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Some structures of marine natural products

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Some structures of marine natural products

by

Janet Sue Finer-Moore

A Dissertation Submitted to the
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The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
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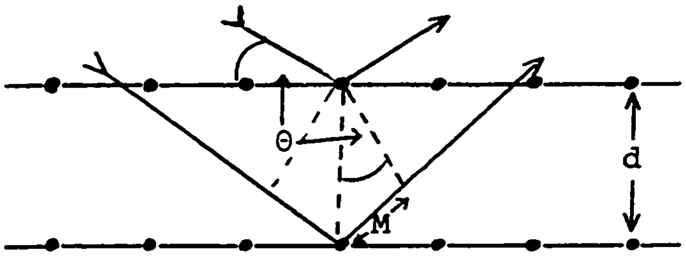
INTRODUCTION

X-ray Methods

At the beginning of the 20th century physicists predicted and then observed the diffraction of X-rays from a three-dimensional periodic array of atoms. When an X-ray beam was directed so as to make certain angles with respect to the planes of atoms in a crystal it was no longer propagated through the crystal but reflected, much the same as visible light from a mirror. This phenomenon occurs when the difference in path length of radiation specularly reflected from parallel planes of atoms in a crystal is equal to some multiple of the wavelength of the radiation. The reflected X-rays then constructively interfere with one another to produce the diffracted beam. It is easy to show this condition is met when $2d\sin\theta = n\lambda$ where d = the spacing between the parallel planes of atoms, λ = the wavelength of the X-rays, θ = the angle made by X-rays with respect to the planes of atoms and n = any integer.



Difference in path length, 2M, = $2d\sin\theta$

A simple set of measurements gives the lattice symmetry and the dimensions of the repeating unit (unit cell) of a crystal. Sets of parallel equally spaced planes intersect the lattice points. Each set of planes divides the unit cell into an integral number of parts and is repeated in each unit cell in the crystal. From the spacing of a set of lattice planes θ can be calculated and one then knows how to direct an X-ray beam with respect to the crystal in order to observe a diffracted beam. In a single crystal X-ray experiment a crystal is rotated until it is in the correct position with respect to the X-ray beam for diffraction to occur and a detector moves into position to measure the intensity of the diffracted beam.

The diffracted beam can be described by the structure factor: $F_{hkl} = \int_V \rho(x,y,z)\exp\{2\pi i(hx + ky + lz)\}dV$ where ρ = electron density at position x, y, z in the crystal; h, k and l are integers identifying the set of diffracting planes; and integration is over one repeating unit of the crystal. Rather than integrate over the unit cell one may approximate the structure factor by summing the contributions of the individual atoms in the unit cell: $F_{hkl} = \sum_{j=1}^{N} f_j\exp\{2\pi i(hx_j + ky_j + lz_j)\}$ where f_j describes the scattering power of the j^{th} atom. This Fourier series is conveniently related to the electron density of the crystal by a Fourier transform: $\rho(x,y,z) = 1/V \sum\sum\sum_{hkl} F_{hkl}\cdot \exp\{-2\pi i(hx + ky + lz)\}$ where summation is over the indices of all reflections. If it were possible to measure the structure factors, the electron density distribution in a crystal could be immediately calculated. Unfortunately the structure factors are complex numbers and no way of measuring them has yet been devised. The quantities measured, the intensities, are proportional to the square of the moduli of the structure factors, $|F_{hkl}|^2$. The complex portions (phases) of the structure factors are lost in the measurement process and must be recovered in order to solve the crystal structure.

There are two basic approaches to the so-called phase problem. If some information is known about the electron density distribution in a crystal an approximate set of phased structure factors can be calculated. These in turn can be used to calculate an improved electron density distribution which may be accurate enough to give a rough picture of the majority of the structure. A crystal structure with a heavy atom (an atom with a significantly higher atomic number than the other atoms in the structure) can usually be solved in this way. There is a straightforward method for obtaining the heavy atom position without knowing any of the phases of the structure factors. If the crystal structure is not too large, fairly accurate phases can then be calculated from the heavy atom position.

When nothing is initially known about the electron density distribution in a crystal, which is the case for most structures without heavy atoms, phase information may be obtained directly from the measured intensities. In the single crystal X-ray diffraction experiment hundreds, often thousands, of intensities are measured and their values depend on a relatively small number of atom position vectors: $|F_{\vec{h}}|^2 = |\sum_{j=1}^{N} f_j \exp\{2\pi i\vec{h}\cdot\vec{r}\}|^2$. Therefore the intensities, or the structure factor magnitudes, $|F_{\vec{h}}|$, are not independent of each other but must be connected by various relationships, and it is by means of these relationships that their phases are derived.

More useful than the structure factor magnitudes are the magnitudes of the unitary structure factors: $U_{\vec{h}} = F_{\vec{h}}/\sum_{j=1}^{N} f_j = \sum_{j=1}^{N} n_j \exp 2\pi i\vec{h}\cdot\vec{r}_j$ where $n_j = f_j/\sum_{j=1}^{N} f_j$. This is because the scattering factors, f_j, in the equations for the structure factors are functions of the scattering angle, θ. The f_j decrease as the angle of scattering from the crystal planes increases. Obviously the structure factor magnitudes will also fall off with increasing values of θ. For the unitary structure factors such angular dependence is, for all practical purposes, eliminated and their magnitudes depend only on the arrangement of atoms in the structure. The normalized structure factors are defined by $E_{\vec{h}} = U_{\vec{h}}/\langle|U_{\vec{h}}|^2\rangle^{\frac{1}{2}}$. They are also independent of θ but are more convenient to work with than the $U_{\vec{h}}$s.

A widely used method for obtaining phases from normalized structure factor magnitudes was developed by considering an equality discovered by Sayre. Sayre used the fact that the electron density function was always positive to derive the equation $F_{\vec{h}} = C_{\vec{h}}\sum_{\vec{h}'} F_{\vec{h}'} F_{\vec{h}-\vec{h}'}$ for structures with only one kind of atom (1). Each product $F_{\vec{h}'} F_{\vec{h}-\vec{h}'}$ is a vector with magnitude and phase. If a product is especially large it will dominate the sum and the phase of the sum will approximately equal the phase of this product: $\phi_{\vec{h}} \simeq \phi_{\vec{h}'} + \phi_{\vec{h}-\vec{h}'}$, where $\phi_{\vec{h}}$ is the phase of the structure factor $F_{\vec{h}}$. This relationship between phases of structure factors in equal-atom structures holds for the phases of large Es in structures with atoms of approximately the same atomic number. The probability of the relationship being correct is related to the magnitudes of $E_{\vec{h}}$, $E_{\vec{h}'}$, and $E_{\vec{h}-\vec{h}'}$, and to the number of independent atoms in the structure.

In practice this relationship is applied to the subset of Es with magnitudes larger than about 1.5 (∿10-15% of those measured). For each large $E_{\vec{h}}$ several possible relationships involving other Es in the subset can usually be written. While one indication of the phase of $E_{\vec{h}}$ may have a rather low probability, the probability of a phase being correct when there are multiple indications for it is very high. Phasing is initiated with a few phases which have been arbitrarily assigned to define the origin in the crystal. These known phases can be used to calculate phases for a few other Es, and these phases in turn enter into phase equations for other Es. The process continues until every E in the subset has been assigned a phase. A Fourier transform of the phased Es gives a well-resolved E map which shows individual atoms. The atom positions can be used to calculate phases for the entire set of structure factors. There are computer programs which now carry out this entire phasing procedure quite automatically and have made it possible to solve many 30-40 atom structures in a few weeks.

Organic chemists, especially in the area of natural products, have been quick to exploit X-ray methods of determining equal-atom structures. As a tool for determining the structures of natural products, X-ray diffraction has several advantages. A straightforward crystal structure problem can be solved in a short time and results accurately define the relative stereochemistry and sometimes even the absolute configuration of the molecule. Although the complete relative stereochemistries of molecules have many times been assigned by other methods of structure determination, the indications for a particular configuration are often ambiguous and wrong assignments have been made. A crystal structure may be done without any previous information about the compound while other methods may depend on comparisons to known structures and fail if the compound has, say, a completely new carbon skeleton.

A disadvantage of X-ray methods is that a single crystal of about .1 mm or greater on each side is necessary for the experiment. Though the crystal need not contain a heavy atom, the size of structures without heavy atoms which can be solved by present methods is limited to about 100 atoms. The majority of natural products are small molecules and the 100 atom limit is not very restrictive. However, natural products which crystallize with 100 or more independent light atoms are not uncommon and X-ray crystallographers are challenged to extend their methods to handle problems of this complexity.

Applications to Marine Chemistry

In recent years marine natural products chemistry has become a major area for application of X-ray crystallography. Research in this field has begun with the isolation and characterization of marine secondary metabolites. Knowledge of the structures of the metabolites has lead to investigations into their biogenesis, synthesis, and their biological and ecological importance.

A chemist interested in the biogenesis of marine natural products searches the known structures to discover patterns which allow him to postulate what kinds of chemical reactions are occurring in the marine organisms. His hypotheses can then become starting points for biosynthetic experimentation. Even with relatively few structures to work with natural products chemists are devising reasonable biosynthetic schemes by relying on the well-established principles of terrestrial natural products chemistry. In particular it is generally assumed that the basic biosynthetic pathways carefully worked out for terrestrial organisms are also valid for marine organisms and that divergence from these pathways appears as a perturbation in the terrestrial scheme. This is a reasonable assumption since the structures of marine and terrestrial secondary metabolites are very similar and the known pathways can readily account for most marine structures. But marine natural products have been novel enough to insure that there is new chemistry, unique to the marine environment, still to be discovered.

New structural information can be helpful for the taxonomic classification of marine organisms. Structurally similar metabolites unique to a certain group of organisms may indicate close biological relationships within the group. Where morphological divisions are not clear secondary metabolites could perhaps serve as taxonomic markers.

Structurally similar secondary metabolites isolated from different classes of marine organisms, on the other hand, are ecologically significant. One organism may obtain a secondary metabolite directly from another, possibly its food source or symbiotic partner, and elaborate it. Often such metabolites are toxic or show some other biological activity.

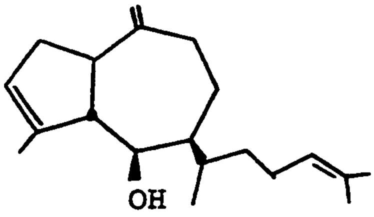
X-ray crystallography has helped open up many areas of research in the marine sciences and will remain an important part of the field as long as it continues to stimulate ideas and provide insight into the chemistry and biology of marine life. Clearly the chemist applying crystallography to marine natural products must be able to choose those structural problems which will result in new and significant information. Acquiring the ability to identify such important problems is at least as challenging as mastering crystallographic theory and technique.

A BIOSYNTHETIC PROBLEM: DITERPENES FROM *DICTYOTACEAE*

History of the Problem

The *Phaeophyta*, also called the brown algae, are multicellular primitive plants distinguished by their particular combination of pigments, which give them an olive green to brown color, and their metabolism, which produces laminarin, mannitol and various fats for storage as food reserves in the cells (2). Almost all species grow in the ocean close to shore, in areas which are alternately submerged and exposed by the tides, or areas slightly beyond the intertidal zone which are always covered with shallow water (2). As a division the brown algae are most abundant in cold waters but genera of the family *Dictyotaceae* are common in tropical and subtropical regions (2). Members of this family have distinct morphological features: they are ribbon-like or fan-shaped and branched with the branches arranged in one plane, and their growth is initiated either by a single apical cell or a row of apical cells (2). Algae of the *Dictyotaceae* family are convenient subjects for scientific investigation because of their accessibility and distinct form. They have attracted the attention of marine scientists by their suspected toxicity and by the unusual metabolites which have been isolated from them in initial investigations.

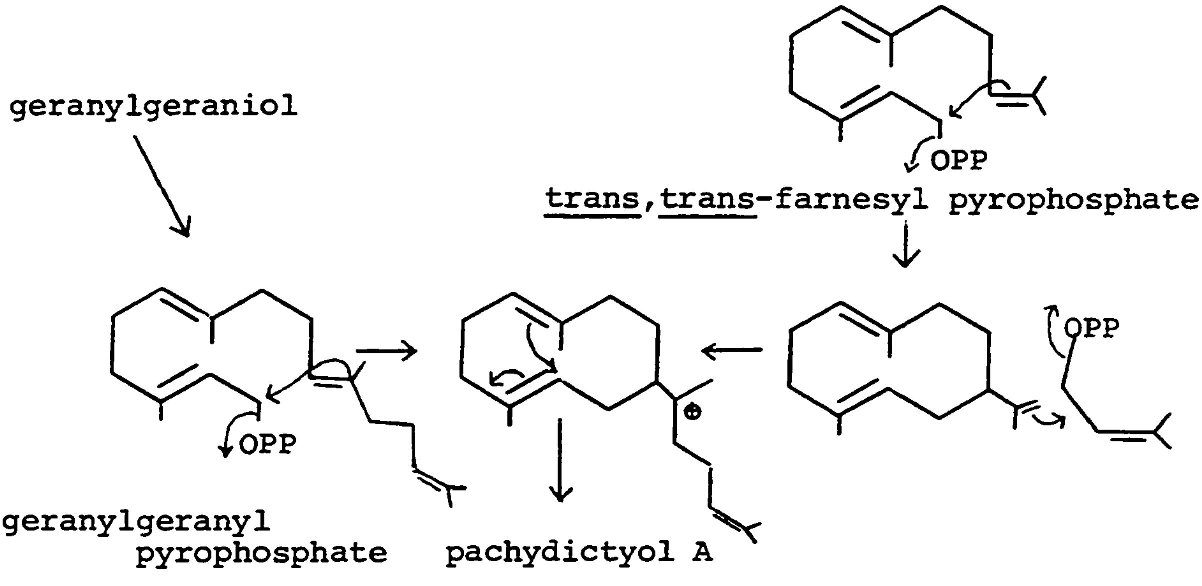
One of the most important results of the investigation of the *Dictyotaceae* has been the discovery of several unique diterpenes which may have been formed by an unusual cyclization of the standard diterpene precursor. The first diterpene isolated from a *Dictyotaceae* species proved mildly active against *Staphylococcus aureus*, but of greater significance than its biological activity was its perhydroazulene ring system (3). This ring system is common in sesquiterpenes but had not previously been encountered in a diterpene. The new diterpene was called pachydictyol A after the brown alga *Pachydictyon coriaceum* from which it had been isolated. An X-ray structure analysis of its p-bromophenylurethane derivative was done and its absolute stereochemistry determined. At least six different diterpenes having the same carbon skeleton as pachydictyol A but different patterns of oxygenation have now been identified (4,5,6). Interestingly, none of these compounds was isolated from a *Pachydictyon* species but from the morphologically similar *Dictyota* genus, and pachydictyol A itself was found in *Dictyota hespera* (7). It has been suggested that the presence of pachydictyol A-related diterpenes is a distinguishing feature of a subclass of *Dictyotaceae* including the genera *Pachydictyon*, *Dictyota* and *Dilophus*, all of which are morphologically difficult to distinguish (7,8).



pachydictyol A

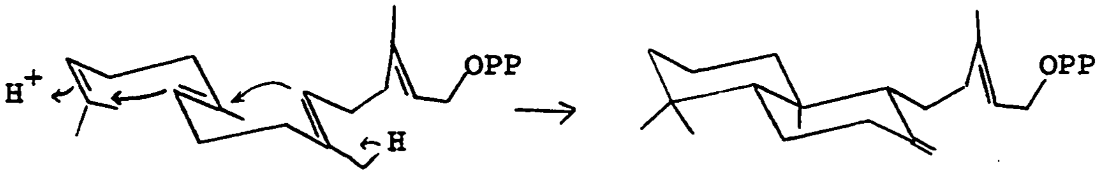
Two possible biosyntheses were postulated for pachydictyol A (3). Because the perhydroazulene ring system is common in sesquiterpenes it was reasonable to propose a biosynthesis involving cyclization of trans,trans-farnesol, addition of an isoprene unit to the isopropyl group of the cyclized intermediate, and finally, closure of the ten-membered ring. Alkylation by γ,γ-dimethylallyl pyrophosphate is common in natural products chemistry (9).

Alternatively, cyclization of geranylgeraniol in a manner analogous to that of farnesol followed by ring closure would also give the correct skeleton.



Two biosynthetic routes to pachydictyol A

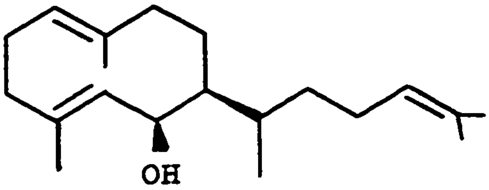
Geranylgeraniol is considered the precursor of most diterpenes but usually undergoes a concerted ring closure, initiated by nucleophilic attack on its terminal double bond, to give the bicyclic intermediate copalyl pyrophosphate (10). It also occasionally cyclizes to form the 14-ring cembrane skeleton (10).



geranylgeranyl pyrophosphate

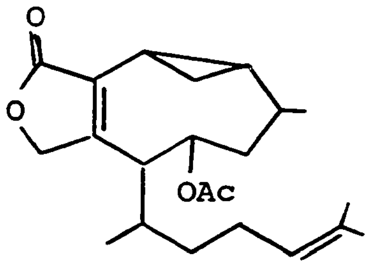
copalyl pyrophosphate

A monocyclic diterpene isolated from *Dilophus ligulatus* may be biogenetically related to pachydictyol A-type compounds. Dilophol was assigned a structure on the basis of chemical and spectral evidence along with biosynthetic considerations (11). The compound looks like it could have been formed by one of the two schemes proposed for pachydictyol A without a final ring closure step.



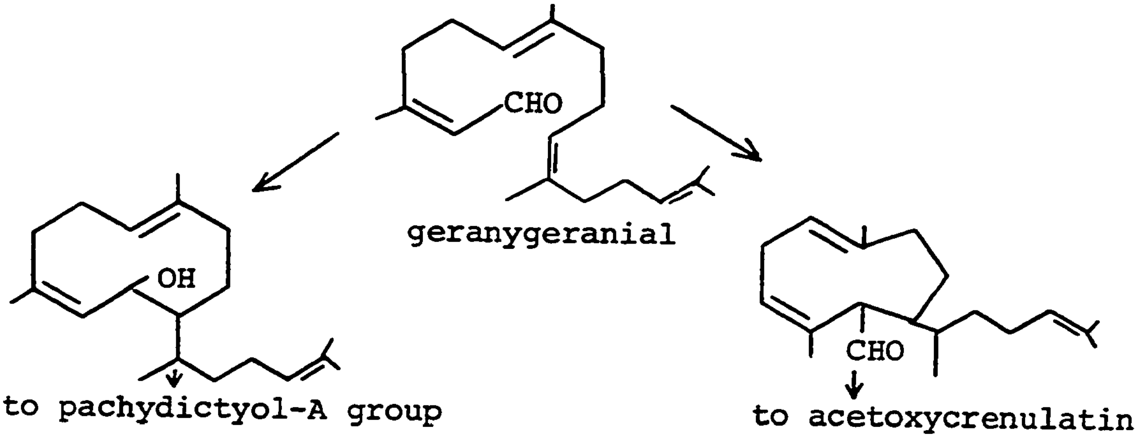
dilophol

Another diterpene, acetoxycrenulatin, has been isolated from Pachydictyon coriaceum and Dictyota crenulata (7). The structure as determined by spectral and chemical data is shown below. The data did not define the stereochemistry at all of the centers.



acetoxycrenulatin

Although acetoxycrenulatin looks quite different from dilophol and the pachydictyol A-type compounds, Fenical has suggested these compounds are all derived from the same precursor (7). Geranylgeranial could cyclize in two different ways to produce a ten-membered ring intermediate (leading to pachydictyol A-related compounds) and a nine-membered ring (leading to acetoxycrenulatin).



Two possible cyclizations of geranylgeranial

None of the biosynthetic schemes suggested for these diterpenes have been experimentally tested and it would probably be difficult to do so. It was hoped that identification of new diterpenes from Dictyotaceae would give more clues about the correct biosyntheses, possibly adding weight to already proposed schemes.

Dictyoxepin

Background

Dictyoxepin was one of two diterpenes isolated from the brown alga Dictyota acutiloba (12). Fresh samples of the algae were extracted in ether and the ether soluble portion was subjected to extensive chromatography to give the two new compounds. Analysis by mass spectrometry gave the molecular formulas $C_{20}H_{32}O_2$ and $C_{20}H_{32}O$ for dictyoxepin and the second diterpene, dictyolene, respectively. Much information about the functionalities of dictyoxepin could be obtained from its ^1H NMR and ^{13}C NMR spectra. However, its skeleton was apparently novel and its characterization by spectral and chemical means would require too much time and too much of the precious and unstable sample to be practical. X-ray diffraction analysis was chosen as the most convenient method of completing the structure determination. The p-bromophenylurethane derivative of dictyoxepin formed crystals suitable for the X-ray experiment.

Experimental

In preliminary measurements crystals of the dictyoxepin derivative were indexed in the hexagonal crystal class with cell constants $\underset{\sim}{a} = \underset{\sim}{b} = 14.238(3)\text{Å}$ and $\underset{\sim}{c} = 23.306(3)\text{Å}$, and a calculated density of 1.18 g/cc for six molecules $C_{27}H_{36}O_3NBr$ in the unit cell.[1] The systematic absence of all 0 0 l reflections with $l \neq 6N$ indicated space group $P6_1$ or its enantiomer $P6_5$. Integrated intensities of all reflections with h, k and $l \geq 0$ and $2\theta \geq 114.1°$ were measured using a minimum scan rate of 1°/minute. Three standard reflections periodically measured to monitor crystal decomposition showed no decline in intensity during data collection. Data were corrected for Lorentz, polarization and background effects and 1576 out of 2174 measured reflections were judged observed

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[1] A Syntex $P2_1$ fully-automated four-circle diffractometer with graphite monochromated CuKα radiation ($\lambda = 1.5418\text{Å}$) was used for all X-ray experiments described in this dissertation. Accurate cell constants were determined by least-squares refinement of 15 centered reflections with 2θ values between 35° and 45°. Integrated intensities were measured with an ω-scan technique. Unless otherwise stated, 1° scans with background measurements .5° on either extreme of the scan were used. Scan rate varied according to the estimated intensity of a reflection. The least intense reflections were measured at the minimum scan rate.

$(F_o^2 \geq 3\sigma(F_o^2))$.[1]

The presence of a bromine in the dictyoxepin derivative (approximately 13% of the electron density of the molecule) simplified the solution of the crystal structure. Location of the bromine position by means of a Patterson synthesis gave a rough approximation of the phases of the structure factors and two subsequent F_o syntheses were sufficient to locate all 32 nonhydrogen atoms (13,14b). Positions and anisotropic thermal parameters for all nonhydrogens were refined by full-matrix least-squares.[2] Theoretical positions and isotropic temperature factors for all the hydrogens were also allowed to refine. In the final stages of refinement corrections were made for anomalous scattering

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[1] $|F_{rel}| = (I/Lp)^{1/2}$ where $L = 1/\sin 2\theta$ and $p = .5(1 + \cos^2\chi \cos^2 2\theta)/(1 + \cos^2\chi) + .5(1 + \cos\chi\cos^2 2\theta)/(1 + \cos\chi)$ where 2θ is the Bragg angle of the reflection and χ is the angle between the X-ray beam off the target and the X-ray beam off the monochromator.

[2] The quantity minimized in all least-squares refinements was $\Sigma\, \omega_{hkl}(|F_o|-|kF_c|)^2$ where $\omega_{hkl} = 1/\sigma_{hkl}^2$. The expression used for the anisotropic temperature factor of the i^{th} atom in the asymmetric unit transformed to the j^{th} equivalent position is as follows: $\exp ij = \exp\{-[(h^2)_j \beta_{11_i} + (k^2)_j \beta_{22_i} + (2\,hk)_j \beta_{12_i} + (2\,hl)_j \beta_{13_i} + 2(kl)_j \beta_{23_i}]\}$. The method for calculating the coefficients β_{11}, etc. is given by H. A. Levy (14a).

by the bromine. The final unweighted R-factor for the observed reflections, $R = \Sigma(|F_o|-|kF_c|)/\Sigma|F_o|$, was .053 for the correct configuration (space group $P6_5$) compared to .054 for its enantiomer. The difference in these two R-factors, though small, is statistically significant (15). This choice of enantiomers correctly predicted the directions of the inequalities in intensities for 12 of the 16 most enantiomorph-sensitive Friedel pairs.

Results

Figure 1 is a computer generated perspective drawing of the p-bromophenylurethane derivative of dictyoxepin. The conformation shown correlates well with the ^1H NMR spectra of the free alcohol. The ring junction of this bicyclic molecule is cis with the bridgehead methyl equatorial and the bridgehead hydrogen axial. The six-membered ring is in the chair conformation with the hydroxyl group equatorial and the side chain axial. The configurations at the asymmetric centers are 5(S), 6(R), 7(S), 10(S) and 11(R). Table 1a lists atom positions for the structure. Table 1b and 1c include selected bond distances and angles. Bond distances and angles are generally in agreement with accepted values (16). We attribute the unusual distances in the side chain to the large thermal motions of the side chain atoms. Under

Figure 1. A computer generated perspective drawing of dictyoxepin, with hydrogens omitted for clarity.

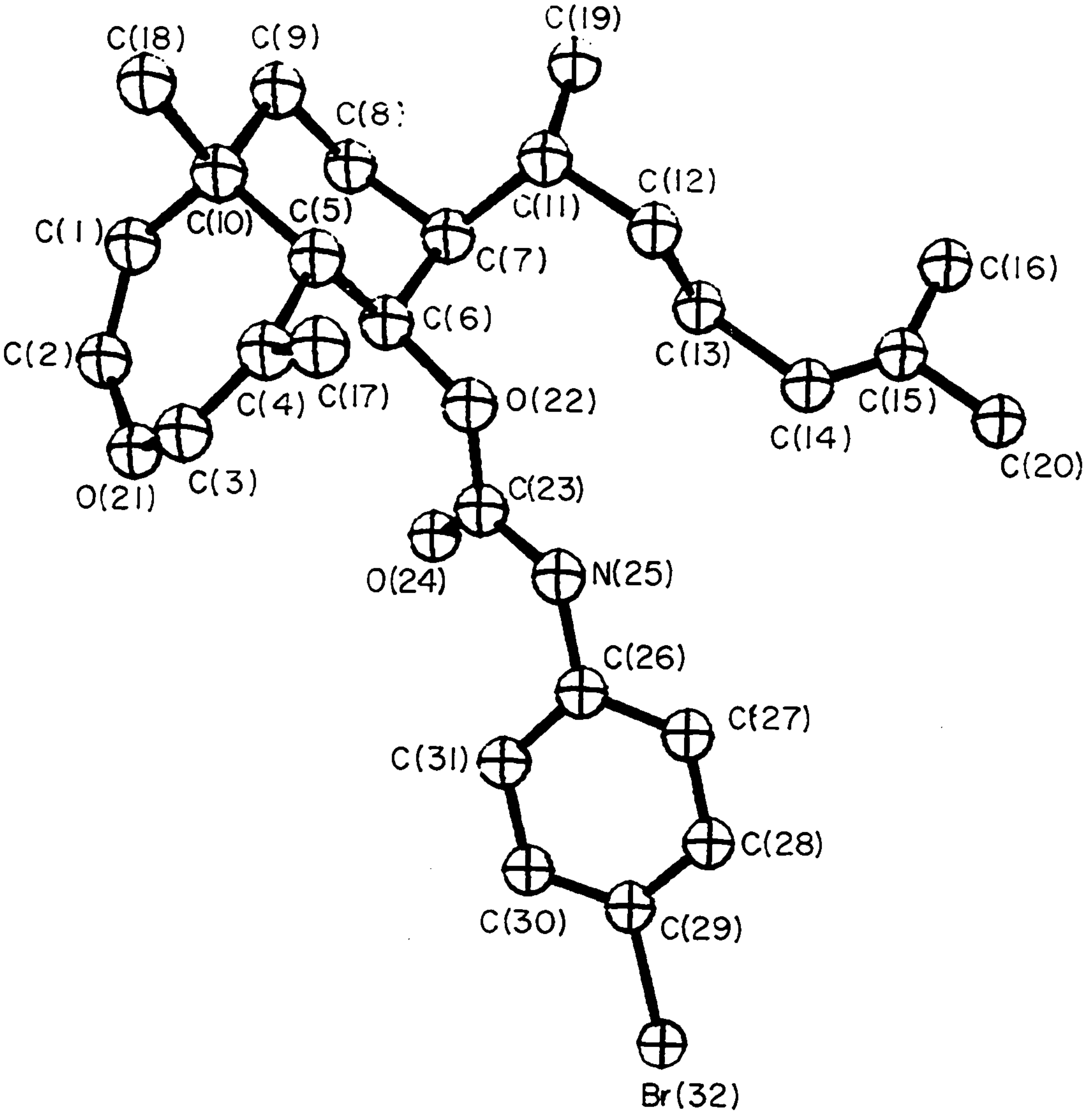

C(18)
C(9)
C(8)
C(19)
C(1)
C(10)
C(5)
C(11)
C(12)
C(7)
C(16)
C(6)
C(2)
C(13)
C(4)
C(17)
O(22)
C(15)
C(14)
C(20)
O(21)
C(3)
C(23)
O(24)
N(25)
C(26)
C(27)
C(31)
C(28)
C(30)
C(29)
Br(32)

Table 1a. Fractional coordinates for the nonhydrogen atoms of dictyoxepin. Standard deviation of the least significant figures are given in parentheses. The numbering scheme refers to figure 1.

C(1)	.5587(7)	.4542(14)	.1288(5)
C(2)	.5336(14)	.3529(20)	.1405(6)
C(3)	.3952(11)	.2547(9)	.0742(6)
C(4)	.3596(7)	.3200(7)	.0556(5)
C(5)	.3816(6)	.4210(6)	.0876(4)
C(6)	.3235(6)	.3959(7)	.1442(3)
C(7)	.3299(7)	.4974(8)	.1737(4)
C(8)	.4530(8)	.5703(8)	.1839(5)
C(9)	.5165(8)	.6023(9)	.1275(5)
C(10)	.5027(7)	.5013(8)	.0955(4)
C(11)	.2745(8)	.5521(8)	.1417(4)
C(12)	.1479(10)	.4832(10)	.1359(5)
C(13)	.0893(13)	.4446(17)	.1931(7)
C(14)	-.0457(18)	.3633(16)	.1799(9)
C(15)	-.1072(13)	.3987(16)	.1858(7)
C(16)	-.0974(35)	.4944(28)	.1978(12)
C(17)	.2939(9)	.2953(9)	.0019(5)
C(18)	.5585(9)	.5379(9)	.0358(5)
C(19)	.3077(14)	.6605(12)	.1648(6)
C(20)	-.2232(17)	.3289(39)	.1725(9)
O(21)	.4522(10)	.2591(9)	.1209(5)
O(22)	.2107(4)	.3136(4)	.1326(2)
C(23)	.1632(6)	.2312(6)	.1692(4)
O(24)	.2038(4)	.2217(5)	.2128(3)
N(25)	.0609(5)	.1621(5)	.1513(3)
C(26)	-.0107(7)	.0592(7)	.1750(4)
C(27)	-.1219(8)	.0199(9)	.1729(6)
C(28)	-.1933(8)	-.0810(11)	.1956(8)
C(29)	-.1557(9)	-.1426(8)	.2183(5)
C(30)	-.0487(9)	-.1085(7)	.2189(4)
C(31)	.0239(7)	-.0054(7)	.1977(4)
Br(32)	-.2555(1)	-.2795(1)	.2500(1)

Table 1b. Selected bond distances of dictyoxepin.[a] In parentheses after each distance is the standard deviation of its least significant figure. Values in the second column have been corrected for thermal motion of the atoms.[b]

C(1) - C(2)	1.330(14)	
C(1) - C(10)	1.490(13)	
C(2) - O(21)	1.337(13)	
C(3) - O(21)	1.340(12)	
C(3) - C(4)	1.334(11)	
C(4) - C(5)	1.507(10)	
C(4) - C(17)	1.494(13)	
C(5) - C(6)	1.503(9)	
C(5) - C(10)	1.531(10)	
C(6) - C(7)	1.560(11)	
C(6) - O(22)	1.464(7)	
C(7) - C(8)	1.544(11)	
C(7) - C(11)	1.549(11)	
C(8) - C(9)	1.532(13)	
C(9) - C(10)	1.541(13)	
C(10) - C(18)	1.558(12)	
C(11) - C(12)	1.568(13)	
C(11) - C(19)	1.473(14)	1.529(14)
C(12) - C(13)	1.523(16)	
C(13) - C(14)	1.705(22)	
C(15) - C(14)	1.218(16)	1.249(21)
C(15) - C(16)	1.327(21)	1.463(29)
C(15) - C(20)	1.473(23)	

[a] All bond distances are reported in angstroms.

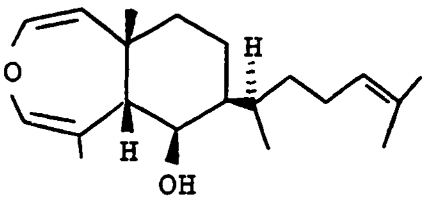
[b] The corrected distance, with the second atom assumed to ride on the first, is given by $d = d_o + (\bar{r}_2^2 - \bar{\varepsilon}_2^2 - \bar{r}_1^2 + \bar{\varepsilon}_1^2)/2d_o$, where d_o = uncorrected distance, $\bar{r}_i^2$ = mean square radial displacement of atom i, and $\bar{\varepsilon}_i^2$ = mean square component of displacement of atom i in the direction defined by the interatomic vector.

Table 1c. Selected bond angles of dictyoxepin.[a] In parentheses after each angle is the standard deviation of its least significant figure.

C(10) - C(1) - C(2)	132.9(8)
C(1) - C(2) - O(21)	129.9(9)
C(2) - O(21) - C(3)	121.8(8)
O(21) - C(3) - C(4)	131.6(9)
C(3) - C(4) - C(5)	122.2(7)
C(3) - C(4) - C(17)	121.3(8)
C(5) - C(4) - C(17)	116.5(6)
C(4) - C(5) - C(6)	112.4(6)
C(4) - C(5) - C(10)	113.1(5)
C(6) - C(5) - C(10)	110.5(6)
C(5) - C(6) - C(7)	113.3(5)
C(5) - C(6) - O(22)	106.3(5)
C(7) - C(6) - O(22)	110.8(5)
C(6) - C(7) - C(8)	102.3(6)
C(6) - C(7) - C(11)	116.4(6)
C(8) - C(7) - C(11)	115.3(7)
C(7) - C(8) - C(9)	111.7(7)
C(8) - C(9) - C(10)	110.9(7)
C(9) - C(10) - C(1)	108.7(7)
C(9) - C(10) - C(5)	109.0(6)
C(9) - C(10) - C(18)	108.2(7)
C(1) - C(10) - C(5)	112.5(7)
C(1) - C(10) - C(18)	108.5(7)
C(5) - C(10) - C(18)	109.7(7)
C(7) - C(11) - C(12)	116.2(7)
C(7) - C(11) - C(19)	111.9(8)
C(12) - C(11) - C(19)	110.7(8)
C(11) - C(12) - C(13)	113.7(9)
C(12) - C(13) - C(14)	108.4(11)
C(13) - C(14) - C(15)	119.8(14)
C(14) - C(15) - C(16)	136.2(20)
C(14) - C(15) - C(20)	119.4(18)
C(16) - C(15) - C(20)	104.1(19)

[a] All bond angles are reported in degrees.

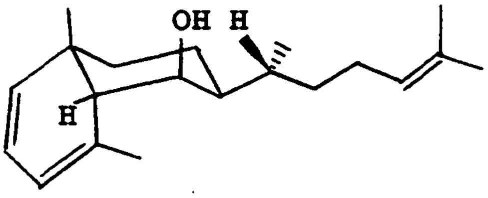
conditions of excessive thermal motion measuring distances from the centers of electron density ellipses is known to be inaccurate. When distances are averaged over the paths of thermal motion somewhat more accurate results are obtained. Some distances corrected for thermal motion are included in table 1b. For complete tables of atomic positions and thermal parameters, bond distances, bond angles, and observed and calculated structure factor magnitudes, refer to the published communication (12).



dictyoxepin

Discussion

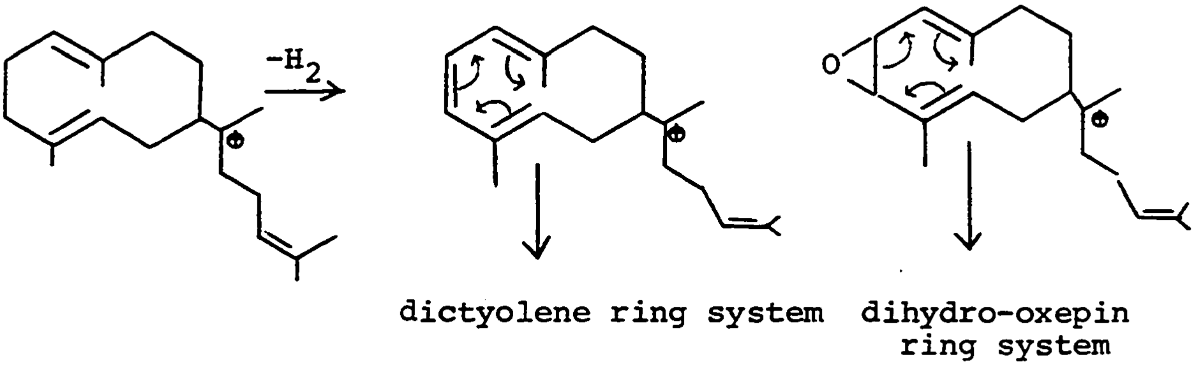
The structure of dictyolene, including stereochemistry, was deduced mainly from its UV, IR, ^{1}H NMR and ^{13}C NMR spectra, and has now been confirmed by total synthesis (17). There is a cis ring junction between the two six-membered rings and the saturated ring is in the chair conformation with the bridgehead methyl and hydroxyl groups axial and C(11) equatorial. The configuration at C(11) is the same as in dictyoxepin.



dictyolene

The discovery of dictyoxepin and dictyolene is significant because of the novelty of their structures. They are the first diterpenes of their particular structural type to be isolated. A few related structures can be found among the sesquiterpenes. Occidentalol (18) and the norsesquiterpenoid dehydrochaecynenes (19) have a cis-fused decalin ring system like dictyolene while occidenol (20) and miscandenin (21) have the same ring system as dictyoxepin.

The biosyntheses of dictyolene and dictyoxepin probably proceed through a germacrene-type intermediate. Transannular cyclization of the cyclodecadiene portion of the intermediate would give a trans-fused decalin system (22). However, if cyclodecadiene is first dehydrogenated to form the 1,3,5-trans,cis,trans conjugated triene, a disrotatory ring closure is thermally allowed and gives the cis-fused system of dictyolene (23). Tomita and Hirose suggest epoxidation of trans,cis,trans-cyclodecatriene followed by a Cope rearrangement as a likely path to the dihydro-oxepin system (20). If this were the biosynthetic route leading to dictyoxepin one might expect the reverse Cope rearrangement to occur on simple heating, but the ^{1}H NMR at 100°C showed only a reversible shift of the NH proton in the p-bromophenylurethane derivative. While disappointing, this is not inconsistent with the hypothetical scheme.



Possible routes to dictyoxepin and dictyolene

Dictyodial

Background

A diterpene dialdehyde with an unusual nine-membered ring skeleton was isolated from lipid extracts of Dictyota crenulata. Methylene chloride extraction of the acetone soluble portion of the lipid fraction followed by several chromatographic separations gave dictyodial, $C_{20}H_{30}O_2$. A series of ^{13}C and ^{1}H NMR studies allowed a biogenetically plausible structure to be drawn for the diterpene but the complete stereochemistry of the molecule could not be deduced. Reduction of dictyodial gave a crystalline diol and an X-ray structure analysis was undertaken.

Experimental

The diol crystals were large but not clear or well-formed. They belonged to the orthorhombic crystal class with a calculated density of 1.07 g/cc for eight molecules of $C_{20}H_{34}O_2$ in the unit cell and cell constants $\underset{\sim}{a}$ = 12.256(4)Å, $\underset{\sim}{b}$ = 8.1420(8)Å and $\underset{\sim}{c}$ = 38.101(4)Å. Systematic extinctions in the data indicated the chiral space group $P2_12_12_1$, implying there were two molecules of the diol in the asymmetric unit. One octant of data with $2\theta \leq 114.1°$ (CuKα) was measured using a minimum scan rate of 1°/minute. Three standard reflections chosen to monitor decomposition of the crystal showed no decline in intensity during data collection. 1802 of the 2973 recorded intensities (60.6%) were considered observed after corrections for Lorentz, polarization and background effects.

The structure was solved by obtaining phases directly from the magnitudes of the structure factors using triple product phase relationships. Phasing of the 300 highest Es was carried out with the computer program MULTAN, which uses a multi-solution weighted tangent formula approach (24). This approach did not work well for two reasons. First, the structure was fairly complex — 44 independent nonhydrogen atoms — and the probability of phase relationships being accurate decreases with increasing size of a structure. Second, MULTAN had difficulty finding good origin defining reflections. Ideally, three special reflections are chosen to define the origin in space group $P2_12_12_1$, that is, reflections with phases restricted to 0 or π, or to ± π/2, depending on the parity of the reflection's indices. If three special reflections cannot be found which both define the origin and are useful in starting the phasing procedure one or more general reflections (reflections with unrestricted phases) are chosen. Using general reflections turns out to be both less accurate and more time-consuming than using special reflections. In the case of the diol three general reflections were chosen for origin definition.

To offset these two problems, MULTAN was rerun using as large a starting set as possible in a reasonable amount of computing time. Increasing the number of starting set reflections significantly increases the chances of generating a correct set of phases. MULTAN was modified to represent the phases of the starting set reflections with magic integers (25). Using the magic integer representation decreases the number of phase sets to be calculated for a given number of starting set reflections. Of the 192 phase sets generated one had outstanding figures of merit and an E map calculated from this set of phases showed 35 of the 44 independent atoms. The remaining atoms were located by means of an F_o synthesis. Hydrogens were located on a difference map and assigned isotropic temperature factors equal to those of the heavy atoms they were bonded to plus 1.0. Nonhydrogens were anisotropically refined by full-matrix least-squares while only the positions of the hydrogens were varied. Refinement converged to an unweighted R-factor of .091 for the observed reflections.

Results

Figure 2 is a computer generated perspective drawing of the diol. Dictyodial is a member of a class of diterpenes with the rare xeniane skeleton. An X-ray diffraction analysis of xenicin, the first example of the xeniane skeleton, determined both its structure and absolute configuration (26). Dictyodiol has been drawn with the same absolute stereochemistry as xenicin (2(R), 3(R), 10(S)). The double bonds at C(1) and C(6) both have the E configuration. Both molecules in the asymmetric unit have the same geometry within experimental error. The conformation of the nine-membered ring is the same as that in xenicin except for the presence of an extra sp^2 center. Dihedral angles of the nine-membered ring are listed in table 2e. The two hydroxyl groups are involved in hydrogen bonding and the bonding scheme is presented in table 2f. Fractional coordinates, bond distances, bond angles and

Figure 2. A computer generated perspective drawing of one molecule from the crystal structure of dictyodiol. Hydrogens are omitted for clarity.

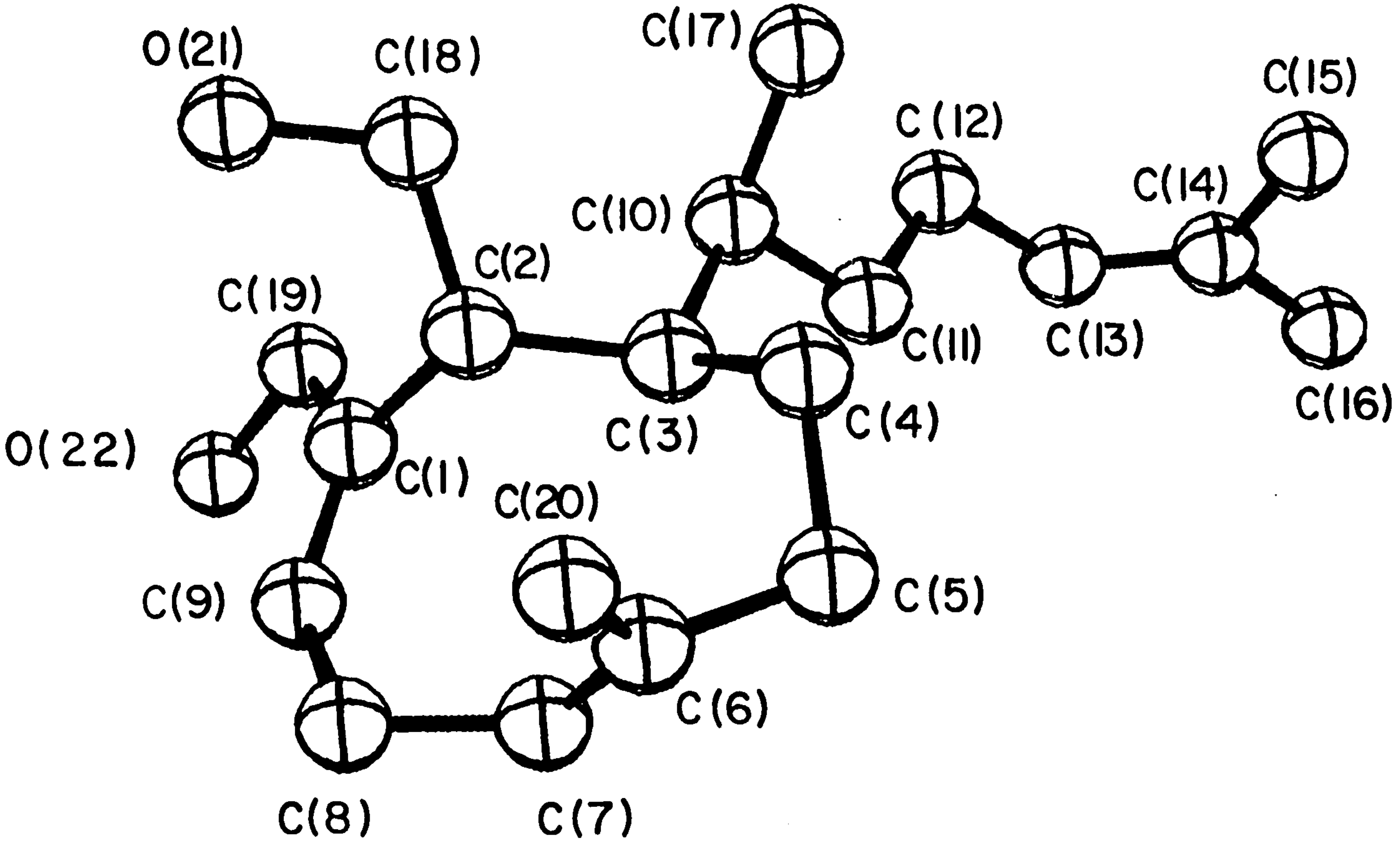

O(21)
C(18)
C(17)
C(15)
C(12)
C(14)
C(10)
C(2)
C(19)
C(11)
C(13)
C(3)
C(4)
C(16)
O(22)
C(1)
C(20)
C(9)
C(5)
C(6)
C(8)
C(7)

Table 2a. Fractional coordinates for dictyodiol. Standard deviations of the least significant figures are given in parentheses. Hydrogens are assigned the same numbers as the heavy atoms to which they are bonded. The numbering scheme refers to figure 2.

