

الجمهورية الجزائرية الديمقراطية الشعبية
وزارة التعليم العالي و البحث العلمي
جامعة منتوري قسنطينة

قسم الكيمياء

كلية العلوم الدقيقة

رقم الترتيب

رقم التسلسل

مذكرة
مقدمة لنيل شهادة الماجستير في العلوم
تخصص كيمياء عضوية
شعبة كيمياء النبات
تحت عنوان

Pulicaria crista (Forsk)

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الإهداء

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تشكرات

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CCM : Chromatographie sur couche mince

CC : Chromatographie sur colonne

CP : Chromatographie sur papier

R_f : Facteur de retardement (retardation factor)

RMN : Résonance Magnétique Nucléaire

¹³C : Carbone 13

¹H : Proton

ppm : Partie par million

δ : Déplacement chimique

J(Hz) : Constante de couplage exprimée en hertz

s : Singulet

d : Doublet

dd : Doublet de doublets

m : Multiplet

SMIE : Spectrométrie de masse en mode impact électronique

m/z : Masse / charge électrique

UV : Ultra_Violet

الفهرس

2	
4	
	<i>Pulicaria crispa</i>	:
6	-1
6	-2
8	-3
9 <i>Pulicaria</i>	-4
13	-5
14	
		الفصل الثاني:
21	-1
21	-2
22	-3
27	-4
30	-5
35	-6
36	-7
37	-8
40	-9
42	-10
43	-11
45	-12
45	-1
45	-2
47	-3
61	

	:	
69 <i>Pulicaria crispa</i>	
69	I
69	II
71	-III
	:	
78	
79 $E \equiv F_{421} \equiv F_{4P}$	-I
87 $C \equiv D_P \equiv D_{P1} \equiv D_6 \equiv F_{P2}$	-II
95	-III
97	

المقدمة

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[20] .

Ecotypes

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Biotypes

%25

162

[1]

[2]

%15

3000

[2]

Pulicaria crisper

المراجع

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الفصل الأول :

الدراسة النظرية لنبات البتلات

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:(1)

-1-

Embranchement	Spermatophytæ		
Sous embranchement	Angiospermae		
Classe	Dicotylédones		
Ordre	Campanulaes		
Famille	Compositae		
Sous famille	Tubuliflorae		
Tribu	Inuleae		
Genre	<i>Pulicaria</i>		
Espèce	<i>Pulicaria crispa</i>		

_____ -2 :

5 80

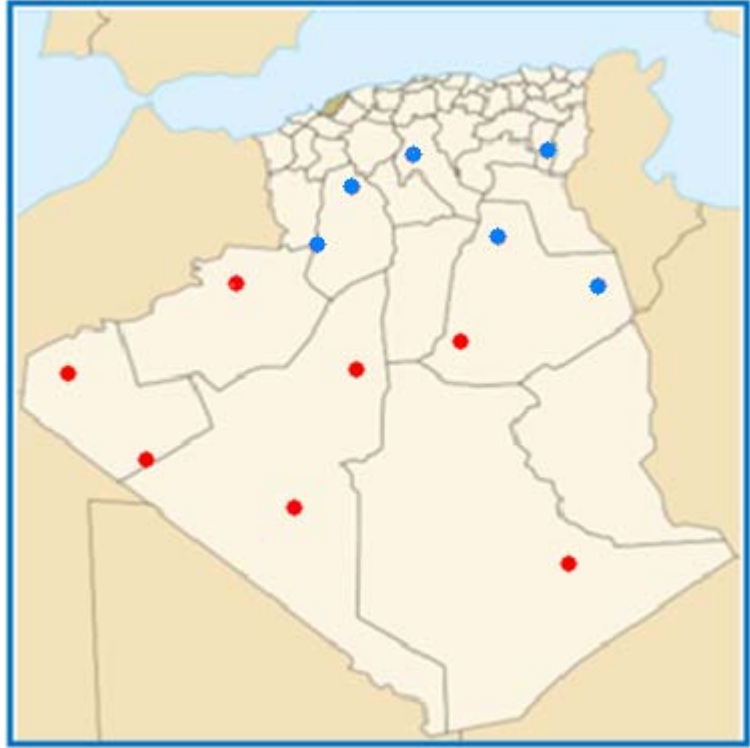
Pulicaria

: [5 4 3] 4 16 [2 1]

(*Francoeuria crispa* (Cass)): *Pulicaria crispa* (Forsk). Benth. et Hook

.(1)

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: -1-

60-40

:Pulicaria crispa

5

(2)

[3]



Pulicaria crispa

: -2-

: _____ -3

[12-8]

[16-13 ، 7 ، 6] :

[14 7]

[14]

[17-14]

. [19]

[18]

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(acétylènes) (β-caryophyllene) و مشتقات
 التيمول (thymol derivatives) [1 3 4 5].

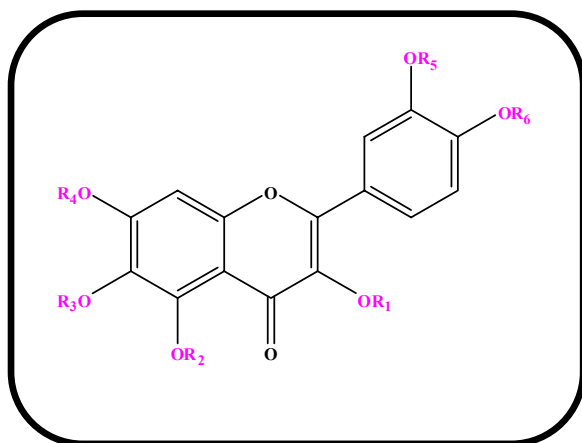
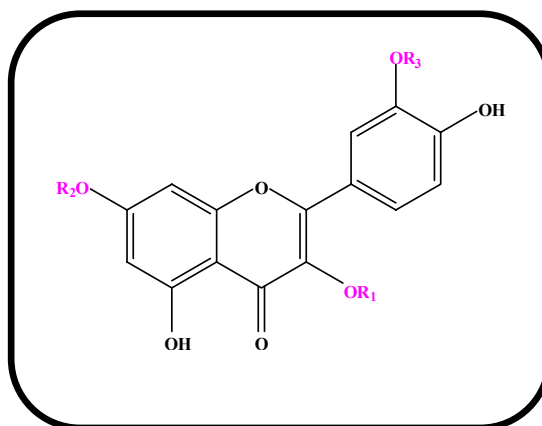
Pulicaria (3) (2)

Pulicaria -2-

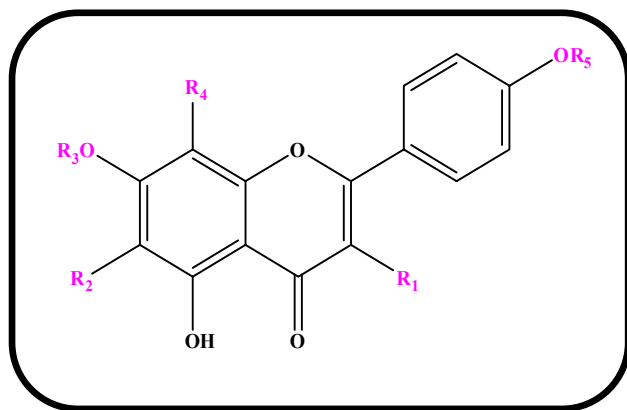
1	Quercetin	<i>P. crispa</i>	[15],[30-31], [13]
2	Quercetin 3-methyl ether	<i>P. crispa</i>	[15]
		<i>P. insica</i>	[28]
3	Quercetin 7-methyl ether (Rhamnetin)	<i>P. undulata</i>	[32]
4	Quercein 3,7-dimethyl ether	<i>P. undulata</i>	[26], [32]
		<i>P. insica</i>	[28]
5	Quercetin 3-glucoside	<i>P. arabica</i>	[25]
		<i>P. crispa</i>	[15]
6	Quercetin 3-galactoside	<i>P. insica</i>	[28]
7	Quercetin 3-glucuronide	<i>P. arabica</i>	[25]
		<i>P. dysenterica</i>	[20]
8	Quercetin 7-glucoside	<i>P. crispa</i>	[15]
		<i>P. undulata</i>	[32]
9	Rhamnetin 3-galactoside	<i>P. crispa</i>	[30], [13]
10	Quercetin 7-glucuronide	<i>P. sicula</i>	[1]
11	Quercetin 3-rutinoside	<i>P. paludosa</i>	[1]
12	Quercetin 3-rhamnoglucoside	<i>P. paludosa</i>	[1]
13	Quercetin 3-diglucuronide	<i>P. paludosa</i>	[1]
		<i>P. sicula</i>	
14	Isorhamnetin 3-glucoside	<i>P. paludosa</i>	[1]
15	Isorhamnetin 3-galactoside	<i>P. paludosa</i>	[1]
16	Isorhamnetin 3-rhamnoglucoside	<i>P. paludosa</i>	[1]
17	Isorhamnetin 3-rhamnogalactoside	<i>P. paludosa</i>	[1]
18	Patuletin 7-glucoside	<i>P. odora</i>	[1]