C(1)	-.2334(10)	.3517(15)	.3014(3)
C(2)	-.3258(9)	.3705(13)	.3278(2)
C(3)	-.2846(11)	.3699(13)	.3678(3)
C(4)	-.3605(10)	.2622(15)	.3922(3)
C(5)	-.3270(12)	.0785(15)	.3926(3)
C(6)	-.3380(11)	.0137(12)	.3564(3)
C(7)	-.2468(13)	.0187(14)	.3363(3)
C(8)	-.2474(11)	.0312(13)	.2972(3)
C(9)	-.2008(10)	.2066(15)	.2883(3)
C(10)	-.2676(12)	.5442(14)	.3847(3)
C(11)	-.1783(9)	.5297(17)	.4139(3)
C(12)	-.1528(12)	.6878(19)	.4337(3)
C(13)	-.0775(11)	.6580(18)	.4629(3)
C(14)	-.0992(13)	.6347(19)	.4960(3)
C(15)	-.2071(14)	.6299(25)	.5103(4)
C(16)	-.0154(16)	.6092(28)	.5234(4)
C(17)	-.3682(12)	.6277(16)	.3999(3)
C(18)	-.3996(9)	.5166(15)	.3196(3)
C(19)	-.1762(11)	.5086(17)	.2907(3)
C(20)	-.4480(10)	-.0236(14)	.3428(3)
O(21)	-.4383(6)	.5119(10)	.2840(1)
O(22)	-.0859(7)	.4742(10)	.2679(2)
C(1')	.2815(10)	.0920(13)	.3022(2)
C(2')	.1747(10)	.1155(13)	.3241(2)
C(3')	.1986(9)	.1175(14)	.3645(3)
C(4')	.1088(11)	.0225(15)	.3853(3)
C(5')	.1324(13)	-.1624(15)	.3887(3)
C(6')	.1485(9)	-.2331(15)	.3522(3)
C(7')	.2477(10)	-.2367(14)	.3383(3)
C(8')	.2778(12)	-.2223(15)	.3005(3)
C(9')	.3191(10)	-.0492(13)	.2922(3)
C(10')	.2207(8)	.2905(13)	.3820(2)
C(11')	.2986(10)	.2642(18)	.4134(3)
C(12')	.3331(12)	.4272(15)	.4311(3)
C(13')	.4122(11)	.3977(18)	.4615(3)
C(14')	.3915(12)	.3825(19)	.4949(3)
C(15')	.2761(14)	.3877(22)	.5085(4)
C(16')	.4767(16)	.3523(28)	.5219(4)
C(17')	.1197(11)	.3834(15)	.3924(3)
C(18')	.1071(10)	.2636(17)	.3122(3)
C(19')	.3380(9)	.2507(13)	.2912(3)
C(20')	.0467(11)	-.2662(21)	.3319(3)
O(21')	.0830(6)	.2498(11)	.2751(2)

Table 2a. (Continued)

O(22')	.4375(7)	.2336(11)	.2737(2)
H(2)	-.375(10)	.262(17)	.325(3)
H(3)	-.217(12)	.306(17)	.369(3)
H(4A)	-.358(11)	.330(19)	.415(3)
H(4B)	-.451(12)	.279(18)	.383(3)
H(5A)	-.396(12)	.042(20)	.411(4)
H(5B)	-.252(12)	.061(18)	.400(4)
H(7)	-.176(11)	.017(19)	.348(3)
H(8A)	-.328(11)	.023(19)	.286(3)
H(8B)	-.177(12)	-.060(19)	.289(3)
H(9)	-.130(11)	.196(17)	.269(3)
H(10)	-.235(12)	.624(17)	.367(3)
H(11A)	-.118(13)	.487(20)	.407(4)
H(11B)	-.214(12)	.435(19)	.432(4)
H(12A)	-.240(13)	.754(20)	.442(4)
H(12B)	-.113(13)	.797(21)	.412(4)
H(13)	-.003(12)	.661(21)	.462(4)
H(15A)	-.265(18)	.720(25)	.515(5)
H(15B)	-.217(15)	.582(25)	.529(5)
H(15C)	-.270(17)	.617(26)	.492(5)
H(16A)	.041(17)	.570(25)	.514(4)
H(16B)	-.027(17)	.593(27)	.546(5)
H(16C)	.007(16)	.697(27)	.537(5)
H(17A)	-.445(13)	.624(20)	.382(4)
H(17B)	-.372(12)	.739(20)	.397(3)
H(17C)	-.402(12)	.552(19)	.421(4)
H(18A)	-.457(11)	.552(18)	.330(3)
H(18B)	-.343(10)	.618(17)	.328(3)
H(19A)	-.216(12)	.598(18)	.278(3)
H(19B)	-.145(11)	.600(19)	.309(3)
H(20A)	-.505(12)	-.103(20)	.359(3)
H(20B)	-.458(12)	-.004(21)	.315(4)
H(20C)	-.486(12)	.080(20)	.342(4)
H(21)	-.391(11)	.547(17)	.266(3)
H(22)	-.059(10)	.483(17)	.252(3)
H(2')	.132(12)	.025(19)	.318(3)
H(3')	.262(11)	.032(17)	.371(3)
H(4'A)	.034(12)	.068(19)	.373(4)
H(4'B)	.103(12)	.070(18)	.407(4)
H(5'A)	.092(13)	-.210(20)	.403(4)
H(5'B)	.189(12)	-.197(20)	.403(4)
H(7')	.311(11)	-.205(17)	.357(3)
H(8'A)	.209(12)	-.277(19)	.284(3)
H(8'B)	.351(12)	-.286(20)	.294(3)
H(9')	.400(10)	-.067(16)	.281(3)
H(10')	.271(11)	.361(17)	.363(3)
H(11'A)	.261(12)	.197(18)	1433(3)

Table 2a. (Continued)

H(11'B)	.373(12)	.217(19)	.407(3)
H(12'A)	.260(13)	.477(19)	.441(3)
H(12'B)	.368(13)	.497(20)	.412(4)
H(13')	.479(12)	.408(20)	.452(4)
H(15'A)	.235(16)	.429(23)	.496(4)
H(15'B)	.283(14)	.444(24)	.528(4)
H(15'C)	.242(15)	.291(22)	.519(5)
H(16'A)	.544(16)	.234(28)	.507(4)
H(16'B)	.476(17)	.353(26)	.540(5)
H(16'C)	.498(17)	.433(25)	.527(5)
H(17'A)	.040(13)	.404(20)	.374(4)
H(17'B)	.130(12)	.531(20)	.401(4)
H(17'C)	.071(12)	.331(20)	.410(4)
H(18'A)	.139(12)	.371(19)	.319(4)
H(18'B)	.022(12)	.286(20)	.327(4)
H(19'A)	.269(11)	.350(17)	.281(3)
H(19'B)	.363(10)	.328(18)	.315(3)
H(20'A)	.010(13)	-.361(23)	.347(4)
H(20'B)	.074(13)	-.314(22)	.309(4)
H(20'C)	.002(13)	-.185(22)	.326(4)
H(21')	.047(11)	.211(18)	.289(3)
H(22')	.476(11)	.300(19)	.266(3)

Table 2b. Bond distances of dictyodiol. The standard deviation of the least significant figure of each distance is given in parentheses.

C(1) - C(2)	1.52(1)
C(1) - C(9)	1.35(2)
C(1) - C(19)	1.51(2)
C(2) - C(3)	1.61(1)
C(2) - C(18)	1.53(2)
C(3) - C(4)	1.58(2)
C(3) - C(10)	1.57(1)
C(4) - C(5)	1.55(2)
C(5) - C(6)	1.48(2)
C(6) - C(7)	1.36(2)
C(6) - C(20)	1.48(2)
C(7) - C(8)	1.49(2)
C(8) - C(9)	1.57(2)
C(10) - C(11)	1.57(2)
C(10) - C(17)	1.52(2)
C(11) - C(12)	1.53(2)
C(12) - C(13)	1.47(2)
C(13) - C(14)	1.30(2)
C(14) - C(15)	1.43(2)
C(14) - C(16)	1.48(2)
C(18) - O(21)	1.44(1)
C(19) - O(22)	1.43(1)
C(1') - C(2')	1.56(2)
C(1') - C(9')	1.30(1)
C(1') - C(19')	1.53(1)
C(2') - C(3')	1.57(1)
C(2') - C(18')	1.53(2)
C(3') - C(4')	1.56(2)
C(3') - C(10')	1.58(1)
C(4') - C(5')	1.54(2)
C(5') - C(6')	1.52(2)
C(6') - C(7')	1.33(2)
C(6') - C(20')	1.49(2)
C(7') - C(8')	1.49(2)
C(8') - C(9')	1.53(2)
C(10') - C(11')	1.54(1)
C(10') - C(17')	1.50(2)
C(11') - C(12')	1.55(2)
C(12') - C(13')	1.53(2)
C(13') - C(14')	1.30(2)
C(14') - C(15')	1.51(2)
C(14') - C(16')	1.49(2)
C(18') - O(21')	1.45(1)
C(19') - O(22')	1.40(1)

Table 2c. Bond angles of dictyodiol. The standard deviation of the least significant figure of each angle is given in parentheses.

C(2)	- C(1)	- C(9)	123.8(10)
C(2)	- C(1)	- C(19)	116.0(10)
C(9)	- C(1)	- C(19)	120.2(10)
C(1)	- C(2)	- C(3)	113.1(9)
C(1)	- C(2)	- C(18)	112.6(8)
C(3)	- C(2)	- C(18)	112.6(8)
C(2)	- C(3)	- C(4)	112.0(9)
C(2)	- C(3)	- C(10)	115.2(8)
C(4)	- C(3)	- C(10)	109.9(9)
C(3)	- C(4)	- C(5)	112.6(10)
C(4)	- C(5)	- C(6)	108.1(9)
C(5)	- C(6)	- C(7)	116.1(12)
C(5)	- C(6)	- C(20)	118.9(11)
C(7)	- C(6)	- C(20)	124.1(10)
C(6)	- C(7)	- C(8)	124.2(13)
C(7)	- C(8)	- C(9)	106.1(9)
C(1)	- C(9)	- C(8)	127.4(10)
C(3)	- C(10)	- C(11)	108.3(10)
C(3)	- C(10)	- C(17)	116.9(11)
C(11)	- C(10)	- C(17)	109.2(9)
C(10)	- C(11)	- C(12)	115.5(11)
C(11)	- C(12)	- C(13)	111.4(12)
C(12)	- C(13)	- C(14)	129.1(13)
C(13)	- C(14)	- C(15)	124.2(14)
C(13)	- C(14)	- C(16)	124.1(15)
C(15)	- C(14)	- C(16)	111.7(13)
C(2)	- C(18)	- O(21)	111.7(9)
C(1)	- C(19)	- O(22)	110.9(10)
C(2')	- C(1')	- C(9')	124.3(10)
C(2')	- C(1')	- C(19')	115.0(9)
C(9')	- C(1')	- C(19')	120.6(10)
C(1')	- C(2')	- C(3')	111.7(9)
C(1')	- C(2')	- C(18')	113.1(8)
C(3')	- C(2')	- C(18')	112.5(9)
C(2')	- C(3')	- C(4')	111.3(9)
C(2')	- C(3')	- C(10')	117.1(8)
C(4')	- C(3')	- C(10')	110.3(8)
C(3')	- C(4')	- C(5')	113.3(11)
C(4')	- C(5')	- C(6')	108.5(10)
C(5')	- C(6')	- C(7')	119.6(11)
C(5')	- C(6')	- C(20')	115.8(11)
C(7')	- C(6')	- C(20')	123.7(10)
C(6')	- C(7')	- C(8')	127.7(11)
C(7')	- C(8')	- C(9')	110.7(9)
C(1')	- C(9')	- C(8')	129.7(11)

Table 2c. (Continued)

C(3') - C(10') - C(11')	108.0(9)
C(3') - C(10') - C(17')	114.7(9)
C(11') - C(10') - C(17')	112.0(8)
C(10') - C(11') - C(12')	112.9(11)
C(11') - C(12') - C(13')	111.7(11)
C(12') - C(13') - C(14')	129.1(13)
C(13') - C(14') - C(15')	121.2(13)
C(13') - C(14') - C(16')	123.6(14)
C(15') - C(14') - C(16')	115.1(12)
C(2') - C(18') - O(21')	109.7(9)
C(1') - C(19') - O(22')	116.3(9)

Table 2d. Observed and calculated structure factor magnitudes for dictyodiol.

H = 0

K	L	FO	FC
0	4	43	43
0	6	104	104
0	8	26	26
0	10	222	222
0	12	62	62
0	14	40	42
0	16	67	65
0	18	85	85
0	20	14	11
0	22	15	15
0	24	10	6
0	26	15	13
0	28	28	28
0	30	21	21
0	32	24	24
0	34	10	13
0	36	10	11
0	40	13	10
1	1	57	54
1	2	10	8
1	3	95	96
1	4	76	77
1	5	43	46
1	6	52	52
1	7	97	95
1	8	116	117
1	9	135	135
1	10	26	25
1	11	30	30
1	12	35	32
1	13	23	19
1	16	57	56
1	17	35	35
1	18	35	34
1	19	42	38
1	20	27	29
1	22	30	33
1	23	29	29
1	24	20	21
1	25	20	19
1	26	13	11
1	33	13	15
1	34	23	24
2	0	6	4
2	3	5	5
2	4	15	14
2	6	5	5
2	8	8	8
2	9	19	21
2	14	8	11
2	15	10	10
2	17	8	11
2	18	10	9
2	19	9	7
2	20	9	12
2	21	8	7
2	22	11	12
2	23	10	13
2	24	19	21
2	26	13	13
2	27	15	16
2	28	13	12
2	30	9	7
2	34	14	13
2	38	14	12
2	39	7	2
3	1	44	40
3	2	54	51
3	3	22	24
3	4	11	2
3	5	13	12
3	6	56	54
3	7	81	80
3	8	60	61
3	9	103	103
3	10	32	35
3	11	14	16
3	12	14	17
3	14	38	38
3	15	31	30
3	16	6	8
3	18	20	21
3	21	20	21
3	22	16	13
3	23	24	24
3	24	26	28
3	25	18	20
3	26	14	13
3	27	22	21
3	28	11	12
3	29	37	35
3	31	13	12
3	32	25	25
3	33	27	26
3	36	12	12
3	39	10	3
4	0	82	80
4	1	52	47
4	2	146	145
4	3	38	33
4	4	11	9
4	5	81	80
4	6	48	45
4	7	36	35
4	8	42	40
4	9	25	26
4	10	7	6
4	11	49	48
4	12	19	16
4	13	23	20
4	14	42	46
4	15	30	31
4	16	68	69
4	17	10	8
4	18	29	29
4	19	17	15
4	20	17	16
4	21	16	17
4	22	17	19
4	24	9	2
4	25	9	5
4	26	18	19
4	27	19	19
4	28	14	13
4	30	38	39
4	32	8	7
4	33	21	19
4	34	15	13
4	35	8	11
4	36	9	3
5	1	14	13
5	3	27	25
5	5	16	16
5	6	25	22
5	7	35	40
5	8	28	29
5	9	45	48
5	11	13	12
5	12	21	18
5	15	17	16
5	17	19	18
5	18	22	26
5	20	13	12
5	21	13	12
5	22	9	8
5	23	15	16
5	24	9	12
5	25	8	6
5	27	22	25
5	31	9	6
6	0	9	9
6	1	9	11
6	6	9	7
6	10	12	10
6	14	9	3
6	18	9	4
6	19	14	13
6	24	8	10
6	27	11	7
6	29	8	9
6	30	8	9
7	1	21	23
7	3	11	12
7	4	26	24
7	6	29	27
7	7	16	15
7	8	23	19
7	9	14	16
7	10	14	13
7	11	9	4
7	16	11	13
7	18	17	14
7	20	9	5
7	23	13	13
7	24	10	12
7	25	8	8
8	0	49	45
8	1	9	6
8	2	21	19
8	3	16	15
8	6	24	25
8	9	8	2

H = 1

K	L	FO	FC
0	2	8	7
0	3	7	7
0	4	13	13
0	6	8	7
0	7	23	22

Table 2d. (Continued)

0	8	14	11	1	26	15	17	3	2	50	48	4	29	18	17
0	9	20	21	1	27	8	9	3	3	39	40	4	30	13	17
0	11	7	7	1	29	10	7	3	4	51	49	4	31	9	8
0	13	20	21	1	30	17	17	3	5	46	45	4	33	11	4
0	14	24	24	1	31	15	17	3	6	63	63	5	1	8	10
0	15	39	38	1	32	16	13	3	7	26	27	5	2	23	25
0	16	12	13	1	34	11	14	3	8	17	20	5	3	7	8
0	17	21	19	1	35	13	15	3	9	7	5	5	4	22	22
0	18	17	16	1	36	12	14	3	10	42	41	5	5	16	17
0	19	12	10	1	37	10	9	3	11	8	10	5	6	37	39
0	20	12	10	1	39	10	8	3	12	22	23	5	7	20	16
0	21	12	13	2	0	94	93	3	13	23	25	5	8	9	6
0	23	6	3	2	1	143	142	3	14	29	30	5	9	26	28
0	24	11	13	2	2	166	167	3	15	22	24	5	10	13	13
0	25	21	20	2	3	85	87	3	16	17	16	5	11	19	16
0	27	18	19	2	4	146	147	3	17	13	14	5	13	18	20
0	28	23	25	2	5	41	40	3	18	20	17	5	15	11	9
0	29	12	10	2	6	92	90	3	19	12	13	5	16	12	12
0	30	11	13	2	7	97	97	3	20	27	28	5	17	14	17
0	33	12	9	2	8	32	31	3	21	21	23	5	18	18	18
0	34	9	8	2	9	88	88	3	23	12	14	5	19	16	19
0	35	10	2	2	10	33	33	3	25	8	10	5	20	8	3
1	0	119	118	2	11	38	38	3	26	10	9	5	21	25	23
1	1	5	6	2	12	18	18	3	27	17	18	5	22	12	9
1	2	83	86	2	13	15	16	3	28	8	12	5	24	10	12
1	3	44	45	2	14	55	57	3	30	35	38	5	26	13	14
1	4	26	26	2	15	24	22	3	31	9	8	5	27	11	12
1	5	79	78	2	16	7	5	3	32	15	15	5	28	12	12
1	6	24	24	2	17	9	11	3	33	9	5	5	29	9	7
1	7	46	45	2	18	27	26	3	34	19	19	5	31	18	16
1	8	11	12	2	19	63	62	3	35	9	9	5	33	8	7
1	9	35	36	2	20	15	18	3	36	13	9	5	34	9	8
1	10	66	68	2	21	9	9	3	38	10	12	6	1	23	24
1	11	30	26	2	22	7	10	4	4	20	17	6	2	37	39
1	12	52	53	2	23	19	19	4	5	9	10	6	3	62	64
1	13	39	40	2	24	25	25	4	6	6	4	6	4	46	50
1	14	10	9	2	26	15	17	4	7	10	10	6	5	27	27
1	15	26	22	2	27	36	37	4	8	7	4	6	6	45	46
1	16	32	28	2	28	21	21	4	9	8	9	6	7	19	19
1	17	30	27	2	29	19	20	4	10	7	3	6	8	11	10
1	18	22	21	2	30	18	15	4	11	20	17	6	9	9	10
1	19	16	16	2	31	14	16	4	13	13	13	6	10	15	13
1	20	30	26	2	33	24	27	4	15	7	8	6	11	19	19
1	21	58	54	2	34	11	10	4	19	12	10	6	12	20	21
1	22	20	18	2	35	11	10	4	20	9	6	6	14	10	6
1	23	38	37	2	36	15	11	4	21	10	9	6	15	25	27
1	24	18	17	3	0	51	49	4	23	10	7	6	16	25	27
1	25	23	25	3	1	20	17	4	26	14	10	6	17	14	16

Table 2d. (Continued)

6	18	10	11	0	20	60	62	1	35	11	11	3	23	12	13
6	20	14	12	0	21	10	7	1	37	13	11	3	24	19	22
6	21	21	19	0	22	52	52	1	38	11	5	3	25	9	12
6	22	19	22	0	23	12	16	2	3	5	5	3	26	27	27
6	23	12	11	0	24	45	48	2	4	12	14	3	27	11	13
6	26	12	12	0	25	64	66	2	5	6	6	3	28	17	16
6	27	17	16	0	26	22	21	2	6	12	13	3	29	15	14
6	30	8	4	0	27	35	36	2	7	12	13	3	30	16	12
7	0	18	18	0	29	11	9	2	8	6	5	3	31	26	30
7	1	14	16	0	30	20	20	2	9	5	8	3	32	8	13
7	3	19	24	0	31	20	24	2	13	11	12	3	33	28	28
7	4	13	14	0	32	30	27	2	14	9	10	3	34	20	19
7	5	9	9	0	33	20	16	2	15	17	19	3	38	10	8
7	9	23	14	0	37	20	19	2	17	14	15	4	0	9	9
7	10	15	15	0	38	9	6	2	19	8	12	4	1	55	55
7	11	13	13	0	40	10	8	2	20	10	14	4	2	71	69
7	13	16	14	1	0	19	20	2	21	13	18	4	3	25	27
7	15	10	9	1	1	56	56	2	22	12	11	4	4	16	16
7	17	13	9	1	2	19	19	2	23	16	15	4	5	42	44
7	19	16	12	1	3	81	81	2	24	14	15	4	6	13	11
7	20	16	16	1	4	87	83	2	25	9	11	4	7	43	46
7	22	9	8	1	5	32	32	2	30	14	13	4	8	26	27
7	24	7	7	1	6	65	62	2	31	10	8	4	9	16	17
8	1	11	4	1	7	35	34	2	33	10	12	4	10	25	28
8	3	8	6	1	8	14	15	2	34	8	8	4	11	26	27
8	17	12	4	1	9	41	44	2	36	9	8	4	13	13	12
				1	10	19	19	2	38	8	10	4	14	10	9
	H =	2		1	11	49	48	3	0	16	14	4	15	21	19
K	L	FO	FC	1	12	9	7	3	1	51	47	4	16	27	27
0	0	193	199	1	13	45	46	3	2	29	27	4	17	9	9
0	1	19	22	1	14	30	32	3	3	51	50	4	18	15	17
0	2	50	50	1	15	33	33	3	4	54	54	4	20	28	25
0	4	139	138	1	16	43	43	3	5	61	60	4	22	37	38
0	5	166	166	1	17	16	16	3	6	27	28	4	24	22	23
0	6	23	25	1	18	30	27	3	7	46	44	4	25	9	10
0	7	140	140	1	19	13	10	3	8	26	24	4	26	19	21
0	8	37	36	1	20	24	22	3	9	21	19	4	27	42	45
0	9	8	9	1	21	8	7	3	10	19	19	4	29	20	19
0	10	120	120	1	22	12	13	3	11	6	9	4	30	19	20
0	11	57	51	1	23	18	20	3	12	14	13	4	31	10	11
0	12	33	34	1	24	14	20	3	13	24	26	4	33	14	14
0	13	88	87	1	25	24	23	3	14	13	15	4	34	17	16
0	14	72	68	1	27	27	27	3	15	17	17	5	0	14	14
0	15	93	91	1	29	21	21	3	16	26	25	5	2	8	7
0	16	66	65	1	30	17	20	3	17	7	9	5	3	27	26
0	17	68	65	1	31	17	20	3	18	11	6	5	4	29	31
0	18	36	34	1	32	20	15	3	19	9	9	5	5	13	13
0	19	11	15	1	34	10	10	3	21	9	11	5	6	24	26

Table 2d. (Continued)

5	7	18	21	8	16	9	3	1	19	28	28	3	0	59	58
5	8	16	16					1	20	25	25	3	1	38	37
5	9	12	16		H = 3			1	22	9	10	3	2	64	66
5	10	33	35	K	L	FO	FC	1	23	23	25	3	3	94	95
5	11	20	20	0	1	9	5	1	24	10	12	3	4	20	22
5	12	21	24	0	2	22	23	1	26	10	8	3	5	24	25
5	14	18	20	0	3	21	21	1	27	14	14	3	6	31	28
5	15	10	9	0	4	20	21	1	31	17	20	3	7	13	13
5	19	16	17	0	5	5	6	1	32	11	8	3	8	32	30
5	20	13	15	0	7	9	11	1	33	28	30	3	9	25	26
5	21	15	13	0	8	28	28	1	39	10	3	3	10	9	10
5	22	9	10	0	9	25	23	1	40	8	4	3	11	14	13
5	28	11	12	0	10	39	40	2	0	24	24	3	12	7	5
5	33	13	11	0	11	10	12	2	1	55	53	3	13	34	33
6	0	11	11	0	12	11	9	2	2	30	26	3	14	7	7
6	1	10	7	0	13	28	28	2	4	91	91	3	15	16	17
6	4	7	7	0	14	23	20	2	5	6	8	3	16	7	9
6	8	8	9	0	16	18	17	2	6	97	96	3	17	26	27
6	20	10	8	0	17	9	7	2	7	10	9	3	18	18	19
6	21	10	9	0	19	16	20	2	8	48	52	3	19	8	11
6	22	12	9	0	20	15	15	2	9	36	37	3	21	23	24
6	23	11	6	0	21	13	17	2	10	33	33	3	23	36	37
6	29	8	5	0	24	7	5	2	11	16	17	3	24	14	10
7	0	9	6	0	25	13	13	2	12	73	72	3	25	27	28
7	1	11	10	0	28	18	17	2	13	57	55	3	27	14	12
7	2	15	13	0	29	13	11	2	14	68	69	3	28	13	8
7	3	8	10	0	30	10	4	2	15	21	19	3	29	24	26
7	4	13	15	0	31	27	27	2	16	33	33	3	30	23	21
7	5	17	15	0	32	13	10	2	17	25	24	3	31	18	16
7	8	10	5	0	34	15	15	2	18	25	25	3	32	16	14
7	9	9	13	1	0	40	41	2	19	13	13	3	35	16	13
7	11	16	13	1	1	89	89	2	20	40	39	4	1	13	14
7	14	20	23	1	2	59	61	2	21	19	23	4	4	11	10
7	16	13	14	1	3	60	62	2	22	26	26	4	5	14	10
7	17	9	6	1	4	80	81	2	23	14	16	4	6	10	11
7	18	17	17	1	5	57	56	2	24	48	49	4	7	8	10
7	19	10	11	1	6	36	35	2	25	28	30	4	8	8	7
7	20	12	15	1	7	79	78	2	26	42	42	4	9	8	4
7	22	8	9	1	9	58	58	2	27	11	9	4	10	8	5
7	24	8	10	1	10	13	16	2	28	13	14	4	12	9	8
8	0	8	4	1	11	37	41	2	29	23	23	4	15	15	11
8	1	17	15	1	12	15	13	2	30	20	17	4	17	10	10
8	3	21	21	1	13	10	11	2	31	16	17	4	19	8	8
8	4	15	15	1	14	16	13	2	32	13	7	4	23	17	14
8	6	11	15	1	15	49	48	2	33	13	11	4	24	13	12
8	8	13	9	1	16	32	32	2	35	8	6	4	25	8	12
8	11	11	10	1	17	52	51	2	38	14	10	4	33	11	13
8	13	9	3	1	18	43	43	2	39	13	12	5	0	56	56

Table 2d. (Continued)

5	1	25	27
5	2	27	25
5	3	33	32
5	4	12	14
5	5	9	9
5	6	9	12
5	7	16	17
5	8	12	8
5	9	17	15
5	10	11	14
5	12	27	28
5	13	16	16
5	15	23	21
5	18	23	23
5	19	17	17
5	20	16	14
5	22	10	9
5	23	12	13
5	26	9	4
5	29	9	10
5	30	9	5
5	31	10	10
5	32	8	7
6	1	41	43
6	3	33	33
6	4	13	14
6	5	15	15
6	6	39	39
6	7	10	14
6	8	13	15
6	9	35	34
6	10	33	29
6	11	19	19
6	12	21	23
6	13	11	12
6	14	15	18
6	16	21	20
6	19	13	13
6	20	16	15
6	21	17	19
6	22	15	16
6	23	21	19
6	24	19	18
6	25	19	20
6	26	21	21
6	28	14	14
6	29	7	5
7	5	12	12
7	6	9	9
7	7	19	20
7	8	11	13
7	13	16	15
7	14	10	8
7	17	15	12
7	18	12	10
7	19	11	13
7	20	10	9
7	23	10	10
8	9	8	5

H = 4

K	L	FO	FC
0	0	29	33
0	1	12	10
0	2	5	2
0	3	61	60
0	4	37	37
0	5	83	83
0	6	100	98
0	7	138	139
0	8	7	7
0	9	20	19
0	10	36	32
0	11	59	57
0	12	38	33
0	13	25	25
0	14	43	39
0	15	81	76
0	16	10	6
0	17	63	60
0	18	38	39
0	19	49	50
0	21	44	47
0	22	43	42
0	23	9	5
0	24	42	44
0	25	14	11
0	26	16	13
0	27	21	25
0	28	57	59
0	29	15	15
0	30	8	5
0	31	9	9
0	33	22	20
0	35	18	17
0	36	11	11
0	37	8	5
0	38	12	11
1	0	21	20
1	1	18	19
1	2	32	32
1	3	28	29
1	4	31	31
1	5	36	36
1	6	80	83
1	7	24	21
1	8	24	23
1	9	50	47
1	10	36	34
1	11	19	15
1	12	30	28
1	13	22	22
1	14	54	52
1	15	45	45
1	16	28	28
1	17	18	21
1	18	17	19
1	20	24	26
1	21	15	16
1	22	14	14
1	23	9	10
1	26	11	14
1	27	37	40
1	28	11	11
1	29	15	17
1	30	12	12
1	31	18	17
1	32	23	22
1	34	12	8
1	35	10	9
2	1	13	12
2	6	6	9
2	8	6	4
2	9	7	5
2	11	10	10
2	12	11	12
2	14	6	7
2	17	14	15
2	19	17	17
2	20	10	8
2	21	21	24
2	22	10	12
2	23	11	9
2	24	8	10
2	26	11	13
2	27	10	8
2	28	9	6
2	29	12	11
2	30	12	6
2	33	12	12
2	35	9	10
3	0	56	57
3	1	8	9
3	2	28	27
3	3	41	38
3	4	38	38
3	5	52	50
3	6	9	10
3	7	31	28
3	8	8	8
3	9	9	9
3	10	9	14
3	11	29	31
3	12	17	15
3	13	15	14
3	14	17	15
3	15	24	25
3	16	27	28
3	17	11	12
3	18	8	5
3	19	10	7
3	20	18	16
3	21	11	11
3	22	22	26
3	24	12	15
3	25	25	25
3	26	27	28
3	27	21	20
3	28	15	13
3	29	23	24
3	30	11	14
3	31	15	19
3	32	9	7
3	33	13	15
3	35	10	7
4	0	13	11
4	1	49	48
4	2	26	26
4	3	40	42
4	4	13	13
4	5	35	32
4	6	22	23

Table 2d. (Continued)

4	7	19	19	6	25	9	6	0	30	16	14	2	11	10	9
4	8	7	7	6	27	10	7	0	31	14	10	2	12	16	16
4	9	11	10	7	0	10	7	0	32	16	16	2	13	10	10
4	11	15	14	7	1	13	13	0	34	15	14	2	14	38	35
4	12	28	27	7	2	13	11	0	36	10	10	2	15	30	27
4	13	20	17	7	3	18	17	0	37	9	10	2	16	51	47
4	14	23	23	7	4	9	11	1	0	8	6	2	17	9	9
4	16	10	9	7	5	17	17	1	1	19	20	2	18	18	16
4	17	16	16	7	6	10	8	1	3	9	11	2	19	20	20
4	18	32	32	7	7	8	11	1	4	18	15	2	20	48	48
4	20	31	30	7	9	9	10	1	5	13	17	2	21	32	31
4	21	24	27	7	11	17	19	1	6	35	34	2	22	16	20
4	22	13	17	7	13	11	15	1	7	63	60	2	23	27	27
4	23	43	47	7	14	22	23	1	8	51	52	2	24	11	12
4	24	22	23	7	16	12	14	1	9	45	42	2	25	18	19
4	25	11	6	7	18	8	5	1	10	41	43	2	26	38	39
4	26	13	14	7	19	13	12	1	11	23	23	2	29	8	8
4	27	17	17	7	20	10	10	1	12	44	45	2	30	14	15
4	29	21	22	7	21	13	14	1	13	33	32	2	31	16	14
4	30	16	15	8	0	11	9	1	14	23	22	2	32	21	23
4	31	10	12	8	1	11	7	1	15	17	16	2	33	14	15
4	33	14	13	8	3	9	4	1	16	21	23	2	34	9	6
5	0	7	7	8	7	12	7	1	17	44	45	2	36	12	7
5	1	23	27	8	8	9	11	1	19	25	27	3	1	22	23
5	3	18	19	8	9	11	10	1	20	19	20	3	2	20	18
5	4	25	25	8	10	10	12	1	21	20	21	3	3	26	27
5	5	9	12	8	11	9	2	1	22	8	10	3	4	22	17
5	6	23	21					1	23	15	18	3	5	25	26
5	7	19	15		H =	5		1	24	19	20	3	6	32	33
5	9	25	25	K	L	FO	FC	1	25	20	23	3	7	25	26
5	10	20	23	0	1	33	32	1	26	18	18	3	8	37	39
5	12	13	12	0	4	28	28	1	27	13	11	3	9	8	11
5	13	11	13	0	5	10	11	1	29	21	21	3	10	7	7
5	15	16	18	0	6	18	19	1	30	21	18	3	11	9	7
5	16	14	15	0	7	32	30	1	31	12	13	3	12	9	4
5	17	15	13	0	8	12	13	1	33	12	13	3	14	14	16
5	18	10	6	0	10	21	18	1	34	8	8	3	15	10	12
5	20	15	16	0	11	15	15	1	36	11	12	3	16	19	19
5	22	9	8	0	12	11	10	1	37	12	10	3	17	11	15
5	23	14	13	0	14	25	27	2	0	52	53	3	18	17	19
5	25	13	9	0	15	6	6	2	2	56	51	3	20	19	23
5	26	10	9	0	16	26	28	2	3	28	28	3	21	16	14
5	29	9	4	0	18	12	13	2	4	47	44	3	22	13	11
6	8	8	8	0	20	16	16	2	5	28	33	3	23	41	39
6	17	9	8	0	21	12	9	2	6	28	27	3	24	26	26
6	18	12	6	0	24	14	11	2	7	48	46	3	25	24	22
6	19	8	10	0	25	30	32	2	8	32	31	3	26	17	10
6	21	11	5	0	27	19	21	2	9	43	41	3	28	25	24

Table 2d. (Continued)

3	30	13	12	6	18	12	11	1	0	16	16	3	0	22	21
3	31	17	14	6	19	13	14	1	1	15	12	3	1	7	5
3	33	15	10	6	20	12	17	1	2	26	27	3	2	10	8
3	34	9	10	6	22	12	4	1	3	7	10	3	3	11	10
3	35	8	7	6	24	10	11	1	4	24	26	3	4	12	10
4	3	10	9	6	25	8	9	1	5	14	15	3	5	10	12
4	4	11	14	6	26	10	8	1	6	16	14	3	6	11	7
4	5	10	11	7	0	11	6	1	7	20	20	3	7	21	19
4	10	8	10	7	1	12	6	1	8	31	33	3	8	12	13
4	12	10	11	7	5	8	10	1	9	29	31	3	9	10	9
4	13	10	6	7	8	13	12	1	10	57	57	3	11	15	13
4	14	8	4	7	12	11	12	1	11	49	46	3	12	29	28
4	15	8	9	7	18	10	13	1	12	13	15	3	13	17	17
4	18	17	18	7	19	9	7	1	13	18	20	3	15	13	13
4	19	13	11	8	3	8	2	1	16	21	20	3	16	17	16
4	22	9	8	8	7	7	5	1	17	7	8	3	17	36	36
4	23	13	14					1	18	11	12	3	18	8	10
4	27	15	11		H =	6		1	19	22	24	3	19	19	21
4	32	10	9	K	L	FO	FC	1	20	14	15	3	20	16	17
5	1	14	12	0	0	46	45	1	21	17	19	3	22	26	27
5	2	17	15	0	1	36	34	1	23	18	17	3	25	25	26
5	3	21	22	0	2	33	34	1	24	13	11	3	26	22	23
5	4	18	18	0	3	8	7	1	26	21	23	3	27	30	27
5	6	15	18	0	4	64	64	1	27	16	13	3	32	9	7
5	7	26	26	0	5	10	12	1	28	12	8	4	0	27	26
5	8	10	7	0	6	8	7	1	29	20	22	4	1	9	12
5	10	10	8	0	7	61	59	1	34	9	6	4	2	40	40
5	11	8	12	0	8	32	26	2	3	16	14	4	3	11	12
5	14	15	15	0	9	35	36	2	5	9	11	4	8	11	9
5	15	10	9	0	11	29	29	2	6	10	10	4	9	21	21
5	18	11	11	0	12	16	18	2	7	15	17	4	10	18	21
5	20	11	14	0	13	37	35	2	9	16	18	4	11	12	12
5	22	22	23	0	14	11	15	2	10	7	5	4	12	20	21
5	23	18	19	0	15	7	11	2	11	18	16	4	13	16	16
5	25	13	16	0	17	32	33	2	13	9	11	4	14	24	26
5	28	11	9	0	18	32	33	2	14	13	11	4	15	13	17
5	30	7	6	0	19	9	10	2	15	11	9	4	17	10	10
6	0	9	4	0	20	10	12	2	17	12	17	4	18	34	37
6	1	12	13	0	21	16	17	2	18	10	11	4	19	22	22
6	2	15	17	0	22	24	24	2	19	7	13	4	20	41	39
6	4	36	37	0	23	31	31	2	22	14	16	4	21	22	21
6	8	21	24	0	26	50	55	2	23	8	10	4	22	14	13
6	9	30	30	0	28	27	28	2	24	12	9	4	23	22	24
6	10	17	15	0	30	15	13	2	27	13	11	4	24	14	14
6	12	11	8	0	31	9	9	2	28	9	5	4	25	8	8
6	13	23	21	0	32	19	18	2	29	12	9	4	27	10	5
6	14	22	19	0	34	12	13	2	30	9	10	4	28	13	14
6	16	23	23	0	36	14	12	2	35	7	5	5	0	24	23

Table 2d. (Continued)

5	1	16	12
5	4	18	21
5	5	16	20
5	7	19	20
5	8	12	10
5	10	10	6
5	11	12	13
5	12	8	9
5	13	15	17
5	15	11	12
5	17	13	13
5	18	14	13
5	19	14	16
5	20	13	10
5	23	12	10
5	27	12	10
5	28	11	7
6	1	11	8
6	2	14	8
6	7	9	10
6	10	10	5
6	11	11	10
6	12	10	8
6	13	10	11
6	16	9	8
6	23	11	5
6	24	9	7
7	1	14	14
7	4	10	5
7	6	13	10
7	8	9	5
7	9	8	6
7	14	9	8
7	16	7	9

H = 7

K	L	FO	FC
0	2	10	10
0	4	13	15
0	5	7	8
0	6	16	18
0	9	9	10
0	10	7	9
0	14	7	4
0	15	10	4
0	17	8	8
0	18	14	13
0	20	12	12
0	21	8	8
0	23	9	3
0	26	10	10
0	27	10	7
0	28	15	16
0	31	8	7
1	1	7	4
1	2	25	24
1	3	9	7
1	4	25	28
1	5	8	9
1	6	8	8
1	7	14	11
1	8	24	28
1	10	15	18
1	11	23	23
1	13	17	16
1	14	22	20
1	15	13	14
1	16	20	19
1	19	7	7
1	20	28	29
1	21	10	11
1	23	16	19
1	24	31	29
1	25	20	19
1	26	22	21
1	27	8	6
1	28	8	5
1	29	12	10
1	30	15	11
1	31	9	12
1	33	12	8
2	0	19	19
2	1	25	25
2	2	13	16
2	3	12	10
2	4	16	18
2	5	12	11
2	6	14	17
2	7	31	29
2	8	22	21
2	9	13	16
2	11	35	38
2	12	10	9
2	15	10	15
2	16	16	19
2	17	33	35
2	18	22	21
2	19	16	15
2	22	19	18
2	23	27	26
2	24	13	10
2	25	13	12
2	27	11	12
2	28	16	15
2	29	11	16
2	30	12	7
2	32	11	7
2	33	7	5
3	1	12	12
3	2	13	15
3	3	15	18
3	4	17	20
3	5	9	7
3	7	9	8
3	8	19	18
3	9	11	12
3	10	23	25
3	11	22	22
3	12	10	17
3	13	18	18
3	14	26	25
3	16	17	18
3	17	11	14
3	18	17	17
3	19	10	11
3	20	16	16
3	21	16	14
3	22	16	14
3	23	9	11
3	24	21	23
3	27	10	7
3	28	9	6
4	0	13	9
4	1	9	4
4	2	10	10
4	5	10	8
4	9	8	10
4	10	10	7
4	11	8	13
4	12	10	13
4	16	14	14
4	18	8	4
4	20	9	8
4	21	8	4
4	22	12	5
4	26	13	7
4	28	9	7
5	0	16	11
5	2	19	16
5	4	11	11
5	5	10	14
5	6	18	18
5	7	18	19
5	8	10	6
5	10	18	18
5	13	14	10
5	14	10	12
5	15	19	20
5	17	13	11
5	18	9	10
5	19	11	7
5	21	8	6
5	22	8	7
5	25	8	8
5	26	8	6
6	1	13	10
6	6	12	12
6	8	20	22
6	12	14	11
6	16	16	11
6	18	8	7
6	19	17	14
6	21	7	4
7	3	9	8
7	10	9	2
7	11	8	9

H = 8

K	L	FO	FC
0	0	22	23
0	1	17	18
0	2	37	37
0	4	29	31
0	5	29	28
0	6	13	15
0	7	16	19
0	8	15	16
0	10	17	17
0	11	15	14
0	12	15	14
0	13	14	18
0	14	36	34

Table 2d. (Continued)

0	15	16	14
0	16	33	32
0	17	12	13
0	19	14	17
0	20	29	31
0	21	26	30
0	22	23	25
0	24	16	18
0	25	13	13
0	26	21	21
0	29	14	13
0	30	9	6
0	33	12	14
1	0	13	16
1	1	12	16
1	3	17	21
1	5	23	24
1	6	20	23
1	8	17	19
1	9	16	16
1	11	16	16
1	12	10	15
1	13	22	23
1	14	10	13
1	15	12	12
1	16	8	3
1	17	14	13
1	21	13	13
1	22	16	18
1	23	14	12
1	25	10	9
2	1	14	11
2	5	12	14
2	7	9	5
2	9	13	10
2	11	23	26
2	13	11	11
2	14	9	9
2	15	10	5
2	17	13	10
2	22	11	11
2	28	8	6
2	31	11	8
3	0	33	36
3	2	26	29
3	4	15	14
3	5	17	19
3	6	19	19
3	7	25	25
3	8	31	31
3	9	17	18
3	10	14	12
3	11	13	12
3	12	11	12
3	13	19	23
3	14	10	6
3	16	10	8
3	17	16	17
3	19	17	20
3	26	9	10
3	27	11	8
3	29	8	10
3	30	10	3
4	1	20	20
4	2	11	9
4	4	21	20
4	5	24	27
4	6	23	24
4	7	16	16
4	9	15	11
4	10	17	20
4	11	22	22
4	13	14	16
4	14	25	25
4	16	20	21
4	17	10	12
4	18	11	8
4	19	8	9
4	23	8	12
5	2	16	16
5	3	10	9
5	7	8	7
5	8	16	17
5	11	10	9
5	14	10	7
6	6	11	6
6	10	10	6
6	11	10	7
7	0	12	10
7	1	8	14
7	2	10	10
7	3	12	14
7	4	9	4
7	5	11	10

H = 9

K	L	FO	FC
0	1	22	24
0	2	8	7
0	3	11	10
0	7	15	15
0	8	12	11
0	13	10	14
0	17	16	15
0	19	16	16
0	20	9	8
0	21	13	9
0	23	9	5
0	29	10	9
1	0	27	28
1	1	21	24
1	2	30	31
1	4	16	14
1	5	18	14
1	6	17	14
1	7	10	13
1	8	15	11
1	9	9	13
1	14	15	11
1	15	11	4
1	17	9	9
1	20	14	13
1	26	8	6
1	30	7	4
2	0	8	9
2	2	15	14
2	3	14	14
2	4	18	17
2	5	9	15
2	6	10	8
2	7	10	11
2	8	39	39
2	11	20	17
2	14	21	24
2	17	11	13
2	18	11	17
2	20	13	13
2	22	11	12
2	25	13	9
2	26	13	10
2	29	10	3
3	0	23	24
3	1	16	20
3	3	21	21
3	4	24	24
3	6	12	19
3	10	13	12
3	11	12	16
3	12	8	9
3	13	14	14
3	14	16	13
3	16	13	13
3	17	9	15
3	19	12	11
3	20	10	6
3	23	9	8
3	25	12	13
4	0	9	3
4	1	12	13
4	13	16	13
4	15	9	6
4	18	10	8
4	20	9	5
5	1	9	12
5	2	10	11
5	3	11	12
5	4	11	6
5	5	13	8
5	7	8	5
5	9	12	11
5	11	10	10
5	13	9	5
5	14	9	6
5	15	9	7
6	5	10	8
6	6	10	6
6	8	15	14
6	10	18	10

H = 10

K	L	FO	FC
0	2	12	11
0	5	26	29
0	8	9	8
0	9	15	16
0	10	10	14
0	11	14	13
0	15	12	9
0	16	18	17
0	18	13	13
0	22	21	19

Table 2d. (Continued)

0	27	8	7
1	0	13	6
1	1	15	18
1	3	20	21
1	4	9	7
1	5	10	5
1	7	11	7
1	8	17	15
1	9	13	11
1	14	9	9
1	16	13	10
1	24	9	3
1	25	8	5
2	2	12	8
2	4	8	3
2	7	14	13
2	24	7	5
3	0	18	20
3	3	10	9
3	4	14	11
3	8	10	9
3	10	22	21
3	11	15	14
3	14	8	5
3	17	11	6
3	22	7	9
4	0	18	19
4	3	11	10
4	5	11	14
4	6	19	21
4	9	11	3
4	11	14	13
4	14	9	13
4	16	12	11
4	18	8	7
4	20	13	8
5	5	8	4
5	11	7	5
5	13	8	7

H = 11

K	L	FO	FC
0	1	9	7
0	2	12	16
0	4	9	6
0	7	9	12
0	12	14	10
0	15	11	10
0	17	11	6
0	19	8	1
0	21	10	7
1	3	12	14
1	4	17	15
1	5	19	20
1	9	16	18
1	12	13	11
1	13	12	14
1	14	8	7
1	15	9	8
1	16	10	7
1	20	8	4
2	0	18	19
2	3	10	5
2	4	17	19
2	5	11	9
2	7	10	4
2	8	12	7
2	10	18	19
2	11	13	13
2	12	16	17
2	14	9	10
2	16	9	4
2	17	9	6
2	18	12	13
2	20	15	11
3	0	12	12
3	3	14	13
3	4	12	6
3	5	11	10
3	7	14	15
3	9	9	7
3	14	9	12
4	3	11	7
4	5	11	10
4	9	9	9
4	11	8	6

H = 12

K	L	FO	FC
0	0	9	9
0	5	9	11
0	6	8	5
0	8	11	10
0	9	14	10
0	13	9	9
0	17	11	8
1	0	10	9
1	6	14	13
1	7	8	10
2	0	13	11
2	3	9	6
2	4	8	7
2	5	13	10
2	7	9	12
2	12	10	2
3	0	7	10
3	7	9	4
3	10	11	12

H = 13

K	L	FO	FC
0	2	9	5
1	2	9	5
1	4	8	1
1	5	7	2
1	7	8	3

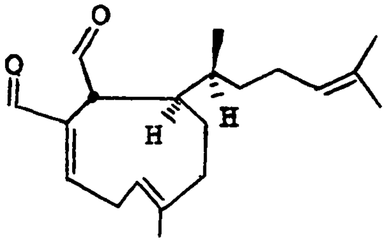
Table 2e. Dihedral angles for the nine-membered rings of both molecules of dictyodiol (°).