19	Quercetagetin 3,7-dimethyl ether	<i>P. dysenterica</i>	[20]• [22]
		<i>P. arabica</i>	[25]
20	Quercetagetin 3',4'-dimethyl ether	<i>P. arabica</i>	[24]
21	Quercetagetin 3,5,7-trimethyl ether	<i>P. arabica</i>	[25]
22	Quercetagetin 3,7,3'-trimethyl ether	<i>P. dysenterica</i>	[20]
23	Quercetagetin 3,7,4'-trimethyl ether (oxyyanin B)	<i>P. dysenterica</i>	[23]
24	Quercetagetin 3,5,7,3'-tetramethyl ether	<i>P. arabica</i>	[25]
25	Quercetagetin 3,7,3',4'-tetramethyl ether	<i>P. dysenterica</i>	(20)
26	Quercetagetin 3,5,6,7,3'-pentamethyl ether	<i>P. arabica</i>	[24]
27	Quercetagetin 3,5,6,7,4'-pentamethyl ether	<i>P. arabica</i>	[24]
28	Kaempferol	<i>P. crispa</i>	[31]
29	Kaempferol 3-methyl ether	<i>P. undulata</i>	[26]
		<i>P. insica</i>	[28]
30	Kaempferol 7-methyl ether (Rhamnocitrin)	<i>P. undulata</i>	[32]
31	Kaempferol 3-glucoside	<i>P. dysenterica</i>	[20]• [23]
32	Kaempferol 3-galactoside	<i>P. insica</i>	[28]
33	5,6,8-trihydroxy-7,4'-dimethoxy flavone	<i>P. paludosa</i>	[21]
34	Apigenin 7-glucoside	<i>P. crispa</i>	[30]• [13]
35	Scutellarein	<i>P. dysenterica</i>	[22]
36	Scutellarein 7,4'-dimethyl ether	<i>P. paludosa</i>	[21]
37	Dihydroquercetin (taxifolin)	<i>P. undulata</i>	[26]
38	Dihydroquercetin 7-methyl ether	<i>P. undulata</i>	[26]
		<i>P. insica</i>	[28]
39	Dihydroquercetin 7,3'-dimethyl ether	<i>P. undulata</i>	[26]
40	Dihydrokaempferol	<i>P. undulata</i>	[26]• [32]
41	Dihydrokaempferol 7-methyl ether	<i>P. undulata</i>	[27]
42	Eriodictyol 7-methyl ether	<i>P. undulata</i>	[27]
43	6-hydroxy kaempferol 3,6-dimethyl ether	<i>P. paludosa</i>	[21]
44	6-hydroxy kaempferol 3,7-dimethyl ether	<i>P. dysenterica</i>	[20]• [22]
45	6-hydroxy kaempferol 3-methyl ether 6-glucoside	<i>P. dysenterica</i>	[22]
46	6-hydroxy kaempferol 3,6,7-trimethyl ether	<i>P. dysenterica</i>	[22]
47	6-hydroxy kaempferol 3,7,4'-trimethyl ether	<i>P. dysenterica</i>	[20]
48	6-hydroxy kaempferol 6-methyl ether7-glucoside	<i>P. odora</i>	[1]
49	Sulphated 6-hydroxy flavone	<i>P. burchardii</i>	[29]
50	Traces of sulfated flavonoid	<i>P. arabica</i>	[25]

المركب	R ₁	R ₂	R ₃
1	H	H	H
2	Me	H	H
3	H	Me	H
4	Me	Me	H
5	Glu	H	H
6	Gal	H	H
7	Gluc	H	H
8	H	Glu	H
9	Gal	Me	H
10	H	Gluc	H
11	Rut	H	H
12	Rha-glu	H	H
13	Diglu	H	H
14	Glu	H	Me
15	Gal	H	Me
16	Rha-glu	H	Me
17	Rha-gal	H	Me

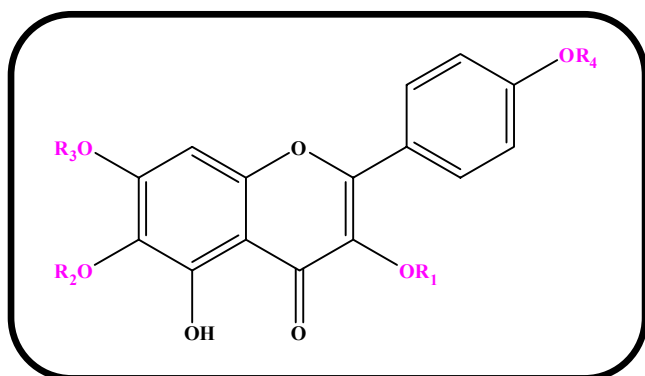
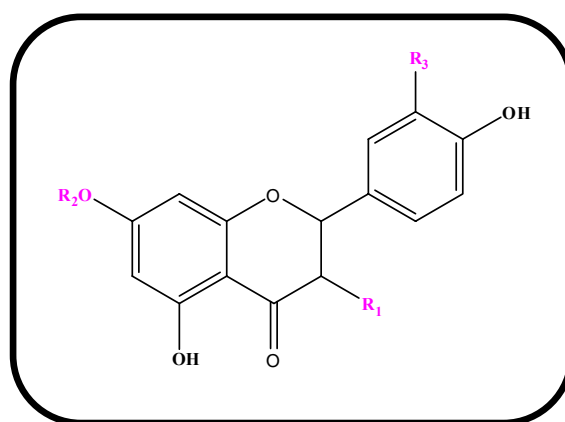


المركب	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆
18	H	H	Me	Glu	H	H
19	Me	H	H	Me	H	H
20	H	H	H	H	Me	Me
21	Me	Me	H	Me	H	H
22	Me	H	H	Me	Me	H
23	Me	H	H	Me	H	Me
24	Me	Me	H	Me	Me	H
25	Me	H	H	Me	Me	Me
26	Me	Me	Me	Me	Me	H
27	Me	Me	Me	Me	H	Me



المركب	R ₁	R ₂	R ₃	R ₄	R ₅
28	OH	H	H	H	H
29	OMe	H	H	H	H
30	OH	H	Me	H	H
31	OGlu	H	H	H	H
32	OGal	H	H	H	H
33	H	OH	Me	OH	Me
34	H	H	Glu	H	H
35	H	OH	H	H	H
36	H	OH	Me	H	Me

المركب	R ₁	R ₂	R ₃
37	OH	H	OH
38	OH	Me	OH
39	OH	Me	OMe
40	OH	H	H
41	OH	Me	H
42	H	Me	OH



المركب	R ₁	R ₂	R ₃	R ₄
43	Me	Me	H	H
44	Me	H	Me	H
45	Me	Glu	H	H
46	Me	Me	Me	H
47	Me	H	Me	Me
48	H	Me	Glu	H

Glu : Glucose

Gal : Galactose

Rut : Rutinose

Gluc : Glucuronide

Rha-glu : Rhamnoglucosyl

Rha-gal : Rhamnogalactosyl

Diglu : Diglucuronide

[32]، [36]	الزيوت الأساسية (les huiles essentiels)
[22]، [23]، [35]	الكومارينات (les coumarines)
[23]، [27]	مشتقات الثيمول (les dérivées de thymol)
[35]	القلويدات (les alkaloides)
[19]، [33]، [38]، [40]، [41]، [43]، [50]	السيكوي تيربينات اللكتونية ومشتقاتها (les sesquiterpene lactones et ces dérivées)
[49] [7] [46] [34] [45]	التربينات (les terpenoides) التربينات الثلاثية (les triterpenes) Les guianolides et eudesmanolides Les guaianolide sesquiterpenes Germacrane sesuiterpenes
[21]، [42]، [44]، [47]	مشتقات الكاريوفيلان (les dérivées du caryophylenes)
[48]	les dérivées du acide hardwickiic
[37]	Les isopimarane

-5- _____ :

[51 6]

[52]

[7] (carminative)

Pulicaria

[55 54 41]

Inuleae

(sternutatoire)

[29]

hémorroïdes

[55]

[56].

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الفصل الثاني

المفردات

-1- _____ :

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9000

[1].

-2- _____ :

Flavus

Flavonoide

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[2]

(Angiospermes)

[3].

"Albert Szent-Györgyi"

[4] C

P

1952 طرف "Geissman"

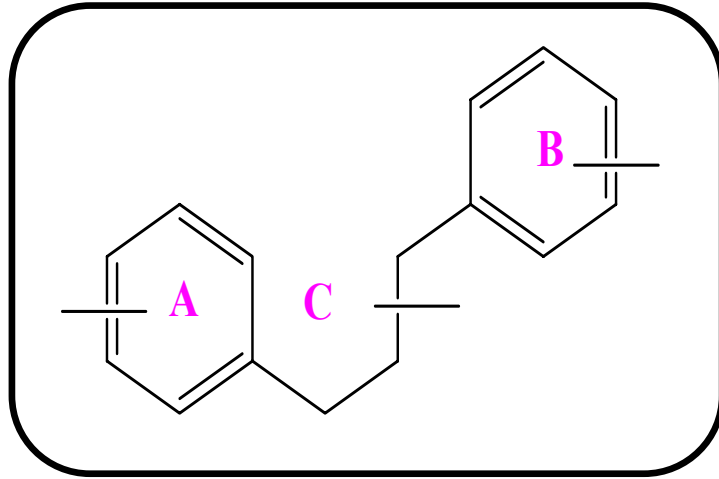
(C₆-C₃-C₆)

15

3

(A et B) C₆

[5] (1)



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: _____ -3

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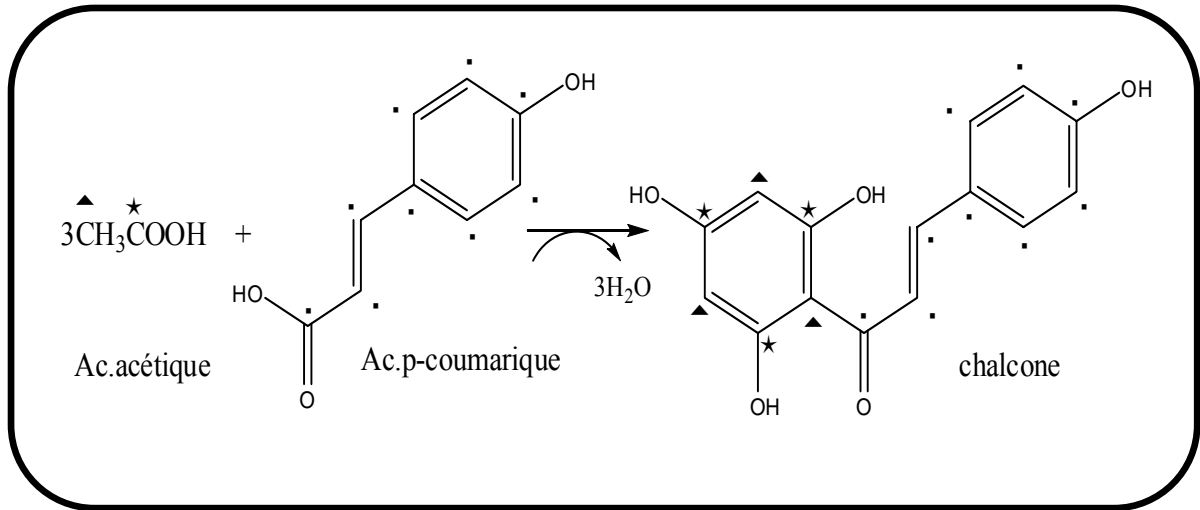
^{14}C

Robinson

[6] 1936

.(2)

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: _____ -1-3

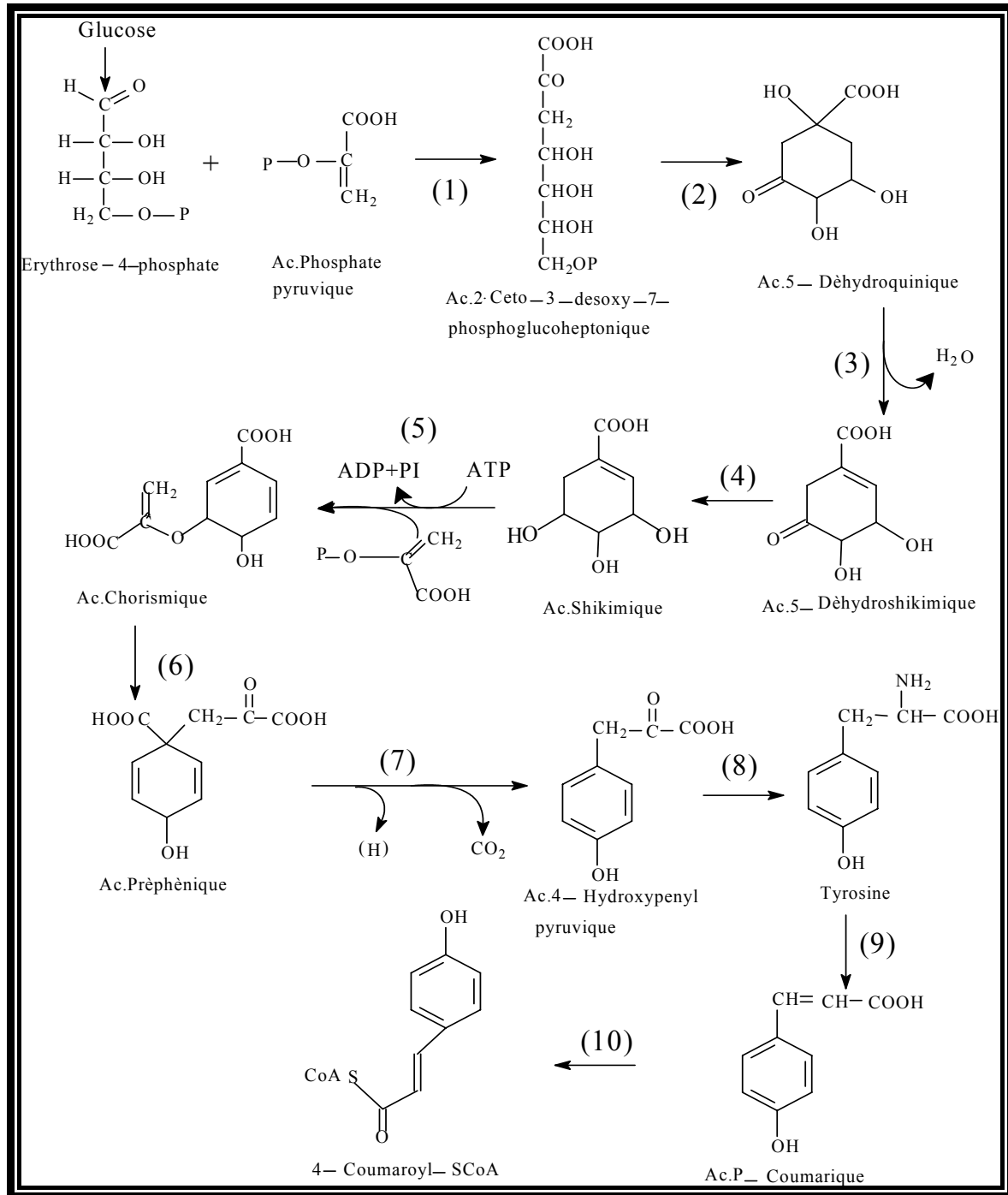
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B

[6] 1955 Davis

.(1)

C₃



p-coumarique

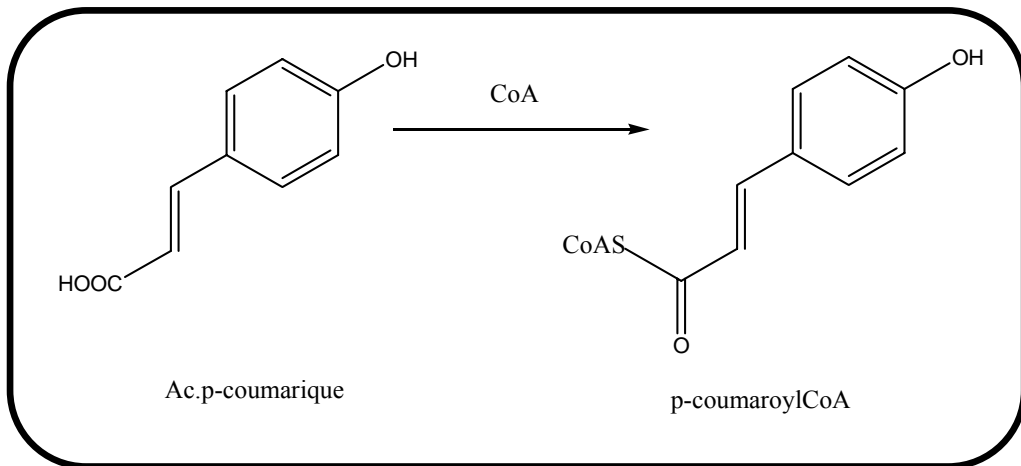
:1-

(1)