	Molecule 1	Molecule 2 (primed numbers)
C(1) - C(2) - C(3) - C(4)	-137	-140
C(1) - C(2) - C(3) - C(10)	97	91
C(2) - C(3) - C(4) - C(5)	87	88
C(3) - C(4) - C(5) - C(6)	- 62	- 55
C(4) - C(5) - C(6) - C(7)	93	90
C(4) - C(5) - C(6) - C(20)	- 76	- 79
C(5) - C(6) - C(7) - C(8)	-152	-148
C(6) - C(7) - C(8) - C(9)	112	102
C(7) - C(8) - C(9) - C(1)	- 51	- 43
C(8) - C(9) - C(1) - C(2)	- 1	- 5
C(8) - C(9) - C(1) - C(19)	178	179
C(9) - C(1) - C(2) - C(3)	92	92
C(9) - C(1) - C(2) - C(18)	-138	-140

Table 2f. Intermolecular distances for dictyodiol (Å).

Atom 1	 2	symmetry operation	distance
O(22)	O(21')	x, y, z	2.77
O(22)	O(21')	-x, .5+y, .5-z	2.78
O(21)	O(22')	x-1, y, z	2.76
O(21)	O(22')	-x, .5+y, .5-z	2.84

structure factor magnitudes are included in tables 2a, 2b, 2c, and 2d, respectively.



dictyodial

Dictyolactone

Background

A diterpene lactone very similar to dictyodial was isolated from the digestive gland of the sea hare Aplysia depilans. The new metabolite almost certainly originated in a species of brown algae. Aplysia depilans feeds mainly on the brown alga Dictyota dichotoma and several of the pachydictyol A-related compounds produced by Dictyota species have been isolated from the sea hare's digestive gland (27). Saponification of the acetone extracts of homogenized digestive glands from A. depilans followed by chromatography of the unsaponified portion gave dictyolactone, $C_{20}H_{30}O_2$. From analysis of UV, IR, ^1H NMR and ^{13}C NMR spectra, and from comparision of the spectra to those of dictyodial, a structure was proposed for dictyolactone and confirmed by X-ray diffraction analysis.

Experimental

Large white crystals from n-hexane belonged to the orthorhombic crystal class with a calculated density of 1.09 g/cc for eight molecules $C_{20}H_{30}O_2$ in the unit cell and unit cell constants $\underset{\sim}{a}$ = 8.279(4)Å, $\underset{\sim}{b}$ = 11.909(13)Å and $\underset{\sim}{c}$ = 37.143(21)Å. After examination of systematic extinctions, space group $P2_12_12_1$ was assigned.

The crystal initially chosen for the X-ray experiment scattered poorly. Only those reflections with $2\theta \leq 110.1°$ (CuKα) were measured. The minimum scan rate was set at 1°/minute. Only about 43% of the reflections measured were judged observed for this first crystal. Later the dictyolactone sample was recrystallized and data collection was repeated on a better crystal. This time the unique reflections with $2\theta \leq 114.1°$ were measured and 1634 of the 2863 recorded intensities (57% of the data) were considered observed after corrections for Lorentz, polarization and background effects.

The same approach as was used to solve the structure of the dictyodial reduction product was chosen for dictyolactone. Both compounds had crystallized in the same space group with approximately the same cell constants so similar problems in solving their crystal structures were anticipated. MULTAN was used to generate as many phase sets for the highest 250 Es as was possible in a reasonable amount of computer time. Origin defining reflections included only one general reflection, and six other reflections — four special and two general reflections — were chosen for the starting set. Phases of the two general reflections in the starting set were represented by magic integers. Absolute figures of merit (an index of the self-consistency of a phase set) for the 192 possible solutions ranged from .4036 to 1.023, all abnormally low values. Two other figures of merit indicated the best solution was one with an absolute figure of merit of only .7635, and an E map from this set showed all but three of the nonhydrogen atoms. It is interesting that the best phase set for dictyodiol also had a rather low self-consistency index while its other two figures of merit were very good. Normally the absolute figure of merit is a very reliable indication of the correctness of a phase set in space groups with translational symmetry (24).

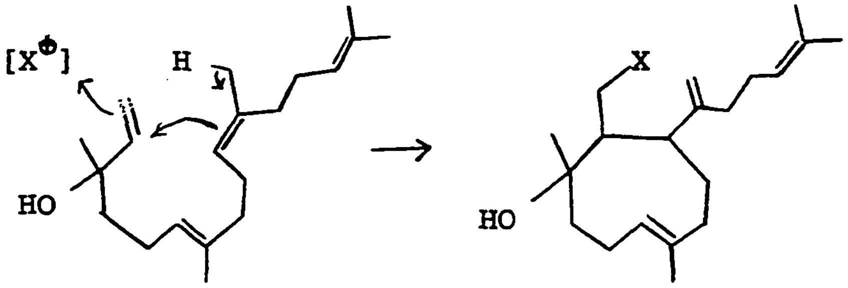
The three remaining carbon atoms were found from an F_o synthesis and theoretical positions were calculated for the hydrogens. Heavy atoms were anisotropically refined by full-matrix least-squares. Hydrogens were assigned the same isotropic temperature factors as the heavy atoms to which they were bonded plus 1.0 and only their positions were refined in least-squares. The unweighted R-factor for the observed reflections was .086.

Results

The structure of dictyolactone is the same as that of dictyodial except that it has a lactone functionality instead of two aldehyde groups. Its three-dimensional structure is shown in the computer generated drawing, figure 3. The conformation of the nine-membered ring is the same as in the dictyodiol structure. The geometries of both molecules in the asymmetric unit are the same within experimental error and there are no exceptional bond distances or angles. Tables 3a, 3b, 3c and 3d are fractional coordinates, bond distances, bond angles and structure factor magnitudes, respectively. Dihedral angles of the nine-membered ring are listed in table 3e. There are no short intermolecular contacts in the crystal structure.

Discussion

The pachydictyol A-type compounds as well as dictyoxepin and dictyolene have sesquiterpene analogues and their biosyntheses are most likely patterned after those of their corresponding sesquiterpenes. The biosyntheses of dictyodial and dictyolactone are less certain. Vanderah *et al*. have suggested two possible routes to the xeniane skeleton (26). One involves cyclization of *cis*,*trans*,*trans*-geranylgeraniol to an 11-membered ring intermediate followed by transannular cyclization to the caryophyllene ring system, and finally, oxidative cleavage of the cyclobutane ring. The other involves oxidative cyclization of geranyllinalool:



The structure proposed for acetoxycrenulatin has the xeniane carbon skeleton so the scheme suggested by Fenical for the biosynthesis of this compound would also account for the biosyntheses of dictyodial and dictyolactone. This scheme is attractive since it proposes a precursor, geranylgeranial, which could as well cyclize to a germacrene-type intermediate and eventually form pachydictyol A and related compounds or dictyoxepin and dictyolene.

Figure 3. A computer generated perspective drawing of one molecule from the crystal structure of dictyolactone. Hydrogens are omitted for clarity.

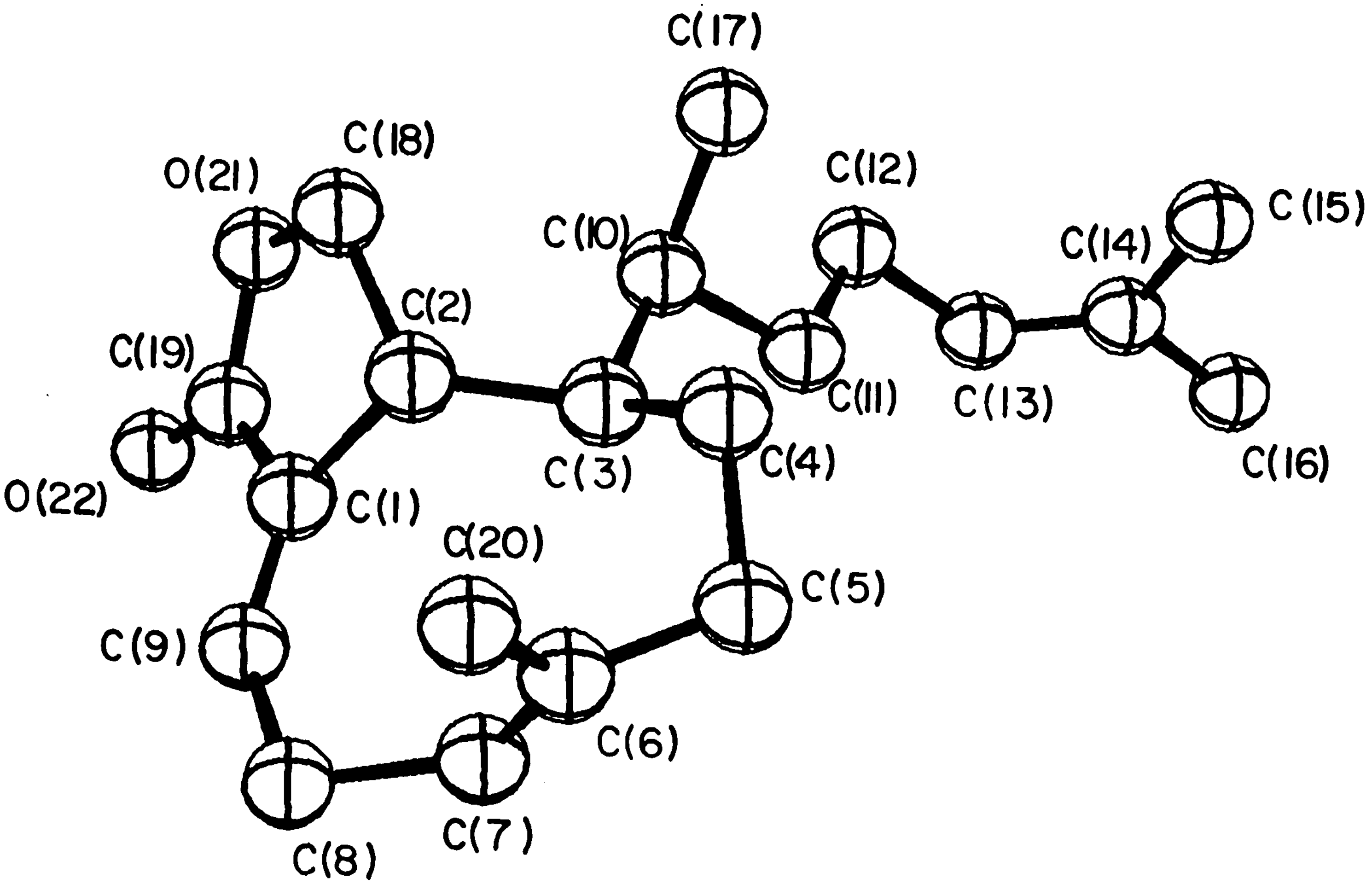

C(17)
C(18)
O(21)
C(12)
C(15)
C(10)
C(14)
C(2)
C(19)
C(11)
C(13)
C(3)
C(4)
O(22)
C(1)
C(16)
C(20)
C(5)
C(9)
C(6)
C(7)
C(8)

Table 3a. Fractional coordinates for dictyolactone. Standard deviations of the least significant figures are given in parentheses. Hydrogens are assigned the same numbers as the heavy atoms to which they are bonded. The numbering scheme refers to figure 3.

C(1)	-.2014(16)	.0699(12)	.9545(3)
C(2)	-.1637(14)	-.0377(11)	.9321(3)
C(3)	-.1609(14)	-.0152(11)	.8893(3)
C(4)	-.2640(15)	-.1050(12)	.8686(3)
C(5)	-.4476(16)	-.0790(14)	.8664(3)
C(6)	-.5104(16)	-.0557(15)	.9023(4)
C(7)	-.5151(16)	.0496(14)	.9165(3)
C(8)	-.5119(16)	.0842(14)	.9557(3)
C(9)	-.3401(19)	.1143(13)	.9646(3)
C(10)	.0094(15)	-.0056(13)	.8731(3)
C(11)	-.0051(16)	.0761(12)	.8384(3)
C(12)	.1588(17)	.0971(15)	.8212(3)
C(13)	.1424(19)	.1776(12)	.7890(3)
C(14)	.1312(18)	.1511(13)	.7550(3)
C(15)	.1356(25)	.0287(14)	.7411(4)
C(16)	.1021(27)	.2332(15)	.7255(4)
C(17)	.0909(18)	-.1136(13)	.8629(3)
C(18)	.0055(18)	-.0647(15)	.9471(3)
C(19)	-.0473(20)	.1117(16)	.9660(4)
C(20)	-.5525(20)	-.1619(14)	.9265(4)
O(21)	.0763(12)	.0418(10)	.9610(2)
O(22)	-.0193(15)	.2032(10)	.9818(3)
C(1')	.0747(17)	-.4304(12)	.9530(3)
C(2')	.1082(16)	-.5326(12)	.9278(3)
C(3')	.1130(13)	-.4998(12)	.8852(3)
C(4')	.0077(17)	-.5861(12)	.8639(3)
C(5')	-.1781(14)	-.5558(14)	.8620(3)
C(6')	-.2352(17)	-.5428(13)	.8980(3)
C(7')	-.2358(16)	-.4423(15)	.9144(3)
C(8')	-.2381(16)	-.4125(12)	.9546(3)
C(9')	-.0646(18)	-.3876(12)	.9643(3)
C(10')	.2838(16)	-.4920(13)	.8694(3)
C(11')	.2739(17)	-.4089(12)	.8350(3)
C(12')	.4407(18)	-.3873(13)	.8178(3)
C(13')	.4173(20)	-.3089(12)	.7850(3)
C(14')	.3944(19)	-.3417(12)	.7517(3)
C(15')	.3890(27)	-.4579(17)	.7388(4)
C(16')	.3697(26)	-.2613(15)	.7211(4)
C(17')	.3620(18)	-.6015(13)	.8579(3)
C(18')	.2786(17)	-.5651(14)	.9426(3)
C(19')	.2258(19)	-.3962(15)	.9678(3)
C(20')	-.2774(19)	-.6474(14)	.9206(4)
O(21')	.3496(11)	-.4651(9)	.9605(2)

Table 3a. (Continued)

O(22')	.2552(15)	-.3121(9)	.9865(2)
H(2)	-.272(16)	-.098(11)	.938(3)
H(3)	-.282(16)	.038(11)	.888(3)
H(4A)	-.204(16)	-.126(12)	.845(4)
H(4B)	-.248(17)	-.174(12)	.881(3)
H(5A)	-.469(16)	-.030(12)	.852(3)
H(5B)	-.535(17)	-.129(12)	.852(3)
H(7)	-.472(17)	.108(11)	.895(3)
H(8A)	-.630(16)	.144(11)	.965(3)
H(8B)	-.558(16)	.061(11)	.969(3)
H(9)	-.305(16)	.185(10)	.982(3)
H(10)	.082(16)	.018(11)	.898(3)
H(11A)	-.067(17)	.055(12)	.813(3)
H(11B)	-.145(18)	.121(12)	.835(3)
H(12A)	.229(18)	.135(12)	.843(3)
H(12B)	.279(18)	.053(12)	.823(3)
H(13)	.142(16)	.243(11)	.787(4)
H(15A)	.019(21)	.025(15)	.760(4)
H(15B)	.203(20)	.026(13)	.719(4)
H(15C)	.251(23)	.029(16)	.753(4)
H(16A)	.171(22)	.241(14)	.718(5)
H(16B)	.085(22)	.199(13)	.705(4)
H(16C)	-.068(21)	.249(14)	.727(4)
H(17A)	.034(17)	-.134(12)	.844(4)
H(17B)	.267(18)	-.098(12)	.865(3)
H(17C)	.069(17)	-.170(12)	.882(4)
H(18A)	.009(17)	-.126(11)	.967(3)
H(18B)	.100(19)	-.074(13)	.915(4)
H(20A)	-.433(19)	-.178(13)	.925(4)
H(20B)	-.573(19)	-.102(13)	.949(4)
H(20C)	-.725(18)	-.174(13)	.917(4)
H(2')	-.019(16)	-.598(11)	.931(3)
H(3')	-.013(15)	-.460(11)	.889(3)
H(4'A)	.046(16)	-.594(12)	.839(4)
H(4'B)	.060(16)	-.657(11)	.870(3)
H(5'A)	-.211(17)	-.430(11)	.835(3)
H(5'B)	-.307(17)	-.603(12)	.850(3)
H(7')	-.237(18)	-.384(11)	.894(3)
H(8'A)	-.382(17)	-.360(11)	.965(3)
H(8'B)	-.279(17)	-.436(11)	.967(3)
H(9')	-.026(15)	-.317(10)	.985(3)
H(10')	.348(17)	-.456(12)	.898(3)
H(11'A)	.160(16)	-.431(11)	.815(3)
H(11'B)	.233(16)	-.352(12)	.838(3)
H(12'A)	.540(17)	-.359(12)	.839(3)
H(12'B)	.465(16)	-.474(11)	.811(3)
H(13')	.416(18)	-.245(12)	.786(4)
H(15'A)	.266(22)	-.476(16)	.755(4)

Table 3a. (Continued)

H(15'B)	.402(20)	-.465(13)	.700(4)
H(15'C)	.428(19)	-.490(15)	.747(4)
H(16'A)	.473(21)	-.241(14)	.716(5)
H(16'B)	.341(23)	-.278(14)	.701(4)
H(16'C)	.175(23)	-.253(15)	.720(5)
H(17'A)	.310(17)	-.631(12)	.842(4)
H(17'B)	.523(19)	-.601(13)	.861(3)
H(17'C)	.356(17)	-.667(12)	.878(4)
H(18'A)	.257(18)	-.632(12)	.951(3)
H(18'B)	.379(18)	-.572(13)	.915(3)
H(20'A)	-.157(17)	-.676(12)	.924(3)
H(20'B)	-.340(17)	-.572(12)	.948(3)
H(20'C)	-.430(18)	-.670(12)	.903(3)

Table 3b. Bond distances of dictyolactone. The standard deviation of the least significant figure of each distance is given in parentheses.

C(1) - C(2)	1.56(2)
C(1) - C(9)	1.32(2)
C(1) - C(19)	1.43(2)
C(2) - C(3)	1.61(1)
C(2) - C(18)	1.54(2)
C(3) - C(4)	1.57(2)
C(3) - C(10)	1.54(2)
C(4) - C(5)	1.55(2)
C(5) - C(6)	1.46(2)
C(6) - C(7)	1.36(2)
C(6) - C(20)	1.59(2)
C(7) - C(8)	1.51(2)
C(8) - C(9)	1.50(2)
C(10) - C(11)	1.62(2)
C(10) - C(17)	1.50(2)
C(11) - C(12)	1.52(2)
C(12) - C(13)	1.54(2)
C(13) - C(14)	1.30(2)
C(14) - C(15)	1.55(2)
C(14) - C(16)	1.49(2)
C(18) - O(21)	1.49(2)
C(19) - O(21)	1.33(2)
C(19) - O(22)	1.26(2)
C(1') - C(2')	1.56(2)
C(1') - C(9')	1.33(2)
C(1') - C(19')	1.43(2)
C(2') - C(3')	1.63(1)
C(2') - C(18')	1.56(2)
C(3') - C(4')	1.56(2)
C(3') - C(10')	1.53(2)
C(4') - C(5')	1.58(2)
C(5') - C(6')	1.43(2)
C(6') - C(7')	1.34(2)
C(6') - C(20')	1.54(2)
C(7') - C(8')	1.54(2)
C(8') - C(9')	1.51(2)
C(10') - C(11')	1.62(2)
C(10') - C(17')	1.52(2)
C(11') - C(12')	1.54(2)
C(12') - C(13')	1.55(2)
C(13') - C(14')	1.31(2)
C(14') - C(15')	1.46(2)
C(14') - C(16')	1.50(2)
C(18') - O(21')	1.48(2)
C(19') - O(21')	1.34(2)
C(19') - O(22')	1.24(2)

Table 3c. Bond angles of dictyolactone. The standard deviation of the least significant figure of each angle is given in parentheses.

C(2)	- C(1)	- C(9)	130.9(12)
C(2)	- C(1)	- C(19)	105.4(12)
C(9)	- C(1)	- C(19)	123.5(13)
C(1)	- C(2)	- C(3)	113.1(10)
C(1)	- C(2)	- C(18)	99.3(10)
C(3)	- C(2)	- C(18)	112.1(9)
C(2)	- C(3)	- C(4)	111.3(10)
C(2)	- C(3)	- C(10)	114.4(9)
C(4)	- C(3)	- C(10)	110.8(10)
C(3)	- C(4)	- C(5)	114.9(11)
C(4)	- C(5)	- C(6)	109.9(10)
C(5)	- C(6)	- C(7)	122.6(14)
C(5)	- C(6)	- C(20)	116.3(14)
C(7)	- C(6)	- C(20)	120.5(12)
C(6)	- C(7)	- C(8)	128.5(14)
C(7)	- C(8)	- C(9)	107.1(10)
C(1)	- C(9)	- C(8)	131.8(13)
C(3)	- C(10)	- C(11)	106.8(10)
C(3)	- C(10)	- C(17)	116.5(12)
C(11)	- C(10)	- C(17)	110.4(9)
C(10)	- C(11)	- C(12)	111.6(11)
C(11)	- C(12)	- C(13)	110.6(12)
C(12)	- C(13)	- C(14)	127.5(14)
C(13)	- C(14)	- C(15)	123.3(13)
C(13)	- C(14)	- C(16)	124.4(14)
C(15)	- C(14)	- C(16)	112.2(11)
C(2)	- C(18)	- O(21)	107.8(12)
C(1)	- C(19)	- O(21)	115.2(14)
C(1)	- C(19)	- O(22)	127.0(15)
O(21)	- C(19)	- O(22)	117.7(14)
C(18)	- O(21)	- C(19)	106.2(11)
C(2')	- C(1')	- C(9')	130.0(13)
C(2')	- C(1')	- C(19')	107.3(12)
C(9')	- C(1')	- C(19')	122.1(12)
C(1')	- C(2')	- C(3')	113.6(10)
C(1')	- C(2')	- C(18')	98.2(10)
C(3')	- C(2')	- C(18')	112.2(9)
C(2')	- C(3')	- C(4')	108.8(10)
C(2')	- C(3')	- C(10')	114.1(9)
C(4')	- C(3')	- C(10')	111.1(10)
C(3')	- C(4')	- C(5')	114.5(11)
C(4')	- C(5')	- C(6')	107.9(10)
C(5')	- C(6')	- C(7')	121.5(14)
C(5')	- C(6')	- C(20')	119.9(14)
C(7')	- C(6')	- C(20')	118.2(12)

Table 3c. (Continued)

C(6') - C(7') - C(8')	130.3(14)
C(7') - C(8') - C(9')	105.3(10)
C(1') - C(9') - C(8')	132.6(12)
C(3') - C(10') - C(11')	107.0(10)
C(3') - C(10') - C(17')	116.6(12)
C(11') - C(10') - C(17')	108.9(9)
C(10') - C(11') - C(12')	112.5(11)
C(11') - C(12') - C(13')	108.3(12)
C(12') - C(13') - C(14')	125.6(13)
C(13') - C(14') - C(15')	126.4(13)
C(13') - C(14') - C(16')	122.9(14)
C(15') - C(14') - C(16')	110.7(12)
C(2') - C(18') - O(21')	108.4(11)
C(1') - C(19') - O(21')	114.7(13)
C(1') - C(19') - O(22')	128.1(15)
O(21') - C(19') - O(22')	117.2(14)
C(18') - O(21') - C(19')	106.2(11)

Table 3d. Observed and calculated structure factor magnitudes for dictyolactone.

H = 0

K	L	FO	FC
0	2	136	143
0	4	12	15
0	6	100	100
0	8	34	32
0	10	210	209
0	12	131	129
0	14	65	63
0	16	35	31
0	18	53	53
0	20	20	19
0	22	46	49
0	24	56	58
0	26	10	9
0	28	32	40
0	32	7	8
0	34	34	37
0	38	5	0
0	40	17	17
1	1	12	12
1	2	5	3
1	3	4	4
1	4	7	7
1	5	11	11
1	6	9	9
1	7	8	8
1	8	3	3
1	9	9	9
1	10	11	10
1	12	7	6
1	14	7	6
1	15	14	12
1	16	17	16
1	17	21	22
1	22	9	8
1	23	8	9
1	24	5	7
1	26	8	10
1	28	5	7
1	31	8	9
1	34	8	9
1	38	7	4
2	1	79	78
2	2	141	132
2	3	138	132
2	4	200	189
2	5	228	217
2	6	76	72
2	7	221	210
2	8	24	18
2	9	82	76
2	10	147	134
2	11	86	75
2	12	64	60
2	13	164	153
2	14	104	97
2	15	57	53
2	16	38	39
2	17	101	94
2	18	19	19
2	19	38	34
2	20	30	29
2	21	12	17
2	22	45	38
2	23	55	58
2	24	32	32
2	25	13	14
2	26	22	21
2	27	25	25
2	28	13	10
2	29	39	36
2	30	25	26
2	31	15	8
2	32	8	10
2	33	13	15
2	34	6	8
2	35	15	16
2	38	7	5
3	1	11	11
3	2	13	13
3	3	8	7
3	4	5	7
3	5	7	6
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3	10	17	17
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3	14	17	17
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3	16	9	9
3	19	5	4
3	20	9	9
3	21	7	8
3	23	6	8
3	24	8	6
3	25	5	5
3	27	12	13
3	28	12	12
3	29	7	6
3	30	6	7
3	31	9	7
3	36	5	6
4	0	55	55
4	1	17	20
4	2	44	39
4	3	33	28
4	4	16	14
4	5	58	55
4	6	92	86
4	7	80	80
4	8	51	46
4	9	16	11
4	10	93	83
4	11	39	34
4	12	10	6
4	13	51	49
4	14	21	17
4	15	69	65
4	16	16	9
4	17	72	70
4	18	42	44
4	19	45	48
4	20	20	13
4	21	64	61
4	22	21	18
4	23	47	42
4	24	20	16
4	25	13	11
4	26	13	10
4	27	55	53
4	28	16	17
4	29	13	11
4	30	6	7
4	32	8	4
4	35	8	9
4	36	5	5
5	1	12	12
5	3	5	6
5	5	10	12
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5	14	5	6
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5	20	5	4
5	21	5	4
5	24	8	9
5	25	7	7
5	27	8	7
5	32	9	9
6	0	33	37
6	1	22	23
6	2	26	24
6	3	17	18
6	4	19	13
6	5	7	10
6	6	39	39
6	7	12	4
6	8	56	50
6	9	39	30
6	10	57	59
6	11	17	15
6	12	31	32
6	13	16	16
6	14	8	8
6	15	33	30
6	16	28	30
6	17	11	8
6	18	7	7
6	19	7	1
6	20	11	12
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6	25	22	23
6	26	8	1
6	27	21	19
6	28	11	5
6	29	5	7
6	30	8	10
6	33	6	4
6	35	7	7
7	3	8	8

Table 3d. (Continued)

4	25	11	11	6	8	12	13	8	1	16	17	0	5	6	5
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4	27	10	11	6	10	34	34	8	3	7	7	0	7	3	1
4	28	8	6	6	11	24	27	8	5	6	7	0	8	3	2
4	29	14	12	6	12	7	8	8	6	15	18	0	9	17	18
4	31	17	17	6	13	20	21	8	7	20	22	0	10	15	13
4	32	15	13	6	14	14	14	8	11	11	12	0	12	19	21
4	33	7	6	6	16	6	6	8	13	5	9	0	13	10	11
4	37	6	4	6	17	14	14	8	17	5	6	0	14	3	3
4	38	4	4	6	19	12	13	8	19	7	7	0	15	6	6
5	1	28	29	6	20	8	8	8	20	12	11	0	16	10	10
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5	3	38	41	6	22	9	9	8	22	5	4	0	18	16	16
5	4	5	3	6	24	8	7	8	27	7	6	0	19	6	7
5	5	27	28	6	25	6	5	8	29	4	2	0	20	8	7
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5	7	7	6	6	27	9	8	9	1	5	6	0	22	5	5
5	8	43	46	6	28	9	10	9	3	6	8	0	23	5	5
5	9	33	33	6	29	10	9	9	4	14	17	0	24	5	4
5	10	25	27	6	31	6	3	9	5	8	9	0	25	7	8
5	11	41	40	6	32	7	7	9	6	6	7	0	26	5	4
5	12	25	25	6	33	6	6	9	8	8	9	0	27	5	6
5	13	28	29	6	34	6	6	9	10	7	9	0	33	5	3
5	14	6	5	7	0	4	2	9	11	5	6	1	0	104	104
5	15	14	14	7	1	6	5	9	13	7	8	1	1	107	108
5	16	22	22	7	2	13	12	9	14	6	7	1	2	158	163
5	17	24	27	7	3	14	16	9	16	6	9	1	3	81	84
5	18	20	22	7	4	19	21	9	18	8	10	1	4	124	134
5	19	10	13	7	5	16	18	9	19	11	11	1	5	26	28
5	20	11	11	7	6	16	18	9	20	6	7	1	6	58	63
5	22	10	11	7	7	7	7	9	21	6	6	1	7	65	69
5	23	14	14	7	8	15	15	10	1	5	4	1	8	33	36
5	25	9	10	7	9	17	17	10	2	7	7	1	9	88	98
5	26	8	8	7	10	21	22	10	4	6	8	1	10	15	20
5	27	7	7	7	11	10	12	10	5	7	8	1	12	11	11
5	28	8	7	7	12	7	8	10	13	6	8	1	14	35	34
5	30	9	10	7	14	6	8	10	14	6	7	1	15	15	18
5	31	5	4	7	15	5	5	10	16	5	5	1	16	11	14
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5	33	5	3	7	19	10	9	11	4	5	5	1	18	31	29
5	35	9	9	7	20	6	7					1	19	56	56
6	1	24	25	7	21	12	13		H =	2		1	20	25	20
6	2	11	11	7	23	20	21	K	L	FO	FC	1	21	35	36
6	3	9	12	7	25	12	12	0	0	19	19	1	22	15	14
6	4	7	9	7	26	6	6	0	1	30	30	1	23	11	9
6	5	18	16	7	30	8	8	0	2	12	11	1	24	17	16
6	6	24	25	7	32	7	7	0	3	14	15	1	25	22	25
6	7	33	32	8	0	10	11	0	4	10	11	1	26	26	24

Table 3d. (Continued)

7	4	7	6
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7	12	10	11
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8	2	18	20
8	3	28	28
8	4	12	17
8	5	12	10
8	6	7	7
8	7	21	24
8	8	18	21
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8	12	12	9
8	13	10	9
8	14	10	10
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8	17	15	18
8	18	8	9
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10	4	5	6
10	6	18	24
10	8	9	12
10	9	8	5
10	12	13	15
10	17	5	2
10	19	6	5
10	20	8	7
10	21	6	8

H = 1

K	L	FO	FC
0	1	34	40
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0	4	62	67
0	6	25	30
0	7	53	61
0	8	88	97
0	9	99	107
0	10	17	17
0	11	31	35
0	12	22	22
0	13	14	15
0	14	18	15
0	15	26	26
0	16	15	14
0	18	14	16
0	19	23	26
0	20	23	24
0	21	8	9
0	22	6	6
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0	30	5	3
0	31	10	9
0	34	6	7
1	0	95	104
1	1	4	5
1	2	61	67
1	3	27	29
1	4	26	28
1	5	78	86
1	6	33	36
1	7	45	50
1	8	16	19
1	9	44	50
1	10	54	59
1	11	20	24
1	12	62	68
1	13	47	53
1	14	13	17
1	15	29	32
1	16	41	43
1	17	11	11
1	18	26	28
1	19	14	17
1	20	21	22
1	21	15	15
1	22	22	20
1	26	10	8
1	27	5	4
1	28	12	13
1	30	8	12
1	31	6	6
1	33	9	12
1	34	11	11
1	36	8	10
2	0	29	31
2	1	48	47
2	2	36	38
2	3	70	73
2	4	17	20
2	5	26	29
2	6	26	27
2	7	26	27
2	8	31	35
2	9	24	22
2	11	41	42
2	12	10	12
2	13	41	42
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2	15	34	37
2	16	34	34
2	17	12	14
2	18	4	2
2	19	19	18
2	20	10	9
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2	22	27	29
2	23	18	21
2	25	7	8
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2	27	7	7
2	28	9	7
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2	30	12	16
2	31	6	2
2	32	6	6
2	35	9	10
2	36	6	7
3	0	28	29
3	1	11	11
3	2	22	25
3	3	42	42
3	4	84	86
3	5	27	26
3	6	70	69
3	7	16	16
3	8	36	35
3	9	47	48
3	10	14	14
3	11	28	29
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3	14	15	16
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3	32	20	18
3	33	7	5
3	34	7	6
3	37	5	6
3	39	4	3
4	0	25	25
4	1	20	22
4	2	31	31
4	3	40	42
4	4	58	58
4	5	18	18
4	6	20	20
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4	8	25	26
4	9	18	15
4	10	15	17
4	12	14	16
4	13	33	30
4	14	45	43
4	15	17	16
4	16	17	20
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4	18	14	17
4	19	22	23
4	20	21	22
4	21	11	12
4	22	21	24
4	24	9	11

Table 3d. (Continued)

1	27	23	23	3	5	9	5	4	24	10	10	6	19	7	6
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1	29	6	6	3	7	26	30	4	26	9	9	6	21	6	7
1	30	16	14	3	8	34	34	4	27	9	10	6	22	5	6
1	31	8	6	3	9	29	28	4	28	10	10	6	23	5	4
1	32	14	16	3	10	19	20	4	29	8	8	6	25	7	7
1	33	15	13	3	11	18	19	4	30	5	5	7	0	34	36
1	35	8	6	3	12	43	42	4	34	6	5	7	1	5	4
1	36	6	5	3	13	22	18	5	0	9	10	7	2	9	10
1	37	6	5	3	14	64	64	5	1	21	16	7	3	16	18
1	38	6	6	3	15	16	19	5	2	9	11	7	4	12	12
1	39	10	10	3	16	21	22	5	3	44	42	7	5	18	19
2	0	9	9	3	17	25	24	5	4	5	5	7	6	23	22
2	1	10	10	3	18	20	19	5	5	41	43	7	7	10	6
2	2	5	5	3	19	25	25	5	6	23	21	7	8	12	12
2	3	11	10	3	20	31	30	5	7	14	15	7	9	13	13
2	4	3	8	3	21	29	28	5	8	11	8	7	10	11	12
2	5	15	17	3	22	27	26	5	9	22	21	7	11	10	12
2	6	14	14	3	23	17	20	5	10	27	25	7	12	12	14
2	8	7	8	3	24	16	14	5	11	10	9	7	13	9	12
2	9	11	12	3	25	31	32	5	12	16	18	7	14	17	18
2	10	9	8	3	26	19	18	5	13	23	22	7	15	10	10
2	11	7	6	3	27	15	17	5	15	9	8	7	16	10	9
2	12	5	6	3	28	19	18	5	16	29	29	7	18	13	13
2	13	5	3	3	29	19	19	5	17	29	28	7	19	16	14
2	15	5	5	3	30	11	9	5	18	32	36	7	20	7	7
2	16	6	5	3	31	17	15	5	19	27	25	7	22	14	11
2	17	10	10	3	32	7	6	5	20	19	18	7	25	11	9
2	18	4	4	3	34	11	10	5	21	18	16	7	27	9	6
2	19	9	7	3	35	5	5	5	23	6	7	7	28	10	11
2	20	4	6	3	36	16	14	5	24	17	16	7	30	6	4
2	21	8	9	3	37	8	6	5	25	25	26	7	31	6	4
2	22	13	12	4	0	4	4	5	26	18	18	8	1	5	5
2	23	6	7	4	1	9	10	5	27	12	11	8	3	5	5
2	24	13	13	4	2	6	6	5	29	6	7	9	0	21	18
2	25	10	9	4	3	6	5	5	30	13	12	9	1	7	9
2	26	7	8	4	4	7	6	5	31	7	8	9	2	11	10
2	28	9	8	4	5	4	3	5	34	8	4	9	3	7	5
2	29	6	7	4	7	6	5	5	36	6	6	9	4	6	6
2	30	8	7	4	9	12	12	6	0	6	7	9	5	5	7
2	31	7	6	4	10	7	8	6	2	10	9	9	6	10	10
2	32	8	9	4	11	13	11	6	3	4	3	9	7	12	14
2	36	6	5	4	12	4	5	6	4	4	4	9	8	9	9
3	0	3	2	4	16	10	9	6	6	6	7	9	10	14	14
3	1	49	51	4	19	11	11	6	8	7	8	9	13	7	8
3	2	46	47	4	20	9	9	6	14	8	10	9	16	5	5
3	3	26	26	4	21	15	14	6	15	5	5	9	21	7	9
3	4	38	38	4	22	10	11	6	17	5	7	9	24	5	2

Table 3d. (Continued)

10	3	6	5	1	6	36	36	2	22	22	22	4	6	17	16
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11	1	6	7	1	8	12	12	2	24	6	6	4	8	22	20
11	2	5	5	1	9	15	20	2	25	12	12	4	9	20	22
11	8	7	8	1	10	31	34	2	26	9	9	4	10	11	9
11	12	6	4	1	11	5	8	2	27	6	6	4	11	8	7
11	13	5	3	1	12	23	22	2	28	22	22	4	12	33	31
				1	13	19	20	2	29	18	20	4	13	17	17
	H =	3		1	14	22	21	2	30	20	21	4	14	8	7
K	L	FO	FC	1	15	16	16	2	31	19	18	4	15	13	13
0	1	28	29	1	16	16	19	2	32	14	12	4	16	20	21
0	2	94	93	1	18	11	11	2	33	7	7	4	17	6	3
0	3	4	5	1	19	6	8	2	34	9	9	4	18	27	26
0	4	60	61	1	20	7	6	3	0	27	27	4	19	5	4
0	6	7	9	1	21	12	13	3	1	20	22	4	20	8	8
0	7	59	66	1	23	12	12	3	2	22	22	4	21	15	15
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0	9	93	97	1	25	8	7	3	4	19	20	4	23	16	18
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0	11	21	19	1	27	6	8	3	6	32	32	4	25	17	18
0	12	9	12	1	28	6	7	3	8	11	12	4	26	5	7
0	13	12	12	1	30	15	15	3	9	12	13	4	28	9	10
0	14	42	42	1	31	12	12	3	10	14	15	4	29	21	19
0	15	11	12	1	32	9	12	3	11	10	11	4	30	20	18
0	16	5	5	1	33	7	8	3	12	11	11	4	31	13	12
0	17	6	1	1	37	5	6	3	13	22	22	4	32	10	8
0	18	27	27	2	0	13	14	3	14	11	11	4	33	8	9
0	20	18	23	2	1	36	35	3	15	24	21	4	34	5	6
0	21	14	9	2	2	48	51	3	16	17	15	5	0	5	5
0	22	9	10	2	3	30	32	3	17	13	14	5	1	16	14
0	23	10	9	2	4	58	61	3	18	7	7	5	2	8	5
0	24	8	9	2	5	18	16	3	19	6	7	5	3	16	13
0	25	5	4	2	6	25	25	3	22	10	11	5	4	26	26
0	27	6	8	2	7	56	58	3	23	18	17	5	5	13	12
0	28	18	19	2	8	25	26	3	24	15	15	5	6	10	11
0	29	20	22	2	9	32	33	3	25	10	10	5	7	17	17
0	30	21	21	2	10	15	14	3	26	12	13	5	8	20	21
0	32	8	8	2	11	11	10	3	27	13	14	5	9	9	9
0	33	13	12	2	12	22	26	3	28	16	17	5	13	9	8
0	36	12	12	2	13	44	42	3	31	11	12	5	14	16	15
0	37	6	8	2	14	12	12	3	32	8	8	5	15	10	12
0	38	9	9	2	15	10	11	3	33	7	8	5	16	5	5
1	0	10	10	2	16	27	26	3	34	8	6	5	17	7	5
1	1	51	52	2	17	23	22	3	36	6	4	5	18	11	13
1	2	30	32	2	18	12	15	4	1	43	40	5	19	5	7
1	3	6	6	2	19	26	26	4	2	26	26	5	20	12	15
1	4	23	23	2	20	11	10	4	3	53	53	5	21	7	8
1	5	32	36	2	21	24	25	4	4	38	37	5	22	17	16

Table 3d. (Continued)

5	23	6	5	7	18	10	11	0	1	42	40	2	1	70	67
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5	25	11	10	7	21	6	6	0	3	19	18	2	3	22	23
5	27	11	10	7	22	10	11	0	4	55	56	2	4	33	32
5	28	14	13	7	23	9	9	0	5	59	57	2	5	19	20
5	30	6	5	7	26	6	4	0	6	39	34	2	6	15	15
5	31	11	10	8	0	13	15	0	7	29	27	2	7	35	35
5	33	8	9	8	2	8	9	0	8	10	8	2	8	23	17
5	34	6	4	8	3	7	7	0	9	13	12	2	10	19	21
6	0	27	26	8	4	10	12	0	10	6	6	2	11	43	40
6	1	25	23	8	5	11	9	0	11	53	52	2	12	11	10
6	3	10	9	8	6	12	14	0	13	5	5	2	13	14	17
6	4	12	15	8	7	10	11	0	14	7	7	2	14	10	9
6	5	5	4	8	10	6	6	0	15	20	21	2	15	29	28
6	6	9	6	8	11	7	9	0	16	18	16	2	16	19	19
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6	8	14	16	8	13	8	8	0	19	18	16	2	18	7	9
6	9	19	19	8	15	8	9	0	21	17	19	2	19	9	9
6	11	30	30	8	16	8	8	0	22	19	20	2	20	12	12
6	13	13	16	8	17	8	9	0	24	8	8	2	22	23	20
6	14	9	8	8	18	14	15	0	26	17	16	2	24	11	13
6	15	7	7	8	19	9	9	0	28	38	38	2	25	7	9
6	16	6	5	8	20	7	8	0	30	6	9	2	26	27	29
6	17	18	19	8	21	13	13	0	33	22	21	2	27	12	13
6	19	6	7	8	22	10	9	0	34	7	6	2	28	18	19
6	20	5	8	8	28	8	7	1	1	15	14	2	29	8	7
6	21	14	15	9	1	9	10	1	2	21	20	2	31	6	7
6	22	12	12	9	2	5	4	1	3	17	18	2	32	11	11
6	23	16	18	9	3	8	10	1	4	15	14	2	33	9	9
6	24	18	18	9	5	7	8	1	5	12	12	2	34	9	9
6	25	15	14	9	6	6	6	1	6	15	15	3	0	9	7
6	26	9	9	9	7	6	8	1	7	7	5	3	1	10	11
6	27	7	7	9	8	6	8	1	8	7	7	3	2	18	17
6	28	8	6	9	9	5	5	1	9	6	5	3	3	10	9
6	30	5	3	9	16	7	7	1	10	9	11	3	4	9	11
6	33	5	3	9	19	5	2	1	11	9	9	3	5	10	11
7	2	7	8	10	0	9	8	1	12	9	10	3	6	11	12
7	3	14	14	10	1	7	7	1	14	10	13	3	7	10	12
7	5	8	8	10	2	6	7	1	15	8	9	3	10	4	3
7	6	6	4	10	4	9	10	1	16	5	3	3	13	5	6
7	8	10	12	10	11	7	9	1	18	6	4	3	14	5	4
7	10	12	14	10	12	8	10	1	19	4	3	3	15	4	5
7	11	8	9	10	15	6	5	1	22	6	5	3	19	16	15
7	12	7	7	10	17	5	4	1	25	10	10	3	20	6	5
7	13	7	8					1	26	9	10	3	21	8	8
7	14	7	7		H =	4		1	28	13	12	3	22	9	8
7	16	6	6	K	L	FO	FC	1	29	8	7	3	23	5	4
7	17	6	6	0	0	55	51	2	0	28	27	3	24	8	8

Table 3d. (Continued)

3	25	8	8	5	24	5	5	8	20	9	9	1	22	5	8
3	26	10	9	6	0	33	31	8	21	6	7	1	23	8	9
3	30	5	5	6	2	5	1	8	22	5	5	1	24	7	7
3	31	5	5	6	3	8	6	9	6	5	4	1	25	10	10
3	33	6	5	6	4	5	4	9	9	5	3	1	26	21	21
4	0	30	27	6	6	23	21	10	1	6	5	1	27	6	7
4	1	41	39	6	7	9	8	10	3	6	6	1	28	10	9
4	2	19	20	6	8	28	25	10	4	8	9	1	29	8	10
4	3	14	16	6	9	11	10	10	6	5	5	1	32	7	6
4	4	7	3	6	10	22	21	10	8	5	4	2	0	6	7
4	6	27	28	6	11	10	11	10	13	5	6	2	2	7	6
4	7	12	13	6	12	10	10	10	16	5	5	2	3	14	15
4	8	15	16	6	13	14	15					2	5	16	15
4	9	21	21	6	14	18	16		H =	5		2	6	4	3
4	10	21	19	6	15	14	12	K	L	FO	FC	2	7	17	18
4	11	26	27	6	16	15	15	0	1	5	3	2	9	8	9
4	12	10	12	6	17	23	23	0	3	22	22	2	10	7	8
4	13	26	26	6	18	14	15	0	5	11	11	2	11	6	7
4	15	20	18	6	19	12	10	0	6	10	10	2	12	12	14
4	16	22	21	6	20	25	26	0	7	8	9	2	13	5	5
4	18	28	27	6	21	7	7	0	9	15	15	2	14	6	5
4	19	15	15	6	22	11	11	0	12	9	11	2	18	6	7
4	20	7	7	6	23	8	7	0	18	8	10	2	22	7	8
4	21	8	10	6	24	9	11	0	20	12	14	2	23	7	8
4	22	7	6	6	27	7	6	0	21	5	6	2	28	6	6
4	23	25	25	6	30	4	3	0	23	7	7	2	32	7	7
4	25	9	9	6	31	5	5	0	27	6	6	3	0	38	35
4	26	24	23	7	6	6	5	0	31	5	4	3	1	10	9
4	27	16	13	7	13	7	8	1	0	20	20	3	2	16	14
4	28	9	9	7	15	8	9	1	1	20	17	3	3	21	20
4	29	16	14	7	16	5	4	1	2	44	42	3	4	29	28
4	33	7	8	8	0	20	16	1	3	8	7	3	5	15	13
5	1	9	8	8	1	13	14	1	4	12	15	3	6	30	30
5	2	6	8	8	2	11	9	1	6	41	42	3	7	5	4
5	4	5	5	8	3	11	12	1	7	4	4	3	8	8	9
5	5	8	8	8	5	9	9	1	8	19	19	3	9	21	20
5	6	7	8	8	6	7	7	1	9	17	19	3	10	16	16
5	8	5	6	8	8	9	9	1	10	13	14	3	11	22	23
5	11	7	7	8	9	16	17	1	11	9	8	3	12	6	5
5	12	7	7	8	10	6	7	1	13	14	16	3	13	17	18
5	15	6	7	8	11	8	9	1	14	14	12	3	14	16	15
5	16	7	9	8	13	13	12	1	15	13	12	3	15	12	13
5	17	13	14	8	14	5	5	1	16	22	20	3	16	7	3
5	18	8	7	8	15	6	7	1	17	28	32	3	17	16	17
5	19	5	4	8	16	6	4	1	18	5	3	3	18	7	9
5	20	6	5	8	17	7	6	1	19	13	14	3	19	9	12
5	22	12	12	8	18	5	3	1	20	6	7	3	21	10	12
5	23	5	4	8	19	8	9	1	21	19	21	3	22	7	6

Table 3d. (Continued)

3	24	6	9	6	18	8	8	1	8	19	15	4	0	11	11
3	25	12	12	6	22	5	5	1	10	18	19	4	2	7	6
3	27	8	8	7	0	12	11	1	11	11	12	4	3	14	15
3	28	11	9	7	2	9	10	1	12	16	14	4	4	6	5
3	32	7	7	7	3	9	10	1	13	10	10	4	5	15	14
4	0	15	14	7	5	16	15	1	14	8	7	4	6	7	4
4	2	12	12	7	6	5	4	1	15	5	3	4	8	7	6
4	3	8	8	7	7	11	10	1	16	17	19	4	9	11	11
4	5	5	3	7	8	6	2	1	17	7	9	4	10	5	4
4	6	9	7	7	9	15	14	1	19	17	20	4	12	6	7
4	7	5	7	7	11	5	4	1	20	13	13	4	13	7	7
4	8	6	6	7	12	8	10	1	23	7	9	4	15	11	10
4	10	11	13	7	13	5	5	1	26	9	8	4	16	6	6
4	11	6	5	7	15	8	6	1	28	5	6	4	18	5	3
4	12	14	14	7	17	5	3	1	29	6	8	4	20	5	5
4	18	7	8	7	19	11	10	2	0	14	14	4	22	5	4
4	20	6	5	7	21	9	7	2	1	7	9	5	0	13	13
4	24	5	3	7	22	7	6	2	2	16	15	5	1	8	8
4	29	6	5	8	1	7	7	2	4	7	10	5	2	13	13
5	0	14	14	8	3	6	3	2	5	15	16	5	3	13	12
5	1	17	17	8	4	5	4	2	7	5	5	5	4	8	8
5	3	7	7	8	6	7	5	2	8	11	9	5	6	26	23
5	4	19	21	8	9	6	5	2	10	8	4	5	7	8	7
5	5	16	17	9	2	6	7	2	17	5	5	5	8	16	15
5	6	5	6	9	3	8	6	2	20	8	8	5	9	6	7
5	7	15	14	9	7	6	7	2	26	6	6	5	10	13	13
5	9	16	18	9	8	5	5	3	1	20	20	5	12	6	5
5	10	9	9	9	9	9	7	3	2	18	18	5	13	11	9
5	11	8	8	9	10	5	2	3	3	21	18	5	14	6	5
5	13	9	8	9	12	5	5	3	4	10	9	5	16	20	18
5	14	15	14					3	5	5	4	5	17	6	6
5	15	12	13		H =	6		3	6	28	25	5	18	14	13
5	16	9	9	K	L	FO	FC	3	7	20	22	5	20	9	6
5	19	18	19	0	1	24	24	3	8	17	15	5	23	6	8
5	20	9	9	0	4	12	13	3	9	14	15	5	24	5	3
5	21	11	11	0	6	6	5	3	10	13	15	5	25	7	5
5	25	6	6	0	7	16	15	3	11	11	10	6	1	6	6
5	28	6	4	0	11	7	6	3	12	11	13	6	2	5	6
5	29	5	5	0	15	8	8	3	14	10	8	6	3	9	8
6	0	6	5	0	19	5	4	3	15	7	4	6	7	6	5
6	2	6	7	1	0	13	12	3	16	8	4	6	9	9	9
6	3	6	6	1	1	21	19	3	17	13	12	6	12	6	7
6	4	6	6	1	2	29	32	3	18	6	7	6	13	9	7
6	5	6	7	1	3	14	15	3	19	13	12	6	15	8	7
6	6	10	10	1	4	30	28	3	20	6	7	6	23	4	4
6	12	7	7	1	5	24	27	3	21	7	8	7	0	6	6
6	15	7	7	1	6	17	14	3	23	17	17	7	1	16	14
6	16	8	7	1	7	11	13	3	27	5	4	7	4	9	7

Table 3d. (Continued)

K	L	FO	FC
7	6	14	12
7	9	7	7
7	10	5	7
7	11	10	11
7	13	10	9
7	16	6	5
7	18	8	7
7	20	5	4
8	4	6	3
9	1	11	11
9	8	4	4
9	10	5	4

H = 7

K	L	FO	FC
0	1	14	14
0	2	5	5
0	3	14	12
0	5	22	24
0	7	13	14
0	8	14	12
0	9	6	4
0	10	13	14
0	11	10	11
0	13	9	7
0	17	23	23
0	19	25	25
0	20	8	7
0	21	9	10
0	24	9	7
0	25	4	5
1	2	5	5
1	5	5	2
2	0	11	13
2	2	29	28
2	3	5	6
2	5	21	20
2	6	12	11
2	7	10	9
2	8	10	10
2	10	12	13
2	11	8	4
2	12	20	19
2	13	9	9
2	14	9	8
2	15	8	7
2	17	14	12
2	18	6	6
2	19	14	15
2	20	6	5
2	21	5	5
2	22	10	9
2	24	10	10
3	5	7	5
3	8	5	3
4	0	21	19
4	1	12	10
4	2	17	15
4	3	9	7
4	4	11	11
4	5	5	2
4	6	8	7
4	8	8	7
4	9	10	7
4	10	13	14
4	12	18	17
4	13	10	8
4	14	6	4
4	15	7	6
4	18	7	5
4	19	8	7
4	20	8	7
4	22	7	7
5	0	5	5
5	18	5	1
6	1	9	7
6	3	6	7
6	5	8	10
6	7	7	4
6	8	7	6
6	10	6	6
6	11	6	6
6	12	5	4
6	16	5	5

H = 8

K	L	FO	FC
0	0	17	15
0	1	12	10
0	3	7	5
0	4	7	6
0	5	7	7
0	6	10	10
0	8	7	6
0	12	7	6
0	17	5	4
1	3	8	7
1	4	7	7
1	7	6	6
1	12	6	4
1	13	4	3
2	0	7	8
2	1	5	6
2	2	9	6
2	4	11	9
2	6	8	6
2	7	8	5
2	8	5	4
2	10	5	6
2	15	6	4
2	17	4	4
3	2	6	2
3	3	5	4
3	7	5	2
3	9	6	6
3	12	6	4
3	13	5	4
3	15	4	3
4	5	7	5
4	6	6	4
4	7	5	2
4	10	5	5
5	4	4	2
5	6	4	2

Table 3e. Dihedral angles for the nine-membered rings of both molecules of dictyolactone (°).

	Molecule 1	Molecule 2 (primed numbers)
C(1) - C(2) - C(3) - C(4)	-132	-133
C(1) - C(2) - C(3) - C(10)	102	103
C(2) - C(3) - C(4) - C(5)	84	86
C(3) - C(4) - C(5) - C(6)	- 52	- 56
C(4) - C(5) - C(6) - C(7)	91	92
C(4) - C(5) - C(6) - C(20)	- 81	- 80
C(5) - C(6) - C(7) - C(8)	-154	-158
C(6) - C(7) - C(8) - C(9)	97	98
C(7) - C(8) - C(9) - C(1)	- 38	- 35
C(8) - C(9) - C(1) - C(2)	- 6	- 7
C(8) - C(9) - C(1) - C(19)	180	-177
C(9) - C(1) - C(2) - C(3)	87	88
C(9) - C(1) - C(2) - C(18)	-154	-154

STUDIES OF MARINE ECOLOGY

Symbiosis and Antibiosis

The success of an organism in the marine environment depends on its ability to compete successfully for nutrients and use them efficiently, dispose of its wastes, and defend itself against predators. One or more of these abilities may be enhanced by a symbiotic association with another organism. There is some confusion in the literature about the meaning of the term symbiosis, but its original definition describes all cases of heterospecific organisms living together (28). According to this definition a symbiotic association may be obligatory or facultative and may benefit one or both of its members. Common types of symbiosis include parasitism, where cohabitation is at the expense of the host, commensalism, where the host is unaffected by the relationship, and mutualism, where both host and symbiont benefit from the relationship (28). Every major type of symbiosis is represented in the marine environment and specific examples are often quite bizarre (29). Of particular importance for the study of natural products are those cases where the association is very intimate and involves some exchange of products, for there is a possibility that transferred material includes secondary metabolites. When an interesting natural product is isolated from the host of such a relationship the question of its origin is raised. If it turns out the symbiont was involved in its synthesis one wonders if and how the metabolite benefits the host.

Antibiosis refers to that type of interaction where one organism produces special products harmful to others (30). The activity of the products is usually selective; they are harmful only to certain forms of life. Antibiosis is an important part of the ecology of the marine environment. Where space or nutrients are scarce, organisms which produce substances that inhibit the growth of competitors are at an advantage. Many immobile or slow-moving marine organisms with exposed bodies depend on a chemical defense system for survival. Animals which do not have the ability to manufacture the chemicals necessary for their defense often appropriate them from their prey. Much research in marine natural products chemistry involves the isolation and characterization of the specific chemicals responsible for the defense of an organism. Examination of the defensive secretions of marine organisms has usually led to the discovery of toxic secondary metabolites.

Metabolites from Opisthobranch Molluscs

Dolabelladiene

Background Opisthobranch molluscs are soft-bodied shell-less animals with no apparent mechanical means of defense but a reputation for being very toxic (31). Research has shown that the unusual natural products found in these organisms are often related to the opisthobranchs' diet. One particular type of opisthobranch mollusc, the sea hare, has the ability to sequester undegraded metabolites from its food source in its digestive gland. This ability is well-documented and may contribute to the chemical defense of the sea hare since many of the stored metabolites are toxic (3, 32, 33, 34).

The sea hare *Aplysia kurodai* was found to contain several bromo-compounds (35). Extractions of the dried sea hares gave the three new compounds aplysin, debromoaplysin and aplysinol (36). *Aplysia kurodai* was known to feed on red algae of the *Laurencia* genus. Isolation from the red alga *Laurencia intermedia* of laurinterol and debromolaurinterol, two compounds easily converted to aplysin and debromoaplysin in an *in vitro* experiment, suggested the new Aplysin metabolites may have actually originated in the sea hare's food source (34, 37). This theory obtained further support when methanol extracts of *Laurencia okamurai* yielded aplysin, debromoaplysin and aplysinol as well as laurinterol and debromolaurinterol (38).

More recently the two brominated diterpenes aplysin-20 and isoaplysin-20 were isolated from *Aplysia kurodai* (39, 40). Since the two compounds did not consistently occur in the sea hare it was suspected they were diet dependent. An examination of the red algae on which the sea hares fed led to the isolation of an isomer of aplysin-20, probably its precursor (41).

Kato and Scheuer succeeded in isolating aplysiatoxin and debromoaplysiatoxin, two components of a toxic fluid from the digestive gland of the sea hare *Stylocheilus longicauda* (42). When sea hares of this species were observed eating the blue-green alga *Lyngbya gracilis* it too was examined and debromoaplysiatoxin was isolated from its extracts (43). In large doses debromoaplysiatoxin and aplysiatoxin are lethal for mice and in smaller doses debromoaplysiatoxin inhibits P-388 lymphocytic mouse leukemia (43).

The *Laurencia* metabolites pacifenol, johnstonol and pacifidiene as well as polyhalogenated monoterpenes from *Plocamium coccineum* and *Plocamium cartilagineum* have been isolated from the digestive glands of *Aplysia* species (33, 44). On the other hand, the digestive glands contained none of the lipids normally associated with the sea hares' diet and no degraded algal metabolites (33). In an experiment, starved sea hares were fed only the red alga *Laurencia pacifica*. Later, *Laurencia* metabolites were found in their digestive glands but no *Plocamium* metabolites (33). Similarly, sea hares fed only *Plocamium coccineum* had only *Plocamium* metabolites in their digestive glands.

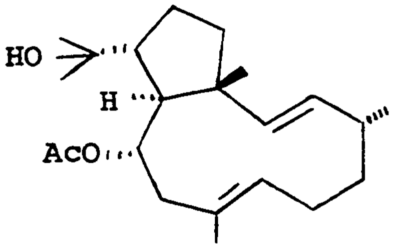
When acetone extracts of the digestive glands of the sea hare *Dolabella californica* were chromatographed fourteen distinct diterpenes were isolated (32). In view of the evidence presented above these diterpenes were presumed to be of dietary origin, probably algal metabolites. Unfortunately the feeding preferences of this nocturnal opisthobranch are not known. Spectral information indicated the compounds were structurally similar alcohols and their corresponding acetates. An examination of the ^{1}H NMR and ^{13}C NMR spectra of dolabelladiene, one of the monoacetate diterpenes, yielded some structural information but the data could not be reconciled to any of the known diterpene skeletons.

Experimental Crystallization of dolabelladiene from hexane gave large, clear parallelepipeds with orthorhombic symmetry. A density of 1.08 g/cc was calculated for four molecules of $C_{22}H_{36}O_3$ in the unit cell. Accurate cell contants were determined: $\underset{\sim}{a}$ = 8.778(1)Å, $\underset{\sim}{b}$ = 9.470(1)Å, and $\underset{\sim}{c}$ =

25.785(2)Å, and from systematic extinctions the space group was identified as $P2_12_12_1$. Data were measured using a minimum scan speed of 1°/minute. One octant of data with $2\theta \leq 114.1°$ (CuKα) was measured and after corrections for Lorentz, polarization and background effects 1540 reflections, 90.4% of the data, were considered observed. Three check reflections measured after every 50 data points showed negligible decomposition of the crystal.

The direct methods program MULTAN was chosen to directly phase the largest 150 Es for the structure. The best set of phases among 64 possible solutions was used to calculate an E map. A 19 atom fragment was chosen from the map and a subsequent F_o synthesis revealed the remaining atoms. Anisotropic least-squares refinement of the heavy atoms and least-squares refinement of theoretical positions and isotropic temperature factors of all 36 hydrogens converged to a conventional R-factor of .033 for the observed reflections.

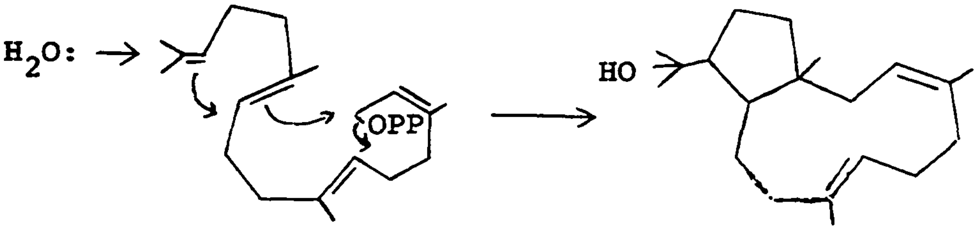
Results The unique carbon skeleton of dolabelladiene has a 5- and an 11-membered ring with a trans ring junction. There are trans double bonds at C(2) and C(7) in the large ring. A computer generated drawing, figure 4, shows the conformation of the molecule. The absolute stereochemistry was not defined by the experiment. All substituents except the bridgehead methyl have the α configuration. Bond distances and angles include no irregular values and are listed in tables 4b and 4c, respectively. Fractional coordinates for all of the atoms are compiled in table 4a. For a table of structure factor magnitudes refer to the published communication (45).



dolabelladiene

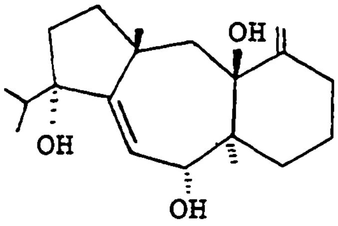
Discussion The remaining 13 metabolites from D. californica all had the same skeleton as dolabelladiene (32). Their structures were determined by spectral analysis, chemical transformations and comparison to dolabelladiene. D. californica's food source has not yet been discovered so it has been impossible to confirm the suspicion that these compounds as well as dolabelladiene are algal metabolites.

The biosynthetic scheme proposed for this new class of diterpenes involves a concerted cyclization of geranylgeraniol pyrophosphate (45). Cis,trans-farnesyl pyrophosphate cyclizes in a somewhat similar manner to give an 11-membered ring intermediate which leads into many classes of sesquiterpenes (46).



Proposed biosynthesis of dolabellane skeleton

Two other Dolabella metabolites were isolated from the cytotoxic extracts of D. auricularia (31). The structure of dolatriol was determined by X-ray diffraction. Its novel tricyclic skeleton is actually very similar to that of dolabelladiene and could be derived from the latter by transannular cyclization of the 11-membered ring. The other metabolite isolated was the acetate of dolatriol.



dolatriol

Figure 4. A computer generated perspective drawing of dolabelladiene with hydrogens omitted for clarity.

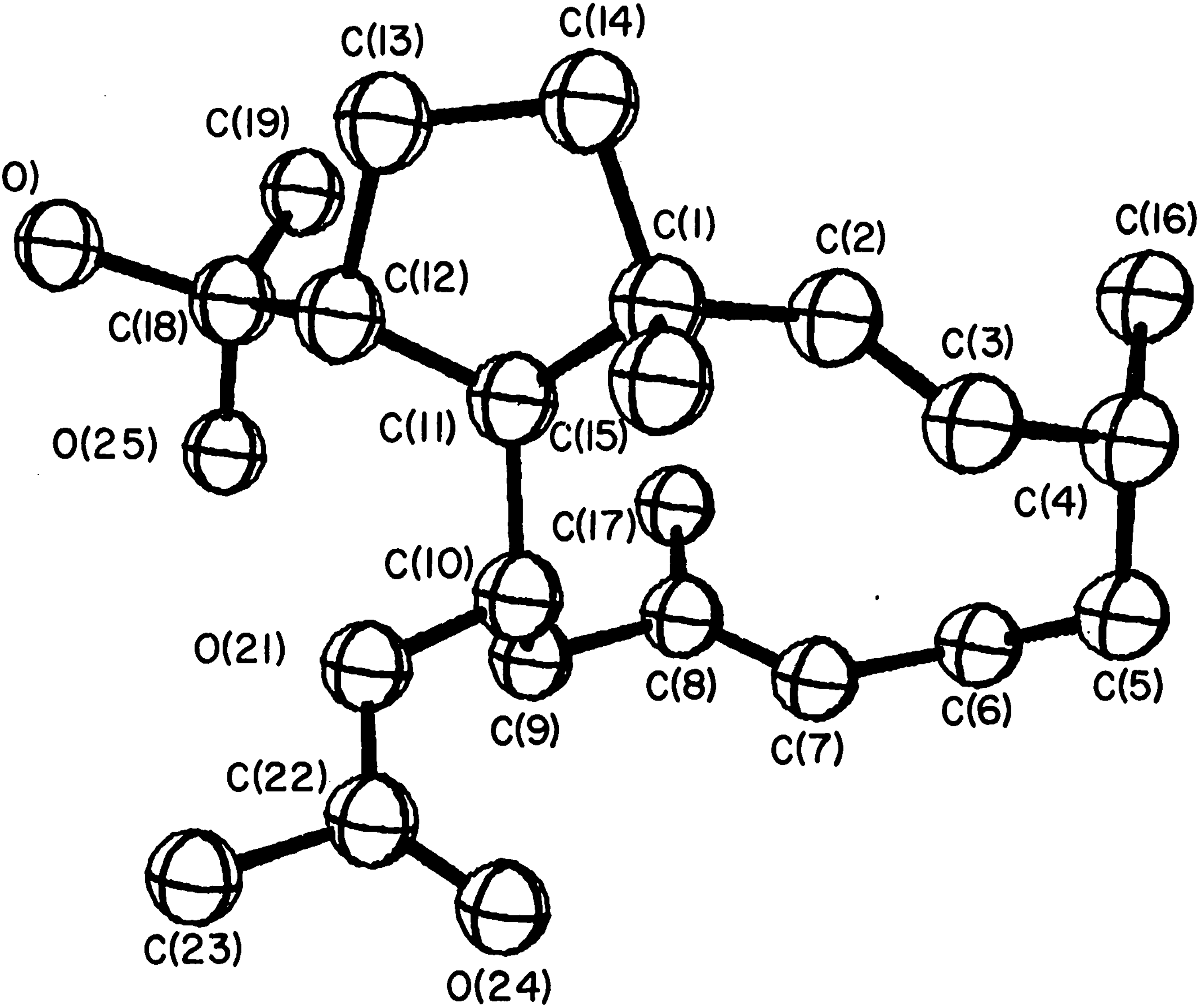

C(13)
C(14)
C(19)
C(20)
C(1)
C(2)
C(16)
C(12)
C(18)
C(3)
O(25)
C(11)
C(15)
C(4)
C(17)
C(10)
O(21)
C(8)
C(9)
C(7)
C(6)
C(5)
C(22)
C(23)
O(24)

Table 4a. Fractional coordinates for the nonhydrogen atoms of 10-acetoxy-18-hydroxy-2,7-dolabelladiene. Standard deviations of the least significant figures are given in parentheses. The numbering scheme refers to figure 4.

C(1)	-.1300(2)	.4865{2)	.0814(1)
C(2)	-.2797(3)	.5629(3)	.0771(1)
C(3)	-.3249(3)	.6781(3)	.1020(1)
C(4)	-.4795(3)	.7467(3)	.1001(1)
C(5)	-.5612(3)	.7421(3)	.1529(1)
C(6)	-.6127(3)	.5975(4)	.1718(1)
C(7)	-.4859(3)	.5045(3)	.1901(1)
C(8)	-.4540(3)	.3722(3)	.1773(1)
C(9)	-.3095(3)	.3046(3)	.1966(1)
C(10)	-.1695(3)	.3731(2)	.1723(1)
C(11)	-.1505(2)	.3467(2)	.1132(1)
C(12)	-.0186(3)	.2492(2)	.0957(1)
C(13)	.0323(3)	.3079(3)	.0421(1)
C(14)	-.0807(3)	.4234(3)	.0287(1)
C(15)	-.0029(3)	.5782(3)	.1030(1)
C(16)	-.5798(3)	.6944(3)	.0557(1)
C(17)	-.5516(4)	.2860(4)	.1421(1)
C(18)	-.0574(3)	.0899(2)	.0945(1)
C(19)	-.1787(4)	.0521(3)	.0552(1)
C(20)	.0877(3)	.0051(3)	.0851(1)
O(21)	-.0319(2)	.3231(2)	.1983(1)
C(22)	.0169(3)	.3895(3)	.2406(1)
C(23)	.1609(3)	.3269(3)	.2607(1)
O(24)	-.0498(3)	.4875(2)	.2598(1)
O(25)	-.1220(2)	.0489(1)	.1433(1)

Table 4b. Bond distances of 10-acetoxy-18-hydroxy-2,7-dolabelladiene. Standard deviations of the least significant figures are given in parentheses.

C(1) - C(2)	1.504(3)
C(1) - C(11)	1.569(3)
C(1) - C(14)	1.545(3)
C(1) - C(15)	1.520(3)
C(2) - C(3)	1.325(3)
C(3) - C(4)	1.506(4)
C(4) - C(5)	1.540(4)
C(4) - C(16)	1.526(4)
C(5) - C(6)	1.521(5)
C(6) - C(7)	1.496(4)
C(7) - C(8)	1.325(4)
C(8) - C(9)	1.505(4)
C(8) - C(17)	1.492(4)
C(9) - C(10)	1.524(4)
C(10) - C(11)	1.553(3)
C(10) - O(21)	1.461(3)
C(11) - C(12)	1.547(3)
C(12) - C(13)	1.557(3)
C(12) - C(18)	1.547(3)
C(13) - C(14)	1.517(4)
C(18) - C(19)	1.513(4)
C(18) - C(20)	1.525(4)
C(18) - O(25)	1.434(3)
O(21) - C(22)	1.329(3)
C(22) - C(23)	1.489(4)
C(22) - O(24)	1.204(3)

Table 4c. Bond angles of 10-acetoxy-18-hydroxy-2,7-dolabelladiene. The standard deviation of the least significant figure of each angle is given in parentheses.

C(2) - C(1) - C(11)	110.1(2)
C(2) - C(1) - C(14)	111.5(2)
C(2) - C(1) - C(15)	113.1(2)
C(11) - C(1) - C(14)	99.5(2)
C(11) - C(1) - C(15)	112.0(2)
C(14) - C(1) - C(15)	109.7(2)
C(1) - C(2) - C(3)	128.5(2)
C(2) - C(3) - C(4)	127.5(2)
C(3) - C(4) - C(5)	112.3(2)
C(3) - C(4) - C(16)	113.9(2)
C(5) - C(4) - C(16)	112.7(2)
C(4) - C(5) - C(6)	116.5(2)
C(5) - C(6) - C(7)	114.2(2)
C(6) - C(7) - C(8)	129.5(2)
C(7) - C(8) - C(9)	119.9(2)
C(7) - C(8) - C(17)	123.1(3)
C(9) - C(8) - C(17)	116.9(3)
C(8) - C(9) - C(10)	111.3(2)
C(9) - C(10) - C(11)	115.0(2)
C(9) - C(10) - O(21)	109.8(1)
C(11) - C(10) - O(21)	108.0(2)
C(10) - C(11) - C(12)	117.5(2)
C(10) - C(11) - C(1)	112.9(2)
C(1) - C(11) - C(12)	105.4(1)
C(11) - C(12) - C(13)	105.1(2)
C(11) - C(12) - C(18)	115.0(2)
C(13) - C(12) - C(18)	113.1(2)
C(12) - C(13) - C(14)	105.7(2)
C(13) - C(14) - C(1)	105.3(2)
C(12) - C(18) - C(19)	113.5(2)
C(12) - C(18) - C(20)	109.4(2)
C(12) - C(18) - O(25)	109.4(2)
C(19) - C(18) - C(20)	111.0(2)
C(19) - C(18) - O(25)	104.2(2)
C(20) - C(18) - O(25)	109.0(2)
C(10) - O(21) - C(22)	119.3(2)
O(21) - C(22) - C(23)	111.8(2)
O(21) - C(22) - O(24)	123.0(2)
C(23) - C(22) - O(24)	125.2(2)

9-isocyanopupukeanane and 2-isocyanopupukeanane

Background Another opisthobranch mollusc, the nudibranch, has shown an ability to use metabolites from its food for its own defense. The nudibranch *Phyllidia varicosa* secretes a potent toxin which protects it from fish and crustaceans. Small quantities of the toxin were originally isolated from the mucus secretion of the nudibranch and characterized as a new isocyanide (47). Later *P. varicosa* was discovered feeding on a sponge, a *Hymeniacidon* species, and extraction of the sponge yielded large quantities of the toxic isocyanide. A series of chemical transformations showed the isocyanide had a novel carbon skeleton so a crystal structure analysis of the crystalline phenylthiourea derivative of the compound was undertaken.

Experimental for 9-isocyanopupukeanane Crystals of the isonitrile derivative were thin plates with monoclinic symmetry and accurate cell constants of $\mathbf{a}$ = 13.837(3)Å, $\mathbf{b}$ = 9.989(2)Å, $\mathbf{c}$ = 16.808(3)Å and β = 110.27(1)°. The calculated density for four molecules $C_{23}H_{34}N_2S$ in the unit cell was 1.13 g/cm^3. Systematic extinctions in the data indicated space group $P2_1$ and, therefore, two molecules in the asymmetric unit. Intensities of all hkl and $hk\bar{l}$ reflections with $2\theta \leq$

114.1° (CuKα) were measured with a minimum scan rate of 1°/minute. The intensities of three periodically measured standard reflections did not change significantly during data collection. The recorded intensities were corrected for Lorentz, polarization and background effects and 1709 of the 3133 unique reflections (55%) were judged observed.

MULTAN was used to phase the 300 highest Es for the structure and both sulfur positions were obtained from an E map of the best phase set. A series of Fourier syntheses served to locate the remaining nonhydrogen atoms in the structure. Theoretical positions for the hydrogen atoms were calculated and the hydrogen contribution was added during refinement of the structure. All nonhydrogens were anisotropically refined by full-matrix least-squares. Hydrogens were assigned isotropic temperature factors of 4.0 and their positions were refined by least-squares. The final unweighted R-factor for the observed reflections was .089.

Results for 9-isocyanopupukeanane A three-dimentsional view of one molecule of the phenylthiourea derivative is shown in a computer generated drawing, figure 5. Both molecules in the asymmetric unit have the same structure. The tricyclic, irregular sesquiterpene skeleton of the isocyanide has been named pupukeanane after the place of collection of *P. varicosa* and its sponge prey. Carbons 1, 2, 3, 6, 7, 8, 9 and 10 make up a bicyclo[2.2.2]octane ring system. The six-membered rings have twisted boat conformations and the five-membered ring has the envelope conformation with C(6), the flap, approximately .65Å from the plane of the other atoms in the ring. The absolute configuration of the molecule could not be determined from the X-ray data. C(12) has the β configuration while C(11) and C(13) have the α configuration.

Table 5a lists the fractional coordinates for the heavy atoms in the structure. Selected bond distances and angles are compiled in tables 5b and 5c, respectively. Some of the bond distances are unusually long or short and a comparison of the bond distances of one molecule in the asymmetric unit to those of the other show some major discrepancies. This questionable geometry is probably due to the large amount of thermal motion of some of the atoms. None of the bond distances were corrected for thermal motion. Rather, accurate geometry for the pupukeanane skeleton was determined from the crystal structure of an isomer of 9-isocyanopupukeanane. For complete tables of fractional coordinates, bond distances, bond angles and structure factor magnitudes for the 9-isocyanopupukeanane derivative refer to the published communciation (47).

Figure 5. A computer generated perspective drawing of the phenylthiourea derivative of 9-isocyanopupukeanane. Hydrogens are omitted for clarity.

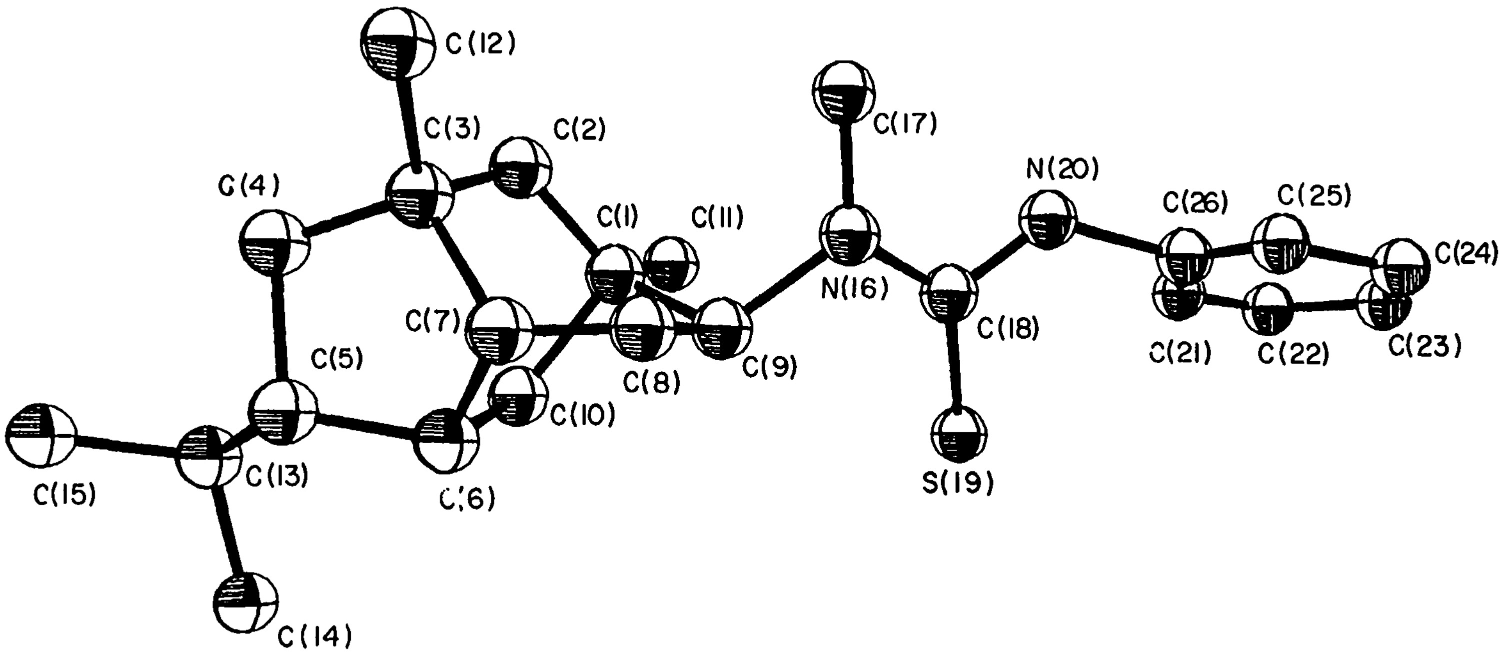

C(12)
C(3)
C(2)
C(17)
N(20)
C(26)
C(25)
C(4)
C(1)
C(11)
C(24)
N(16)
C(7)
C(18)
C(5)
C(8)
C(9)
C(21)
C(22)
C(23)
C(10)
S(19)
C(15)
C(13)
C(6)
C(14)

Table 5a. Fractional coordinates of the nonhydrogen atoms of 9-isocyanopupukeanane. The standard deviations of the least significant figures are given in parentheses. The numbering scheme refers to figure 5.

C(1)	.1862(13)	.8072(17)	.3196(11)
C(2)	.1598(18)	.9119(16)	.2495(12)
C(3)	.0912(13)	.8688(19)	.1662(12)
C(4)	.1376(14)	.8175(19)	.1053(11)
C(5)	.1475(11)	.6613(18)	.1139(9)
C(6)	.1221(12)	.6362(15)	.1911(9)
C(7)	.0399(11)	.7369(19)	.1853(8)
C(8)	.0099(20)	.7406(23)	.2552(15)
C(9)	.1066(13)	.7482(22)	.3465(11)
C(10)	.2187(15)	.6794(18)	.2739(11)
C(11)	.2750(17)	.8426(27)	.3954(15)
C(12)	-.0027(22)	.9728(27)	.1170(16)
C(13)	.2516(14)	.6189(21)	.1063(11)
C(14)	.2730(22)	.4742(23)	.1310(18)
C(15)	.2607(16)	.6369(22)	.0235(12)
N(16)	.0593(13)	.8447(13)	.4020(10)
C(17)	.0140(13)	.9768(15)	.3722(9)
C(18)	.0727(10)	.7959(18)	.4782(12)
S(19)	.1358(4)	.6472(5)	.5208(3)
N(20)	.0389(10)	.8742(15)	.5254(7)
C(21)	.1258(15)	.8128(20)	.6836(15)
C(22)	.1223(26)	.7977(25)	.7565(15)
C(23)	.0223(20)	.8030(21)	.7709(15)
C(24)	-.0746(16)	.8241(21)	.6984(16)
C(25)	-.0507(13)	.8440(16)	.6231(10)
C(26)	.0296(11)	.8413(16)	.6162(8)
C(1')	.3101(15)	.2197(28)	.6791(12)
C(2')	.2684(14)	.3215(22)	.7123(12)
C(3')	.3384(13)	.3574(17)	.8026(13)
C(4')	.3069(13)	.2800(15)	.8772(10)
C(5')	.3844(13)	.1543(17)	.8985(9)
C(6')	.4309(11)	.1608(19)	.8282(9)
C(7')	.4458(17)	.3049(18)	.8185(14)
C(8')	.4866(11)	.3298(15)	.7338(10)
C(9')	.4065(13)	.2771(19)	.6608(12)
C(10')	.3412(13)	.0980(17)	.7420(11)
C(11')	.2278(11)	.1555(25)	.5968(8)
C(12')	.3345(24)	.5085(20)	.8155(19)
C(13')	.3328(15)	.0334(19)	.9142(10)
C(14')	.3078(22)	.0487(24)	.9991(17)
C(15')	.4005(20)	-.0909(22)	.9249(15)
N(16')	.4355(9)	.2055(13)	.6011(7)
C(17')	.4925(17)	.0867(17)	.6317(14)
C(18')	.4236(15)	.2418(18)	.5172(8)

Table 5a. (Continued)

S(19')	.3622(5)	.3799(4)	.4748(4)
N(20')	.4733(8)	.1570(17)	.4782(8)
C(21')	.3730(11)	.1731(14)	.3272(7)
C(22')	.3778(15)	.1949(19)	.2413(11)
C(23')	.4589(25)	.2196(22)	.2300(13)
C(24')	.5488(13)	.2281(17)	.2947(10)
C(25')	.5660(14)	.2070(18)	.3825(10)
C(26')	.4563(12)	.1802(14)	.3990(9)

Table 5b. Selected bond distances for 9-isocyanopupukeanane. The standard deviation of the least significant figure of each distance is given in parentheses.

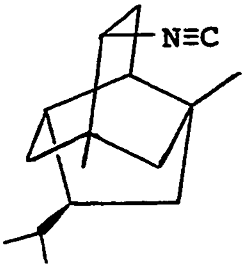
C(1) - C(2)	1.52(2)
C(2) - C(3)	1.46(2)
C(3) - C(4)	1.48(2)
C(4) - C(5)	1.57(2)
C(5) - C(6)	1.48(2)
C(6) - C(7)	1.50(2)
C(7) - C(8)	1.38(2)
C(8) - C(9)	1.65(3)
C(1) - C(9)	1.45(2)
C(1) - C(10)	1.63(2)
C(1) - C(11)	1.47(3)
C(3) - C(12)	1.64(3)
C(3) - C(7)	1.58(2)
C(5) - C(13)	1.54(2)
C(13) - C(14)	1.50(3)
C(13) - C(15)	1.45(2)
C(6) - C(10)	1.62(2)
C(9) - N(16)	1.63(2)
N(16) - C(17)	1.45(2)
C(1') - C(2')	1.38(2)
C(2') - C(3')	1.53(3)
C(3') - C(4')	1.65(2)
C(4') - C(5')	1.61(2)
C(5') - C(6')	1.53(2)
C(6') - C(7')	1.47(2)
C(7') - C(8')	1.72(2)
C(8') - C(9')	1.44(2)
C(1') - C(9')	1.57(2)
C(1') - C(10')	1.57(3)
C(1') - C(11')	1.59(3)
C(3') - C(12')	1.53(2)
C(3') - C(7')	1.50(2)
C(5') - C(13')	1.47(2)
C(13') - C(14')	1.59(3)
C(13') - C(15')	1.53(3)
C(6') - C(10')	1.67(2)
C(9') - N(16')	1.40(2)
N(16') - C(17')	1.42(2)

Table 5c. Selected bond angles of 9-isocyanopupukeanane. The standard deviation of the least significant figure of each angle is given in parentheses.

C(9)	- C(1)	- C(2)	121(1)
C(10)	- C(1)	- C(2)	102(1)
C(11)	- C(1)	- C(2)	114(2)
C(9)	- C(1)	- C(11)	108(2)
C(9)	- C(1)	- C(10)	101(1)
C(10)	- C(1)	- C(11)	108(1)
C(1)	- C(2)	- C(3)	116(1)
C(2)	- C(3)	- C(4)	118(2)
C(2)	- C(3)	- C(7)	104(1)
C(2)	- C(3)	- C(12)	116(2)
C(4)	- C(3)	- C(7)	101(1)
C(4)	- C(3)	- C(12)	109(2)
C(7)	- C(3)	- C(12)	107(2)
C(3)	- C(4)	- C(5)	109(1)
C(4)	- C(5)	- C(6)	102(1)
C(4)	- C(5)	- C(13)	109(1)
C(6)	- C(5)	- C(13)	122(1)
C(5)	- C(6)	- C(7)	103(1)
C(5)	- C(6)	- C(10)	109(1)
C(7)	- C(6)	- C(10)	105(1)
C(3)	- C(7)	- C(6)	101(1)
C(3)	- C(7)	- C(8)	116(2)
C(6)	- C(7)	- C(8)	114(2)
C(7)	- C(8)	- C(9)	114(2)
C(1)	- C(9)	- C(8)	101(1)
C(1)	- C(9)	- N(16)	116(1)
C(8)	- C(9)	- N(16)	102(1)
C(1)	- C(10)	- C(6)	110(1)
C(5)	- C(13)	- C(14)	110(2)
C(5)	- C(13)	- C(15)	116(2)
C(14)	- C(13)	- C(15)	108(2)
C(9)	- N(16)	- C(17)	123(1)
C(9)	- N(16)	- C(18)	113(1)
C(17)	- N(16)	- C(18)	124(1)
C(9')	- C(1')	- C(2')	108(2)
C(10')	- C(1')	- C(2')	111(1)
C(11')	- C(1')	- C(2')	112(2)
C(9')	- C(1')	- C(11')	112(1)
C(9')	- C(1')	- C(10')	111(1)
C(10')	- C(1')	- C(11')	103(2)
C(1')	- C(2')	- C(3')	111(1)
C(2')	- C(3')	- C(4')	113(1)
C(2')	- C(3')	- C(7')	110(1)
C(2')	- C(3')	- C(12')	109(2)
C(4')	- C(3')	- C(7')	102(1)

Table 5c. (Continued)

C(4')	- C(3')	- C(12')	109(1)
C(7')	- C(3')	- C(12')	114(2)
C(3')	- C(4')	- C(5')	102(1)
C(4')	- C(5')	- C(6')	103(1)
C(4')	- C(5')	- C(13')	111(1)
C(6')	- C(5')	- C(13')	122(1)
C(5')	- C(6')	- C(7')	104(1)
C(5')	- C(6')	- C(10')	106(1)
C(7')	- C(6')	- C(10')	111(1)
C(3')	- C(7')	- C(6')	101(1)
C(3')	- C(7')	- C(8')	113(2)
C(6')	- C(7')	- C(8')	109(1)
C(7')	- C(8')	- C(9')	106(1)
C(1')	- C(9')	- C(8')	115(1)
C(1')	- C(9')	- N(16')	115(2)
C(8')	- C(9')	- N(16')	118(1)
C(1')	- C(10')	- C(6')	104(1)
C(5')	- C(13')	- C(14')	111(1)
C(5')	- C(13')	- C(15')	112(2)
C(14')	- C(13')	- C(15')	107(2)
C(9')	- N(16')	- C(17')	115(1)
C(9')	- N(16')	- C(18')	128(1)
C(17')	- N(16')	- C(18')	116(1)



9-isocyanopupukeanane

<u>Experimental for 2-isocyanopupukeanane</u> Some time after the structure of 9-isocyanopupukeanane had been determined an isomer of the toxin was isolated from the same source. 2-isocyanopupukeanane crystallized from hexane and its crystal structure was investigated. A large crystal of the isomer chosen for the experiment belonged to the orthorhombic space group $P2_12_12_1$ with accurate cell constants of $\underset{\sim}{a}$ = 6.981(2)Å, $\underset{\sim}{b}$ = 9.969(2)Å and $\underset{\sim}{c}$ = 21.113(4)Å, and a calculated density for Z = 4 of 1.05 g/cc. Integrated intensities for one octant of reflections with $2\theta \leq 114.1°$ (CuKα) were recorded. Initially the minimum scan rate was set at 1°/minute but was changed to 2°/minute when the intensities of three standard reflections had decreased 20%. The intensities of the standards were periodically measured throughout data collection to monitor crystal decomposition. They showed a rapid linear decrease with time and by the

end of data collection each was 50-60% of its original value. All measured intensities and their sigmas were rescaled to correct for crystal decomposition, then corrected for Lorentz, polarization and background effects. After making these corrections 911 of 1195 unique reflections were considered observed.

Structure factors were converted to Es and a good set of phases for the largest 150 Es was determined using MULTAN. An E map showed 12 out of 17 nonhydrogen atoms and a subsequent F_o synthesis revealed the entire structure. Nonhydrogens were anisotropically refined by full-matrix least-squares. At this point all 25 hydrogens were included in their theoretical positions and isotropically refined. Refinement converged at an unweighted R-factor of .047 for the observed reflections.

Results for 2-isocyanopupukeanane As can be seen from the computer generated drawing, figure 6, the isonitrile has the pupukeanane skeleton with the isocyano substituent at C(2). The conformation of the molecule is basically the same as that of 9-isocyanopupukeanane. C(6) is .55Å removed from the least-squares plane through the other carbons in the five-membered ring. Tables 6a, 6b, 6c and 6d are fractional coordinates, bond distances, bond angles and structure factor magnitudes for the crystal structure. Bond distances

Figure 6. A computer generated perspective drawing of 2-isocyanopupukeanane with hydrogens omitted for clarity.

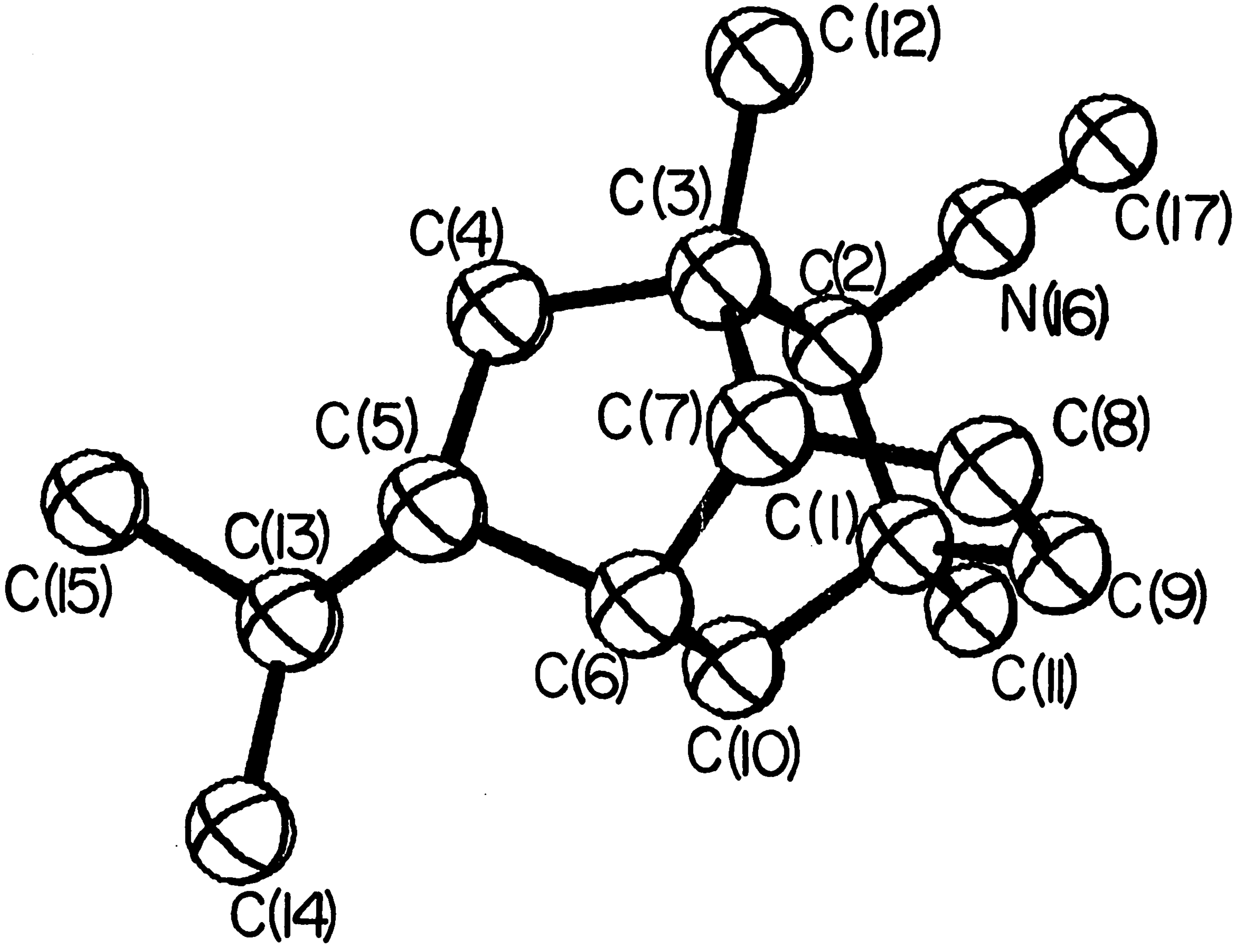

C(12)
C(17)
C(3)
C(4)
C(2)
N(16)
C(7)
C(8)
C(5)
C(1)
C(15)
C(13)
C(9)
C(6)
C(11)
C(10)
C(14)

Table 6a. Fractional coordinates and temperature factors for 2-isocyanopupukeanane. Standard deviations of the least significant figures are given in parentheses. Hydrogens are assigned the same numbers as the heavy atoms to which they are bonded. The numbering scheme refers to figure 6.