p-coumarique

Ac.p-coumaroyl CoA إلى Ac.p-coumarique

(3) الذي يكون جاهزا للاتحاد مع Malonyl-CoA



Ac.p-coumaroyl CoA Ac.p-coumarique :-3-

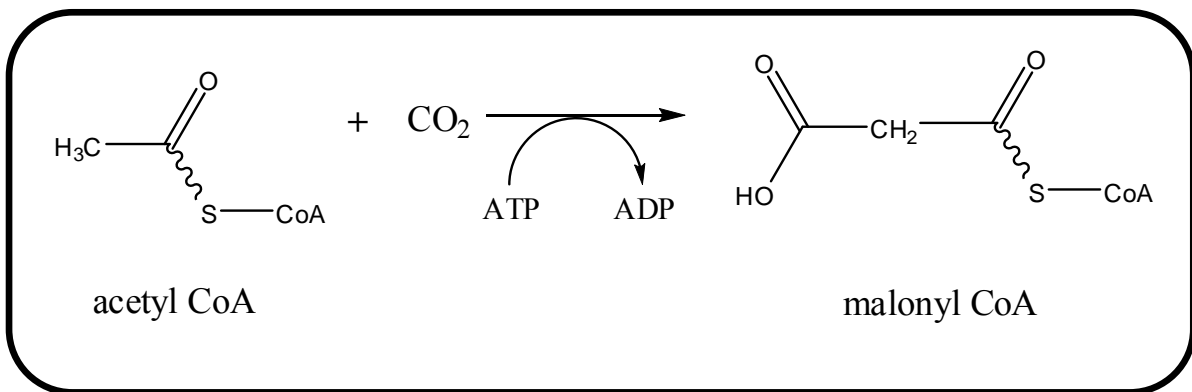
: _____ -2-3

: ●

Malonyl-CoA

A

: (4) Acetyl-CoA

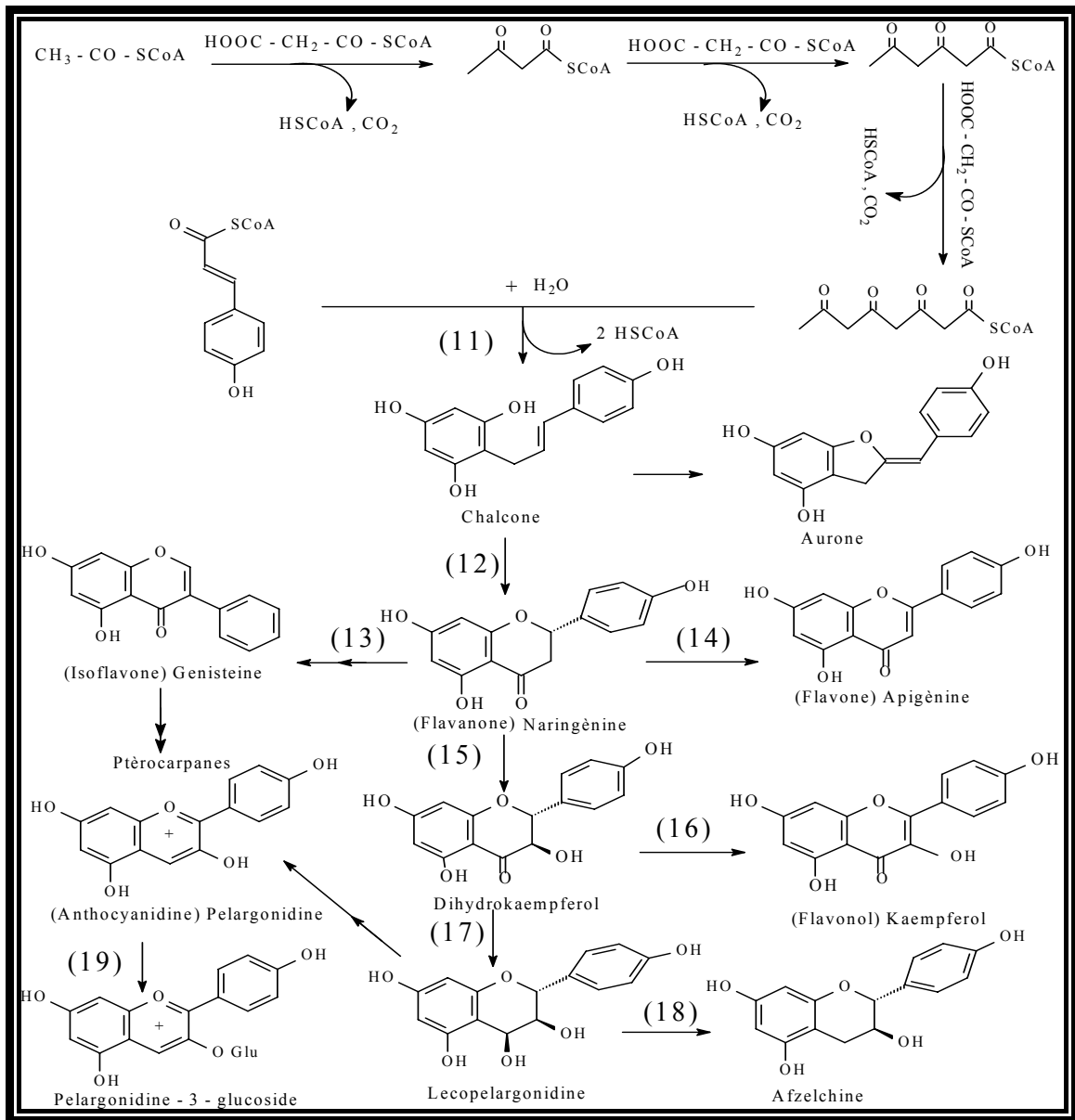


Malonyl-CoA :-4-

[7]

(-2-) p-coumaroyl-CoA Malonyl-CoA

(1)



[7]

:-2-

: -1-

1	Aldolase, 3-désoxy-O-arabinoheptulosonate-7 phosphate synthase ou DHAP synthase
2	Déshydroquinone synthase
3	Déshydroquinone déshydratase
4	Shikimate déshydrogénase
5	Complexe shikimate kinase
6	Chorismate mutase
7	Préphénate déshydrogénase
8	Aminotransférases
9	Tyrosine ammonia-lyase
10	P-coumarate CoA-ligase
11	Chalcone synthase
12	Chalcone isomérase
13	2-hydroxyisoflavanone synthase
14	Flavone synthase
15	(2S)-Flavanone 3-hydroxylase
16	Flavonol synthase
17	Dihydroflavonol 4-réductase
18	Flavan-3,4-cis-diol 4-réductase
19	Anthocyanidin/flavonol 3-O glucosyltransférase

: _____ -4

...

: _____ -1-4

A

% 90 7 5

A

B

2'

4'

[8]

6'

: _____ -2-4

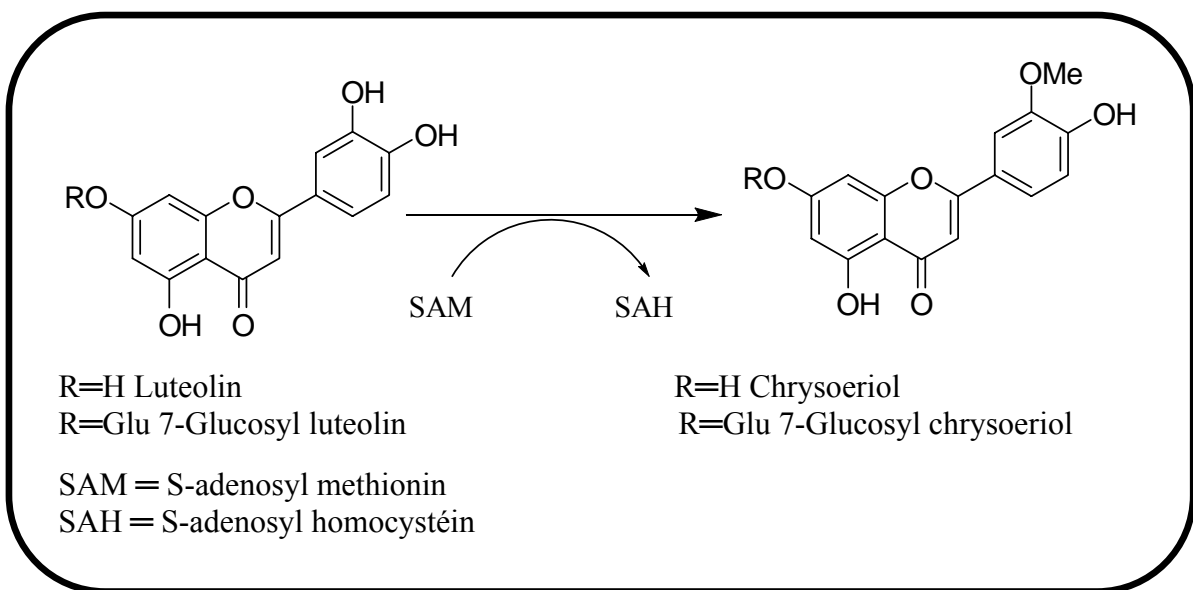
O-méthyl-transférase

(SAM)

B (3')

: (5)

[9] Lutéoline



Chrysoeriol Luteolin

:-5-

(D-allose D-galactose D-glucose) Hexoses :

(D-xylose L-rhamnose L-arabinose D-apioses) Pentoses

(O-hétérosidique)

3

700

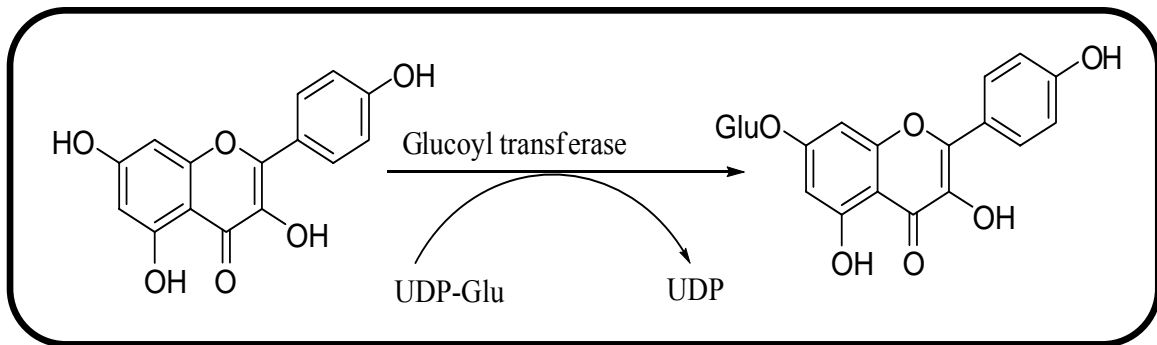
7

[1] 1400

UDP-Glu

(Glycosyl transférase)

(6) (glucose Uridine diphosphate)



C-7

-6-

:C-hétérosides

C-glycosyl flavonoides

Glucose)