C(1)	-.1534(6)	-.2817(3)	-.2918(1)
C(2)	-.3480(6)	-.3424(3)	-.3107(1)
C(3)	-.3815(6)	-.3329(3)	-.3841(1)
C(4)	-.4978(6)	-.2039(4)	-.3981(2)
C(5)	-.3523(7)	-.0974(3)	-.4208(1)
C(6)	-.1624(6)	-.1551(4)	-.3968(1)
C(7)	-.1842(6)	-.3030(3)	-.4140(1)
C(8)	-.0227(6)	-.3920(4)	-.3897(2)
C(9)	.0083(6)	-.3686(4)	-.3187(2)
C(10)	-.1412(6)	-.1440(3)	-.3243(1)
C(11)	-.1352(8)	-.2675(3)	-.2203(1)
C(12)	-.4767(7)	-.4579(3)	-.4117(2)
C(13)	-.4039(8)	.0469(4)	-.4038(2)
C(14)	-.2412(11)	.1425(5)	-.4242(3)
C(15)	-.5961(10)	.0874(5)	-.4332(2)
N(16)	-.3572(5)	-.4799(3)	-.2883(1)
C(17)	-.3616(8)	-.5878(5)	-.2701(2)
H(2)	-.459(5)	-.292(3)	-.287(1)
H(4A)	-.603(7)	-.225(4)	-.431(2)
H(4B)	-.564(5)	-.170(3)	-.357(1)
H(5)	-.343(5)	-.103(3)	-.468(1)
H(6)	-.048(6)	-.119(3)	-.417(1)
H(7)	-.201(5)	-.316(3)	-.462(1)
H(8A)	.094(6)	-.381(4)	-.412(2)
H(8B)	-.057(6)	-.489(4)	-.399(2)
H(9A)	.002(7)	-.460(4)	-.295(2)
H(9B)	.126(5)	-.321(3)	-.311(1)
H(10A)	-.237(5)	-.082(3)	-.306(1)
H(10B)	-.011(5)	-.110(3)	-.318(1)
H(11A)	-.234(6)	-.205(4)	-.203(2)
H(11B)	-.144(7)	-.348(3)	-.200(1)
H(11C)	-.004(8)	-.230(5)	-.209(2)
H(12A)	-.613(6)	-.481(4)	-.388(1)
H(12B)	-.509(5)	-.438(3)	-.456(1)
H(12C)	-.394(8)	-.528(5)	-.405(2)
H(13)	-.416(5)	.052(3)	-.356(1)
H(14A)	-.251(8)	.137(5)	-.474(2)
H(14B)	-.287(10)	.227(6)	-.409(2)
H(14C)	-.105(10)	.122(6)	-.405(2)
H(15A)	-.700(8)	.031(5)	-.416(2)
H(15B)	-.620(10)	.185(6)	-.427(3)
H(15C)	-.575(8)	.085(5)	-.482(2)

Table 6b. Bond distances of 2-isocyanopupukeanane. The standard deviation of the least significant figure of each distance is given in parentheses.

C(1) - C(2)	1.540(5)
C(1) - C(9)	1.532(5)
C(1) - C(10)	1.537(4)
C(1) - C(11)	1.521(4)
C(2) - C(3)	1.570(4)
C(2) - N(16)	1.452(4)
C(3) - C(4)	1.549(5)
C(3) - C(7)	1.544(5)
C(3) - C(12)	1.527(5)
C(4) - C(5)	1.546(6)
C(5) - C(6)	1.531(6)
C(5) - C(13)	1.525(5)
C(6) - C(7)	1.526(5)
C(6) - C(10)	1.543(4)
C(7) - C(8)	1.523(6)
C(8) - C(9)	1.532(5)
C(13) - C(14)	1.544(8)
C(13) - C(15)	1.532(8)
N(16) - C(17)	1.142(5)

Table 6c. Bond angles of 2-isocyanopupukeanane. The standard deviation of the least significant figure of each angle is given in parentheses.

C(2) - C(1) - C(9)	109.4(3)
C(2) - C(1) - C(10)	106.5(3)
C(2) - C(1) - C(11)	111.6(3)
C(9) - C(1) - C(10)	107.4(3)
C(9) - C(1) - C(11)	111.1(3)
C(10) - C(1) - C(11)	110.8(3)
C(1) - C(2) - C(3)	111.3(3)
C(1) - C(2) - N(16)	109.0(3)
C(3) - C(2) - N(16)	111.9(3)
C(2) - C(3) - C(4)	108.5(3)
C(2) - C(3) - C(7)	106.3(3)
C(2) - C(3) - C(12)	113.1(3)
C(4) - C(3) - C(7)	103.3(3)
C(4) - C(3) - C(12)	112.1(3)
C(7) - C(3) - C(12)	113.0(3)
C(3) - C(4) - C(5)	106.6(3)
C(4) - C(5) - C(6)	102.0(3)
C(4) - C(5) - C(13)	114.9(4)
C(6) - C(5) - C(13)	118.8(3)
C(5) - C(6) - C(7)	101.5(3)
C(5) - C(6) - C(10)	112.6(3)
C(7) - C(6) - C(10)	108.3(3)
C(3) - C(7) - C(6)	100.3(3)
C(3) - C(7) - C(8)	114.3(3)
C(6) - C(7) - C(8)	114.2(3)
C(7) - C(8) - C(9)	110.1(3)
C(1) - C(9) - C(8)	110.2(3)
C(1) - C(10) - C(6)	111.9(2)
C(5) - C(13) - C(14)	110.1(4)
C(5) - C(13) - C(15)	111.1(4)
C(14) - C(13) - C(15)	111.6(4)
C(2) - N(16) - C(17)	178.8(4)

Table 6d. Observed and calculated structure factor magnitudes for 2-isocyanopupukeanane.

H = 0				3	2	14	14	5	13	13	12	9	3	7	6
K	L	FO	FC	3	3	26	25	5	14	4	4	9	4	3	3
0	2	33	34	3	4	25	26	5	15	8	9	9	5	11	11
0	4	72	85	3	5	16	15	5	16	16	16	9	9	2	2
0	6	100	117	3	6	3	2	5	17	11	11	9	10	2	1
0	8	56	56	3	7	3	3	5	19	1	1	9	12	2	1
0	10	91	97	3	8	12	12	6	0	11	11	10	0	3	3
0	12	6	6	3	9	2	2	6	1	19	20	10	1	5	5
0	14	6	6	3	10	2	2	6	2	4	4	10	3	4	4
0	16	15	15	3	11	7	8	6	3	1	0	10	4	3	2
0	20	1	1	3	12	9	8	6	4	17	17	10	5	3	3
0	22	2	2	3	13	5	5	6	5	11	11	10	6	3	3
1	1	67	86	3	14	12	13	6	6	12	12				
1	2	1	1	3	15	2	2	6	7	5	4	H = 1			
1	3	71	82	3	16	2	1	6	8	2	2	K	L	FO	FC
1	4	66	72	3	17	3	3	6	9	12	12	0	1	11	9
1	5	27	28	3	18	4	4	6	10	12	13	0	2	98	123
1	6	17	17	3	19	4	4	6	11	3	3	0	3	60	65
1	7	6	5	3	20	3	3	6	12	2	2	0	4	9	9
1	8	21	21	3	21	3	3	6	13	2	3	0	5	37	39
1	9	12	12	4	0	41	41	6	14	11	11	0	6	13	13
1	10	30	31	4	1	10	10	6	15	14	14	0	7	35	35
1	11	45	44	4	2	18	18	6	16	3	4	0	8	53	53
1	12	6	6	4	3	34	35	6	17	4	4	0	9	3	1
1	13	28	28	4	4	30	29	6	19	1	1	0	10	11	10
1	14	9	9	4	5	8	9	7	1	7	7	0	11	5	5
1	15	6	7	4	6	9	10	7	2	2	3	0	12	24	23
1	16	2	3	4	7	13	13	7	3	7	7	0	14	7	8
1	18	1	2	4	8	13	14	7	4	3	2	0	15	8	8
1	20	1	1	4	10	3	3	7	5	4	5	0	18	3	4
1	21	2	2	4	12	15	15	7	7	9	9	0	19	4	4
2	0	18	19	4	13	9	9	7	9	9	10	0	20	4	3
2	1	48	52	4	14	18	18	7	10	1	1	1	0	13	12
2	2	24	26	4	16	16	16	7	11	3	4	1	1	67	78
2	3	45	48	4	17	10	11	7	12	3	4	1	2	39	40
2	5	8	10	4	20	5	5	7	14	4	4	1	3	12	12
2	6	12	13	4	21	4	5	8	1	8	9	1	4	33	34
2	7	2	1	5	1	20	19	8	2	8	7	1	5	31	30
2	8	3	4	5	2	20	21	8	3	5	6	1	6	8	8
2	9	25	24	5	3	32	31	8	4	5	4	1	7	6	6
2	10	12	11	5	4	6	6	8	5	3	3	1	8	9	9
2	11	15	15	5	6	23	23	8	6	9	9	1	9	33	31
2	12	10	10	5	7	8	8	8	7	4	3	1	10	16	16
2	13	6	6	5	8	10	9	8	8	6	6	1	11	23	21
2	14	2	1	5	9	2	2	8	9	6	6	1	12	17	17
2	15	4	4	5	10	13	12	8	12	2	2	1	13	1	0
2	17	5	4	5	11	11	11	8	13	2	2	1	14	8	8
2	18	3	3	5	12	2	1	9	1	2	2	1	15	2	2

Table 6d. (Continued)

1	18	2	2	4	9	10	11	7	2	10	10				
2	0	2	1	4	10	10	9	7	3	6	7		H =	2	
2	1	43	45	4	11	6	5	7	4	4	3	K	L	FO	FC
2	2	19	19	4	12	6	6	7	5	7	7	0	0	24	24
2	3	6	6	4	13	14	15	7	6	8	8	0	1	2	1
2	4	20	21	4	14	6	6	7	7	5	5	0	2	7	5
2	5	31	30	4	15	10	10	7	8	4	4	0	3	26	27
2	6	13	14	4	16	11	11	7	9	3	4	0	4	32	35
2	7	2	1	4	17	5	4	7	10	3	3	0	5	24	26
2	8	10	10	4	18	6	6	7	11	8	8	0	6	1	1
2	9	20	19	4	19	6	5	7	12	5	5	0	7	22	22
2	10	12	12	4	20	3	4	7	13	4	4	0	8	13	13
2	12	10	10	5	0	33	32	7	14	4	3	0	9	28	28
2	13	9	8	5	1	11	11	7	15	2	2	0	10	8	8
2	14	4	4	5	2	7	8	7	16	4	4	0	11	11	11
2	15	16	16	5	3	11	10	8	0	25	24	0	13	2	2
2	16	3	3	5	4	6	5	8	1	12	12	0	14	15	14
2	17	5	5	5	5	18	17	8	2	4	3	0	18	5	5
2	19	2	2	5	6	11	11	8	3	6	6	0	19	3	4
2	21	3	3	5	7	4	4	8	4	8	8	0	20	2	2
3	0	6	6	5	8	11	12	8	5	2	2	1	0	30	30
3	1	20	20	5	10	13	13	8	6	9	10	1	1	47	48
3	2	34	35	5	11	4	4	8	7	8	8	1	2	41	42
3	3	24	23	5	13	14	15	8	8	4	4	1	3	27	28
3	4	6	7	5	14	8	8	8	9	3	2	1	4	16	16
3	5	10	10	5	15	12	13	8	10	12	11	1	5	14	13
3	6	6	5	5	16	3	4	8	11	2	2	1	6	11	10
3	7	20	19	5	17	3	3	8	13	6	5	1	7	11	11
3	8	11	12	5	18	3	4	8	14	4	3	1	8	8	8
3	9	4	3	6	0	7	7	8	15	4	3	1	9	8	8
3	10	7	6	6	1	12	12	9	0	3	3	1	10	12	11
3	11	8	8	6	2	17	17	9	1	8	8	1	11	7	6
3	12	8	9	6	3	13	13	9	2	4	3	1	12	8	9
3	13	6	6	6	4	5	5	9	3	11	11	1	13	7	7
3	15	5	6	6	5	8	9	9	4	2	1	1	14	3	3
3	16	13	12	6	6	4	4	9	5	7	6	1	15	7	7
3	17	9	9	6	7	10	10	9	6	4	4	1	16	14	15
3	18	3	3	6	8	5	5	9	7	2	2	1	17	4	4
3	20	3	3	6	9	6	6	9	8	3	2	1	18	4	5
4	0	22	23	6	10	2	2	9	9	3	3	1	19	6	6
4	1	27	28	6	11	13	13	9	10	4	4	1	20	2	2
4	2	29	29	6	12	7	7	9	11	6	5	1	22	2	2
4	3	17	18	6	13	5	5	9	12	4	4	2	0	25	25
4	4	8	8	6	14	3	3	10	0	4	3	2	1	26	27
4	5	18	17	6	15	3	2	10	2	3	3	2	2	23	24
4	6	17	15	6	17	5	5	10	3	2	2	2	3	10	10
4	7	17	17	7	0	14	14	10	6	3	2	2	4	37	39
4	8	9	9	7	1	14	14	10	7	4	4	2	5	10	11

Table 6d. (Continued)

2	6	18	18	4	18	9	9	8	5	3	4	1	9	14	16
2	7	22	21	4	19	5	6	8	6	5	5	1	11	4	4
2	8	8	8	4	20	2	2	8	7	5	5	1	12	7	7
2	9	8	7	5	0	11	11	8	8	11	11	1	13	14	14
2	10	7	6	5	1	3	4	8	9	3	3	1	14	10	10
2	11	10	10	5	2	21	21	8	10	2	2	1	15	3	3
2	12	23	22	5	3	7	7	8	12	5	5	1	17	9	9
2	13	8	8	5	4	3	2	8	13	4	4	1	18	9	9
2	14	7	7	5	5	9	9	9	1	8	8	1	19	6	6
2	15	6	7	5	6	5	5	9	2	4	4	2	0	24	21
2	16	12	11	5	8	11	10	9	4	5	5	2	1	37	39
2	17	11	11	5	10	5	5	9	7	3	3	2	2	17	18
2	18	3	3	5	11	4	4	9	8	3	3	2	3	9	10
2	19	3	3	5	12	10	10	9	9	4	4	2	4	26	27
3	0	28	27	5	15	3	4	9	11	2	3	2	5	15	15
3	1	18	18	5	16	2	2	10	1	2	1	2	6	19	19
3	2	6	6	6	0	8	9	10	4	2	1	2	7	16	16
3	3	25	25	6	1	10	9	10	5	3	2	2	8	13	13
3	4	14	14	6	2	4	5	10	6	3	3	2	9	19	19
3	5	28	28	6	3	3	4					2	10	14	14
3	6	13	13	6	4	7	7		H =	3		2	11	10	11
3	7	5	5	6	5	7	8	K	L	FO	FC	2	12	5	5
3	8	22	21	6	6	4	3	0	1	10	10	2	13	11	11
3	10	4	4	6	8	7	7	0	2	21	20	2	14	22	22
3	11	5	5	6	9	3	3	0	3	18	16	2	15	10	10
3	12	2	2	6	10	6	6	0	4	12	13	2	16	8	8
3	13	15	14	6	11	5	5	0	5	3	3	2	17	6	7
3	14	17	17	6	12	6	6	0	6	11	13	2	18	8	8
3	15	17	17	6	13	10	10	0	7	11	10	2	19	3	3
3	16	4	4	6	14	3	3	0	8	15	16	2	20	4	3
3	18	4	4	6	15	8	9	0	9	4	4	3	0	8	9
3	19	3	3	6	17	3	2	0	10	6	6	3	1	20	19
3	20	4	5	7	0	3	3	0	12	13	12	3	2	19	18
4	1	22	22	7	1	19	19	0	13	7	6	3	3	25	26
4	2	20	20	7	2	18	19	0	15	10	9	3	4	7	7
4	3	30	29	7	3	4	4	0	16	4	3	3	5	12	12
4	4	3	3	7	4	8	8	0	17	10	10	3	6	5	4
4	5	9	9	7	5	5	5	0	18	2	3	3	7	9	8
4	6	11	11	7	6	5	5	0	19	4	5	3	8	9	10
4	7	13	12	7	8	5	5	1	0	19	19	3	9	5	4
4	8	3	2	7	9	12	12	1	1	18	16	3	10	5	4
4	9	14	13	7	10	3	4	1	2	11	11	3	11	16	15
4	11	2	2	7	11	8	8	1	3	38	38	3	12	9	10
4	12	5	5	7	12	11	11	1	4	17	17	3	13	13	12
4	13	6	6	7	13	3	3	1	5	25	25	3	14	3	2
4	14	4	4	7	16	2	2	1	6	8	8	3	15	8	8
4	15	7	6	8	2	20	20	1	7	3	3	3	16	4	4
4	16	8	8	8	3	3	3	1	8	13	13	3	17	10	10

Table 6d. (Continued)

3	18	2	2	7	3	12	12	1	4	15	15	4	7	10	9
4	0	12	12	7	4	13	13	1	5	6	6	4	10	3	3
4	1	18	17	7	5	5	5	1	6	11	11	4	11	5	6
4	2	4	4	7	6	5	5	1	7	3	3	4	12	7	7
4	3	5	5	7	7	7	8	1	8	3	4	4	14	3	4
4	4	14	14	7	8	4	3	1	9	4	4	5	0	3	3
4	5	4	4	7	10	7	7	1	10	13	14	5	1	12	13
4	6	5	6	7	11	9	9	1	11	8	8	5	2	15	15
4	7	6	5	7	13	4	4	1	12	4	4	5	3	4	4
4	8	3	3	7	14	5	5	1	13	4	4	5	4	5	6
4	9	8	8	8	0	16	17	1	14	5	5	5	5	9	8
4	10	6	5	8	1	4	5	1	15	7	6	5	6	3	3
4	11	7	8	8	2	9	10	1	16	4	5	5	7	4	4
4	12	5	6	8	3	4	4	1	17	3	4	5	8	7	7
4	13	3	2	8	4	3	3	1	18	2	1	5	11	6	5
4	14	11	11	8	7	4	3	2	1	8	7	5	12	7	7
4	15	4	4	8	8	6	6	2	2	4	3	5	14	4	4
4	16	6	6	8	9	5	5	2	3	5	5	5	15	4	4
4	17	4	4	8	10	5	5	2	4	6	6	6	0	3	3
5	1	6	7	8	11	2	2	2	6	5	5	6	1	16	16
5	2	10	10	8	12	2	2	2	7	6	7	6	2	9	9
5	3	10	10	9	1	3	2	2	9	5	4	6	4	7	7
5	5	6	6	9	2	3	3	2	10	2	2	6	5	9	9
5	6	3	3	9	4	2	3	2	11	8	8	6	6	7	7
5	7	5	4	9	5	2	1	2	12	7	6	6	7	2	2
5	10	6	5	9	6	4	4	2	13	7	7	6	8	6	5
5	12	5	5	9	8	4	3	2	14	4	5	6	9	6	6
5	13	5	5					2	16	5	5	6	10	5	6
5	14	4	4		H =	4		3	0	9	10	6	11	5	5
5	15	4	4	K	L	FO	FC	3	1	5	6	6	12	5	5
5	16	2	2	0	0	32	30	3	2	4	4	6	14	6	6
5	18	2	2	0	1	8	7	3	3	5	6	7	1	6	6
6	0	13	13	0	2	21	20	3	4	12	12	7	2	4	5
6	1	8	8	0	3	2	2	3	5	5	5	7	3	8	8
6	2	7	7	0	4	10	9	3	6	8	9	7	4	6	6
6	3	13	14	0	5	13	12	3	8	5	4	7	5	5	6
6	4	5	4	0	6	5	5	3	10	7	6	7	6	3	4
6	5	3	4	0	8	4	3	3	12	3	3	7	9	8	7
6	6	4	4	0	10	5	5	3	13	5	5	7	11	3	3
6	7	10	10	0	11	9	8	3	14	3	2	7	12	4	4
6	8	4	5	0	12	6	6	3	15	5	5	8	1	3	3
6	10	5	5	0	14	7	7	3	16	4	4	8	3	2	1
6	11	7	7	0	15	5	5	4	0	2	2	8	4	4	4
6	12	3	2	0	17	3	3	4	1	10	11	8	6	3	3
6	13	8	8	1	0	16	16	4	2	7	6	8	7	3	3
6	14	5	5	1	1	8	8	4	3	3	2	8	8	3	3
7	1	11	12	1	2	11	10	4	4	6	6	8	9	2	3
7	2	10	11	1	3	8	7	4	5	2	2	9	1	3	3

Table 6d. (Continued)

9	4	2	1

H = 5

K	L	FO	FC
0	1	12	13
0	2	15	14
0	3	7	7
0	4	13	13
0	6	10	10
0	8	5	5
0	9	4	4
0	12	4	4
0	14	3	1
0	15	2	2
0	17	2	1
1	0	3	4
1	1	16	16
1	2	14	14
1	3	7	6
1	4	10	10
1	5	4	4
1	6	3	3
1	7	3	3
1	9	9	9
1	11	4	5
1	12	6	6
1	13	3	3
1	14	2	3
1	17	3	3
2	0	14	14
2	1	7	7
2	2	6	7
2	3	3	3
2	4	10	9
2	5	8	8
2	6	6	6
2	10	6	5
2	12	6	6
2	13	4	3
2	14	4	4
2	15	4	4
3	1	11	11
3	3	7	6
3	4	5	6
3	5	8	7
3	6	3	2
3	7	5	5
3	8	3	3
3	9	3	3
3	10	2	2
3	11	6	6
3	12	4	5
3	13	3	3
3	14	3	3
3	15	4	4
3	16	2	2
4	0	6	6
4	1	8	8
4	2	5	6
4	3	4	4
4	4	4	4
4	5	3	4
4	6	3	4
4	7	4	4
4	9	2	2
4	10	5	5
4	11	4	3
4	12	2	2
4	13	2	2
4	15	3	3
5	0	10	10
5	1	5	7
5	2	8	9
5	3	5	5
5	4	4	4
5	5	6	6
5	6	4	5
5	7	3	4
5	8	4	4
5	9	3	3
5	10	6	5
5	12	5	5
5	13	7	6
6	1	2	2
6	2	6	6
6	3	3	3
6	4	5	6
6	6	4	4
6	7	4	3
6	9	3	3
7	1	4	3
8	2	3	2

H = 6

K	L	FO	FC
0	0	24	23
0	1	5	6
0	2	8	8
0	3	3	3
0	4	3	2
0	5	3	2
0	7	4	4
0	8	5	6
0	9	8	7
0	10	11	12
0	14	3	3
1	1	13	13
1	2	7	7
1	3	8	8
1	4	7	6
1	6	5	5
1	7	6	6
1	8	3	3
1	9	3	2
1	11	9	9
1	12	2	0
1	13	2	3
2	0	6	6
2	2	6	6
2	3	5	6
2	4	3	3
2	5	5	5
2	6	4	3
2	7	5	5
2	10	4	5
2	12	4	4
3	1	4	5
3	3	7	7
3	4	4	3
3	5	3	3
3	6	4	4
3	7	2	2
3	8	2	2
3	9	2	2
3	10	3	3
3	11	2	2
3	12	3	3
4	0	3	3
4	1	3	3
4	2	5	5
4	4	3	4
4	5	4	4
4	6	3	3
4	7	3	3
4	9	2	3
5	0	3	3
5	3	3	4
5	6	3	5
5	9	3	3
6	5	3	3

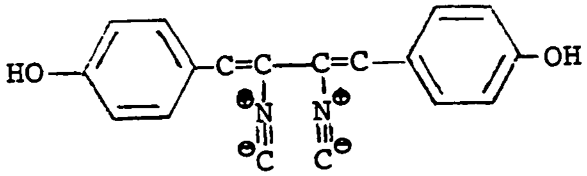
H = 7

K	L	FO	FC
0	2	4	4
0	4	3	3
0	5	4	4
0	7	3	3
0	8	5	5
1	3	3	3
1	4	4	4
1	5	3	3
1	6	3	2
2	1	3	3
2	3	4	4
2	7	2	2
3	4	3	2

and angles agree well with expected values and there are no short intermolecular distances (16).

Discussion The structures of 9-isocyanopupukeanane and its isomer have unusual features. Their pupukeanane skeleton appears to be composed of isoprene units but the units are not joined in a regular head-to-tail manner. No speculation on when or how in the biosynthesis a rearrangement takes place has been published.

Also unknown is the origin of the isocyanide substituents. Prior to 1973 the only known naturally occurring isocyanide was the antibiotic xanthocillin from the fungi Penicillium notatum and Penicillium chrysogenum (48). In 1965 Achenbach and Grisebach studied the incorporation of several labelled compounds into xanthocillin (49). Of the compounds tried, DL-tyrosine-[2-^{14}C] showed significant incorporation, but the labelled carbon appeared only in the butadiene portion of the molecule. Furthermore, when DL-tyrosine-[2-^{14}C-^{15}N] was incorporated into xanthocillin the ^{14}C/^{15}N ratio increased from 10.2 to 61.6, showing the nitrogen of tyrosine did not become part of the isocyanide group.


xanthocillin

Recently a handful of isocyanide sesquiterpenes and diterpenes have been isolated from a variety of sponge species (50, 51, 52, 53, 54, 55). The majority of these compounds were accompanied by their corresponding isothiocyanates and formamides (51, 52, 53, 56). This seems to indicate the isonitrile functionality is derived from a formamide. The following biosynthetic sequence has been proposed: $\rangle\text{-NHCHO} \xrightarrow{-H_2O} \rangle\text{-N}\equiv\text{C} \longrightarrow \rangle\text{-N=C=S}$ (56). A formamide with the pupukeanane skeleton has not yet been isolated.

Crispatone

Background Certain sacoglossan opisthobranch molluscs harbor symbiotic chloroplasts in the tubules of their digestive diverticulum. Examination of the symbionts by electron microscopy show they are closely associated with the animal membrane and completely free of plant cytoplasm and organelles (57). The pigments isolated from the chloroplasts are identical to those in the siphonaceous marine algae on which the sea slugs feed (57). Rather than digest whole algal cells, sacoglossans puncture the cells and suck out the fluid contents (57). It is presumed the symbionts are obtained by this process but how they become established in the host's digestive apparatus is not known.

It is very interesting that the symbiotic chloroplasts can survive independent of the algal cells. Studies of how they function in their host have provided some understanding of the degree of autonomy of cellular chloroplasts. Symbiotic chloroplasts have demonstrated an ability to photosynthetically fix carbon (57, 58, 59, 60). They are able to synthesize α- and β-carotene but appear to have lost the ability to synthesize chlorophylls a and b and xanthophyll, three pigments characteristic of free siphonaceous algae (61). They are also unable to synthesize lamellar proteins or ribulose diphosphate carboxylase, all of which are necessary for chloroplast growth and division, so they probably can't replicate in their host (62). Their life span is unknown, but sea slugs isolated from a source of chloroplasts for six weeks still photosynthetically fix carbon, indicating the plastids can survive for at least that long (57).

The role the symbiotic chloroplasts play in the sacoglossans' metabolism is still obscure. A series of experiments has shown one function of the chloroplasts may be to provide nutrients to tissue with a high metabolic turnover rate. Chemical analyses of sea slugs incubated with $NaH^{14}CO_3$ and exposed to light have shown ^{14}C incorporated into a wide variety of metabolites (57, 58, 59). The fate of the labelled photosynthate was studied by radioautography (57). Specimens of sea slugs incubated with $NaH^{14}CO_3$ and exposed to light were examined by radioautography at intervals of 15, 30, 45, 60, 120, 240 and 540 minutes. Results showed the first host tissues to contain ^{14}C were the terminal bulbs of the digestive diverticula. In time, ^{14}C was found in a number of the sea slug's organs. At the end of the experiment the highest level of radioactivity was in the pedal gland, a mucus producing organ. One experiment showed the turnover rate of ^{14}C in the pedal gland was only 10-12 hours, suggesting the photosynthate was being used to synthesize the mucopolysaccharide secretion of the gland (58). This conclusion was borne out by another investigation in which an estimated 5-10% of the total ^{14}C fixed by chloroplasts was found in their host's pedal gland secretion (63).

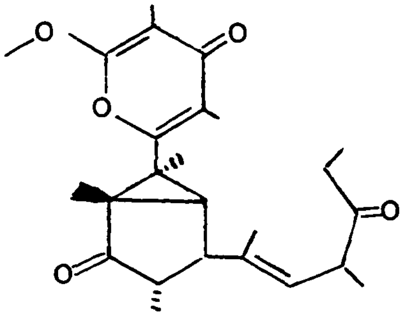
There is also a possibility that symbiotic plastids contribute to the synthesis of secondary metabolites in the sacoglossans. There is no evidence for this yet, but an investigation of the metabolites of the sacoglossans *Tridachia* and *Tridachiella* has been rewarded by the discovery of some unusual compounds. These metabolites were found consistently in sacoglossans, no matter where the specimens were collected, so they are probably not obtained directly from a particular food source (64). Crispatone was isolated from *Tridachia crispata* and initial investigations indicated it was a propionate-derived compound. When attempts to establish its structure by chemical degradation failed it was crystallized from ether/hexane and its crystal structure was determined.

Experimental The crystals of crispatone belonged to the orthorhombic crystal class with a calculated density of 1.12g/cc for Z = 4 and unit cell axes $\underset{\sim}{a}$ = 8.255(7)Å, $\underset{\sim}{b}$ = 13.518(13)Å and $\underset{\sim}{c}$ = 22.017(24)Å. Systematic extinctions in the data unambiguously indicated the chiral space group $P2_12_12_1$. A total of 1911 unique reflections with $2\theta \leq 114.1°$ (CuKα) were measured using a minimum scan rate of 1°/minute. Intensities were corrected for Lorentz, polarization and background effects and 1133 of the reflections (59%) were judged observed and used for refinement of the structure.

The structure was solved by a straightforward application of direct methods. 32 possible phase sets for the 200 largest Es were generated by MULTAN. An E map from the set with the best figures of merit showed all but five nonhydrogen atoms. The crystal structure was completed by means of an F_o synthesis. Nonhydrogens were assigned anisotropic temperature factors and refined by full-matrix least-squares. Hydrogens were included in their theoretical positions and isotropically refined. The final unweighted

R-factor for the observed reflections was .074.

<u>Results</u> Crispatone's carbon skeleton is unique and includes an α-methoxy-γ-pyrone ring joined to a bicyclic ring system composed of a nearly planar 5-membered ring and a cyclopropane ring. The γ-pyrone ring is planar with C(26) .49Å below the plane of the ring as pictured, Figure 7. Distances from the best plane through the five-membered ring are .073Å, .048Å, -.095Å, .101Å and -.067Å for carbons 7, 8, 9, 10 and 11, respectively. The dihedral angles defining the orientation of the γ-pyrone ring with respect to the bicyclic ring system are O(27)-C(5)-C(6)-C(8)=68.41° and C(4)-C(5)-C(6)-C(7)=50.10°. The relative configurations of the asymmetric centers are 6(S*), 7(S*), 8(S*), 10(S*), 11(R*) and 14(R*). Tables 7a, 7b, 7c and 7d are fractional coordinates, bond distances, bond angles and structure factor magnitudes for the structure. Bond distances and angles do not differ significantly from expected values and there are no abnormally short intermolecular contacts (16).



crispatone

Figure 7. A computer generated perspective drawing of crispatone with hydrogens omitted for clarity.

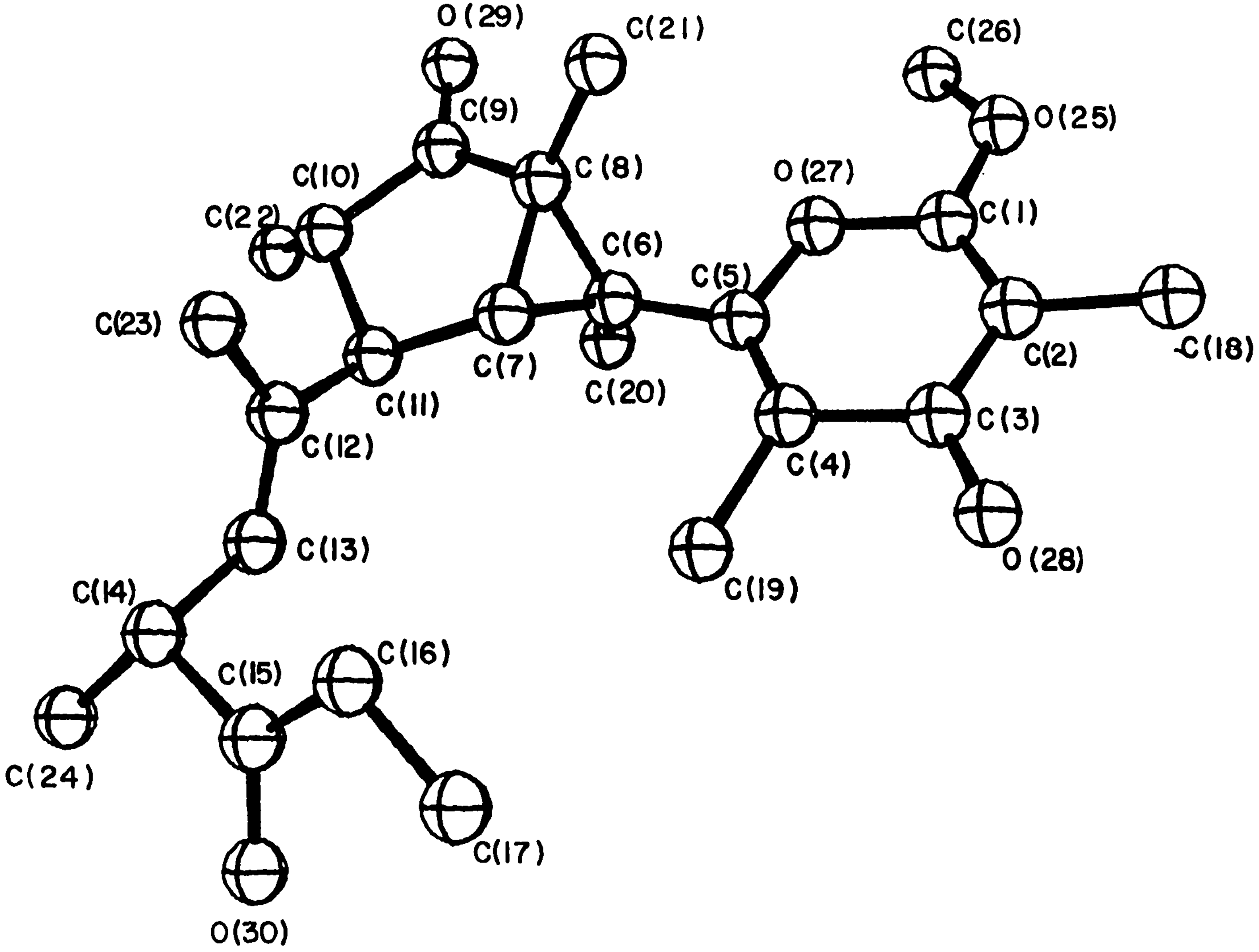

O (29)
C(21)
C(26)
C(9)
O(25)
C(10)
C (8)
O (27)
C(1)
C(22)
C(6)
C(5)
C(23)
C(7)
C(2)
-C(18)
C(11)
C(20)
C(12)
C(3)
C(4)
C(13)
O (28)
C(19)
C(14)
C(15)
C(16)
C(24)
C(17)
O(30)

Table 7a. Fractional coordinates for crispatone. Standard deviations of the least significant figures are given in parentheses. Hydrogens are assigned the same numbers as the heavy atoms to which they are bonded. The numbering scheme refers to figure 7.

C(1)	.0414(14)	-.2235(10)	-.0874(6)
C(2)	-.0059(13)	-.2753(9)	-.1335(5)
C(3)	-.0670(13)	-.2285(9)	-.1843(5)
C(4)	-.0829(13)	-.1182(8)	-.1830(4)
C(5)	-.0459(11)	-.0737(7)	-.1324(5)
C(6)	-.0520(13)	.0356(7)	-.1171(4)
C(7)	-.2074(13)	.0859(6)	-.1322(4)
C(8)	-.1695(12)	.0654(7)	-.0673(4)
C(9)	-.1319(13)	.1645(8)	-.0387(6)
C(10)	-.1838(13)	.2445(8)	-.0818(5)
C(11)	-.2052(12)	.1980(7)	-.1461(4)
C(12)	-.3504(11)	.2276(7)	-.1825(4)
C(13)	-.3304(12)	.2562(7)	-.2395(5)
C(14)	-.4650(13)	.2826(9)	-.2859(5)
C(15)	-.4718(15)	.2002(9)	-.3335(6)
C(16)	-.5266(16)	.1020(10)	-.3095(5)
C(17)	-.5207(19)	.0169(11)	-.3549(6)
C(18)	.0154(17)	-.3890(7)	-.1320(6)
C(19)	-.1393(16)	-.0678(8)	-.2409(4)
C(20)	.1125(13)	.0862(8)	-.1245(5)
C(21)	-.2634(16)	-.0086(9)	-.0288(5)
C(22)	-.0868(18)	.3383(9)	-.0793(6)
C(23)	-.5138(12)	.2174(8)	-.1530(5)
C(24)	-.4216(15)	.3811(8)	-.3191(6)
O(25)	.1032(9)	-.2610(5)	-.0364(4)
C(26)	.1927(18)	-.2012(10)	.0014(6)
O(27)	.0226(8)	-.1221(5)	-.0828(3)
O(28)	-.1169(10)	-.2729(6)	-.2321(3)
O(29)	-.0792(13)	.1760(6)	.0109(4)
O(30)	-.4312(14)	.2104(7)	-.3858(4)
H(7)	-.292(6)	.047(3)	-.154(2)
H(10)	-.275(7)	.260(4)	-.070(3)
H(11)	-.099(9)	.206(5)	-.163(3)
H(13)	-.223(6)	.272(4)	-.257(2)
H(14)	-.565(17)	.320(9)	-.281(6)
H(16A)	-.677(14)	.087(8)	-.299(5)
H(16B)	-.473(7)	.081(4)	-.273(2)
H(17A)	-.585(10)	.038(5)	-.398(3)
H(17B)	-.576(11)	-.044(6)	-.333(3)
H(17C)	-.397(11)	.021(6)	-.368(4)
H(18A)	-.087(13)	-.409(7)	-.140(4)
H(18B)	-.008(17)	-.410(10)	-.079(6)
H(18C)	.132(17)	-.401(9)	-.163(6)

Table 7a. (Continued)

H(19A)	-.251(10)	-.030(5)	-.237(4)
H(19B)	-.139(13)	-.111(8)	-.285(5)
H(19C)	-.019(11)	-.021(6)	-.246(4)
H(20A)	.099(12)	.131(6)	-.112(4)
H(20B)	.143(13)	.097(8)	-.155(5)
H(20C)	.243(19)	.019(10)	-.129(6)
H(21A)	-.156(8)	-.026(4)	.008(3)
H(21B)	-.327(9)	-.069(5)	-.047(3)
H(21C)	-.374(9)	.023(4)	-.003(3)
H(22A)	.033(13)	.321(7)	-.091(5)
H(22B)	-.107(12)	.354(6)	-.050(4)
H(22C)	-.148(9)	.385(5)	-.106(3)
H(23A)	-.506(10)	.158(6)	-.143(4)
H(23B)	-.594(11)	.238(6)	-.171(4)
H(23C)	-.563(8)	.239(5)	-.110(3)
H(24A)	-.207(14)	.378(8)	-.341(5)
H(24B)	-.364(9)	.422(5)	-.304(3)
H(24C)	-.535(10)	.373(5)	-.348(3)
H(26A)	.258(11)	-.166(6)	-.014(4)
H(26B)	.122(12)	-.217(7)	.040(4)
H(26C)	.111(10)	-.137(5)	.009(3)

Table 7b. Bond distances of crispatone. The standard deviation of the least significant figure of each distance is given in parentheses.

C(1) - C(2)	1.29(2)
C(1) - O(25)	1.33(1)
C(1) - O(27)	1.38(1)
C(2) - C(3)	1.38(2)
C(2) - C(18)	1.55(2)
C(3) - C(4)	1.50(2)
C(3) - O(28)	1.28(1)
C(4) - C(5)	1.30(1)
C(4) - C(19)	1.52(1)
C(5) - C(6)	1.52(1)
C(5) - O(27)	1.39(1)
C(6) - C(7)	1.49(1)
C(6) - C(8)	1.52(1)
C(6) - C(20)	1.53(1)
C(7) - C(8)	1.49(1)
C(7) - C(11)	1.55(1)
C(8) - C(9)	1.51(1)
C(8) - C(21)	1.52(1)
C(9) - C(10)	1.50(2)
C(9) - O(29)	1.18(1)
C(10) - C(11)	1.56(1)
C(10) - C(22)	1.50(2)
C(11) - C(12)	1.49(1)
C(12) - C(13)	1.32(1)
C(12) - C(23)	1.50(1)
C(13) - C(14)	1.55(1)
C(14) - C(15)	1.53(2)
C(14) - C(24)	1.56(2)
C(15) - C(16)	1.50(2)
C(15) - O(30)	1.21(1)
C(16) - C(17)	1.52(2)
O(25) - C(26)	1.37(2)

Table 7c. Bond angles of crispatone. The standard deviation of the least significant figure of each angle is given in parentheses.

C(2) - C(1) - O(25)	124.7(12)
C(2) - C(1) - O(27)	124.1(11)
O(25) - C(1) - O(27)	111.0(10)
C(1) - C(2) - C(3)	119.8(12)
C(1) - C(2) - C(18)	119.2(11)
C(3) - C(2) - C(18)	120.9(11)
C(2) - C(3) - C(4)	118.2(10)
C(2) - C(3) - O(28)	124.6(11)
C(4) - C(3) - O(28)	117.1(10)
C(3) - C(4) - C(5)	117.2(9)
C(3) - C(4) - C(19)	117.2(9)
C(5) - C(4) - C(19)	125.6(10)
C(4) - C(5) - C(6)	129.2(10)
C(4) - C(5) - O(27)	123.3(9)
C(6) - C(5) - O(27)	107.3(8)
C(5) - C(6) - C(7)	115.1(8)
C(5) - C(6) - C(8)	116.1(8)
C(5) - C(6) - C(20)	112.6(8)
C(7) - C(6) - C(8)	59.5(6)
C(7) - C(6) - C(20)	122.3(8)
C(8) - C(6) - C(20)	121.5(8)
C(6) - C(7) - C(8)	61.3(6)
C(6) - C(7) - C(11)	118.9(8)
C(8) - C(7) - C(11)	111.6(8)
C(6) - C(8) - C(7)	59.2(6)
C(6) - C(8) - C(9)	114.0(8)
C(6) - C(8) - C(21)	123.5(9)
C(7) - C(8) - C(9)	106.1(8)
C(7) - C(8) - C(21)	123.4(9)
C(9) - C(8) - C(21)	117.0(9)
C(8) - C(9) - C(10)	108.4(9)
C(8) - C(9) - O(29)	125.0(10)
C(10) - C(9) - O(29)	126.4(10)
C(9) - C(10) - C(11)	108.4(9)
C(9) - C(10) - C(22)	115.7(9)
C(11) - C(10) - C(22)	115.8(9)
C(7) - C(11) - C(10)	102.6(8)
C(7) - C(11) - C(12)	111.1(8)
C(10) - C(11) - C(12)	118.0(8)
C(11) - C(12) - C(13)	119.2(9)
C(11) - C(12) - C(23)	117.3(8)
C(13) - C(12) - C(23)	123.3(9)
C(12) - C(13) - C(14)	127.2(9)
C(13) - C(14) - C(15)	108.1(9)
C(13) - C(14) - C(24)	110.0(9)

Table 7c. (Continued)

C(15) - C(14) - C(24)	108.0(9)
C(14) - C(15) - C(16)	114.5(10)
C(14) - C(15) - O(30)	124.0(11)
C(16) - C(15) - O(30)	121.4(11)
C(15) - C(16) - C(17)	115.3(10)
C(1) - O(25) - C(26)	119.4(10)
C(1) - O(27) - C(5)	117.0(8)

Table 7d. Observed and calculated structure factor magnitudes for crispatone.