C₁

C₈ / C₆

(

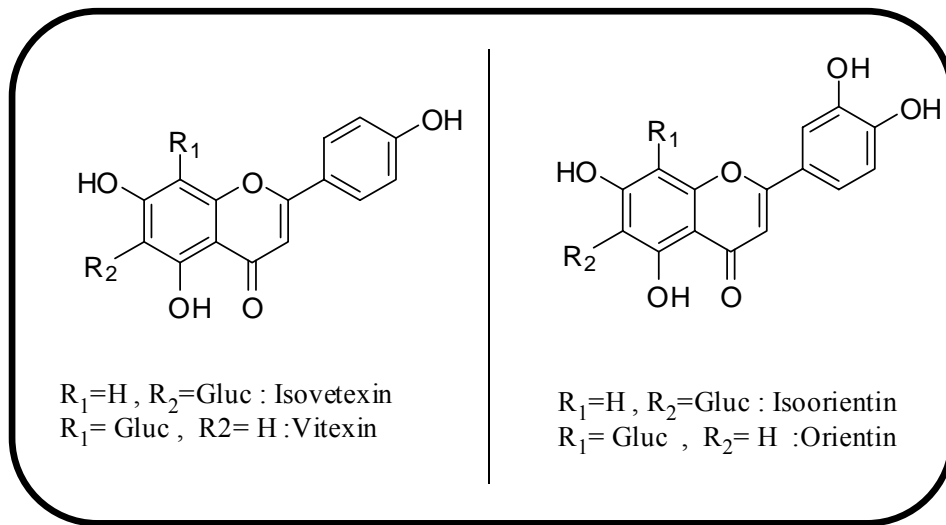
Galactose

5-hydroxy-C-glycosyl flavone

(6↔8 8↔6)

(7)

[10 1] Wessely-Moser



C-glycosyl flavone

: -7-

: _____ -5

[11]

: _____ -1-5

A

‘C-7 C-5

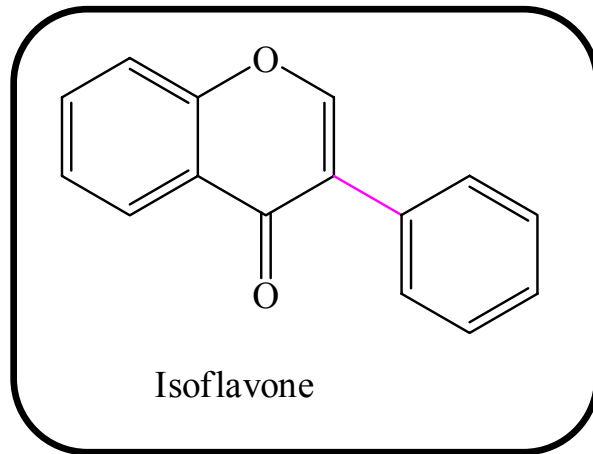
%90

_____ -4-5 :

[13,12] légumineuses

3 A B

.2



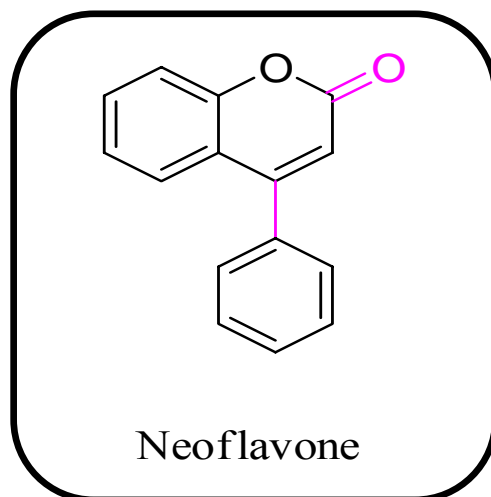
[14]

B

.2

4

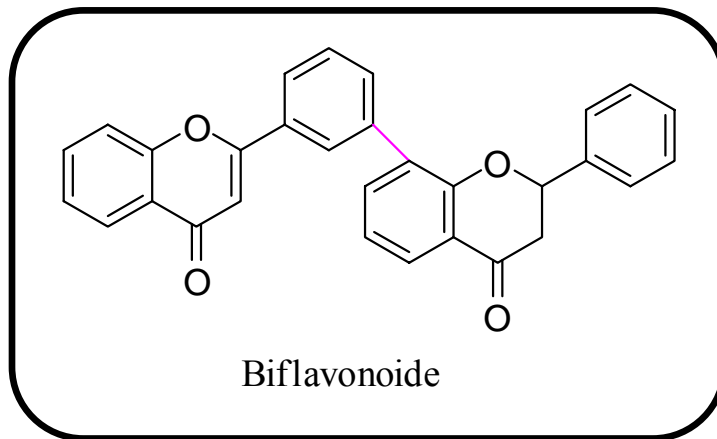
B



[15]

: _____ -5-5

C-8 C-6



: _____ -6-5

C₃

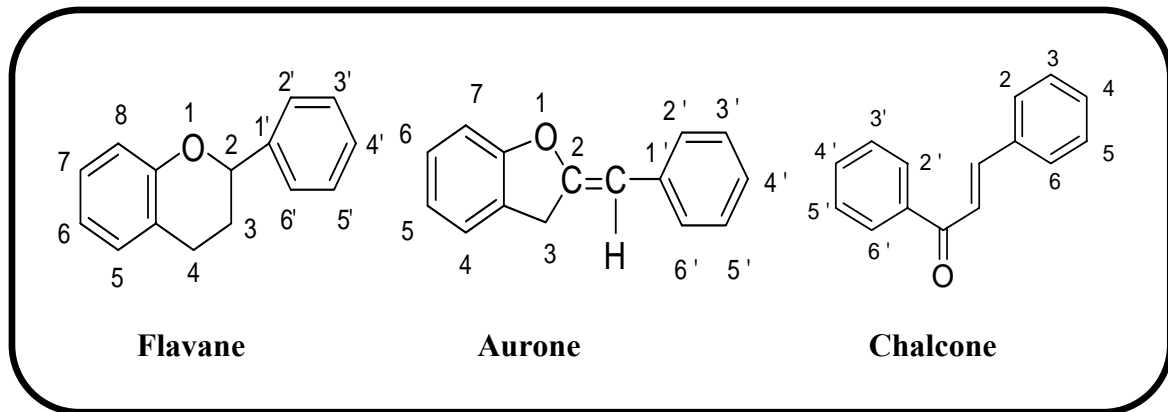
A

B

(α - β insaturé)

.2-benzylidiène coumarone

.(8)



:-8-

(2)

:-2-

Apigenine Luteoline	5, 7, 4' 5, 7, 3', 4'	R=H Flavone		Phenyl-2 chromones
Kaempferol Quercetine	5, 7, 4' 5, 7, 3', 4'	R=OH Flavonol		
Naringenine Butine	5, 7, 4' 7, 3', 4'	R=H Flavanone (dihydroflavone)		
Fustine Taxifoline	5, 7, 3', 4', 5' 5, 7, 3', 4'	R=OH Flavanonol		Phenyl-2 chromanes
Gallocatechine Catéchine	5, 7, 3', 4' 5, 7, 3', 4', 5'	R=H Catechine (Flavanol-3)		
Leucocyanidine Leucodelphinidine	5, 7, 3', 4' 5, 7, 3', 4', 5'	R=OH Leucoanthocyanidine (flavandiol-3,4)		
Apigenidine Lueolidine	5, 7, 4' 5, 7, 3', 4'	R=H Flavylum (anthocyane)		Flavyliums
Cyanidine Delphinidine	5, 7, 3', 4' 5, 7, 3', 4', 5'	R=OH Anthocyanidine		
Daidzein Orobol	7, 4' 5, 7, 3', 4'	Isoflavone		Phenyl-3 chromones

[16]

(téguments externes des fruits)

(...)

3

[17].

(polymères)

(3-O-glycosides)

(3)

[11] (aglycones)

-3-

Flavonoïdes	Aliments
Flavanones	
narigénine	fruits du genre citrus
Flavones	
Chrysin	peau de fruits
Apigénine	persil, thym, romarin, céleri
lutéoline	persil, céleri
Flavonols	
kaempferol	radis, brocoli, thé noir
quercétine	oignon, pomme, olive, vin rouge, tomate
myricétine	canneberge, vin rouge
Flavan-3-ol	
épicatéchine	thé vert, thé noir
catéchine	thé vert, thé noir
épigallocatechine	vin rouge
Anthocyanidols	
cyanidols	cassis, myrtilles
malvidol	raisins, fraises, cassis
apigénidol	framboises, fraises

[21-18]

:

() [22] (4)

[23] 1 25 .

[17] :-4-

(/)	
17.7	الخضر
124.1	الكرنب الأبيض
20.1	البصل الأحمر
338.6	الفلفل
80.8	السبانخ
402.8	أوراق البقدونس
25.9	أوراق الكرفس
	جذور الكرفس
18.4	الفواكه
52.8	البطيخ
1003	الفاولة
5465	العنب
22.3	الجوز
22.8	الكيوي
65.3	الموز
24.7	التفاح
23.3	الإجاص
11.5	البرقوق
	المشمش

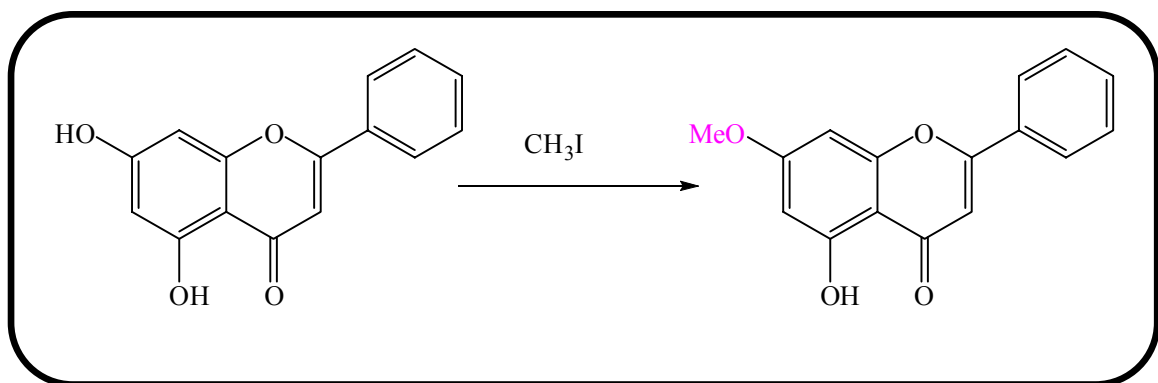
-7- _____ :

[15]

-8 _____ :

5

[2] (9)



-9-

5-OH

(Anhydride acétique)

(AlCl₃)

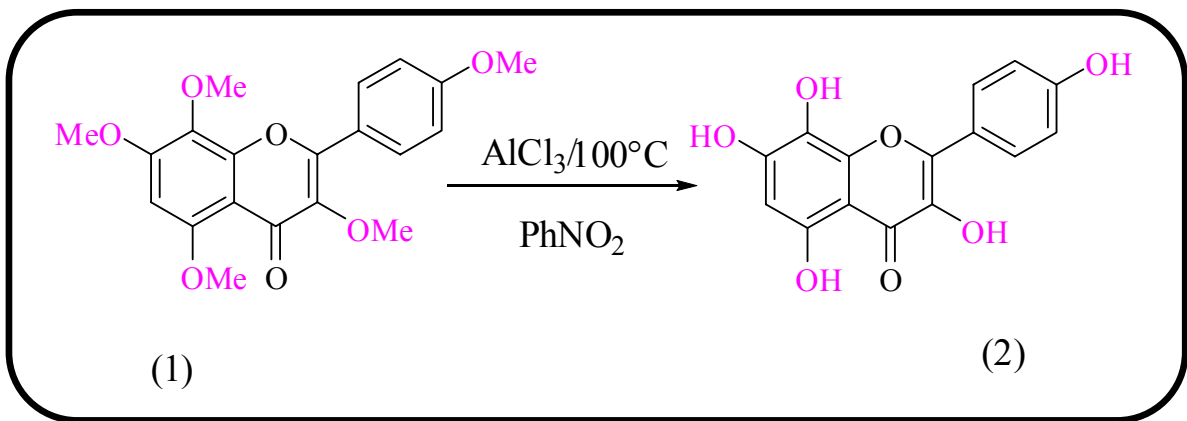
[2]

(2)

(1)

(10)

100°



-10-

5

5

[2]

)

(O-Glycoside

2

(C-Glycoside) C-C

3

7

2

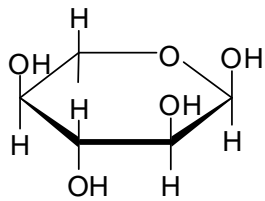
α -glycosides

(5)

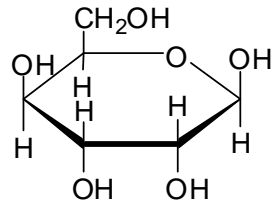
[15] β -glycosides

: -5-

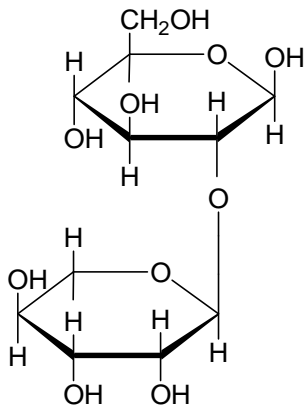
<i>O</i> - β -D-xylosyl(1 → 2)glucose	Sambubioside
<i>O</i> - α -L-rhamnosyl(1 → 2)glucose	Neohesperidoside
<i>O</i> - α -L-rhamnosyl(1 → 6)glucose	Rutinoside
<i>O</i> - α -D-rhamnosyl(1 → 2)glucose	Sophoroside
<i>O</i> - α -D-rhamnosyl(1 → 6)glucose	Gentioboside



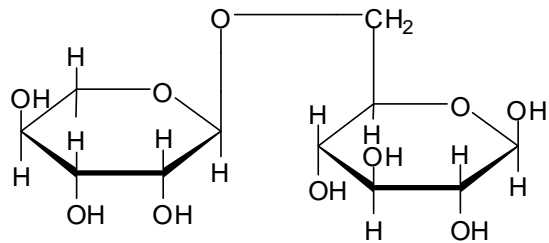
Rhamnose $C_6H_{12}O_5$ $M=164$



Glucose $C_6H_{12}O_6$ $M=180$



$C_{12}H_{22}O_{10}$



Rutinose $C_{12}H_{22}O_{10}$ $M=326$

: _____ -9

($C_6-C_3-C_6$)

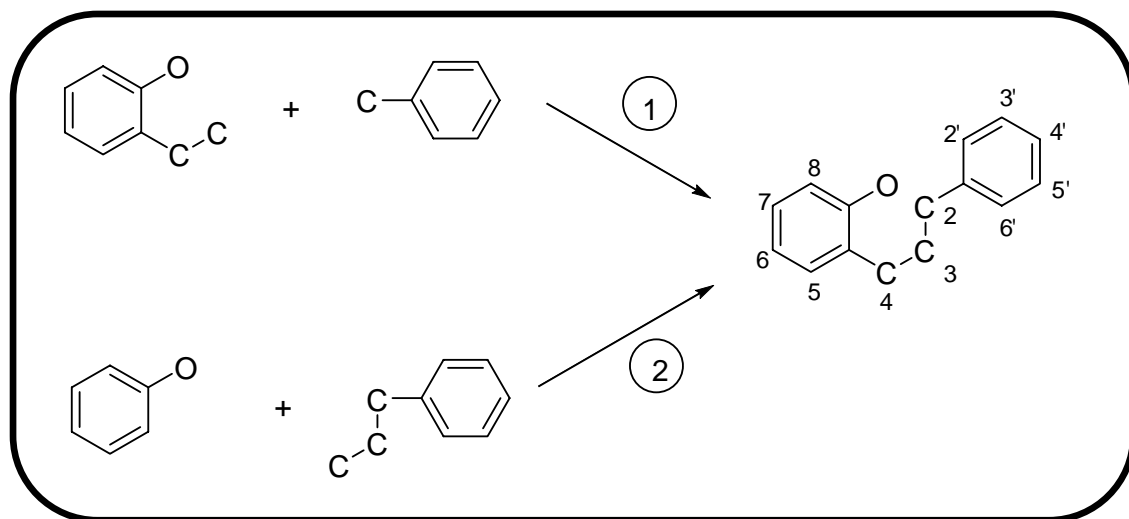
. [24]

(aldéhyde C_6-C_1 (2-hydroxy acétophénone) C_6-C_2 -1

. aromatique)

C_6-C_3 (phénol) C_6 -2

. (11) (dérivés de l'acide cinnamique ou leur équivalent)



C_3-C_6 C_6

C_6-C_1 C_6-C_2

:-11-

C_{15}

(hydrolyse)

(isomérisation)

.O-(alkyl ou sucre) C-(alkyl ou sucre)

● اصطناع الشالكون، الفلافونون و الفلافون:

dérivés de benzaldéhydes

ortho-hydroxyacétophénonnes

()

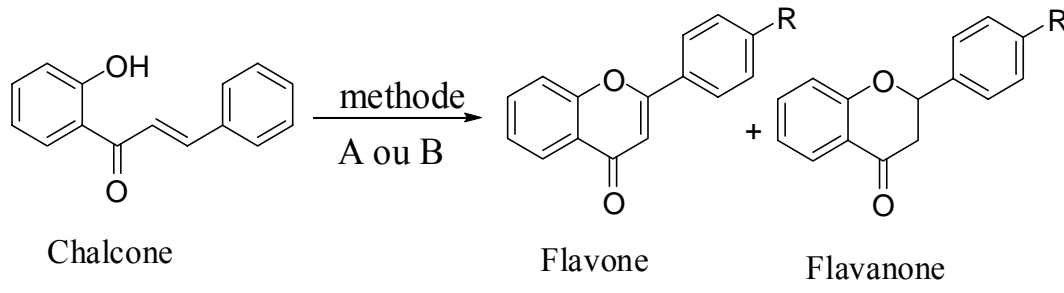
. (12)

B A

. [25]

(déhydrogénation)

. ()



Méthode A : PdCl₂, MeOH, Reflux 4 jours.

Méthode B : PdCl₂ (0.1% mol), 1,4-benzoquinone, MeOH, Reflux 4 jours

: -12-

: _____ -10

*

*

Phytoalexines:

[17]

(. 270-250)

*

[26]

()

[27]

(toniques veineux)

(perméabilité P)

[28]

: [4] *

- Inhibition de l'histidine décarboxylase.
- Inhibition de l'élastase.
- Inhibition de la hyluronicase .
- Inhibition non spécifique de la catéchol-O-méthyltransférase...