H =	0			3	1	23	21	5	15	9	9	9	10	22	23
K	L	FO	FC	3	2	6	8	5	17	5	5	9	11	5	5
0	2	27	27	3	3	51	51	5	18	13	13	9	12	13	13
0	4	82	100	3	4	52	54	6	0	92	85	9	14	7	8
0	6	37	42	3	5	31	30	6	1	53	51	9	16	5	8
0	8	54	55	3	8	8	9	6	2	64	62	9	17	5	5
0	10	12	11	3	9	38	37	6	3	48	46	10	0	9	8
0	12	12	13	3	10	47	43	6	4	29	29	10	2	8	6
0	16	19	19	3	11	36	35	6	5	32	33	10	4	11	13
0	18	19	18	3	12	9	10	6	6	29	29	10	5	6	7
0	20	13	12	3	13	18	19	6	7	8	8	10	6	19	21
0	22	9	9	3	16	6	6	6	10	9	9	10	7	6	6
1	1	36	41	3	17	5	6	6	11	12	12	10	9	15	16
1	2	83	91	3	18	13	12	6	12	5	5	10	14	6	5
1	3	59	62	3	19	6	8	6	13	5	4	11	1	18	19
1	4	25	21	3	20	10	10	6	16	13	15	11	2	5	5
1	5	49	53	3	21	10	10	6	18	8	9	11	4	5	6
1	6	4	0	4	0	71	72	6	19	5	4	11	6	6	6
1	7	29	29	4	1	22	21	7	1	47	41	11	7	8	9
1	9	32	33	4	2	14	14	7	2	29	27	11	8	5	6
1	11	3	2	4	3	32	31	7	3	8	6	11	10	14	15
1	13	20	19	4	4	34	35	7	4	12	13	11	12	5	7
1	14	8	6	4	5	15	16	7	5	11	12	12	1	5	5
1	15	10	9	4	6	10	11	7	6	15	15	12	2	6	7
1	17	5	6	4	7	17	16	7	10	7	7	12	4	6	6
1	18	10	10	4	8	32	31	7	11	6	6	12	5	6	6
1	19	7	7	4	9	40	37	7	12	13	13	12	7	5	7
1	20	8	7	4	10	20	20	7	13	9	8	13	1	5	5
1	22	4	5	4	11	13	14	7	14	4	3	14	1	6	3
2	0	170	181	4	13	5	8	7	16	11	11				
2	1	27	28	4	14	8	8	8	0	19	19		H =	1	
2	2	17	13	4	15	8	8	8	1	20	21	K	L	FO	FC
2	3	48	51	4	16	9	9	8	2	8	8	0	1	39	44
2	4	41	40	4	17	12	11	8	3	14	13	0	2	79	88
2	5	76	77	4	19	5	7	8	5	15	14	0	3	117	132
2	6	5	5	5	1	23	21	8	6	7	6	0	5	60	65
2	7	3	4	5	2	36	35	8	8	22	21	0	6	35	38
2	8	15	15	5	3	39	39	8	9	13	14	0	7	66	72
2	9	58	58	5	4	20	19	8	10	5	6	0	8	4	2
2	10	10	10	5	5	29	29	8	14	11	12	0	9	4	5
2	11	14	14	5	6	29	28	8	16	4	4	0	11	11	12
2	12	25	25	5	7	6	4	8	18	8	9	0	12	28	27
2	13	34	33	5	8	5	4	9	1	8	8	0	13	11	11
2	14	7	6	5	9	20	19	9	2	4	5	0	14	5	5
2	15	13	12	5	10	8	8	9	4	6	8	0	17	16	15
2	16	9	10	5	11	30	29	9	6	11	12	0	18	13	13
2	17	8	7	5	12	8	6	9	7	8	10	0	19	8	8
2	22	5	7	5	13	8	8	9	9	8	9	0	20	13	12

Table 7d. (Continued)

0	21	19	19
1	0	68	73
1	1	91	103
1	2	27	29
1	3	77	84
1	4	14	17
1	5	21	22
1	6	8	6
1	7	17	17
1	8	25	23
1	9	14	16
1	10	24	22
1	11	15	14
1	12	10	9
1	13	4	3
1	14	18	18
1	15	8	7
1	16	9	9
1	17	5	6
1	18	9	9
1	19	10	10
1	20	15	16
1	21	5	3
2	0	23	26
2	1	45	50
2	2	21	22
2	3	21	23
2	4	43	45
2	5	46	47
2	6	27	27
2	7	30	30
2	8	46	44
2	9	11	10
2	10	29	29
2	11	11	9
2	12	32	32
2	13	9	9
2	14	8	8
2	15	12	14
2	18	8	10
2	19	15	14
2	20	5	6
2	21	8	9
3	0	21	20
3	1	41	43
3	2	43	44
3	3	55	58
3	4	39	40
3	5	29	30
3	6	38	36
3	7	5	3
3	8	18	20
3	9	9	9
3	10	11	10
3	11	39	37
3	12	10	11
3	13	13	13
3	14	7	7
3	15	5	6
3	16	5	4
3	20	6	6
3	22	4	4
4	0	8	10
4	1	36	35
4	2	25	24
4	3	36	38
4	4	75	76
4	5	46	47
4	6	11	11
4	7	28	28
4	8	24	23
4	9	14	14
4	10	12	12
4	11	11	11
4	12	11	8
4	13	10	10
4	14	16	16
4	15	8	8
4	18	8	9
4	21	5	5
4	22	6	5
5	0	19	19
5	1	13	12
5	2	21	19
5	3	21	21
5	4	20	21
5	5	8	6
5	6	34	33
5	7	35	34
5	8	22	20
5	9	11	8
5	10	4	5
5	11	13	12
5	12	7	9
5	13	4	3
5	14	11	11
5	16	10	10
5	17	6	7
5	19	7	9
5	20	8	9
6	0	10	6
6	1	30	29
6	2	14	15
6	3	28	26
6	4	30	32
6	5	10	10
6	6	29	29
6	7	8	9
6	8	20	20
6	9	26	25
6	10	10	11
6	12	10	11
6	13	10	10
6	14	8	8
6	15	7	7
6	17	5	6
6	18	9	12
7	0	16	15
7	1	9	10
7	2	45	42
7	3	6	8
7	4	31	30
7	5	23	23
7	6	6	6
7	7	6	5
7	8	9	9
7	9	4	3
7	10	8	8
7	11	9	8
7	13	7	6
7	15	5	4
7	16	5	7
7	17	6	7
7	20	4	4
8	0	6	7
8	1	3	3
8	2	6	7
8	3	13	14
8	4	6	5
8	5	7	8
8	6	12	12
8	7	4	5
8	8	12	12
8	9	7	7
8	10	10	10
8	12	11	11
8	13	9	11
8	14	9	11
8	15	7	7
9	0	6	7
9	1	6	7
9	2	8	8
9	4	10	8
9	5	16	17
9	6	14	14
9	7	13	13
9	8	5	7
9	9	5	6
9	10	5	4
9	11	18	19
9	13	6	6
10	0	4	5
10	1	8	9
10	2	10	11
10	3	9	8
10	4	6	5
10	8	14	15
10	10	9	9
10	12	8	9
11	3	5	6
11	4	9	10
11	5	13	14
11	7	7	9
11	8	6	8
11	10	6	8
11	11	7	8
12	0	4	4
12	4	7	7
13	2	6	5

H = 2

K	L	FO	FC
0	0	139	164
0	1	52	58
0	2	50	49
0	3	51	57
0	4	100	107
0	5	10	3
0	6	19	19
0	7	11	12
0	9	8	9
0	10	26	26

Table 7d. (Continued)

0	11	4	3	3	5	8	9	5	19	5	6	9	5	8	7
0	13	9	8	3	6	39	39	6	0	11	10	9	6	15	15
0	17	12	12	3	7	49	46	6	1	26	24	9	7	15	15
0	20	5	2	3	8	9	9	6	2	29	29	9	8	12	12
1	0	5	5	3	9	13	13	6	3	28	26	9	10	14	14
1	1	83	90	3	10	17	14	6	4	5	5	9	11	10	10
1	2	142	161	3	11	4	3	6	5	10	9	9	12	6	7
1	3	95	106	3	13	8	7	6	6	22	21	9	14	7	8
1	4	5	6	3	14	11	10	6	7	10	10	9	16	4	4
1	5	23	23	3	15	16	15	6	8	5	6	10	0	6	6
1	6	7	6	3	16	8	7	6	9	7	8	10	1	5	5
1	7	33	33	3	17	5	4	6	10	5	4	10	2	7	9
1	8	33	32	3	18	7	6	6	12	11	12	10	3	10	10
1	9	9	7	3	19	8	8	6	13	12	12	10	4	8	7
1	10	16	16	3	20	5	4	6	15	5	6	10	5	13	11
1	11	9	8	4	0	20	19	6	18	5	5	10	6	9	10
1	12	7	7	4	1	21	22	7	0	31	30	10	7	6	8
1	13	7	6	4	2	25	24	7	1	40	38	10	8	10	12
1	14	19	19	4	3	26	26	7	2	19	18	10	9	18	20
1	15	11	11	4	4	34	33	7	3	10	9	10	10	9	9
1	16	17	17	4	5	37	38	7	4	8	7	10	11	5	4
1	17	8	6	4	6	25	26	7	5	12	12	10	12	6	6
1	18	5	7	4	7	5	4	7	6	14	12	10	13	5	7
1	19	15	16	4	8	22	21	7	7	7	6	10	14	6	6
1	20	5	5	4	9	32	32	7	9	11	10	11	0	4	4
2	0	49	51	4	10	19	19	7	10	6	5	11	2	13	13
2	1	14	13	4	11	10	11	7	11	11	13	11	3	9	9
2	2	26	23	4	12	22	21	7	13	5	5	11	8	10	11
2	3	41	41	4	13	13	12	7	14	5	5	12	0	11	12
2	4	36	40	4	14	5	3	7	15	4	6	12	3	7	6
2	5	19	19	4	15	6	7	7	16	8	8	13	1	4	3
2	6	15	17	4	16	10	9	7	19	5	8	13	4	4	4
2	7	5	3	4	18	6	7	8	0	13	14	13	5	5	4
2	8	11	11	4	20	6	5	8	1	19	18				
2	9	24	24	5	0	34	32	8	2	5	4		H =	3	
2	10	6	6	5	1	37	38	8	3	9	8	K	L	FO	FC
2	11	9	10	5	2	38	37	8	4	17	16	0	1	34	36
2	12	21	21	5	3	16	17	8	6	7	8	0	2	32	31
2	13	7	8	5	4	32	31	8	8	10	10	0	3	10	10
2	15	13	13	5	5	3	3	8	9	6	6	0	4	35	35
2	16	8	8	5	6	10	7	8	11	12	12	0	6	11	12
2	17	10	9	5	8	27	26	8	12	11	11	0	7	18	18
2	18	9	9	5	9	11	9	8	13	4	4	0	8	18	19
2	19	5	5	5	12	6	6	8	14	11	11	0	9	16	15
3	1	13	14	5	13	8	9	9	0	5	4	0	10	17	17
3	2	35	39	5	14	7	7	9	2	8	7	0	11	13	13
3	3	20	20	5	15	8	8	9	3	13	12	0	12	4	3
3	4	7	5	5	17	6	7	9	4	10	11	0	13	12	11

Table 7d. (Continued)

0	14	10	10	3	6	40	38	5	17	7	9	10	2	11	11
0	16	14	11	3	7	35	35	6	0	5	6	10	3	9	10
0	17	10	10	3	8	7	7	6	2	12	13	10	4	8	7
0	18	7	7	3	9	14	15	6	3	5	5	10	5	12	12
0	20	7	6	3	10	9	9	6	4	26	25	10	6	11	11
0	21	6	5	3	11	29	29	6	5	12	13	10	9	5	7
0	22	4	4	3	12	6	6	6	6	4	4	10	12	7	10
1	0	11	12	3	13	8	8	6	7	8	9	11	1	6	7
1	1	17	17	3	14	11	10	6	9	13	12	12	3	8	8
1	2	47	50	3	15	7	7	6	10	17	17				
1	3	39	42	3	16	4	4	6	11	4	3		H =	4	
1	4	45	50	3	17	6	6	6	14	5	5	K	L	FO	FC
1	5	20	21	3	18	7	7	7	0	5	5	0	1	9	9
1	6	47	47	3	19	4	4	7	1	20	18	0	2	11	2
1	7	7	7	4	1	4	3	7	2	20	18	0	3	29	28
1	8	18	18	4	2	11	11	7	4	9	9	0	4	51	55
1	9	16	17	4	3	20	20	7	5	10	11	0	5	40	43
1	10	7	9	4	4	26	26	7	6	24	22	0	6	16	16
1	11	18	17	4	5	8	8	7	7	8	8	0	7	13	15
1	12	12	11	4	6	21	19	7	8	8	8	0	8	11	10
1	13	6	4	4	7	8	7	7	11	9	8	0	9	14	15
1	14	7	7	4	8	12	11	7	13	11	12	0	11	12	11
1	16	24	24	4	9	12	11	7	14	7	8	0	13	13	12
1	17	13	13	4	10	13	12	7	15	8	11	0	14	25	25
1	18	7	8	4	11	13	13	8	0	11	11	0	15	5	4
2	0	49	51	4	12	11	10	8	1	22	22	0	16	6	5
2	1	13	12	4	13	7	5	8	3	5	4	0	17	21	20
2	2	33	34	4	14	12	12	8	4	18	18	0	18	5	6
2	3	35	38	4	15	17	17	8	6	6	5	1	0	21	21
2	4	34	37	4	16	13	13	8	7	21	21	1	1	24	24
2	5	22	24	4	17	5	6	8	10	4	4	1	2	16	16
2	6	25	25	4	18	6	7	8	11	10	11	1	3	14	15
2	7	23	23	4	19	4	4	8	13	8	8	1	4	26	27
2	8	20	20	4	20	4	3	9	0	10	11	1	5	20	21
2	9	8	10	5	0	19	18	9	1	10	10	1	6	17	16
2	10	11	11	5	1	17	18	9	2	8	7	1	7	10	12
2	11	12	13	5	2	15	14	9	3	12	11	1	8	4	2
2	13	5	5	5	3	9	9	9	4	6	6	1	10	5	6
2	15	10	10	5	4	15	13	9	5	4	5	1	11	17	17
2	17	14	14	5	5	6	6	9	6	8	8	1	12	10	10
2	18	8	10	5	6	23	23	9	7	15	15	1	14	8	8
2	20	5	6	5	7	13	12	9	8	11	11	1	15	11	12
3	0	11	11	5	8	4	5	9	9	11	12	1	16	8	9
3	1	20	21	5	10	18	17	9	10	8	9	1	18	5	3
3	2	35	33	5	11	17	17	9	11	9	10	2	0	16	17
3	3	23	23	5	13	7	8	9	16	4	3	2	1	11	12
3	4	27	27	5	14	9	7	10	0	5	5	2	2	22	23
3	5	13	13	5	16	13	14	10	1	9	9	2	3	23	23

Table 7d. (Continued)

2	4	30	30	5	4	9	7	9	4	15	14	1	17	5	5
2	5	38	37	5	5	9	8	9	6	8	8	2	1	7	9
2	6	6	7	5	6	12	12	9	7	15	15	2	2	29	29
2	7	8	9	5	7	7	7	9	8	13	13	2	3	11	13
2	8	12	11	5	8	4	3	9	9	4	4	2	4	9	10
2	9	7	7	5	10	12	12	9	12	4	7	2	5	11	14
2	11	6	6	5	11	7	8	9	14	6	6	2	7	10	10
2	12	8	8	5	13	5	4	10	0	13	14	2	9	10	9
2	13	5	6	5	14	12	12	10	2	7	7	2	10	13	13
2	14	19	18	5	15	6	6	10	3	7	7	2	12	5	7
2	16	5	7	6	0	10	10	10	4	9	9	2	13	4	3
2	17	13	13	6	1	16	16	10	5	12	13	2	14	5	5
2	18	7	6	6	2	14	14	10	6	10	10	2	16	4	4
2	20	4	4	6	3	19	18	10	9	5	5	3	0	10	9
3	0	5	6	6	4	18	16	11	1	5	6	3	1	6	5
3	1	22	23	6	5	16	15	11	2	4	5	3	2	8	9
3	3	31	30	6	6	9	8	11	4	7	7	3	3	5	5
3	4	9	9	6	7	8	5	11	6	5	4	3	4	7	7
3	5	11	11	6	9	7	6	11	7	4	4	3	6	11	11
3	6	4	4	6	10	5	2	12	0	6	7	3	7	7	8
3	7	18	17	6	11	8	8	12	1	4	4	3	8	5	5
3	8	15	14	6	12	11	11					3	12	7	6
3	9	13	13	6	14	7	7		H =	5		3	13	11	10
3	10	14	14	6	15	5	6	K	L	FO	FC	3	15	6	7
3	11	11	11	6	16	7	7	0	1	12	13	4	0	5	5
3	12	13	11	7	0	5	6	0	2	7	8	4	1	10	10
3	13	4	4	7	1	5	4	0	3	24	26	4	2	8	8
3	14	11	10	7	3	15	15	0	5	11	13	4	3	13	12
3	15	8	7	7	4	9	10	0	6	19	19	4	4	19	18
3	16	8	8	7	5	14	12	0	7	17	17	4	5	8	8
3	17	5	4	7	7	7	6	0	8	16	15	4	7	4	5
4	1	7	8	7	9	7	7	0	10	10	10	4	8	10	9
4	2	17	16	7	10	10	9	0	12	5	6	4	9	9	9
4	3	22	23	7	11	8	7	0	13	8	9	4	10	5	3
4	4	14	14	7	12	5	6	0	14	17	17	4	12	6	4
4	5	21	20	8	1	6	7	0	15	11	10	4	13	5	7
4	6	18	17	8	2	10	10	0	17	9	11	4	15	7	8
4	7	4	3	8	3	9	8	1	1	4	5	4	17	5	4
4	8	5	6	8	4	10	8	1	3	5	5	5	1	6	5
4	9	12	12	8	5	12	12	1	4	13	14	5	2	10	9
4	11	10	10	8	6	9	9	1	5	5	4	5	3	4	4
4	12	5	5	8	7	6	6	1	6	22	23	5	4	14	14
4	14	5	7	8	9	10	9	1	7	18	18	5	5	6	4
4	15	5	7	8	10	6	6	1	8	17	18	5	6	13	12
5	0	6	7	8	14	7	8	1	9	5	4	5	7	8	7
5	1	12	11	9	0	18	17	1	12	12	11	5	8	4	4
5	2	13	14	9	1	5	6	1	13	8	8	5	10	5	4
5	3	15	16	9	3	7	6	1	15	11	11	5	11	7	7

Table 7d. (Continued)

5	12	5	5
5	14	4	3
6	1	7	5
6	3	13	13
6	4	8	7
6	5	4	5
6	6	10	10
6	8	11	10
6	9	11	10
6	11	5	7
6	13	5	6
6	14	5	7
7	1	8	5
7	3	8	7
7	4	7	6
7	5	6	7
7	6	9	8
7	8	8	7
7	12	5	4
8	2	5	5
8	3	7	7
8	4	6	5
8	6	7	7
8	7	7	7
8	8	6	6
8	9	6	7
9	3	8	6
9	4	6	5
9	10	4	5
10	5	7	7
10	6	5	4
10	9	5	4
11	1	6	4
11	3	7	6
11	4	4	3
12	2	4	3

H = 6

K	L	FO	FC
0	0	5	8
0	1	10	10
0	3	22	24
0	4	6	5
0	6	7	7
0	7	19	18
0	10	10	10
0	11	6	7
0	12	9	8
0	13	7	8
0	14	9	10
0	15	8	9
1	0	14	12
1	1	11	12
1	2	4	4
1	3	10	9
1	4	12	13
1	5	19	19
1	6	8	7
1	7	7	7
1	8	10	9
1	9	9	9
1	11	6	7
1	12	11	13
1	13	9	10
1	14	6	6
1	15	5	6
1	17	5	5
2	0	6	7
2	1	9	10
2	2	12	13
2	3	8	7
2	4	5	7
2	5	12	12
2	6	8	9
2	7	13	13
2	8	6	5
2	9	11	12
2	17	6	5
3	0	8	8
3	1	7	6
3	3	12	11
3	4	10	9
3	10	5	4
3	12	6	8
3	14	5	6
4	0	6	7
4	1	8	8
4	2	11	10
4	4	6	6
4	5	7	6
4	6	8	6
4	7	5	5
4	8	8	8
4	9	7	5
4	10	9	7
4	12	5	4
4	16	4	5
5	0	7	7
5	1	8	8
5	3	11	9
5	4	7	7
5	5	6	4
5	6	5	4
5	7	7	7
5	9	5	4
6	0	9	8
6	1	9	10
6	2	6	6
6	3	6	6
6	6	8	7
6	7	6	4
6	8	7	5
6	11	7	7
6	13	5	6
7	1	11	9
7	5	9	8
7	6	5	6
7	8	6	4
7	9	5	3
7	13	5	5
8	1	8	6
8	2	7	6
8	3	8	7
8	4	4	5
8	5	10	10
8	6	8	7
8	7	6	5
8	8	6	6
8	9	5	3
9	1	5	4
9	2	6	5
9	3	9	7
9	5	6	6
9	7	4	3
10	1	5	3
10	3	4	5
10	4	5	5
10	5	8	6
10	6	4	2

H = 7

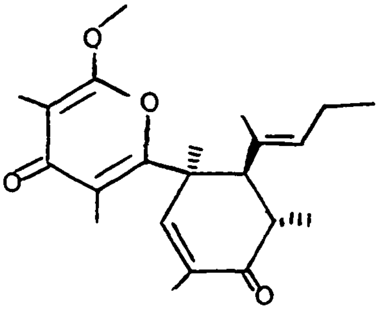
K	L	FO	FC
0	1	6	9
0	5	10	12
0	6	8	7
0	10	6	6
0	14	8	7
1	1	13	12
1	2	9	9
1	3	6	6
1	4	7	9
1	5	5	4
1	6	6	7
1	7	9	10
1	8	4	5
1	9	6	6
1	10	5	3
1	12	7	7
2	1	8	9
2	2	9	8
2	4	5	5
2	7	7	9
2	11	6	7
2	13	4	4
3	1	6	6
3	3	10	11
3	4	5	3
3	7	5	5
3	12	4	3
4	1	6	5
4	4	5	6
4	6	5	4
4	9	5	3
4	13	5	4
5	0	6	5
5	1	7	6
5	2	5	4
5	5	7	6
5	7	5	4
5	8	5	5
5	10	4	4
5	12	5	4
6	2	6	6
7	1	7	7
7	3	7	6
7	4	4	4
7	7	6	5
8	2	5	3
9	0	7	5

TAble 7d. (Continued)

H = 8

K	L	FO	FC
1	10	4	3
2	10	5	5
3	0	6	8
3	1	4	4
4	1	5	5
4	6	5	4
5	0	6	4

Discussion   Crispatone is apparently a polyketide compound which, on inspection, can be divided into eight "propionate" units. Its rare α-methoxy-γ-pyrone ring also appears in tridachione, a metabolite of Tridachiella diomedea. Tridachione has an unprecedented skeleton which looks like it is composed of six "propionate" units. The structure of tridachione was determined by X-ray diffraction (64).



tridachione

Metabolites of Gorgonians and Soft Corals

Zooxanthellae and the metabolism of coelenterates

The coral reefs in the shallow waters of the tropics are occupied by a complex mixture of interdependent organisms. Important in the ecology of the coral reefs are the zooxanthellae, unicellular algae which are symbiotically associated with a variety of coelenterates. They invariably occur in their hosts as single vegetative cells encysted in a thick, complex cell wall (65). They are probably members of the *Dinophyceae* class for they have a nucleus typical of the dinoflagellates and when cultured *in vitro* give rise to motile forms morphologically similar to those produced by species of this algal class (66). Evidently more than one genus is represented in the zooxanthellae, though one particular species, *Gymnodinium microadriaticum*, has been isolated from 13 different host species from distinct phyla and gathered from different parts of the world (67).

When zooxanthellae are incubated with $^{14}CO_3^{-2}$ in sea water and exposed to light they produce a large amount of ^{14}C-labelled organic compounds (68, 69, 70). ^{14}C fixation is substantially less with control samples kept in the dark. When a homogenate of host tissue is added to the sea water the algae rapidly release up to 70% of their labelled material. Not every product is released to the medium. The amount and composition of secreted material depends on host species. When the hosts themselves are incubated with $^{14}CO_2^{-2}$ and exposed to light a significant amount of ^{14}C fixation is again observed and a large proportion of the fixed ^{14}C (20-50%)is found incorporated into host tissues, particularly in host lipids and amino acids (71, 72, 73, 74).
These results are interpreted as evidence that the zooxanthellae photosynthetically fix carbon and are induced

to release some of the photosynthate for use by their hosts.

The degree to which the released products contribute to the nutrition of their hosts is debatable and most likely varies with host species and environmental conditions (65). For example, the reef-building corals are carnivorous organisms whose nutritional requirements can be satisfied by the zooplankton they feed on, but if food is scarce they may depend on their zooxanthellae for normal growth. On the other hand, the xeniid alcyonaceans eat little, if any, zooplankton and thrive in the light. They probably depend heavily on their autotrophic symbionts for survival.

While nourishment may be the main function of the symbiotic zooxanthellae, their role in the synthesis of their host's secondary metabolites should not be ignored. The gorgonians (Order Gorgonacea) and soft corals (Order Alcyonacea) are members of the coelenterate subclass Octocorallia which generally form symbiotic associations with zooxanthellae and whose natural products have been studied by many chemists. The great majority of the diterpenes isolated from the Octocorals have the cembrane skeleton or one easily derived from it. These compounds often occur in high concentrations in the organisms. Some cembranolides even occur in crystalline form in gorgonians (75). Specific diterpene content of the Octocorals varies even among closely related species or specimens of one species collected from different geographical locations (75, 76). This suggests the organisms are hosting different species of zooxanthellae, each with different metabolic capabilities, which are contributing to the diterpene synthesis (75).

Some biosynthetic experiments support this suggestion. Rice *et al*. examined the gorgonian *Pseudoplexaura porosa* and found they could hardly separate the gorgonian's zooxanthellae from crystals of a cembranolide, crassin acetate (77). Histological preparations of *P. porosa* showed no crassin acetate inside the zooxanthellae, but crystals of the compound were closely associated with the tissue containing the symbionts. Curious about the origin of the diterpene, they fed $^{14}CO_3^{-2}$ and ^{14}C-acetate and found small but significant incorporation into the ring of crassin acetate. About ten times more acetate than carbonate incorporated. They could not demonstrate crassin acetate synthesis in free zooxanthellae and concluded host and symbiont worked together to synthesize the compound. Now there is evidence that free zooxanthellae are able to incorporate ^{14}C-mevalonate into crassin acetate (75).

Many of the cembrane-type diterpenes from soft corals and gorgonians are toxins which may afford protection from potential predators or from larvae which might settle and encrust the immobile bodies of these coelenterates. Sarcophine is lethal to the fish Gambusia offinis with an LD_{50} after three hours of 3 mg/liter (78). Crassin acetate in high concentrations is lethal to several types of marine organisms (75). Sinularin, dihydrosinularin, sinulariolide and asperdiol are all active against P-388 lymphocytic leukemia (79, 80). Eunicin, jeunicin and crassin acetate affect the growth and motility of Tetrahymena pyriformis (75). Eunicin and crassin acetate are also mildly antibiotic (81). The discovery that zooxanthellae are involved in producing these various toxins would show the benefits of their symbiotic association with the Octocorals are more than nutritional.

The sesquiterpenes of the Octocorals are a more diverse group than the diterpenes. Several of them have novel carbon skeletons. Skeletons which are precedented usually have the opposite configuration of their terrestrial form (75, 82, 83). Distribution of sesquiterpenes in some Octocorallia species depends on the place the organisms are collected (75, 84). Perhaps this means that sesquiterpene as well as diterpene biosynthesis in the Octocorals is influenced by the symbiotic zooxanthellae.

There are a number of directions to go in exploring the origin of the terpenes from soft corals and gorgonians. It should be possible to design biosynthetic experiments like those of Rice et al. to test the ability of the zooxanthellae to synthesize a particular terpenoid, either by themselves or in conjunction with host tissue (77). A comparison of the terpene content of symbiont-free Octocorals to that of Octocorals with zooxanthellae should also yield significant information. Tursch, for instance, reports that the diterpenoid eunicellin found in the gorgonian *Eunicella stricta* does not occur in a deep-water form of the species which has no zooxanthellae. He also has been unable to isolate any terpenes from soft corals devoid of zooxanthellae (84). Finally, the continued isolation and characterization of new terpenes expands the base of data on which theories are built and with which experiments are planned.

Ophirin

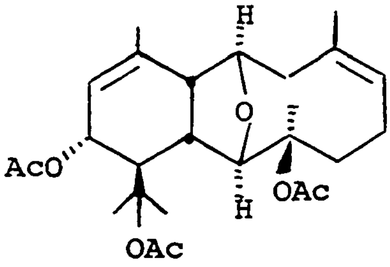
Background Ophirin was isolated from an unidentified gorgonian from the Gulf of Eilet. Spectra of the compound indicated it was a diterpene with three acetate groups and the molecular formula $C_{26}H_{38}O_7$. Portions of the structure were obtained by examination of the ^1H and ^{13}C NMR spectra but certain features of the ^1H NMR spectrum were difficult to interpret and an X-ray analysis was required to complete the structure determination.

Experimental Large, clear crystals of ophirin were orthorhombic with cell constants $\underset{\sim}{a}$ = 8.886(2)Å, $\underset{\sim}{b}$ = 16.670(6)Å and $\underset{\sim}{c}$ = 16.731(6)Å and a calculated density for four molecules

$C_{26}H_{38}O_7$ in the unit cell of 1.24 g/cc. Space group $P2_12_12_1$ was assigned on the basis of systematic extinctions in the data. All unique data with $2\theta \leq 114.1°$ (CuKα) were measured using a minimum scan rate of 1°/minute. The intensities of three standard reflections used to monitor crystal stability did not decline during data collection. All 1951 recorded intensities were corrected for Lorentz, polarization and background effects and 1647 of the reflections (∿84%) were then judged observed.

Structure factors were converted to Es and the 216 Es $\geq$ 1.48 were phased by direct methods. MULTAN generated 64 possible phase sets, none of which were good solutions. MULTAN was then rerun, increasing the number of starting set reflections to six and giving magic integer representation to general starting set reflections. Of the 120 possible phase sets generated one gave an E map which showed the majority of the structure. A fragment chosen from the map was used as input for an F_o synthesis, and the electron density map calculated from the phased structure factors showed the entire molecule. Nonhydrogen atoms were assigned anisotropic thermal parameters and refined by full-matrix least-squares. Hydrogen atoms, in calculated positions with isotropic temperature factors, were included in the model at this point. Refinement of the entire structure, including hydrogens, converged to a standard R-factor of .073 for the observed reflections.

Results The stereochemistry of ophirin's tricyclic structure is shown in the computer generated perspective drawing, figure 8. The ring junctions have a cis-anti-cis configuration. The double bond at C(6) has the E configuration. The acetoxy group at C(3) is exo with respect to the nine-membered ring. The five-membered ring is neither planar nor in an envelope conformation, but is fairly flat. The six-membered ring is also somewhat flat. Some least-squares planes are shown in table 8e and selected dihedral angles are in table 8f. Tables 8a, 8b, 8c and 8d are fractional coordinates of all the atoms, bond distances, bond angles and structure factor magnitudes, respectively. Bond distances and angles are unexceptional and there are no significantly short intermolecular distances (16).



ophirin

Figure 8. A computer generated perspective drawing of ophirin with hydrogens omitted for clarity.

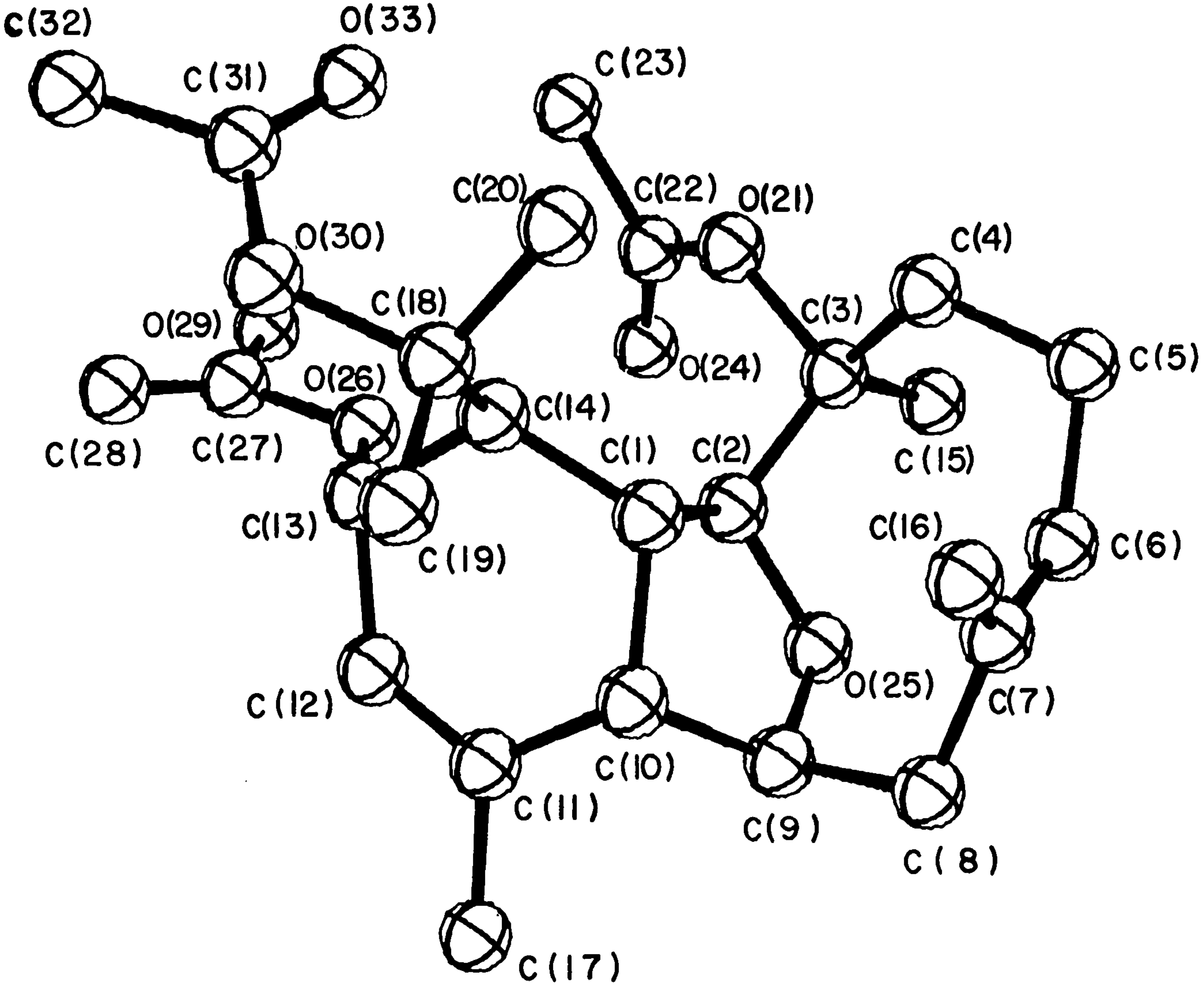

C(32)
O(33)
C(31)
C(23)
C(20)
C(22)
O(21)
C(4)
O(30)
C(18)
C(3)
O(29)
C(5)
O(24)
O(26)
C(14)
C(28)
C(27)
C(1)
C(2)
C(15)
C(16)
C(13)
C(6)
C(19)
O(25)
C(7)
C(12)
C(10)
C(11)
C(9)
C(8)
C(17)

Table 8a. Fractional coordinates for ophirin. Standard deviations of the least significant figures are given in parentheses. Hydrogens are assigned the same numbers as the heavy atoms to which they are bonded. The numbering scheme refers to figure 8.

C(1)	-.1649(8)	.0492(4)	.1394(4)
C(2)	-.0384(8)	.0164(4)	.0865(4)
C(3)	-.0513(9)	.0262(5)	-.0049(4)
C(4)	-.1327(9)	.0994(5)	-.0391(5)
C(5)	-.0486(11)	.1807(6)	-.0442(6)
C(6)	.0428(10)	.1927(4)	.0318(6)
C(7)	-.0047(9)	.2172(5)	.1032(6)
C(8)	.0885(9)	.1903(5)	.1730(5)
C(9)	.0742(8)	.0966(4)	.1877(5)
C(10)	-.0798(8)	.0710(4)	.2171(4)
C(11)	-.0671(9)	-.0014(4)	.2744(4)
C(12)	-.1520(9)	-.0663(4)	.2649(4)
C(13)	-.2726(8)	-.0787(4)	.2035(4)
C(14)	-.3006(7)	-.0080(4)	.1458(4)
C(15)	.1003(9)	.0118(6)	-.0495(5)
C(16)	-.1495(11)	.2584(5)	.1191(7)
C(17)	.0409(12)	.0032(6)	.3428(5)
C(18)	-.4491(8)	.0382(4)	.1661(5)
C(19)	-.4440(10)	.0847(5)	.2436(5)
C(20)	-.5004(9)	.0886(5)	.0954(6)
O(21)	-.1614(6)	-.0378(3)	-.0305(3)
C(22)	-.1331(14)	-.1168(5)	-.0289(6)
C(23)	-.2671(16)	-.1603(6)	-.0612(5)
O(24)	-.0183(9)	-.1465(4)	-.0020(5)
O(25)	.1002(5)	.0533(3)	.1145(3)
O(26)	-.2303(6)	-.1482(3)	.1557(3)
C(27)	-.3019(13)	-.2183(5)	.1712(7)
C(28)	-.2398(15)	-.2840(5)	.1171(7)
O(29)	-.3990(10)	-.2233(4)	.2193(6)
O(30)	-.5704(5)	-.0221(3)	.1835(3)
C(31)	-.6181(10)	-.0760(5)	.1280(6)
C(32)	-.7407(11)	-.1265(5)	.1613(8)
O(33)	-.5687(8)	-.0814(5)	.0617(5)
H(1)	-.194(6)	.105(3)	.118(3)
H(2)	-.029(8)	-.025(4)	.097(4)
H(4A)	-.245(7)	.108(4)	-.003(4)
H(4B)	-.161(7)	.085(3)	-.093(3)
H(5A)	-.119(8)	.211(4)	-.054(4)
H(5B)	.026(11)	.180(6)	-.086(6)
H(6)	.139(9)	.165(4)	.031(5)
H(8A)	.179(6)	.198(3)	.162(3)
H(8B)	.056(6)	.216(3)	.222(3)
H(9)	.160(6)	.083(3)	.225(3)

Table 8a. (Continued)

H(10)	-.125(8)	.120(4)	.245(4)
H(12)	-.142(10)	-.114(5)	.307(5)
H(13)	-.376(9)	-.095(5)	.229(5)
H(14)	-.311(6)	-.042(3)	.098(3)
H(15A)	.171(18)	.065(9)	-.057(9)
H(15B)	.079(7)	.008(4)	-.112(4)
H(15C)	.124(8)	-.041(4)	-.072(4)
H(16A)	-.214(10)	.224(5)	.151(5)
H(16B)	-.210(8)	.263(4)	.069(4)
H(16C)	-.139(9)	.301(4)	.131(5)
H(17A)	.155(12)	-.010(6)	.314(6)
H(17B)	-.012(10)	-.051(5)	.408(6)
H(17C)	.047(16)	.061(8)	.382(8)
H(19A)	-.414(10)	.041(5)	.292(5)
H(19B)	-.548(12)	.101(6)	.268(6)
H(19C)	-.369(9)	.135(4)	.235(4)
H(20A)	-.464(8)	.138(4)	.081(4)
H(20B)	-.600(8)	.126(4)	.129(4)
H(20C)	-.502(14)	.071(8)	.022(7)
H(23A)	-.365(11)	-.153(6)	-.006(5)
H(23B)	-.251(12)	-.215(7)	-.068(6)
H(23C)	-.277(24)	-.152(12)	-.113(12)
H(28A)	-.303(14)	-.303(7)	.071(8)
H(28B)	-.236(28)	-.326(14)	.142(14)
H(28C)	-.147(15)	-.267(7)	.083(7)
H(32A)	-.691(9)	-.169(5)	.203(5)
H(32B)	-.791(10)	-.151(5)	.109(5)
H(32C)	-.795(13)	-.083(7)	.210(7)

Table 8b. Bond distances of ophirin. The standard deviation of the least significant figure of each distance is given in parentheses.

C(1) - C(2)	1.532(10)
C(1) - C(10)	1.547(9)
C(1) - C(14)	1.542(10)
C(2) - C(3)	1.541(10)
C(2) - O(25)	1.454(8)
C(3) - C(4)	1.531(11)
C(3) - C(15)	1.559(11)
C(3) - O(21)	1.510(10)
C(4) - C(5)	1.550(13)
C(5) - C(6)	1.522(14)
C(6) - C(7)	1.331(14)
C(7) - C(8)	1.501(12)
C(7) - C(16)	1.483(13)
C(8) - C(9)	1.586(11)
C(9) - C(10)	1.515(10)
C(9) - O(25)	1.440(9)
C(10) - C(11)	1.547(10)
C(11) - C(12)	1.328(10)
C(11) - C(17)	1.496(12)
C(12) - C(13)	1.499(11)
C(13) - C(14)	1.544(10)
C(13) - O(26)	1.456(8)
C(14) - C(18)	1.565(10)
C(18) - C(19)	1.512(12)
C(18) - C(20)	1.522(12)
C(18) - O(30)	1.502(8)
O(21) - C(22)	1.340(10)
C(22) - C(23)	1.496(17)
C(22) - O(24)	1.221(14)
O(26) - C(27)	1.356(10)
C(27) - C(28)	1.525(14)
C(27) - O(29)	1.182(15)
O(30) - C(31)	1.359(11)
C(31) - C(32)	1.485(13)
C(31) - O(33)	1.197(13)

Table 8c. Bond angles of ophirin. The standard deviation of the least significant figure of each angle is given in parentheses.

C(2) - C(1) - C(10)	102.2(5)
C(2) - C(1) - C(14)	113.2(6)
C(10) - C(1) - C(14)	118.0(6)
C(1) - C(2) - C(3)	118.8(6)
C(1) - C(2) - O(25)	106.5(5)
C(3) - C(2) - O(25)	109.8(6)
C(2) - C(3) - C(4)	119.4(6)
C(2) - C(3) - C(15)	113.2(6)
C(2) - C(3) - O(21)	104.8(6)
C(4) - C(3) - C(15)	110.6(7)
C(4) - C(3) - O(21)	98.7(6)
C(15) - C(3) - O(21)	108.4(6)
C(3) - C(4) - C(5)	119.4(7)
C(4) - C(5) - C(6)	109.1(7)
C(5) - C(6) - C(7)	128.4(8)
C(6) - C(7) - C(8)	115.6(8)
C(6) - C(7) - C(16)	125.3(9)
C(8) - C(7) - C(16)	118.6(8)
C(7) - C(8) - C(9)	111.8(7)
C(8) - C(9) - C(10)	113.6(6)
C(8) - C(9) - O(25)	110.4(6)
C(10) - C(9) - O(25)	106.3(6)
C(1) - C(10) - C(9)	103.6(5)
C(1) - C(10) - C(11)	111.9(5)
C(9) - C(10) - C(11)	110.8(6)
C(10) - C(11) - C(12)	121.4(7)
C(10) - C(11) - C(17)	118.7(6)
C(12) - C(11) - C(17)	119.9(7)
C(11) - C(12) - C(13)	126.9(7)
C(12) - C(13) - C(14)	116.0(6)
C(12) - C(13) - O(26)	107.6(6)
C(14) - C(13) - O(26)	107.8(5)
C(1) - C(14) - C(13)	112.9(6)
C(1) - C(14) - C(18)	111.7(6)
C(13) - C(14) - C(18)	112.1(6)
C(14) - C(18) - C(19)	114.4(6)
C(14) - C(18) - C(20)	110.8(6)
C(14) - C(18) - O(30)	108.5(5)
C(19) - C(18) - C(20)	113.1(6)
C(19) - C(18) - O(30)	101.4(6)
C(20) - C(18) - O(30)	107.8(6)
C(3) - O(21) - C(22)	124.5(7)
O(21) - C(22) - C(23)	108.7(9)
O(21) - C(22) - O(24)	124.3(9)
C(23) - C(22) - O(24)	127.0(9)

Table 8c. (Continued)

C(2) - O(25) - C(9)	110.5(5)
C(13) - O(26) - C(27)	117.4(7)
O(26) - C(27) - C(28)	109.7(9)
O(26) - C(27) - O(29)	122.2(8)
C(28) - C(27) - O(29)	128.1(9)
C(18) - O(30) - C(31)	122.2(6)
O(30) - C(31) - C(32)	110.3(9)
O(30) - C(31) - O(33)	124.7(8)
C(32) - C(31) - O(33)	125.0(9)

Table 8d. Observed and calculated structure factor magnitudes for ophirin.