ATP ases :

[29] Kinase transférase

(piégeurs des radicaux libres)

[30] [28] : [4]

[35] (antivirale) [34 33] [32] [31] (antitumorale)

(marqueurs [36] (antispasmodiques)

. ...[39 38] [37] génétiques)

B A (OH)

C₂-C₃

:-6-

Thymonin	- diurétique	42
Criseliol	- digestive	43
Nepitrine	- anti-inflammatoire - anti-arthrique	44
8-glucosyle Hypolaetine	- anti-inflammatoire - anti-ulcère	45
Fisetine	- anti-inflammatoire	46
Nobilitine	- anti-allergique	47
Tangeritine		48
8-methoxy cirsilineol	- anti-spasmodique - stomachique	42 43
Cirsimaritine	- anti-purique	49
Baicaleine	- antiseptique ()	50
Eupatorine, eupatiline, jaceossidine		51 52
Hispiduline et 6-methoxy apigenine	- traitement des tumeurs	
Quercétine	- traitement du para influenza - anti-malaria () - anticancéreuse	54 55 62 63
3-glucosyl kaempferol	- crises hémorroïdaires	56
3-rutinosyl kaempferol	- troubles cardio-vasculaires	57
3-methyl quercétine	- anti-viral	58
Morine		59
3-methyl Kaempferol	- antipolivirus	60
3-rhamnosyl kaempferol 3-glucosyl kaempferol	- activité analgésique	61

_____ -11

_____ -1

[62 23 20] %50 20

/

(diethyl ether)

(AcOEt)

[63]

(n-BuOH)

_____ -2

(Cellulose)

(Silicagel)

:

(Polyamide, eg. Machry Nagel) SC₆

[64] (OH)

(CPP)

:

.(8 6) 70 5 •

.(18-16) B.A.W (/ /) 4 / 1 / 5 •

(CCM)

:

:

(DC6)

-

.(/ / /) 13 / 3 / 3 / 1 •

.(/ /) 4 / 3 / 3 •

.(/ /) 18 / 1 / 1 •

.(/ / /) 60 / 28 / 7 / 7 •

:

-

.(/ /) 5 / 3 / 1 4 / 2 / 1 •

.(/ /) 8 / 0.5 / 0.5 8 / 1 / 1 •

:

-

. 30 10 •

(DC6)

Séphadex LH 20

-3 _____ :

-1-3 :

: R_f

$R_f =$ _____

)

R_f

R_f

.(

[63]

-2-3 :

356-254

(7)

[24]

: -7-

	UV
. 8 7 5 5,6,7 . .3	.
.3 .5 OH .5 OH 3	.
.(5 OH) 3 OH	.
.	.
.	.
.	.
.5 OH	.

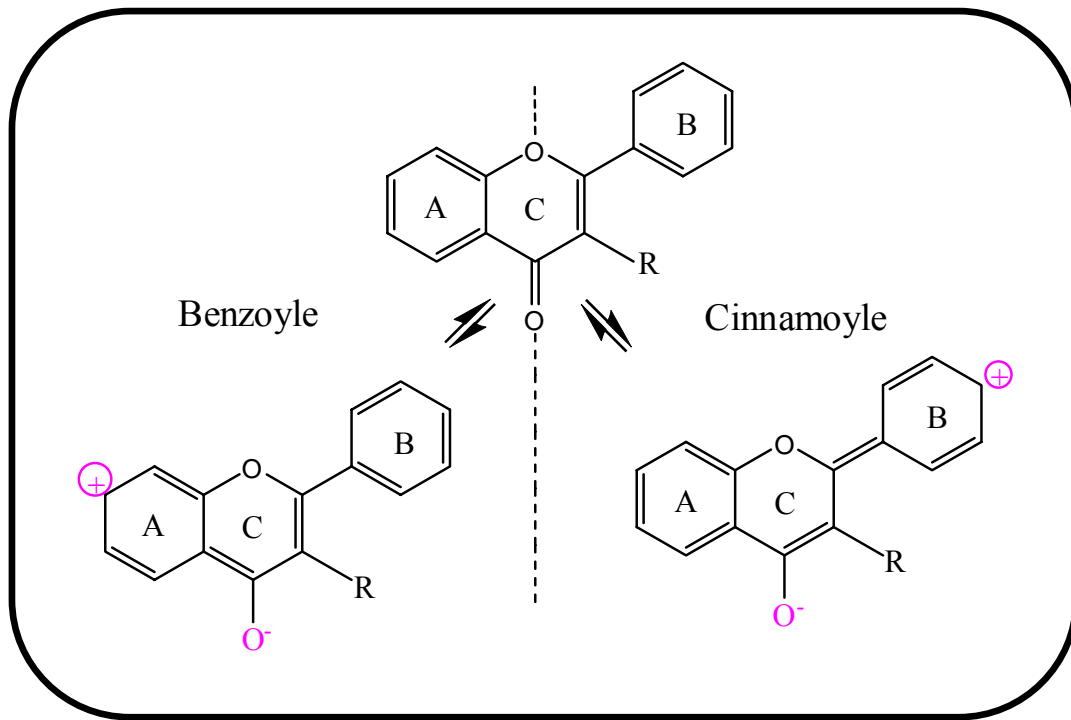
:(UV) -3-3

: -1-3-3

() C₄

.(13)

[64] II I



: -13-

- (300-400 nm) :I
- .B C₄ Cinnamoyl
- C B
- [65]
- (250-280 nm) :II
- .A Benzoyl
- [65] (8)

II I

: -8-

II	I	
280 250	350 320	
280 250	385 352	
275 245	330 300	
275 245	320 Epaulement	
280 270	470 460	

.()

. [65] ()

: -2-3-3

:(NaOMe) NaOH •

. I

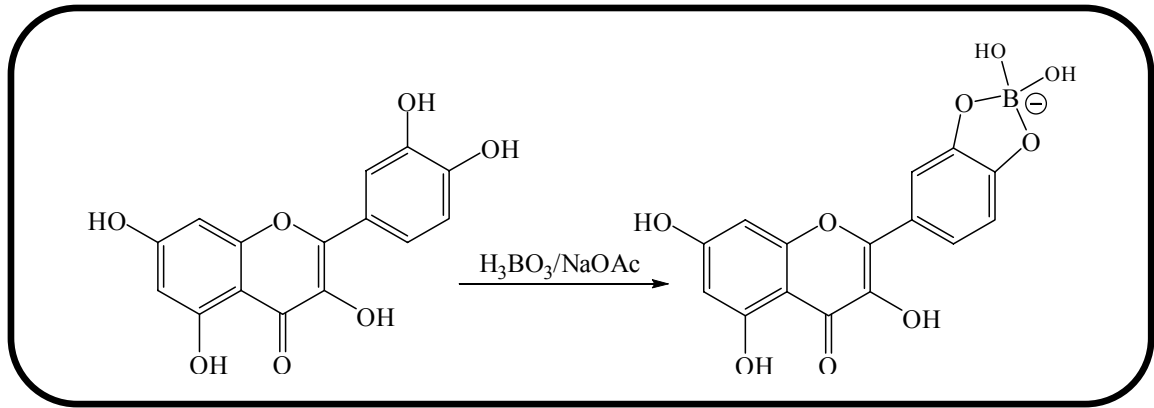
NaOH :NaOAc •

.C₇

NaOAc C₄' C₃ C₇

:NaOAc+H₃BO₃ •

.(14)



(NaOAc+H₃BO₃)

: -14-

• :AlCl₃+HCl AlCl₃

5 3

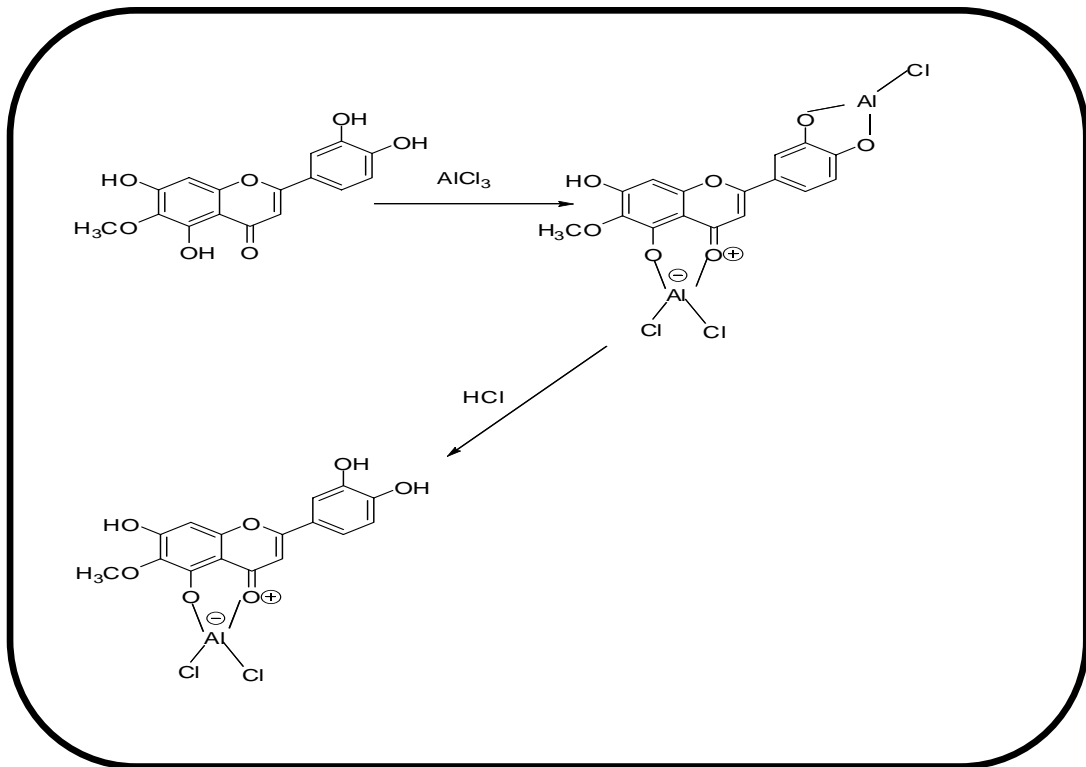
8 7 7 6

B

4' 3'