H =	0			3	12	3	3	6	16	7	5	10	9	8	8
K	L	FO	FC	3	13	8	8	6	17	6	6	10	11	8	7
0	2	5	6	3	14	15	16	7	1	16	16	10	12	9	4
0	4	17	24	3	15	5	4	7	2	41	42	10	14	9	7
0	6	33	39	3	16	6	7	7	3	4	1	11	1	15	14
0	8	7	7	3	17	5	7	7	6	42	43	11	2	10	11
0	10	12	14	4	0	56	56	7	7	9	10	11	3	18	19
0	12	4	6	4	1	27	28	7	8	20	20	11	4	16	16
0	14	6	8	4	2	26	33	7	10	16	16	11	6	8	8
0	16	5	6	4	3	22	23	7	11	4	3	11	8	4	6
0	18	4	4	4	4	49	56	7	13	11	9	11	9	7	7
1	1	2	2	4	5	26	26	7	14	4	5	11	11	9	8
1	2	105	167	4	6	3	2	7	16	3	3	11	12	12	12
1	3	13	11	4	7	12	12	8	0	11	10	12	0	5	6
1	4	88	123	4	8	4	3	8	1	3	4	12	1	15	14
1	5	32	38	4	9	14	16	8	2	3	2	12	2	14	14
1	6	57	73	4	10	3	3	8	3	11	10	12	3	10	9
1	7	12	12	4	13	5	3	8	4	7	7	12	4	8	7
1	8	26	32	4	15	6	5	8	5	21	23	12	5	4	3
1	9	8	10	4	16	5	5	8	6	24	26	12	6	19	20
1	10	23	29	4	17	3	2	8	7	13	10	12	7	7	7
1	13	6	12	5	1	63	69	8	9	8	8	12	8	8	9
1	15	4	11	5	2	31	31	8	12	14	13	12	10	3	2
1	16	7	8	5	3	22	20	8	13	9	8	12	11	8	6
2	0	109	169	5	4	22	20	8	14	9	6	12	13	8	7
2	1	12	14	5	5	22	21	8	15	4	4	13	1	15	16
2	2	23	28	5	6	3	1	8	16	4	4	13	3	8	8
2	3	21	23	5	7	34	34	9	1	32	35	13	4	4	3
2	4	13	17	5	8	25	25	9	2	12	12	13	5	6	6
2	5	20	20	5	9	24	24	9	3	3	3	13	6	11	10
2	6	8	7	5	10	14	13	9	4	5	5	13	7	3	3
2	7	25	26	5	12	15	15	9	5	39	40	13	10	9	7
2	8	6	5	5	13	19	21	9	6	13	13	13	11	8	8
2	9	4	4	5	14	13	13	9	7	5	6	13	12	3	4
2	10	7	6	5	17	6	6	9	8	12	12	14	0	25	25
2	11	18	19	6	0	15	15	9	9	10	9	14	1	16	18
2	13	10	14	6	1	23	20	9	10	20	21	14	2	23	24
2	14	4	7	6	2	51	55	9	14	4	2	14	3	4	6
2	16	3	3	6	3	56	62	9	15	15	13	14	4	4	2
3	1	22	22	6	5	40	40	10	0	15	15	14	5	9	8
3	2	8	5	6	6	66	65	10	1	16	19	14	6	8	10
3	3	44	48	6	7	7	6	10	2	12	13	14	7	13	14
3	4	51	56	6	8	14	13	10	3	31	29	14	8	10	9
3	6	31	36	6	9	17	17	10	4	11	11	14	9	10	9
3	7	20	22	6	10	18	17	10	5	16	16	14	11	5	6
3	8	16	16	6	12	22	22	10	6	10	10	15	1	16	15
3	9	30	31	6	14	6	6	10	7	9	10	15	2	6	4
3	10	10	8	6	15	5	4	10	8	22	21	15	3	26	25

Table 8d. (Continued)

15	4	13	13	1	13	19	17	4	10	17	17	7	8	16	16
15	7	14	14	1	14	11	10	4	11	6	7	7	9	6	6
15	8	12	8	1	15	4	4	4	12	10	11	7	10	7	7
15	9	5	4	1	16	13	11	4	13	19	19	7	11	6	8
15	10	5	4	1	18	7	6	4	14	18	16	7	12	6	5
16	0	8	10	2	0	68	80	4	15	7	7	7	13	7	8
16	1	11	12	2	1	20	20	4	16	10	9	7	14	5	4
16	2	6	3	2	2	30	32	4	17	6	6	7	15	6	6
16	4	4	4	2	3	57	63	5	0	10	11	8	0	24	28
16	5	12	12	2	4	36	37	5	1	52	57	8	1	34	33
16	7	6	8	2	5	23	24	5	2	65	70	8	2	23	23
16	8	6	8	2	6	4	2	5	3	63	66	8	3	23	24
17	3	9	10	2	7	49	45	5	4	17	19	8	4	20	20
17	4	5	7	2	8	38	38	5	5	60	63	8	5	24	25
17	6	7	7	2	9	13	15	5	6	7	8	8	6	19	18
18	0	10	2	2	10	18	18	5	7	25	24	8	7	12	13
18	1	9	11	2	11	10	9	5	8	24	23	8	8	9	11
				2	12	23	25	5	9	17	18	8	9	8	7
H = 1				2	13	13	12	5	10	19	18	8	11	18	18
K	L	FO	FC	2	14	4	2	5	11	6	6	8	12	6	7
0	1	12	12	2	15	9	10	5	12	9	7	8	13	3	2
0	2	31	37	2	16	8	9	5	14	11	11	8	15	3	3
0	3	26	25	3	0	2	0	5	15	4	4	8	16	6	7
0	4	74	80	3	1	49	51	5	16	3	2	9	0	11	11
0	5	72	75	3	2	23	23	6	0	98	110	9	1	24	24
0	6	69	73	3	3	39	38	6	1	19	18	9	2	5	5
0	7	63	65	3	4	14	12	6	2	20	21	9	3	25	24
0	8	13	14	3	5	58	63	6	3	12	12	9	4	14	15
0	9	17	16	3	6	19	19	6	4	10	10	9	5	18	18
0	10	12	10	3	7	29	28	6	5	24	24	9	6	5	6
0	11	5	9	3	8	23	24	6	6	23	23	9	7	17	18
0	12	20	19	3	9	28	27	6	7	12	10	9	8	7	6
0	15	7	8	3	10	10	10	6	8	26	25	9	9	11	12
0	16	9	11	3	11	9	6	6	9	5	7	9	10	5	4
0	18	6	8	3	13	3	1	6	10	16	17	9	11	12	11
1	0	82	100	3	14	10	10	6	11	13	13	9	12	7	7
1	1	72	87	3	15	10	10	6	12	6	6	9	13	9	8
1	2	64	77	3	16	6	6	6	13	10	9	9	14	3	3
1	3	96	117	4	0	4	7	6	14	5	4	9	15	5	4
1	4	66	75	4	1	35	35	6	15	10	9	10	0	5	4
1	5	27	25	4	2	75	84	7	0	12	12	10	1	3	5
1	6	17	17	4	3	63	67	7	1	18	19	10	2	19	18
1	7	21	20	4	4	35	39	7	2	41	41	10	3	16	18
1	8	20	21	4	5	27	27	7	3	47	47	10	4	13	12
1	9	26	24	4	6	14	15	7	4	44	42	10	5	5	6
1	10	20	20	4	7	49	48	7	5	19	17	10	6	11	11
1	11	6	5	4	8	17	16	7	6	7	7	10	7	19	18
1	12	8	9	4	9	22	20	7	7	21	20	10	8	10	10

Table 8d. (Continued)

10	9	8	8
10	10	9	9
10	11	13	13
10	12	15	14
10	13	7	7
10	15	7	6
11	0	12	12
11	1	11	9
11	2	5	5
11	3	10	10
11	4	3	5
11	5	14	13
11	6	19	19
11	7	11	12
11	8	7	6
11	9	18	18
11	10	13	13
11	12	12	12
11	13	9	9
12	0	19	19
12	1	12	8
12	2	15	15
12	3	21	21
12	4	14	14
12	5	5	4
12	6	17	18
12	7	14	15
12	8	8	9
12	10	5	4
12	11	6	7
12	12	11	12
12	13	5	4
13	0	14	15
13	1	20	20
13	2	26	26
13	3	5	4
13	4	8	11
13	7	7	7
13	8	5	6
13	10	14	14
13	11	9	8
13	12	6	5
14	0	7	7
14	1	7	9
14	2	15	15
14	3	12	13
14	4	9	8
14	5	7	6
14	6	8	9
14	8	15	15
14	10	3	2
14	11	6	5
15	1	15	15
15	2	5	13
15	3	3	5
15	4	30	11
15	5	12	11
15	6	5	6
15	8	6	6
15	9	7	5
15	10	7	6
16	0	8	8
16	1	16	16
16	2	8	7
16	3	11	8
16	4	9	9
16	5	4	4
16	6	4	4
16	7	3	4
16	8	8	6
17	0	3	3
17	2	4	5
17	3	3	4
17	4	4	5
17	5	5	5
17	6	4	5
18	0	8	7
18	1	7	6

H = 2

K	L	FO	FC
0	0	84	93
0	1	68	77
0	2	40	44
0	3	56	66
0	4	55	63
0	5	20	19
0	6	35	30
0	7	34	36
0	9	11	11
0	10	33	33
0	11	5	4
0	12	15	15
0	13	7	6
0	14	10	7
0	15	6	6
0	17	15	12
1	0	13	12
1	1	79	89
1	2	23	22
1	3	61	65
1	4	52	55
1	5	17	16
1	6	31	30
1	7	31	31
1	8	29	27
1	9	26	25
1	10	13	12
1	11	19	19
1	12	22	21
1	13	22	21
1	14	6	7
1	15	9	9
2	0	82	89
2	1	95	92
2	2	54	55
2	3	36	35
2	4	39	37
2	5	60	67
2	6	9	8
2	8	18	17
2	9	17	17
2	10	17	17
2	11	11	11
2	12	18	18
2	13	14	13
2	14	10	9
2	15	5	5
2	17	6	6
3	0	102	116
3	1	49	50
3	2	19	17
3	3	39	37
3	4	21	23
3	5	43	44
3	6	10	9
3	7	20	20
3	8	14	14
3	9	8	8
3	10	19	17
3	11	5	4
3	12	9	10
3	14	13	14
3	15	4	3
3	16	7	7
4	0	45	45
4	1	38	39
4	2	32	32
4	3	22	18
4	4	15	14
4	5	23	22
4	6	31	29
4	7	25	24
4	8	23	22
4	9	11	11
4	10	14	13
4	11	23	22
4	12	12	13
4	13	6	5
4	14	10	9
4	15	5	4
4	16	6	6
5	0	10	12
5	1	28	28
5	2	16	16
5	3	38	34
5	5	29	29
5	6	19	18
5	7	6	6
5	8	6	7
5	9	34	34
5	10	9	7
5	11	17	18
5	12	17	17
5	14	15	16
5	15	5	5
5	16	3	4
6	0	13	13
6	1	31	33
6	2	11	11
6	3	16	18
6	4	28	27
6	5	29	28
6	6	29	28
6	7	15	14
6	8	8	8
6	9	13	12
6	10	15	14
6	11	22	22
6	12	14	15
6	13	3	4
6	16	3	4

Table 8d. (Continued)

7	0	44	44	10	0	32	31	14	3	8	7	1	7	20	19
7	1	48	50	10	1	7	9	14	4	11	12	1	8	30	30
7	2	55	54	10	2	20	19	14	5	6	7	1	9	20	21
7	3	32	31	10	3	28	25	14	6	13	12	1	10	8	7
7	4	4	4	10	4	21	22	14	7	8	9	1	11	14	14
7	5	7	7	10	5	21	21	14	8	5	6	1	12	11	11
7	6	14	14	10	6	10	10	14	10	3	3	1	13	11	10
7	7	7	7	10	7	7	6	15	0	3	4	1	14	6	6
7	8	8	7	10	8	14	14	15	1	14	15	1	15	11	11
7	9	14	14	10	10	9	9	15	2	12	12	1	16	10	10
7	10	15	14	10	11	13	14	15	3	13	13	1	17	4	4
7	11	7	6	10	12	3	2	15	4	8	9	2	0	30	31
7	12	10	10	10	13	4	5	15	5	13	13	2	1	17	16
7	13	8	8	11	1	20	19	15	8	4	3	2	2	7	6
7	14	15	15	11	3	13	13	15	9	4	4	2	3	39	42
7	15	9	9	11	5	10	9	16	1	10	9	2	4	23	23
7	16	6	6	11	6	12	10	16	3	5	5	2	5	5	6
8	0	14	14	11	7	15	15	16	5	3	2	2	6	7	9
8	1	16	18	11	8	17	18	17	0	4	4	2	7	29	28
8	2	6	7	11	9	5	5	17	2	7	7	2	8	30	29
8	3	9	9	11	10	9	8	17	3	8	8	2	9	18	17
8	4	37	37	11	11	10	10	17	5	7	7	2	10	15	16
8	5	25	25	11	12	6	6					2	11	16	15
8	6	3	6	12	0	8	8		H =	3		2	12	3	5
8	7	13	13	12	1	8	9	K	L	FC	FC	2	13	11	11
8	8	11	12	12	2	4	3	0	1	7	6	2	14	8	9
8	9	6	8	12	3	12	13	0	2	73	78	2	15	5	6
8	10	14	14	12	4	22	22	0	3	20	20	2	16	4	3
8	11	20	20	12	5	13	13	0	4	14	15	2	17	3	3
8	12	4	5	12	6	20	20	0	5	23	23	3	0	10	10
8	13	5	5	12	7	3	5	0	6	11	8	3	1	59	59
8	14	5	5	12	9	4	3	0	7	35	35	3	2	30	31
8	15	9	9	12	10	4	2	0	8	30	31	3	3	26	27
9	0	4	3	12	11	4	5	0	9	7	6	3	4	15	13
9	1	23	22	13	1	7	7	0	10	12	13	3	5	46	44
9	2	6	6	13	2	16	16	0	11	15	15	3	6	9	9
9	3	13	13	13	3	18	17	0	12	19	18	3	7	21	20
9	4	18	17	13	4	17	17	0	13	4	4	3	8	5	5
9	5	16	15	13	5	13	13	0	14	7	7	3	10	21	20
9	6	14	13	13	6	9	7	0	15	8	6	3	11	9	9
9	7	13	13	13	7	10	11	0	17	3	4	3	12	15	15
9	8	19	19	13	8	18	18	1	0	42	40	3	13	10	10
9	9	16	16	13	9	8	8	1	1	32	32	3	14	10	10
9	11	6	6	13	10	3	1	1	2	29	29	3	15	7	8
9	12	12	13	13	11	4	6	1	3	4	3	3	16	3	3
9	13	12	13	14	0	6	7	1	4	78	80	4	0	27	25
9	14	6	6	14	1	8	8	1	5	25	24	4	1	40	42
9	15	3	3	14	2	8	9	1	6	25	23	4	2	15	15

Table 8d. (Continued)

4	3	26	24	7	4	7	5	10	10	10	10	15	5	8	9
4	4	55	57	7	5	21	21	10	11	19	19	15	6	5	6
4	5	42	39	7	6	7	5	10	13	5	5	16	1	8	7
4	6	18	16	7	7	18	17	11	0	20	19	16	2	4	5
4	7	13	13	7	8	20	19	11	1	8	7	16	3	10	11
4	8	14	14	7	9	14	13	11	2	7	7	16	4	5	5
4	9	8	9	7	10	17	17	11	3	14	13	16	5	4	6
4	10	7	7	7	11	8	8	11	4	5	5	17	0	4	5
4	11	10	10	7	13	5	5	11	6	15	16	17	1	6	6
4	12	9	10	7	15	7	7	11	7	11	11	17	2	6	8
4	13	8	8	8	0	14	15	11	8	18	17				
4	15	5	5	8	1	25	24	11	9	8	7		H =	4	
5	0	6	7	8	2	26	26	11	10	4	4	K	L	FO	FC
5	1	56	56	8	3	29	29	11	11	6	7	0	0	7	7
5	2	46	44	8	4	20	20	12	0	12	12	0	1	7	6
5	3	14	15	8	5	15	15	12	1	3	3	0	2	14	14
5	4	14	14	8	6	5	6	12	2	14	13	0	3	14	14
5	5	25	25	8	7	8	7	12	3	8	7	0	4	33	30
5	6	27	26	8	8	8	7	12	4	14	15	0	5	8	7
5	7	21	21	8	9	12	13	12	5	17	16	0	6	14	14
5	8	17	17	8	11	15	14	12	6	8	8	0	7	12	11
5	9	12	11	8	12	6	8	12	9	8	8	0	8	6	6
5	10	28	28	8	13	3	4	12	10	5	6	0	9	4	4
5	11	8	9	8	14	6	7	12	11	5	5	0	10	12	12
5	12	6	7	8	15	3	3	12	12	9	6	0	11	12	12
5	13	6	5	9	0	19	18	13	0	7	7	0	12	24	24
5	14	9	9	9	1	14	13	13	1	15	15	0	13	13	12
5	15	4	5	9	2	3	3	13	2	9	8	0	14	14	13
5	16	5	4	9	3	26	26	13	3	5	4	0	15	9	9
6	0	20	21	9	4	9	9	13	4	13	14	1	0	43	39
6	1	21	20	9	5	17	16	13	6	12	13	1	1	22	20
6	2	46	43	9	6	16	16	13	7	9	9	1	2	13	13
6	3	7	8	9	7	26	27	13	8	4	5	1	3	30	32
6	4	55	55	9	8	19	19	13	9	5	5	1	4	20	21
6	5	31	29	9	10	8	8	13	10	8	8	1	5	36	34
6	6	11	10	9	11	6	8	13	11	3	4	1	6	39	37
6	7	25	23	9	12	6	7	14	1	19	19	1	7	20	20
6	8	6	5	9	13	11	11	14	2	7	8	1	8	12	11
6	9	11	12	10	0	12	13	14	3	9	8	1	9	21	18
6	10	14	13	10	1	26	24	14	4	11	12	1	11	7	7
6	11	14	13	10	2	15	15	14	5	15	16	1	12	5	5
6	12	4	3	10	3	12	12	14	6	9	10	1	13	9	8
6	13	6	6	10	4	8	8	14	7	5	4	1	14	10	10
6	14	12	13	10	5	11	10	14	9	5	4	1	15	5	6
6	15	4	5	10	6	17	18	15	1	20	20	1	16	5	5
7	1	13	17	10	7	17	17	15	2	10	10	2	0	43	41
7	2	25	23	10	8	3	3	15	3	7	6	2	1	22	21
7	3	31	30	10	9	13	13	15	4	8	7	2	2	48	46

Table 8d. (Continued)

2	3	26	26	5	6	17	17	8	12	7	7	12	11	4	5
2	4	6	4	5	7	15	15	8	14	4	4	13	0	8	9
2	5	28	28	5	8	9	8	9	0	7	5	13	1	13	13
2	6	15	16	5	9	13	13	9	1	24	24	13	2	15	15
2	7	22	22	5	10	14	13	9	2	26	26	13	3	9	9
2	8	12	11	5	11	10	10	9	3	15	15	13	4	5	5
2	9	3	4	5	13	8	9	9	4	22	22	13	5	5	6
2	10	9	9	5	15	4	3	9	5	17	18	13	6	6	6
2	11	13	13	6	0	47	44	9	6	6	6	13	7	4	6
2	12	15	15	6	1	25	25	9	7	14	14	13	8	5	6
2	13	9	9	6	2	39	38	9	9	9	8	13	9	4	5
2	14	9	9	6	3	5	6	9	10	4	4	14	0	14	13
2	15	5	6	6	4	8	9	9	11	4	5	14	1	14	15
2	16	3	4	6	5	6	7	9	12	4	4	14	2	6	7
3	0	35	33	6	6	6	5	10	0	7	6	14	3	14	13
3	1	41	39	6	7	21	21	10	1	11	10	14	4	9	10
3	2	17	16	6	8	32	33	10	3	17	18	14	5	4	5
3	3	21	21	6	9	2	2	10	4	20	20	14	6	8	8
3	4	29	26	6	10	10	10	10	5	15	14	14	7	6	5
3	5	34	34	6	11	13	13	10	6	13	14	15	1	4	5
3	6	28	26	6	12	6	7	10	7	18	18	15	3	7	8
3	7	29	27	6	13	4	4	10	8	13	14	15	4	7	7
3	8	12	12	6	14	3	4	10	9	12	13	15	5	10	11
3	9	6	7	6	15	3	3	10	10	8	7	15	6	5	5
3	10	3	4	7	1	15	16	10	11	5	6	16	0	10	11
3	11	6	7	7	2	25	26	10	12	6	5	16	2	3	3
3	12	3	4	7	3	15	13	10	13	2	2	16	3	7	9
3	16	7	7	7	4	24	24	11	0	6	6	16	4	6	5
4	0	25	25	7	5	11	11	11	1	16	16				
4	1	6	5	7	6	19	19	11	2	21	21		h =	5	
4	2	38	35	7	7	11	11	11	3	3	3	K	L	FO	FC
4	3	30	28	7	8	9	8	11	4	8	9	0	1	5	4
4	4	10	11	7	9	11	10	11	5	7	8	0	2	4	3
4	5	10	9	7	10	6	5	11	6	10	10	0	3	18	18
4	6	9	8	7	12	4	2	11	7	8	7	0	4	3	1
4	7	20	20	7	13	3	3	11	8	16	16	0	5	19	19
4	8	6	6	8	0	18	18	11	9	7	7	0	6	6	5
4	9	11	11	8	1	24	24	11	10	8	8	0	7	3	3
4	10	3	4	8	2	10	9	11	11	3	2	0	9	9	9
4	11	26	26	8	3	23	23	12	1	14	14	0	10	9	8
4	13	6	6	8	4	19	19	12	2	10	11	0	11	5	6
4	16	2	3	8	5	9	7	12	3	7	8	0	12	3	1
5	0	31	30	8	6	9	8	12	4	13	12	0	14	11	11
5	1	30	30	8	7	27	27	12	5	5	5	0	15	3	1
5	2	27	28	8	8	15	15	12	6	12	12	1	0	8	9
5	3	10	9	8	9	15	16	12	7	5	5	1	1	13	13
5	4	48	47	8	10	10	9	12	8	8	8	1	2	14	15
5	5	18	19	8	11	13	14	12	9	5	4	1	3	19	17

Table 8d. (Continued)

1	4	10	9	4	10	16	16	8	1	14	14	12	8	10	10
1	5	17	16	4	11	10	9	8	2	7	7	13	0	19	19
1	6	12	12	4	12	7	7	8	3	3	3	13	1	3	3
1	7	10	10	4	13	6	6	8	4	21	21	13	3	7	5
1	8	13	13	4	14	6	6	8	5	17	17	13	4	6	7
1	9	10	10	4	15	4	4	8	6	11	11	13	7	3	3
1	10	13	13	5	0	17	16	8	8	16	16	14	1	4	3
1	11	11	11	5	1	15	15	8	9	9	9	14	2	8	8
1	12	8	9	5	2	19	19	8	10	7	7	14	3	7	6
1	13	6	6	5	3	19	18	8	11	9	9	14	4	8	7
1	14	10	10	5	4	6	5	8	13	5	5	14	6	4	4
2	0	41	41	5	5	10	10	9	0	12	12	15	2	3	2
2	1	14	13	5	6	9	8	9	1	6	6	15	3	5	6
2	2	17	16	5	7	19	19	9	2	8	8				
2	3	14	12	5	8	17	17	9	3	4	3		H =	6	
2	4	17	17	5	9	16	16	9	4	6	5	K	L	FO	FC
2	5	4	4	5	10	6	7	9	5	11	11	0	0	35	33
2	6	12	11	5	11	12	13	9	6	11	11	0	1	7	8
2	7	22	22	5	12	4	3	9	7	16	16	0	2	38	36
2	8	4	5	5	13	6	7	9	8	11	11	0	3	10	9
2	9	3	3	5	14	2	3	9	9	19	20	0	5	6	5
2	10	4	5	6	0	6	7	9	10	3	2	0	6	10	10
2	11	12	13	6	1	20	19	9	11	4	3	0	7	4	3
2	14	6	6	6	2	5	5	10	0	14	14	0	8	22	22
2	15	5	5	6	4	8	8	10	1	20	21	0	9	5	5
3	0	5	4	6	5	10	10	10	3	12	11	0	11	12	12
3	1	26	25	6	6	24	24	10	4	16	17	0	13	6	5
3	2	33	32	6	7	4	5	10	5	14	14	1	0	8	8
3	3	4	3	6	8	5	5	10	6	10	11	1	1	12	12
3	4	12	10	6	9	12	12	10	7	9	9	1	2	22	21
3	5	20	19	6	10	16	16	10	8	5	5	1	3	19	19
3	6	16	15	6	11	8	9	10	9	3	3	1	4	19	18
3	7	13	13	6	12	6	6	10	11	8	8	1	5	21	22
3	8	9	8	6	13	3	4	11	0	3	3	1	6	18	18
3	9	9	9	7	0	15	15	11	1	10	9	1	7	5	5
3	10	12	12	7	1	5	6	11	2	14	14	1	8	6	5
3	11	13	13	7	2	17	17	11	3	8	7	1	9	11	11
3	12	6	6	7	3	12	11	11	4	12	12	1	11	7	8
3	13	3	4	7	4	8	9	11	5	18	20	1	12	8	8
3	15	4	4	7	5	20	20	11	6	9	9	2	0	15	15
4	0	34	31	7	6	6	7	11	8	6	7	2	1	11	11
4	1	22	22	7	7	7	8	11	9	8	8	2	2	9	8
4	2	13	13	7	8	3	2	11	10	4	4	2	3	21	20
4	3	15	14	7	9	18	19	12	1	10	10	2	5	6	6
4	4	20	20	7	10	4	3	12	3	4	6	2	6	14	14
4	5	19	19	7	11	10	11	12	4	8	8	2	7	7	7
4	6	16	17	7	12	3	3	12	6	5	4	2	8	9	10
4	9	18	19	8	0	6	4	12	7	4	3	2	9	3	4

Table 8d. (Continued)

2	10	11	12	6	8	7	7	11	2	6	7	3	0	23	24
2	11	8	10	6	9	4	3	11	4	3	4	3	1	6	6
2	12	3	4	6	10	5	5	11	8	3	3	3	2	16	16
2	14	5	5	6	11	5	6	11	9	6	8	3	3	22	21
3	0	6	6	6	12	3	4	12	0	6	5	3	4	4	4
3	1	8	7	7	0	10	10	12	3	3	4	3	5	8	9
3	2	5	4	7	1	20	20	12	4	7	8	3	6	5	5
3	3	6	7	7	2	8	7	12	5	8	7	3	7	5	5
3	4	9	10	7	3	9	10	12	7	5	4	3	8	13	14
3	5	17	16	7	4	3	2	13	2	5	4	3	9	9	9
3	6	7	7	7	5	5	5	13	5	2	3	3	10	4	3
3	7	7	7	7	6	19	20	14	0	4	5	3	12	5	6
3	8	13	13	7	8	11	11	14	1	3	4	4	0	16	16
3	9	17	17	7	9	7	7	14	2	4	4	4	1	16	16
3	10	11	10	7	10	7	8					4	2	9	9
3	11	8	9	7	12	5	5		H =	7		4	3	14	13
3	12	11	12	8	0	3	3	K	L	FO	FC	4	4	6	5
3	13	6	7	8	1	9	9	0	1	9	9	4	5	14	14
4	0	3	3	8	2	11	11	0	2	25	25	4	6	13	13
4	1	9	9	8	3	8	8	0	3	4	2	4	7	9	9
4	2	8	9	8	4	9	8	0	4	9	8	4	8	4	5
4	3	21	21	8	5	6	6	0	5	9	8	4	9	6	7
4	4	18	18	8	7	13	14	0	6	29	29	4	10	10	10
4	6	5	4	8	8	9	10	0	10	6	7	5	0	12	11
4	7	20	20	8	9	7	6	0	11	9	8	5	1	9	9
4	9	4	5	8	10	5	5	1	0	37	37	5	2	9	9
4	10	9	9	8	11	5	5	1	1	13	13	5	3	23	24
4	11	3	5	9	1	7	8	1	2	10	10	5	4	5	5
4	13	6	6	9	2	16	17	1	4	16	15	5	6	6	6
5	0	14	14	9	3	19	20	1	5	12	11	5	7	3	2
5	1	4	4	9	4	10	10	1	6	9	10	5	8	5	5
5	2	13	14	9	5	14	14	1	7	5	5	5	9	5	6
5	3	19	19	9	6	10	10	1	8	10	11	5	10	5	5
5	4	6	6	9	7	4	4	1	9	11	11	5	11	4	5
5	6	10	9	9	8	8	8	1	10	6	6	6	0	14	14
5	7	20	21	9	9	7	7	1	11	3	4	6	1	6	6
5	8	10	11	9	10	6	6	2	0	27	26	6	2	3	3
5	9	13	14	9	11	2	3	2	1	5	7	6	3	11	11
5	10	8	8	10	0	7	7	2	2	20	19	6	4	10	9
5	12	4	4	10	1	14	14	2	3	12	12	6	5	5	5
6	0	7	7	10	2	3	4	2	4	8	8	6	6	3	3
6	1	18	19	10	3	6	6	2	5	8	8	6	7	6	7
6	2	10	11	10	4	13	14	2	6	17	17	6	8	7	7
6	3	4	3	10	5	8	8	2	7	9	9	6	9	3	3
6	4	6	7	10	6	4	5	2	8	8	8	6	10	7	6
6	5	14	14	10	7	4	5	2	10	9	9	6	11	4	6
6	6	14	14	10	9	4	4	2	11	8	9	7	1	6	7
6	7	9	10	11	1	8	8	2	12	3	3	7	2	8	8

Table 8d. (Continued)

7	3	5	6
7	4	14	14
7	5	12	13
7	6	4	5
7	8	7	7
7	9	5	5
8	1	8	9
8	2	9	10
8	3	9	9
8	4	8	8
8	5	10	11
8	6	6	5
8	7	5	4
8	8	4	5
8	9	4	5
9	0	4	5
9	1	6	7
9	2	9	10
9	3	8	8
9	6	5	6
9	8	5	5
10	1	3	3
10	3	3	3
10	4	4	4
10	6	8	8
11	0	3	6
11	1	5	6
11	2	6	6
11	4	8	8
11	5	2	3
12	0	5	5
12	1	4	4
12	2	2	3

H = 8

K	L	FO	FC
0	0	12	12
0	1	23	23
0	2	13	13
0	4	10	9
0	5	4	4
0	6	10	9
0	7	5	5
0	8	9	9
0	10	3	2
1	2	7	7
1	4	15	14
1	5	13	13
1	6	9	9
1	7	15	15
1	8	6	6
1	9	5	6
1	10	4	5
2	0	19	20
2	1	16	16
2	2	12	12
2	3	11	11
2	5	7	8
2	6	8	8
2	7	5	5
2	8	5	5
2	9	3	4
3	2	10	10
3	3	14	13
3	4	12	12
3	5	7	7
3	6	5	5
3	7	9	9
3	8	3	4
3	9	3	4
4	0	21	21
4	1	13	13
4	2	7	7
4	3	8	8
4	4	10	10
4	5	5	5
4	6	13	14
4	9	3	3
5	1	5	6
5	2	13	12
5	4	12	13
5	5	3	3
5	6	10	11
5	7	6	5
5	8	6	6
6	0	13	12
6	1	5	5
6	2	4	5
6	3	6	6
6	4	6	7
6	6	5	5
6	7	5	4
6	8	3	3
7	0	4	4
7	1	11	11
7	3	6	7
7	4	7	7
7	5	6	6
7	6	7	8
7	7	3	3
8	1	3	4
8	2	8	9
8	3	9	10
8	4	5	5
9	0	6	7
9	2	4	5
9	3	5	5
10	0	5	6
10	1	5	5

H = 9

K	L	FO	FC
0	1	3	3
0	2	4	5
0	4	5	5
0	6	6	6
1	0	12	12
1	1	5	6
1	2	6	6
1	3	4	4
1	5	6	7
2	1	3	3
2	2	6	6
2	3	7	7
2	6	3	4
3	1	3	3
3	2	2	3
3	3	5	5
3	4	4	4
3	5	4	5
4	0	5	4
4	1	3	3
4	2	4	4
4	4	4	5
4	5	5	5
5	0	3	3
5	3	12	13
5	4	4	4
6	0	5	5
6	1	5	5

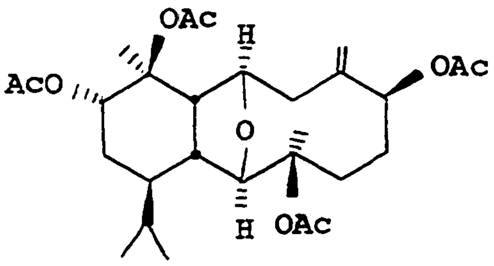
Table 8e. Least squares planes for ophirin. Equations for the planes are of the form Ax+By+Cz=D. Distances (Å) of some atoms from the least squares planes are in brackets.

Plane	Atoms used in calculation	A	B	C	D
1	1, 10, 11, 12, 13, 14, 17	.683	-.480	-.551	2.928
	[C(1), -.24; C(10), .13; C(11), .01; C(12); -.09; C(13), -.02, C(14), .19; C(17), .02]				
2	10, 11, 12, 13, 14	.668	-.400	-.627	3.244
	[C(1), -.47; C(11), -.02; C(12),-.01; C(13), -.02; C(14), .02]				
3	1, 2, 9, 10, 25	-.188	.879	-.437	.213
	[C(1), -.19; C(2), .11; C(9), -.13; C(10), .12; O(25), .01]				
4	1, 2, 9, 25	-.115	.816	-.566	.510
	[C(1), -.03; C(2), .05; C(9), .03; C(10), .50; O(25), -.05]				
5	2, 9, 10, 25	-.339	.831	-.441	.337
	[C(1), -.49; C(2), -.04; C(9), -.07; C(10), .04; O(25), .07]				

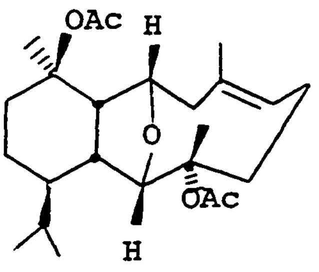
Table 8f. Dihedral angles for the nine-membered ring of ophirin (°).

C(2)	- C(3)	- C(4)	- C(5)	-80
C(3)	- C(4)	- C(5)	- C(6)	41
C(4)	- C(5)	- C(6)	- C(7)	79
C(5)	- C(6)	- C(7)	- C(8)	-154
C(6)	- C(7)	- C(8)	- C(9)	69
C(7)	- C(8)	- C(9)	- O(25)	-51
C(8)	- C(9)	- O(25)	- C(2)	111
C(9)	- O(25)	- C(2)	- C(3)	-139
O(25)	- C(2)	- C(3)	- C(4)	91

Discussion Ophirin's skeleton is made up of isoprene units linked in a regular head-to-tail fashion. It can be viewed as a cembrene skeleton closed with a transannular oxygen bridge and a carbon-carbon bond. Eunicellin, from a gorgonian species, has the same carbon skeleton as ophirin with an oxygen bridge in the same position (85). Acetoxycladiellin and cladiellin, both from a soft coral species, also have the eunicellin carbon skeleton with an oxygen bridge, but the stereochemistry of the ring junctions in these two compounds is different from that in eunicellin and ophirin (86). The structures, but not the absolute configurations, of eunicellin and acetoxycladiellin were determined by X-ray diffraction.



eunicellin



acetoxycladiellin

Sinularene

Background Sinularia mayi is a soft coral species found near Indonesia. Chromatography of hexane extracts of S. mayi yielded several sesquiterpene hydrocarbons (87). The major ones were isolated by gas chromatography and the structure of one of these has been studied.

Sinularene was a novel sesquiterpene with a molecular formula of $C_{15}H_{24}$. An analysis of its IR and NMR spectra showed only that it was tricyclic with an isopropyl group and a five-membered ring bearing an exocyclic methylene. Attempts to determine the structure by chemical degradation also failed. Finally the p-bromobenzoate derivative was prepared and crystals suitable for an X-ray diffraction analysis were obtained from acetone-H_2O.

Experimental The crystals of the sinularene derivative were soft colorless plates with a melting point of only 45°C. A crystal approximately .1 mm X .2 mm X .4 mm was chosen for the single crystal experiment. The crystal was indexed in the monoclinic crystal class and data collection was started at room temperature. However, the reflections looked very broad and had low intensities. The experiment was restarted, this time bathing the crystal in cold nitrogen (-60°C).

Cooling the crystal reduced the thermal motion of the atoms in the crystal and the intensities of the reflections increased by 10-50% of their room temperature values.

Cell constants of the cooled crystal were $\underset{\sim}{a}$ = 17.923(19)Å, $\underset{\sim}{b}$ = 7.140(6)Å, $\underset{\sim}{c}$ = 18.628(9)Å and β = 101.60(7)° and the calculated density was 1.33 g/cc for four molecules $C_{22}H_{28}O_3Br$ and four molecules of acetone in the unit cell. The systematic absence of all reflections with $h + k \neq 2N$ indicated the unit cell was C-centered and, given the chirality of sinularene, space group C2 was assigned. Integrated intensities of all $h\ k\ l$ and $h\ k\ \bar{l}$ reflections with $h + k = 2N$ and $2\theta \leq 114.1°$ (CuKα) were measured with a minimum scan rate of 3°/minute. The scan width used in the ω-scan technique was increased to 3° because reflections were still rather broad. Intensities of three periodically measured standard reflections decreased slowly with time and by the end of data collection had declined 15-20%. Data were corrected for Lorentz, polarization and background effects, but not for the apparent crystal decomposition, and 1138 of the 1670 unique reflections (68%) were judged observed.

Fractional coordinates of the bromine atom were obtained from a Patterson synthesis and used as input for an F_o synthesis. The resulting electron density map showed the entire structure. Nonhydrogen atoms were assigned anisotropic temperature factors and refined by full-matrix least-squares.

Hydrogens were included in their calculated positions with isotropic temperature factors and also refined by least-squares. As the last step in refinement, corrections were made for anomalous scattering by the bromine. The final unweighted R-factor for both possible absolute configurations of the structure was .062.

Results Figure 9 is a computer generated drawing of the contents of one asymmetric unit of the structure. Each molecule of the sinularene derivative is hydrogen bonded to a molecule of acetone: O(16)-O(30)=2.86Å. The tricyclic, rearranged sesquiterpene skeleton of sinularene can be viewed as two six-membered rings, both in a boat conformation, sharing a side (cis ring junction) and connected by a carbon-carbon bond (C(2)-C(8)). The absolute configuration of the molecule could not be determined from the X-ray data but was deduced from a negative Cotton effect of the sinularene ozonolysis product. Comparisons to the absolute configurations of related sesquiterpenes from S. mayi showed this assignment to be reasonable. The configurations at the asymmetric centers are 1(R), 2(S), 5(R), 6(R), 7(S) and 8(R). Bond distances and angles of the structure generally conform to expected values and are listed in tables 9b and 9c (16). Fractional coordinates for all the atoms are included in table 9a. For a table of observed and

Figure 9. A computer generated perspective drawing of the contents of one asymmetric unit from the crystal structure of the p-bromobenzoate derivative of sinularene. Hydrogens are omitted for clarity.

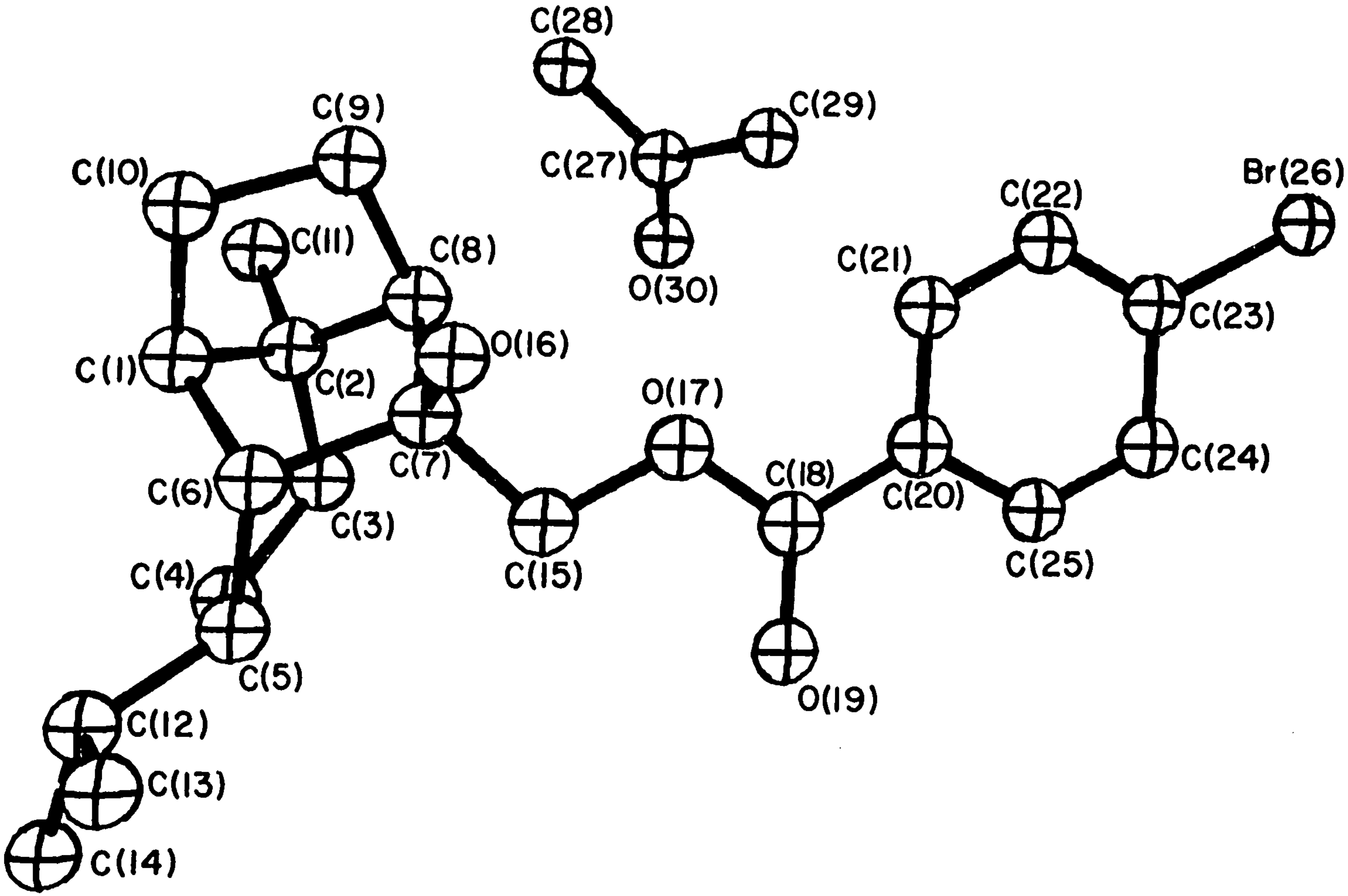

C(28)
C(29)
C(9)
C(27)
Br(26)
C(10)
C(22)
C(11)
C(8)
O(30)
C(21)
C(23)
O(16)
C(1)
C(2)
O(17)
C(7)
C(18)
C(24)
C(6)
C(3)
C(20)
C(15)
C(25)
C(4)
C(5)
O(19)
C(12)
C(13)
C(14)

Table 9a. Fractional coordinates for the nonhydrogen atoms of sinularene. Standard deviations of the least significant figures are given in parentheses. The numbering scheme refers to figure 9.

C(1)	.8946(9)	.0561(35)	.3964(7)
C(2)	.8947(7)	.2285(37)	.3466(8)
C(3)	.8190(7)	.3354(35)	.3302(8)
C(4)	.7608(7)	.2600(36)	.3720(8)
C(5)	.7463(8)	.0465(33)	.3602(7)
C(6)	.8224(8)	-.0451(33)	.3530(8)
C(7)	.8426(8)	-.0389(41)	.2728(7)
C(8)	.9081(8)	.0993(37)	.2823(7)
C(9)	.9818(7)	-.0140(45)	.3185(6)
C(10)	.9693(8)	-.0517(35)	.3954(9)
C(11)	.9583(9)	.3662(28)	.3743(8)
C(12)	.7122(8)	-.0435(35)	.4220(6)
C(13)	.6859(9)	-.2425(36)	.4012(8)
C(14)	.6475(8)	.0728(36)	.4415(7)
C(15)	.7761(8)	.0035(45)	.2103(6)
O(16)	.8667(6)	-.2312(32)	.2603(6)
O(17)	.8029(5)	-.0064(35)	.1439(4)
C(18)	.7510(9)	.0079(45)	.0833(6)
O(19)	.6821(5)	.0198(38)	.0829(5)
C(20)	.7819(8)	.0006(41)	.0146(6)
C(21)	.8586(9)	-.0361(39)	.0155(7)
C(22)	.8848(7)	-.0318(38)	-.0484(8)
C(23)	.8412(9)	.0015(47)	-.1147(7)
C(24)	.7586(9)	.0393(34)	-.1168(6)
C(25)	.7335(8)	.0357(36)	-.0532(8)
Br(26)	.8736(1)	-.0038(29)	-.2018(1)
C(27)	.9874(9)	.5412(38)	.1507(8)
C(28)	1.0520(8)	.5114(52)	.2099(8)
C(29)	.9850(15)	.3745(66)	.0950(16)
O(30)	.9400(7)	.6580(35)	.1442(6)

Table 9b. Bond distances of sinularene. The standard deviation of the least significant figure of each distance is given in parentheses.

C(1) - (C2)	1.54(3)
C(1) - C(6)	1.56(2)
C(1) - C(10)	1.55(3)
C(2) - C(3)	1.53(2)
C(2) - C(8)	1.57(3)
C(2) - C(11)	1.51(3)
C(3) - C(4)	1.52(2)
C(4) - C(5)	1.55(3)
C(5) - C(6)	1.54(2)
C(5) - C(12)	1.55(2)
C(6) - C(7)	1.61(2)
C(7) - C(8)	1.52(3)
C(7) - C(15)	1.52(2)
C(7) - O(16)	1.47(3)
C(8) - C(9)	1.58(3)
C(9) - C(10)	1.51(2)
C(12) - C(13)	1.52(3)
C(12) - C(14)	1.53(3)
C(15) - O(17)	1.41(1)
O(17) - C(18)	1.31(1)
C(18) - O(19)	1.24(2)
C(18) - C(20)	1.49(2)
C(20) - C(21)	1.40(2)
C(20) - C(25)	1.40(2)
C(21) - C(22)	1.37(2)
C(22) - C(23)	1.34(2)
C(23) - C(24)	1.50(2)
C(23) - Br(26)	1.83(1)
C(24) - C(25)	1.35(2)
C(27) - C(28)	1.45(2)
C(27) - C(29)	1.57(5)
C(27) - O(30)	1.18(3)

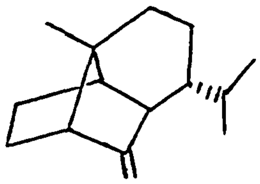
Table 9c. Bond angles of sinularene. The standard deviation of the least significant figure of each angle is given in parentheses.

C(2)	- C(1)	- C(6)	99.1(12)
C(2)	- C(1)	- C(10)	106.5(14)
C(6)	- C(1)	- C(10)	113.2(18)
C(1)	- C(2)	- C(3)	114.2(14)
C(1)	- C(2)	- C(8)	90.5(18)
C(1)	- C(2)	- C(11)	113.9(12)
C(3)	- C(2)	- C(8)	114.0(11)
C(3)	- C(2)	- C(11)	108.6(20)
C(8)	- C(2)	- C(11)	114.9(13)
C(2)	- C(3)	- C(4)	113.1(17)
C(3)	- C(4)	- C(5)	112.7(16)
C(4)	- C(5)	- C(6)	107.6(14)
C(4)	- C(5)	- C(12)	112.4(15)
C(6)	- C(5)	- C(12)	112.2(16)
C(1)	- C(6)	- C(5)	114.5(17)
C(1)	- C(6)	- C(7)	98.7(13)
C(5)	- C(6)	- C(7)	116.0(13)
C(6)	- C(7)	- C(8)	102.9(13)
C(6)	- C(7)	- C(15)	115.4(12)
C(6)	- C(7)	- O(16)	104.5(17)
C(8)	- C(7)	- C(15)	115.4(20)
C(8)	- C(7)	- O(16)	112.4(14)
C(15)	- C(7)	- O(16)	105.9(17)
C(2)	- C(8)	- C(7)	103.7(13)
C(2)	- C(8)	- C(9)	102.7(11)
C(7)	- C(8)	- C(9)	106.1(20)
C(8)	- C(9)	- C(10)	103.0(12)
C(1)	- C(10)	- C(9)	102.4(14)
C(5)	- C(12)	- C(13)	110.3(14)
C(5)	- C(12)	- C(14)	112.6(18)
C(13)	- C(12)	- C(14)	110.9(15)
C(7)	- C(15)	- O(17)	107.9(12)
C(15)	- O(17)	- C(18)	116.2(11)
O(17)	- C(18)	- O(19)	122.9(12)
O(17)	- C(18)	- C(20)	114.4(13)
O(19)	- C(18)	- C(20)	122.7(11)
C(18)	- C(20)	- C(21)	122.1(11)
C(18)	- C(20)	- C(25)	119.7(14)
C(21)	- C(20)	- C(25)	118.2(13)
C(20)	- C(21)	- C(22)	119.8(12)
C(21)	- C(22)	- C(23)	124.5(14)
Br(26)	- C(23)	- C(22)	125.5(14)
Br(26)	- C(23)	- C(24)	117.9(9)
C(22)	- C(23)	- C(24)	116.5(13)
C(23)	- C(24)	- C(25)	118.4(12)

Table 9c. (Continued)

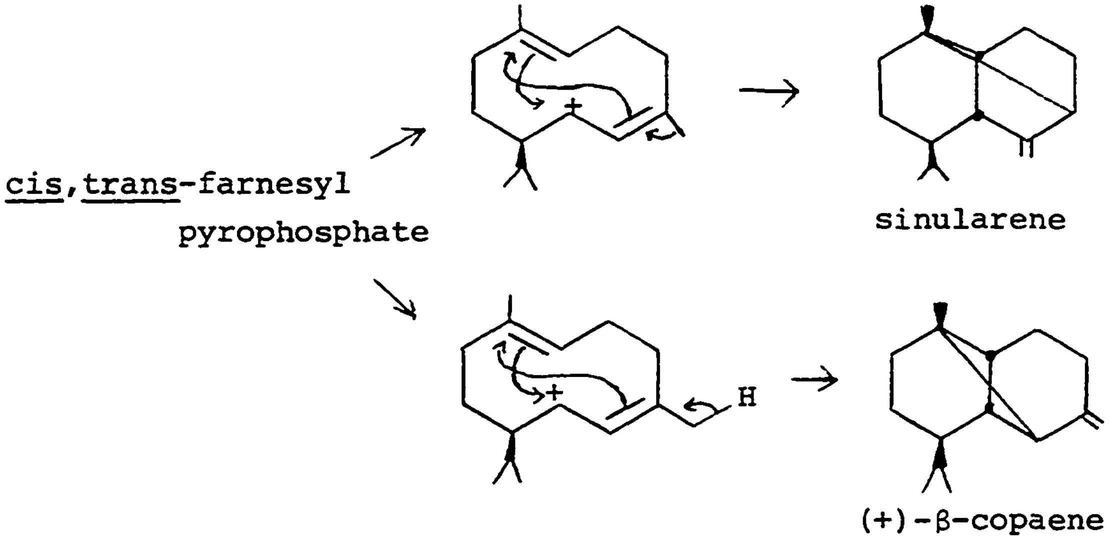
C(20) - C(25) - C(24)	122.6(14)
C(28) - C(27) - C(29)	107.7(22)
C(28) - C(27) - O(30)	129.2(22)
C(29) - C(27) - O(30)	123.0(17)

calculated structure factor magnitudes refer to the published communication (87).



sinularene

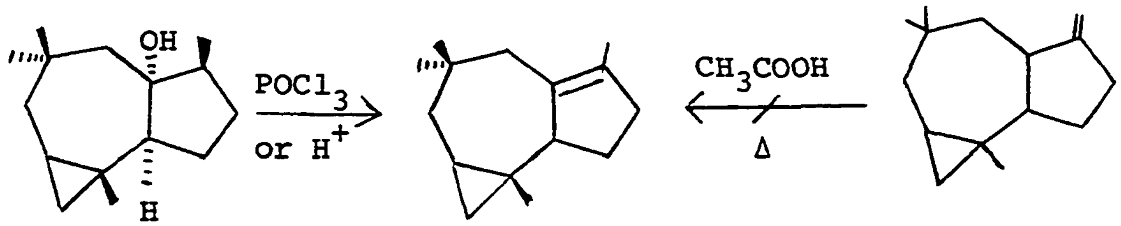
Discussion Sinularene may be biogentically related to (+)-β-copaene, also a metabolite of Sinularia mayi. (+)-β-copaene could be formed by cyclization of cis,trans-farnesyl pyrophosphate. If the cyclization proceeded with a 1,2-methyl shift, sinularene would be formed.



Possible biogenetic relationship between sinularene and (+)-β-copaene

Erectene

Background Great differences in the terpene content of even closely related species in the Octocorallia have often been observed (75). An examination of the terpene fractions of eight species of Sinularia from the Gulf of Eilet showed each species produced different types and amounts of sesquiterpenes The hydrocarbon oil of one of these species, S. erecta, was 1.5% of the dry weight of the animal and consisted almost exclusively of a single sesquiterpene. This compound was named erectene and assigned the molecular formula $C_{15}H_{24}$. Its structure except for stereochemistry was determined by analysis of its IR, UV and NMR spectra and by chemical transformations. It appeared to have the same skeleton as africanol from the soft coral Lemnalia africana (88). If so, it would be expected to isomerize to the elimination product of africanol. Since this reaction did not occur it was suspected the two sesquiterpenes had different stereochemistries. An X-ray diffraction analysis of the crystalline ozonolysis product of erectene was done to define the stereochemical differences.



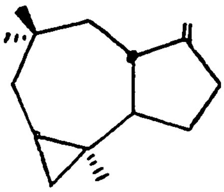
africanol

erectene

Experimental The crystal of the erectene ozonolysis product chosen for the experiment was quite large but photographs of its diffraction pattern showed it did not diffract well. It was cooled in a nitrogen stream (-60°C) during data collection in an effort to improve its scattering power. The cooled crystal had an orthorhombic unit cell with cell constants of $\mathbf{a}$ = 6.429(4)Å, $\mathbf{b}$ = 25.962(8)Å and $\mathbf{c}$ = 30.126(8)Å. A density of 1.10 g/cc was calculated for 16 molecules of $C_{14}H_{24}O$ in the unit cell. The chiral space group $P2_12_12_1$ could be unambiguously assigned after examination of systematic extinctions. Therefore, there were four molecules of the ozonolysis product in each asymmetric unit. All reflections with h, k and l $\geq$ 0 and $2\theta \leq 114.1°$ (CuKα) were measured at a minimun scan rate of 1°/minute. Intensities of three reflections used to monitor crystal decomposition showed less than a 2% decrease during data collection. After the measured intensities had been corrected for Lorentz, polarization and background effects only 1763 of the 3853 reflections (46%) were judged observed.

The structure was solved by phasing the 350 Es $\gtrsim$ 1.48 using MULTAN. For a structure of this size (60 independent atoms) a single phase relationship has a rather low probability of being correct, even if the magnitudes of the Es in the relationship are large. To insure that even at the beginning of the phasing procedure most phases would be determined by more than one phase relationship MULTAN was run using a large starting set which included four special reflections and two general reflections. General reflections were given magic integer representation. One hundred and ninety-two possible phase sets were generated and an E map calculated from one of the more promising sets showed about half of the structure. The new structural information was used in an E recycling procedure to calculate an improved E map (89). This map showed 50 of the 60 independent atoms. The remaining nonhydrogens were found on an F_o synthesis. All 60 atoms were assigned anisotropic temperature factors and refined by full-matrix least-squares. The hydrogen contribution was not considered because it would have been impossible to input 156 atoms into the least-squares program. The final unweighted R-factor for the observed reflections was .119.

Results   Figure 10 is a computer generated drawing of one of the independent molecules in the structure. There is a *trans* ring junction between the 5- and 7-membered rings and a *cis* ring junction between the 3- and 7-membered rings. The hydrogen at C(1) has the β configuration. The 5-membered ring is in the envelope conformation with C(1) as the flap. The absolute stereochemistry of the molecule, determined from its CD spectrum, is 1(S), 2(S), 4(R) and 8(R). Fractional coordinates of all 60 atoms, bond distances, bond angles and structure factor magnitudes are included in tables 10a, 10b, 10c and 10d, respectively. The four independent molecules have the same stereochemistry and any differences in their bond lengths and angles are probably due to the limited amount of data rather than any real differences in their geometries. There are no abnormally short intermolecular contacts in the structure (16).



erectene

Figure 10. A computer generated perspective drawing of one molecule from the crystal structure of the erectene ozonolysis product.

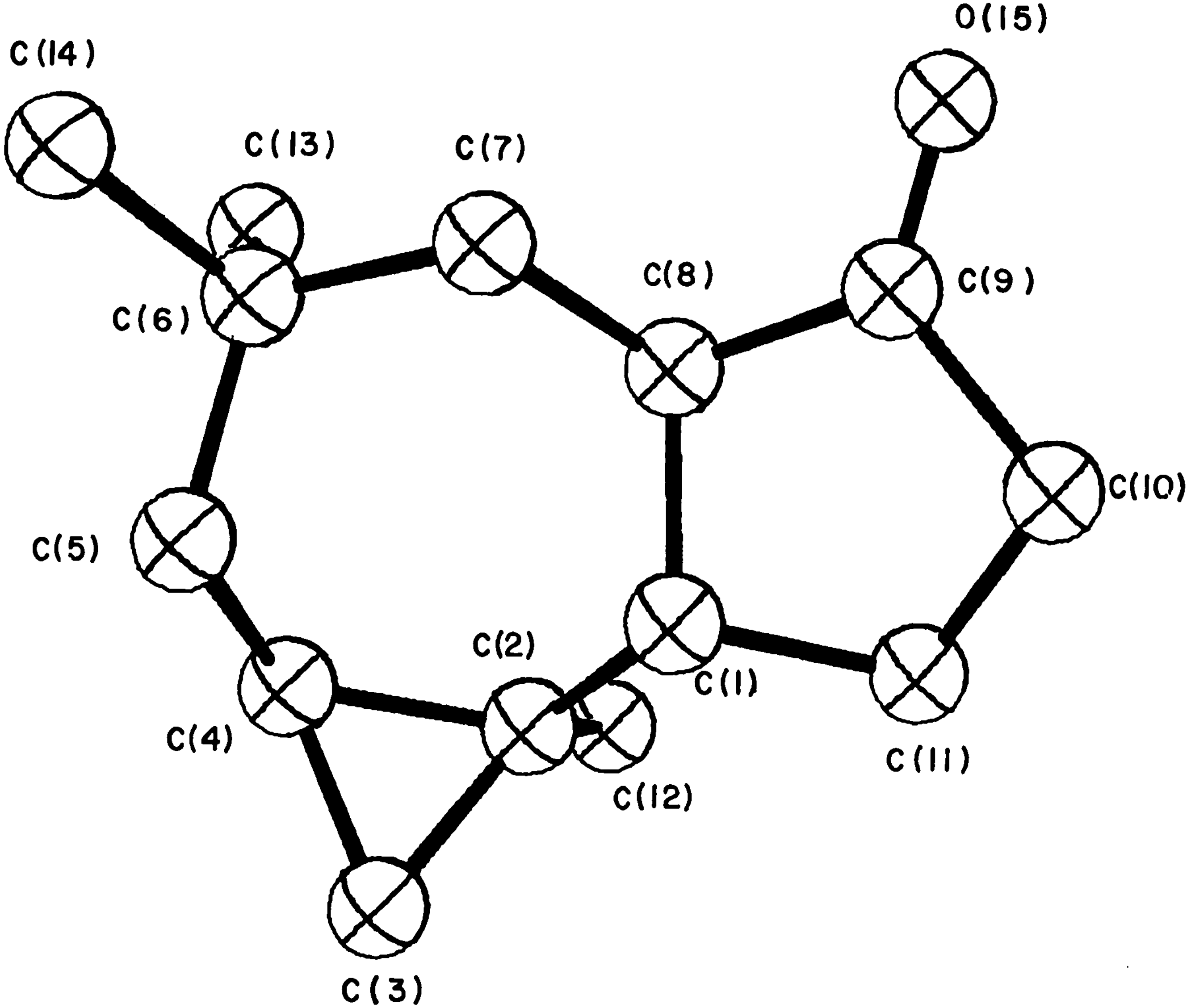

O(15)
C(14)
C(13)
C(7)
C(8)
C(9)
C(6)
C(10)
C(5)
C(2)
C(1)
C(4)
C(12)
C(11)
C(3)

Table 10a. Fractional coordinates for the ozonolysis product of erectene. Standard deviations of the least significant figures are given in parentheses. The numbering scheme refers to figure 10.

C(1)	.0347(41)	.3881(5)	−.0371(5)
C(2)	−.0902(46)	.3383(6)	−.0320(6)
C(3)	.0307(38)	.2896(6)	−.0366(5)
C(4)	−.0284(41)	.3059(6)	.0094(6)
C(5)	.1411(38)	.3246(6)	.0424(6)
C(6)	.0831(42)	.3719(8)	.0692(7)
C(7)	.1146(32)	.4211(6)	.0433(5)
C(8)	−.0138(36)	.4281(5)	.0003(5)
C(9)	.0311(36)	.4798(7)	−.0201(6)
C(10)	.0531(38)	.4748(6)	−.0717(6)
C(11)	−.0230(37)	.4195(5)	−.0800(5)
C(12)	−.3278(38)	.3383(9)	−.0454(7)
C(13)	−.1553(47)	.3697(8)	.0862(6)
C(14)	.2424(45)	.3730(9)	.1110(7)
O(15)	.0317(24)	.5199(4)	−.0003(4)
C(1A)	−.4548(39)	.6050(5)	.0191(5)
C(2A)	−.5582(45)	.6552(6)	.0162(5)
C(3A)	−.4464(39)	.7053(7)	.0269(5)
C(4A)	−.4987(40)	.6923(6)	−.0216(7)
C(5A)	−.3307(44)	.6754(6)	−.0565(6)
C(6A)	−.4029(35)	.6315(7)	−.0850(6)
C(7A)	−.3752(37)	.5809(6)	−.0637(5)
C(8A)	−.5053(33)	.5678(5)	−.0227(5)
C(9A)	−.4719(29)	.5176(7)	−.0039(6)
C(10A)	−.4378(38)	.5159(6)	.0467(5)
C(11A)	−.5229(37)	.5709(5)	.0591(5)
C(12A)	−.7972(40)	.6573(7)	.0298(7)
C(13A)	−.6386(38)	.6372(8)	−.1034(7)
C(14A)	−.2691(35)	.6311(7)	−.1282(6)
O(15A)	−.4656(24)	.4764(4)	−.0261(4)
C(1B)	−.5000(40)	.2506(5)	−.7071(5)
C(2B)	−.6510(37)	.2899(6)	−.7276(6)
C(3B)	−.5698(34)	.3451(6)	−.7325(5)
C(4B)	−.6015(37)	.3079(6)	−.7723(5)
C(5B)	−.4033(34)	.2869(7)	−.7974(6)
C(6B)	−.4196(47)	.2297(7)	−.8112(6)
C(7B)	−.3650(35)	.1937(7)	−.7710(5)
C(8B)	−.5138(40)	.1985(5)	−.7308(5)
C(9B)	−.4367(33)	.1595(6)	−.6938(6)
C(10B)	−.4287(35)	.1879(6)	−.6494(5)
C(11B)	−.5539(39)	.2370(5)	−.6562(5)
C(12B)	−.8884(40)	.2847(8)	−.7167(6)
C(13B)	−.6387(36)	.2184(8)	−.8311(6)
C(14B)	−.2450(33)	.2182(9)	−.8481(6)

Table 10a. (Continued)

O(15B)	-.4195(25)	.1139(4)	-.6997(4)
C(1C)	-.0458(32)	.5148(6)	-.8065(5)
C(2C)	-.1602(40)	.4706(6)	-.7912(6)
C(3C)	-.0527(43)	.4206(6)	-.7819(6)
C(4C)	-.1303(35)	.4537(6)	-.7433(6)
C(5C)	.0067(40)	.4839(7)	-.7138(5)
C(6C)	-.0626(41)	.5389(7)	-.7031(5)
C(7C)	-.0247(39)	.5777(5)	-.7400(5)
C(8C)	-.1096(35)	.5661(6)	-.7850(5)
C(9C)	-.0592(32)	.6075(7)	-.8188(6)
C(10C)	-.0077(34)	.5835(6)	-.8619(5)
C(11C)	-.7013(36)	.5267(7)	-.8585(5)
C(12C)	-.3929(32)	.4628(7)	-.8091(7)
C(13C)	-.3022(35)	.5405(8)	-.6900(7)
C(14C)	.0503(40)	.5607(8)	-.6594(6)
O(15C)	-.0578(22)	.6544(4)	-.8122(4)

Table 10b. Bond distances of the ozonolysis product of erectene. The standard deviation of the least significant figure of each distance is given in parentheses.

C(1) - C(2)	1.53(3)
C(1) - C(8)	1.57(2)
C(1) - C(11)	1.57(2)
C(2) - C(3)	1.49(3)
C(2) - C(4)	1.56(3)
C(2) - C(12)	1.58(4)
C(3) - C(4)	1.50(3)
C(4) - C(5)	1.55(3)
C(5) - C(6)	1.51(3)
C(6) - C(7)	1.51(3)
C(6) - C(13)	1.62(4)
C(6) - C(14)	1.62(3)
C(7) - C(8)	1.55(3)
C(8) - C(9)	1.50(2)
C(9) - C(10)	1.57(2)
C(9) - O(15)	1.20(2)
C(10) - C(11)	1.54(2)
C(1A) - C(2A)	1.47(3)
C(1A) - C(8A)	1.62(2)
C(1A) - C(11A)	1.56(2)
C(2A) - C(3A)	1.52(3)
C(2A) - C(4A)	1.54(3)
C(2A) - C(12A)	1.59(4)
C(3A) - C(4A)	1.54(3)
C(4A) - C(5A)	1.57(3)
C(5A) - C(6A)	1.50(3)
C(6A) - C(7A)	1.47(2)
C(6A) - C(13A)	1.62(3)
C(6A) - C(14A)	1.56(3)
C(7A) - C(8A)	1.53(3)
C(8A) - C(9A)	1.44(2)
C(9A) - C(10A)	1.54(2)
C(9A) - O(15A)	1.26(2)
C(10A) - C(11A)	1.57(2)
C(1B) - C(2B)	1.54(3)
C(1B) - C(8B)	1.53(2)
C(1B) - C(11B)	1.61(2)
C(2B) - C(3B)	1.53(2)
C(2B) - C(4B)	1.46(2)
C(2B) - C(12B)	1.57(3)
C(3B) - C(4B)	1.55(2)
C(4B) - C(5B)	1.58(3)
C(5B) - C(6B)	1.55(3)
C(6B) - C(7B)	1.57(3)

Table 10b. (Continued)

C(6) - C(13B)	1.56(4)
C(6B) - C(14B)	1.61(3)
C(7B) - C(8B)	1.55(3)
C(8B) - C(9B)	1.59(2)
C(9B) - C(10B)	1.53(2)
C(9B) - O(15B)	1.20(2)
C(10B) - C(11B)	1.52(3)
C(1C) - C(2C)	1.44(3)
C(1C) - C(8C)	1.54(2)
C(1C) - C(11C)	1.61(2)
C(2C) - C(3C)	1.50(3)
C(2C) - C(4C)	1.52(3)
C(2C) - C(12C)	1.60(3)
C(3C) - C(4C)	1.53(3)
C(4C) - C(5C)	1.48(3)
C(5C) - C(6C)	1.53(3)
C(6C) - C(7C)	1.52(2)
C(6C) - C(13C)	1.59(3)
C(6C) - C(14C)	1.61(3)
C(7C) - C(8C)	1.49(2)
C(8C) - C(9C)	1.52(2)
C(9C) - C(10C)	1.48(2)
C(9C) - O(15C)	1.23(2)
C(10C) - C(11C)	1.53(3)

Table 10c. Bond angles of the ozonolysis product of erectene. The standard deviation of the least significant figure of each angle is given in parentheses.

C(2)	- C(1)	- C(8)	112.6(16)
C(2)	- C(1)	- C(11)	113.5(17)
C(8)	- C(1)	- C(11)	101.5(12)
C(1)	- C(2)	- C(3)	115.7(22)
C(1)	- C(2)	- C(4)	113.8(18)
C(1)	- C(2)	- C(12)	118.8(17)
C(3)	- C(2)	- C(4)	58.9(12)
C(3)	- C(2)	- C(12)	118.7(17)
C(4)	- C(2)	- C(12)	116.8(19)
C(2)	- C(3)	- C(4)	62.7(12)
C(2)	- C(4)	- C(3)	58.4(12)
C(2)	- C(4)	- C(5)	121.5(16)
C(3)	- C(4)	- C(5)	120.2(21)
C(4)	- C(5)	- C(6)	114.9(19)
C(5)	- C(6)	- C(7)	112.2(16)
C(5)	- C(6)	- C(13)	112.0(18)
C(5)	- C(6)	- C(14)	105.8(18)
C(7)	- C(6)	- C(13)	108.7(18)
C(7)	- C(6)	- C(14)	107.5(18)
C(13)	- C(6)	- C(14)	110.6(17)
C(6)	- C(7)	- C(8)	117.5(16)
C(1)	- C(8)	- C(7)	114.7(15)
C(1)	- C(8)	- C(9)	105.0(13)
C(7)	- C(8)	- C(9)	110.3(15)
C(8)	- C(9)	- C(10)	110.5(14)
C(8)	- C(9)	- O(15)	124.7(15)
C(10)	- C(9)	- O(15)	124.5(15)
C(9)	- C(10)	- C(11)	102.1(13)
C(1)	- C(11)	- C(10)	106.0(14)
C(2A)	- C(1A)	- C(8A)	113.2(15)
C(2A)	- C(1A)	- C(11A)	115.1(17)
C(8A)	- C(1A)	- C(11A)	101.9(12)
C(1A)	- C(2A)	- C(3A)	122.3(23)
C(1A)	- C(2A)	- C(4A)	119.2(19)
C(1A)	- C(2A)	- C(12A)	116.9(17)
C(3A)	- C(2A)	- C(4A)	60.4(12)
C(3A)	- C(2A)	- C(12A)	111.8(16)
C(4A)	- C(2A)	- C(12A)	114.2(18)
C(2A)	- C(3A)	- C(4A)	60.4(11)
C(2A)	- C(4A)	- C(3A)	59.3(12)
C(2A)	- C(4A)	- C(5A)	119.6(15)
C(3A)	- C(4A)	- C(5A)	123.2(21)
C(4A)	- C(5A)	- C(6A)	112.4(20)
C(5A)	- C(6A)	- C(7A)	113.1(15)
C(5A)	- C(6A)	- C(13A)	114.6(17)

Table 10c. (Continued)

C(5A)	- C(6A)	- C(14A)	108.2(17)
C(7A)	- C(6A)	- C(13A)	110.0(17)
C(7A)	- C(6A)	- C(14A)	106.8(16)
C(13A)	- C(6A)	- C(14A)	103.3(15)
C(6A)	- C(7A)	- C(8A)	118.9(16)
C(1A)	- C(8A)	- C(7A)	112.7(14)
C(1A)	- C(8A)	- C(9A)	101.9(12)
C(7A)	- C(8A)	- C(9A)	115.9(15)
C(8A)	- C(9A)	- C(10A)	115.9(14)
C(8A)	- C(9A)	- O(15A)	124.6(15)
C(10A)	- C(9A)	- O(15A)	119.5(15)
C(9A)	- C(10A)	- C(11A)	99.2(13)
C(1A)	- C(11A)	- C(10A)	103.5(13)
C(2B)	- C(1B)	- C(8B)	111.2(16)
C(2B)	- C(1B)	- C(11B)	113.1(17)
C(8B)	- C(1B)	- C(11B)	103.7(12)
C(1B)	- C(2B)	- C(3B)	116.3(18)
C(1B)	- C(2B)	- C(4B)	116.4(18)
C(1B)	- C(2B)	- C(12B)	118.4(16)
C(3B)	- C(2B)	- C(4B)	62.4(11)
C(3B)	- C(2B)	- C(12B)	115.6(16)
C(4B)	- C(2B)	- C(12B)	115.6(17)
C(2B)	- C(3B)	- C(4B)	56.6(11)
C(2B)	- C(4B)	- C(3B)	61.0(11)
C(2B)	- C(4B)	- C(5B)	120.4(16)
C(3B)	- C(4B)	- C(5B)	118.5(18)
C(4B)	- C(5B)	- C(6B)	113.9(18)
C(5B)	- C(6B)	- C(7B)	110.5(15)
C(5B)	- C(6B)	- C(13B)	110.2(19)
C(5B)	- C(6B)	- C(14B)	108.5(18)
C(7B)	- C(6B)	- C(13B)	112.8(18)
C(7B)	- C(6B)	- C(14B)	105.5(18)
C(13B)	- C(6B)	- C(14B)	109.2(16)
C(6B)	- C(7B)	- C(8B)	114.6(17)
C(1B)	- C(8B)	- C(7B)	113.7(16)
C(1B)	- C(8B)	- C(9B)	102.6(12)
C(7B)	- C(8B)	- C(9B)	107.7(16)
C(8B)	- C(9B)	- C(10B)	108.5(13)
C(8B)	- C(9B)	- O(15B)	123.6(16)
C(10B)	- C(9B)	- O(15B)	127.1(16)
C(9B)	- C(10B)	- C(11B)	105.6(14)
C(1B)	- C(11B)	- C(10B)	101.4(14)
C(2C)	- C(1C)	- C(8C)	114.7(16)
C(2C)	- C(1C)	- C(11C)	114.5(15)
C(8C)	- C(1C)	- C(11C)	102.7(12)
C(1C)	- C(2C)	- C(3C)	121.0(21)
C(1C)	- C(2C)	- C(4C)	118.1(17)

Table 10c. (Continued)

C(1C) - C(2C) - C(12C)	118.0(16)
C(3C) - C(2C) - C(4C)	60.9(12)
C(3C) - C(2C) - C(12C)	112.6(16)
C(4C) - C(2C) - C(12C)	113.6(18)
C(2C) - C(3C) - C(4C)	60.3(12)
C(2C) - C(4C) - C(3C)	58.8(12)
C(2C) - C(4C) - C(5C)	119.5(15)
C(3C) - C(4C) - C(5C)	124.2(20)
C(4C) - C(5C) - C(6C)	116.7(19)
C(5C) - C(6C) - C(7C)	114.8(15)
C(5C) - C(6C) - C(13C)	111.0(18)
C(5C) - C(6C) - C(14C)	111.6(17)
C(7C) - C(6C) - C(13C)	108.7(18)
C(7C) - C(6C) - C(14C)	107.1(16)
C(13C) - C(6C) - C(14C)	102.9(15)
C(6C) - C(7C) - C(8C)	118.1(15)
C(1C) - C(8C) - C(7C)	117.5(15)
C(1C) - C(8C) - C(9C)	105.9(13)
C(7C) - C(8C) - C(9C)	112.8(14)
C(8C) - C(9C) - C(10C)	109.8(14)
C(8C) - C(9C) - O(15C)	126.5(16)
C(10C) - C(9C) - O(15C)	123.7(16)
C(9C) - C(10C) - C(11C)	106.7(14)
C(1C) - C(11C) - C(10C)	102.8(12)

Table 10d. Observed and calculated structure factor magnitudes for erectene.

H = 0				2	10	72	66	4	16	9	19	6	23	10	6
K	L	FO	FC	2	11	17	29	4	17	16	15	6	24	19	19
0	2	19	28	2	12	19	16	4	18	17	18	6	25	21	24
0	4	259	363	2	13	36	33	4	19	17	13	6	26	15	16
0	6	105	135	2	14	48	45	4	20	29	28	7	1	11	6
0	8	75	97	2	16	75	71	4	22	14	14	7	2	38	42
0	10	43	56	2	17	37	33	4	25	19	19	7	3	49	49
0	12	96	85	2	18	20	19	5	1	40	46	7	4	44	53
0	14	51	48	2	19	39	39	5	2	43	44	7	5	56	54
0	16	40	37	2	20	27	27	5	3	95	114	7	6	21	29
0	18	38	36	2	24	18	19	5	4	16	18	7	7	35	38
0	24	18	15	2	25	18	19	5	5	84	99	7	8	20	14
0	26	25	24	2	26	15	19	5	6	71	82	7	9	8	3
1	1	12	20	2	28	17	17	5	8	15	7	7	10	86	82
1	2	27	37	3	1	10	16	5	10	20	24	7	11	13	6
1	3	46	66	3	2	10	20	5	11	87	94	7	12	37	35
1	4	90	124	3	3	17	29	5	12	18	17	7	13	34	39
1	5	36	51	3	4	23	33	5	13	43	43	7	15	11	7
1	6	8	12	3	6	50	62	5	14	9	8	7	17	36	34
1	7	14	7	3	7	52	56	5	15	10	6	7	18	28	25
1	8	11	15	3	8	9	15	5	18	13	9	7	20	11	11
1	9	65	62	3	9	21	23	5	19	39	39	7	21	31	31
1	10	9	20	3	11	18	18	5	20	30	32	7	22	16	17
1	11	13	7	3	12	88	90	5	22	18	14	7	24	23	21
1	12	14	9	3	13	27	27	5	23	27	25	7	27	15	16
1	13	17	18	3	14	48	45	5	24	19	21	8	0	59	59
1	14	103	90	3	15	44	42	5	25	12	11	8	1	28	31
1	15	33	32	3	16	72	72	5	26	13	15	8	2	18	23
1	16	18	11	3	17	29	24	5	29	15	13	8	3	9	15
1	17	9	10	3	18	42	41	6	0	67	90	8	4	121	124
1	18	29	28	3	20	28	27	6	1	56	62	8	5	43	45
1	19	18	16	3	21	18	18	6	2	79	103	8	6	15	20
1	22	19	18	3	22	16	18	6	3	143	171	8	7	83	82
1	23	28	27	3	24	20	22	6	4	74	94	8	8	28	34
1	24	28	29	3	25	32	33	6	5	73	66	8	10	101	100
1	25	41	41	3	27	13	14	6	6	29	34	8	11	76	77
1	27	19	22	4	1	36	37	6	7	47	45	8	13	26	21
1	28	16	20	4	2	95	114	6	8	19	20	8	14	15	12
1	29	14	13	4	3	24	25	6	9	19	16	8	15	10	6
2	0	39	65	4	4	90	106	6	10	25	30	8	16	22	18
2	1	52	78	4	5	18	27	6	11	80	80	8	17	23	20
2	2	65	95	4	6	134	134	6	12	25	26	8	18	26	27
2	3	50	63	4	7	59	57	6	13	8	10	8	20	11	10
2	4	27	44	4	8	17	17	6	14	34	36	8	24	14	17
2	5	53	63	4	9	49	42	6	17	17	12	9	3	28	24
2	7	188	214	4	13	41	42	6	18	15	14	9	4	21	19
2	8	11	2	4	14	66	67	6	19	11	8	9	5	53	49
2	9	50	48	4	15	16	23	6	22	19	22	9	6	9	8

Table 10d. (Continued)

9	7	24	25	11	21	36	36	14	8	13	19	17	17	22	24
9	8	10	9	11	23	36	36	14	11	14	19	17	19	30	28
9	9	69	67	11	25	13	16	14	12	22	21	18	0	53	56
9	10	20	15	11	27	16	18	14	13	51	52	18	2	20	16
9	11	18	16	11	28	11	10	14	16	11	11	18	3	43	43
9	13	31	35	12	0	12	22	14	17	47	51	18	5	17	15
9	17	30	31	12	1	13	7	14	18	24	24	18	6	29	29
9	19	28	29	12	2	58	63	14	20	20	21	18	7	27	29
9	21	50	51	12	3	32	31	14	22	12	12	18	8	32	34
9	22	21	21	12	4	19	28	15	1	14	11	18	11	36	35
9	23	43	44	12	5	33	32	15	4	25	30	18	12	15	15
9	24	20	17	12	6	13	13	15	5	13	12	18	13	21	21
9	25	39	39	12	7	23	22	15	6	34	33	18	14	45	46
9	26	16	15	12	9	29	24	15	8	13	16	19	4	13	10
10	0	34	31	12	10	42	43	15	9	26	27	19	5	24	24
10	1	21	27	12	11	18	16	15	12	25	23	19	7	28	28
10	2	33	35	12	12	13	11	15	14	14	8	19	9	16	16
10	3	24	29	12	15	11	5	15	17	28	29	19	10	12	16
10	4	63	62	12	16	18	17	15	21	21	21	19	12	58	58
10	5	25	27	12	17	16	19	15	25	11	12	19	15	35	34
10	6	11	10	12	19	16	14	15	27	11	14	19	16	35	35
10	7	146	146	12	20	15	17	16	0	29	31	19	18	41	38
10	8	43	42	12	21	14	18	16	1	21	24	19	19	14	15
10	9	67	62	12	22	12	10	16	3	12	11	20	0	47	47
10	10	19	22	12	25	19	19	16	4	19	27	20	1	20	25
10	11	19	14	13	1	21	23	16	5	19	22	20	2	43	44
10	13	21	21	13	2	11	12	16	6	44	44	20	3	32	31
10	14	16	23	13	3	41	44	16	7	18	16	20	4	12	15
10	15	24	20	13	5	39	37	16	8	27	26	20	5	36	37
10	16	26	25	13	7	36	37	16	9	34	35	20	7	49	51
10	18	26	23	13	8	24	26	16	11	34	37	20	8	16	16
10	20	23	22	13	9	25	26	16	12	14	16	20	11	33	32
10	22	22	22	13	10	10	9	16	14	17	20	20	13	18	15
10	25	17	16	13	11	43	42	16	15	24	24	20	14	20	23
11	1	23	21	13	13	15	14	16	17	11	13	20	15	16	16
11	2	48	45	13	14	25	27	16	18	26	27	20	20	11	12
11	3	17	20	13	15	46	48	16	19	12	10	21	1	34	34
11	4	56	55	13	17	14	12	17	1	23	21	21	3	18	17
11	6	10	5	13	19	39	39	17	3	20	16	21	4	16	19
11	7	56	51	13	21	26	28	17	4	16	18	21	5	68	69
11	8	11	19	13	25	20	17	17	6	11	5	21	7	36	37
11	9	29	26	14	0	34	33	17	7	12	15	21	8	31	31
11	10	37	35	14	1	45	44	17	8	21	19	21	9	25	24
11	13	28	32	14	2	15	8	17	9	25	27	21	10	16	13
11	16	16	15	14	3	76	76	17	11	12	11	21	11	23	19
11	17	19	21	14	5	9	9	17	13	29	28	21	14	36	37
11	19	13	15	14	6	37	35	17	14	17	17	22	0	74	76
11	20	23	20	14	7	33	35	17	15	21	22	22	1	25	25

Table 10d. (Continued)

22	2	22	21	0	17	17	10	2	14	24	25	4	13	10	10
22	4	68	67	0	18	15	16	2	15	42	48	4	14	33	36
22	5	14	6	0	24	12	10	2	16	26	26	4	15	33	34
22	6	33	33	0	25	30	30	2	17	36	37	4	16	30	35
22	7	19	16	0	26	13	12	2	18	13	12	4	17	12	11
22	9	11	8	0	27	30	28	2	19	18	20	4	18	25	26
22	10	13	21	0	29	22	21	2	22	22	22	4	20	12	7
22	12	25	23	0	31	11	9	2	23	12	12	4	21	15	17
22	13	12	10	1	0	78	83	2	25	12	15	4	23	11	9
22	17	15	10	1	1	9	10	3	0	98	110	4	24	12	13
23	1	22	21	1	2	56	57	3	1	10	13	5	0	12	18
23	2	23	23	1	3	20	26	3	2	89	104	5	1	25	21
23	4	28	28	1	4	13	13	3	3	30	34	5	2	35	37
24	1	31	31	1	5	41	38	3	4	47	56	5	3	26	26
24	2	15	17	1	7	17	20	3	5	26	30	5	4	19	17
24	3	13	10	1	8	42	45	3	6	64	69	5	5	23	22
24	4	13	15	1	9	15	14	3	7	32	36	5	6	33	32
24	5	22	20	1	10	39	35	3	8	25	25	5	7	34	30
24	6	37	36	1	11	29	28	3	9	43	50	5	8	45	44
24	8	17	17	1	12	47	44	3	10	22	23	5	9	14	9
24	12	14	16	1	13	26	28	3	11	38	35	5	10	11	17
25	2	18	12	1	14	26	30	3	12	34	32	5	11	43	53
25	4	11	10	1	15	37	38	3	13	38	41	5	12	25	26
25	7	12	10	1	16	22	23	3	14	12	17	5	13	14	10
25	9	22	18	1	17	37	40	3	15	42	47	5	14	35	34
25	12	11	6	1	18	24	26	3	16	37	35	5	15	31	34
26	0	14	12	1	19	19	23	3	17	19	20	5	16	44	43
26	2	22	20	1	20	28	27	3	19	12	17	5	17	25	28
26	4	13	8	1	21	24	25	3	20	19	18	5	18	40	39
26	7	10	4	1	22	20	25	3	22	10	7	5	20	25	26
26	11	15	9	1	23	40	40	3	23	19	19	5	21	16	18
27	9	11	12	1	24	14	14	3	24	18	19	5	22	16	21
28	0	10	9	1	26	23	26	3	25	14	18	5	23	25	27
				1	27	41	39	3	26	18	21	5	24	11	14
	H =	1		1	29	15	13	3	29	12	13	5	27	19	15
K	L	FO	FC	2	0	202	233	4	0	76	82	6	0	39	31
0	1	9	14	2	1	193	228	4	1	60	62	6	1	20	11
0	2	18	20	2	2	194	228	4	2	92	91	6	2	33	35
0	3	31	28	2	3	124	147	4	3	77	79	6	3	76	66
0	4	124	140	2	4	81	95	4	4	33	29	6	4	64	63
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Table 10d. (Continued)

6	13	33	25	8	15	11	9	10	13	14	9	12	18	20	19
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6	18	32	32	8	20	15	16	10	19	18	21	13	0	10	8
6	19	22	22	8	21	29	31	10	20	15	14	13	1	21	13
6	20	18	22	8	22	12	14	10	21	13	17	13	3	47	42
6	21	24	24	8	23	17	21	10	23	14	15	13	4	13	10
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6	24	13	10	8	26	16	18	10	29	18	6	13	6	27	30
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7	6	38	33	9	6	28	29	11	7	12	11	13	18	40	38
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7	9	30	29	9	9	50	55	11	11	18	13	13	22	14	8
7	10	44	34	9	10	13	12	11	12	28	29	13	26	14	17
7	11	26	24	9	11	28	22	11	13	14	12	13	27	13	15
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7	16	30	33	9	16	19	21	11	19	23	24	14	4	21	20
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8	12	11	12	10	10	45	38	12	15	31	33	15	12	16	11
8	13	23	24	10	11	12	6	12	16	21	20	15	14	20	18
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Table 10d. (Continued)

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15	19	16	19	18	18	12	14	24	4	12	14	1	13	20	25
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15	23	11	11	19	4	13	15	24	7	16	14	1	15	29	28
15	24	13	12	19	5	15	10	24	10	11	7	1	16	22	20
15	25	12	8	19	6	16	19	24	11	22	21	1	17	29	29
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16	12	18	19	19	17	14	9	H = 2				2	0	109	110
16	13	41	41	20	1	25	26	K	L	FC	FC	2	1	103	97
16	14	18	19	20	2	21	23	0	0	296	376	2	2	105	111
16	15	15	14	20	4	24	29	0	1	78	76	2	3	70	65
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16	20	15	13	20	11	26	25	0	5	23	21	2	7	38	41
17	1	11	12	20	12	22	25	0	6	105	113	2	8	27	31
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17	7	11	10	21	1	19	19	0	10	66	59	2	11	33	32
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17	16	28	33	22	7	16	12	0	21	17	18	2	18	11	19
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17	19	13	11	22	9	14	12	0	24	14	11	2	22	13	12
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18	0	40	42	23	3	11	10	1	1	87	104	3	2	51	49
18	1	27	27	23	4	18	23	1	2	47	46	3	3	36	30
18	3	18	18	23	6	23	22	1	3	89	88	3	4	42	37
18	5	20	19	23	8	24	24	1	4	76	76	3	6	50	51
18	6	12	12	23	9	12	11	1	5	58	56	3	8	21	21
18	7	31	32	23	10	14	10	1	6	29	31	3	9	30	30
18	8	24	28	23	11	16	17	1	7	24	23	3	10	21	21
18	9	18	17	23	15	16	14	1	8	54	52	3	11	43	36
18	11	35	34	23	17	11	10	1	9	27	20	3	12	24	19

Table 10d. (Continued)

3	13	48	45	5	15	24	23	7	13	24	21	9	16	28	26
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3	15	29	30	5	17	16	11	7	15	14	15	9	19	46	45
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3	25	25	25	5	25	21	20	7	23	14	17	9	27	15	14
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4	0	73	69	5	27	11	11	7	25	12	15	10	1	31	24
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4	2	65	59	6	0	16	13	8	0	8	17	10	3	39	38
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4	12	32	30	6	10	44	42	8	12	22	17	10	13	23	23
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4	14	15	13	6	12	15	15	8	14	11	11	10	15	12	7
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4	20	11	14	6	17	21	19	8	20	27	27	10	25	12	10
4	21	17	19	6	18	14	14	8	21	26	27	11	0	15	8
4	23	12	12	6	19	15	15	8	22	20	18	11	1	18	22
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4	25	12	10	6	22	14	11	9	0	19	18	11	3	9	13
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5	7	47	44	7	6	15	13	9	9	38	36	11	11	27	23
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Table 10d. (Continued)

11	23	15	15	14	6	17	20	17	24	10	10	22	2	18	21
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11	25	15	16	14	10	13	11	18	1	13	11	22	4	38	37
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12	0	48	47	14	13	19	21	18	4	35	34	22	6	22	22
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12	9	34	35	15	8	13	13	19	2	11	14	23	7	14	15
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13	1	26	22	16	7	16	14	20	4	40	38	24	13	10	7
13	2	12	12	16	9	15	16	20	5	17	18	25	0	20	17
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13	20	13	15	17	11	20	20	21	6	11	4	0	4	72	63
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14	3	25	22	17	20	12	9	21	15	14	13	0	16	16	11
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Table 10d. (Continued)

0	19	15	7	3	9	13	7	5	19	13	13	8	15	18	29
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3	1	15	12	5	14	14	15	8	8	20	21	13	9	13	15
3	2	49	46	5	15	31	32	8	9	13	13	13	13	11	10
3	4	26	25	5	16	14	15	8	10	15	21	13	14	10	17
3	6	17	19	5	17	20	17	8	11	17	17	14	1	11	12
3	7	28	23	5	18	22	21	8	13	22	28	14	3	24	24

Table 10d. (Continued)

14	4	24	25
14	6	19	21
14	8	20	21
14	9	19	19
14	10	19	24
14	13	15	20
15	1	24	25
15	4	16	22
15	6	10	16
15	7	12	15
15	10	16	19
16	0	13	14
16	1	11	12
16	2	14	13
16	4	19	23
16	5	13	18
16	6	14	14
16	7	14	16
16	9	16	19
17	0	15	16
17	6	13	11
17	12	17	22
17	14	11	7
18	4	11	7
18	5	11	15
18	7	14	20
18	9	20	25
19	6	13	15
19	7	11	9
19	15	11	11
20	0	19	23
20	3	12	16
20	4	11	17
22	0	16	17
22	3	12	17
22	5	13	19
24	0	19	20
24	2	11	15
24	3	10	10

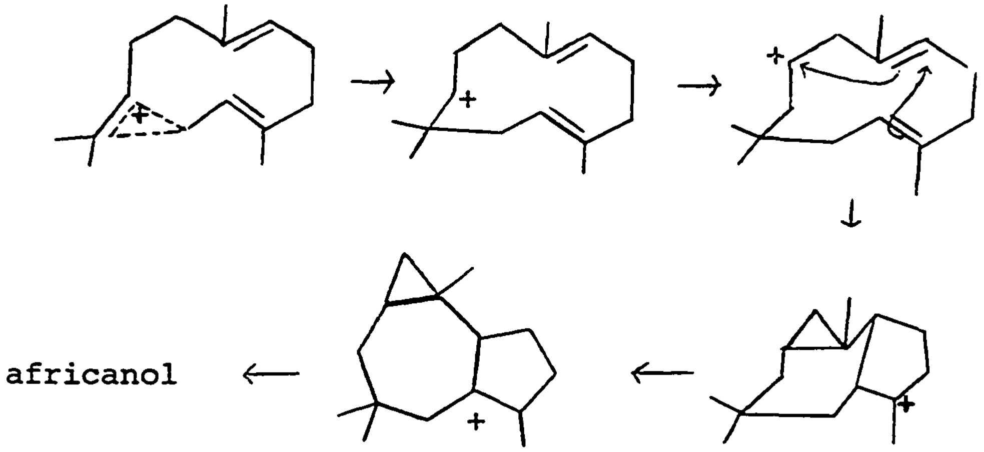
H = 4

K	L	FO	FC
0	0	13	13
0	1	11	11
0	2	69	60
0	3	46	42
0	4	17	13
0	6	60	58
0	8	51	50
0	11	13	15
0	16	12	11
1	0	42	36
1	1	47	42
1	2	29	28
1	3	18	12
1	5	23	22
1	6	33	35
1	7	18	21
1	8	36	38
1	9	13	14
1	10	20	23
1	11	20	22
1	12	20	20
1	13	11	18
1	16	19	23
1	17	16	21
1	18	13	16
1	19	11	10
2	0	36	36
2	1	42	39
2	2	35	38
2	3	44	40
2	4	23	28
2	5	36	38
2	6	20	18
2	9	13	16
2	10	23	28
2	11	17	20
2	12	13	14
2	19	12	10
3	0	30	29
3	1	15	13
3	2	22	18
3	3	21	21
3	5	13	16
3	6	24	21
3	7	15	22
3	8	15	21
3	9	11	17
3	10	15	14
3	14	14	18
4	0	28	24
4	1	43	42
4	2	27	33
4	3	21	18
4	5	52	54
4	6	12	16
4	9	10	12
4	10	13	12
4	11	16	21
4	12	15	17
4	13	24	29
4	15	13	23
4	17	13	15
5	1	12	5
5	2	13	14
5	3	13	23
5	4	15	15
5	6	22	21
5	8	16	16
5	9	11	12
5	11	16	20
5	12	19	20
5	13	13	17
5	15	13	16
5	17	12	15
6	0	12	4
6	1	27	28
6	2	24	26
6	3	17	23
6	5	11	11
6	6	35	43
6	9	13	17
6	10	13	18
6	12	12	16
6	13	18	26
7	0	17	15
7	1	16	22
7	2	16	12
7	4	10	13
7	5	12	13
7	7	14	18
7	11	12	20
7	12	11	19
8	0	12	14
8	1	32	35
8	2	19	26
8	3	17	25
8	4	11	20
8	6	11	16
8	12	12	19
9	0	28	29
9	1	14	8
9	3	10	10
9	4	11	15
9	5	11	15
9	15	13	26
10	0	17	16
10	1	20	20
10	2	20	22
10	3	34	34
10	4	15	15
10	5	11	10
10	7	15	17
10	8	20	29
10	11	11	20
11	0	24	23
11	1	11	14
11	2	19	21
11	8	14	19
11	11	13	19
11	13	13	25
12	1	30	29
12	2	30	29
12	3	11	4
12	4	35	34
12	5	15	13
12	6	21	23
12	7	17	23
12	8	11	8
12	10	14	23
13	2	12	16
13	3	16	13
13	4	11	11
13	5	14	17
13	9	11	15
13	14	12	13
14	9	11	14
14	10	14	15
15	7	12	16
15	13	10	11
16	6	11	9
17	0	15	17
18	0	15	15
18	1	15	15
18	3	12	16
22	0	22	20
22	4	10	14
23	0	10	11

Table 10d. (Continued)

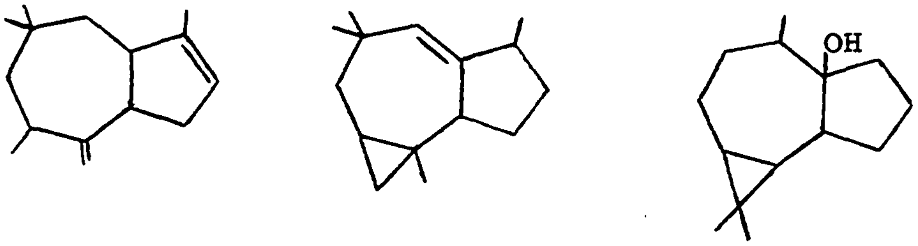
	H =	5	
K	L	FO	FC
0	2	12	14
0	3	14	10
0	5	14	5
0	6	18	15
0	8	37	36
0	9	18	18
0	10	12	12
1	2	11	3
1	4	17	14
1	6	11	14
1	8	17	20
1	11	13	20
2	3	17	15
2	7	11	9
3	4	11	10
4	0	16	16
6	0	24	26
6	1	15	12
6	5	14	24
7	3	11	15
7	4	15	19
8	2	20	21
9	0	11	15
9	1	11	12
9	7	10	15
10	1	34	33
11	0	14	15
12	8	11	10
13	1	13	15
14	0	15	11
14	14	10	7

Discussion Erectene's skeleton differs from that of africanol only in the stereochemistry of the ring junction between the 5- and 7-membered rings. It can be divided by inspection into three isoprenoid units and is probably derived from the normal sesquiterpene precursor, farnesyl pyrophosphate, by a sequence of cyclizations similar to those proposed for africanol (88).



Proposed biosynthesis of africanol

Erectene constituted 95% of the hydrocarbon oil of S. erecta. The remaining 5% contained a mixture of compounds, most of which were sesquiterpenes with skeletons similar to that of erectene. The two most prominent compounds in the mixture were assigned tentative structures on the basis of their spectra. A third compound was identified as palustrol, a sesquiterpene isolated previously from a xeniid (82).



palustrol

Three sesquiterpenes from *S. erecta*

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