.(15)

A



HCl

AlCl₃

: -15-

I

(9)

. [66 63 4] II

[66 64 4]

: (9)

التعليق	(nm)		
	II	I	
	280 250	350 304	MeOH
	280 250	385 352	
3 OR	280 250	357 328	
4' OH		65+ 45+ -1	NaOMe (NaOH)
4' OR		MeOH/ -2	
Orthodi-OH 4' 3 OH 7 8 6 7 A B Orthodi-OH			
4' 3' 3 Tri OH 5' 4' 3' 3 Tetra OH			
7 OH		320 335	
7 OH	20+ 5+		NaOAc
8 6			
7 OR			

3' 4' 7 8 6 7 Di OH 5 7 8 5 6 7 Tri OH 3 3' 4'			
B Orthodi OH		36+ 12+	NaOAc + H ₃ BO ₃
A Orthodi OH (8-7 7-6)	+10 - 15		MeOH/ NaOAc + H ₃ BO ₃
6 5-OH		20+ 17+	MeOH/ AlCl ₃ +HCl
3 OCH ₃ 5 OH		55+ 35+	
5 OH 3 OH		60+ 50+	
B Orthodi OH		40- 20- [360 350]	AlCl ₃ / (AlCl ₃ +HCl)
Orthodi OH Orthodi OH A B Tri OH B		25- 20-	

: /

: (-)

: (+)

:RMN ¹H

-43

B C

A

CDCl₃ :DMSO-d₆

(0-9ppm)

[67 15]

(12 11 10:)

.[68 4] B A

A

:-10-

H-8	H-6	H-5	نوع الفلافونيد
$d(J=2,5 \text{ Hz})$ 6,3– 6,5 ppm	$d(J=2,5 \text{ Hz})$ 6,2 –6,0 ppm	-	5,7-OH
$d(J=2,5 \text{ Hz})$ 6,1–6,4 ppm	$d(J=2,5 \text{ Hz})$ 6,1 –5,9 ppm	-	5-OH,7-O Glc
6,3 ppm (S)	-	-	5,6,7-OR (R=H, Glc)
-	6,3 ppm (S)	-	5,7,8-OR (R=Glc,H)
$d(J=2,5 \text{ Hz})$ 6,7–7 ppm	$d,d(9 \text{ Hz}, 2,5 \text{ Hz})$ 7,1 –6,7 ppm	$d(J=9 \text{ Hz})$ 8,0 ppm	7-OR (R=H, Glc)

B

:-11-

H-6' , H2' $d(J= 8,5 \text{ Hz})$	H-5' , H3' $d(J= 8,5 \text{ Hz})$	
7,9 - 7,7 ppm	7,1 - 6,5 ppm	فلافون
8,1 - 7,9 ppm	7,1 - 6,5 ppm	

B

:-12-

H-6' $dd(J= 8,5; 2,5 \text{ Hz})$	H2' $d(J= 2,5 \text{ Hz})$	نوع الفلافونيد
7,5 - 7,3 ppm	7,3 - 7,2 ppm	Flavone - 3',4'- OH. - 3'- OMe, 4'- OH. - 3'-OH, 4'- OMe.
7,9 - 7,6 ppm	7,7 - 7,5 ppm	Flavonol - 3',4' OH. - 3'-OH, 4' OMe.

C₃

:C

(H-8 ,H-6) A

(6,2-6,4 ppm)

.[68]

.[68] 8-8,5 ppm

C₂

.[68] 3,8-4,5 ppm

:

:

H₁"

(13)

H₁"

:-13-

$\delta H_1''$ ppm	الفلافونيد
5,2 - 4,8	7-O-glucosyl flavonol
6,0 - 5,7	3-O-glucosyl flavonol

5,3 – 5,1	7-O-rhamnosyl flavonol
5,1 – 5,0	3-O-rhamnosyl flavonol

β α

H_1'' β H_2'' H_1''
 H_2'' (diaxial) $(J=7 \text{ Hz})$
 $(J=2 \text{ Hz})$ H_1'' α
 .(equatorial-equatorial)
 .[4] (0,8-1,2 ppm) $(J=6 \text{ Hz})$

Neohesperidose Rutinose

(4,2-4,4 ppm) (7,3-O-rutinosides) $H-1''$
 (0,7-1 ppm) $(J=2 \text{ Hz})$
 $(J=2 \text{ Hz})$ (4,9-5 ppm) (7,3-O-neohesperidosides) $H-1''$
 .[68] (1,1-1,3 ppm)

: _____ -5-3

.()

[69] (IE)

:

B A

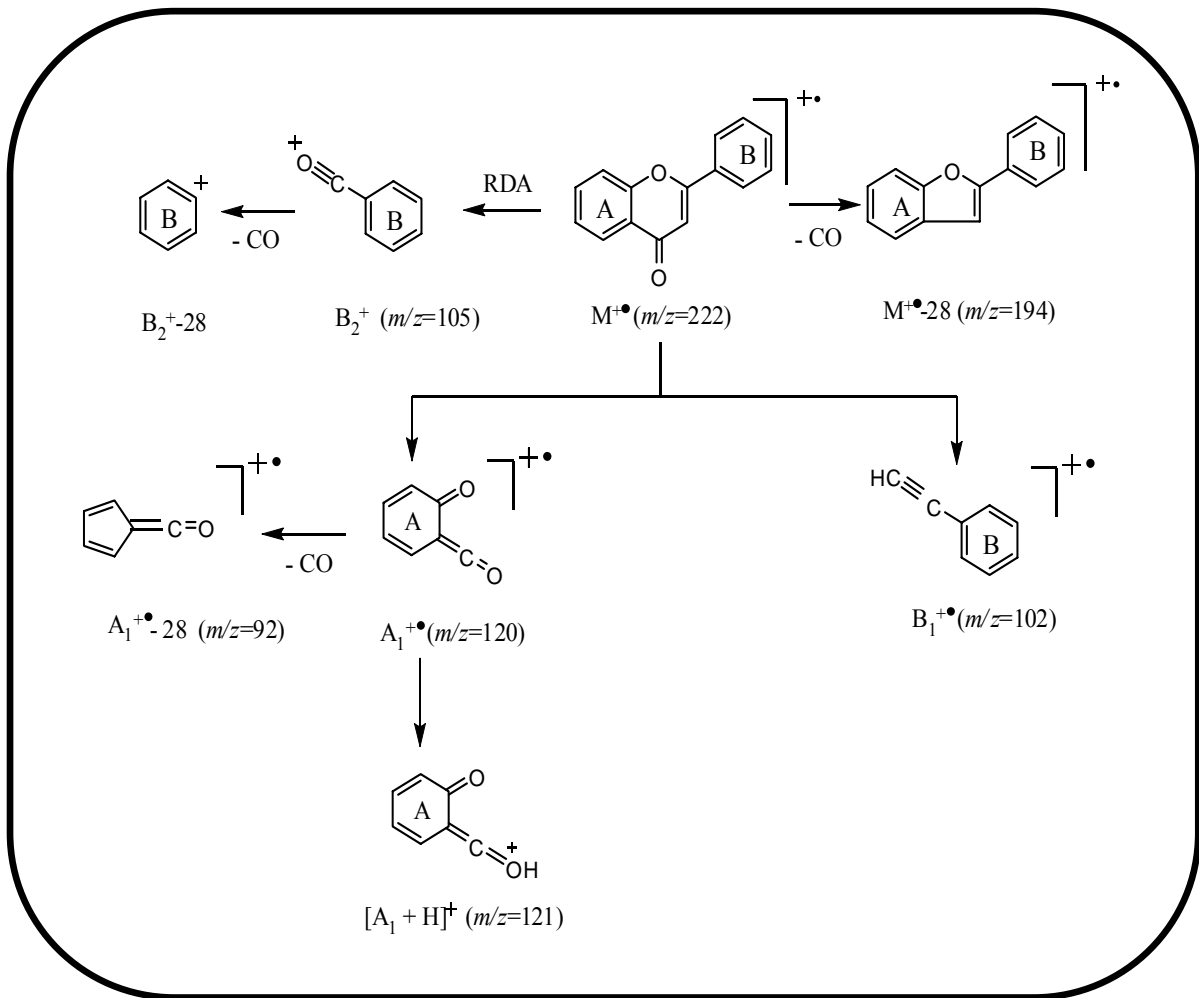
(17) (16)

Electro-spray

FAB

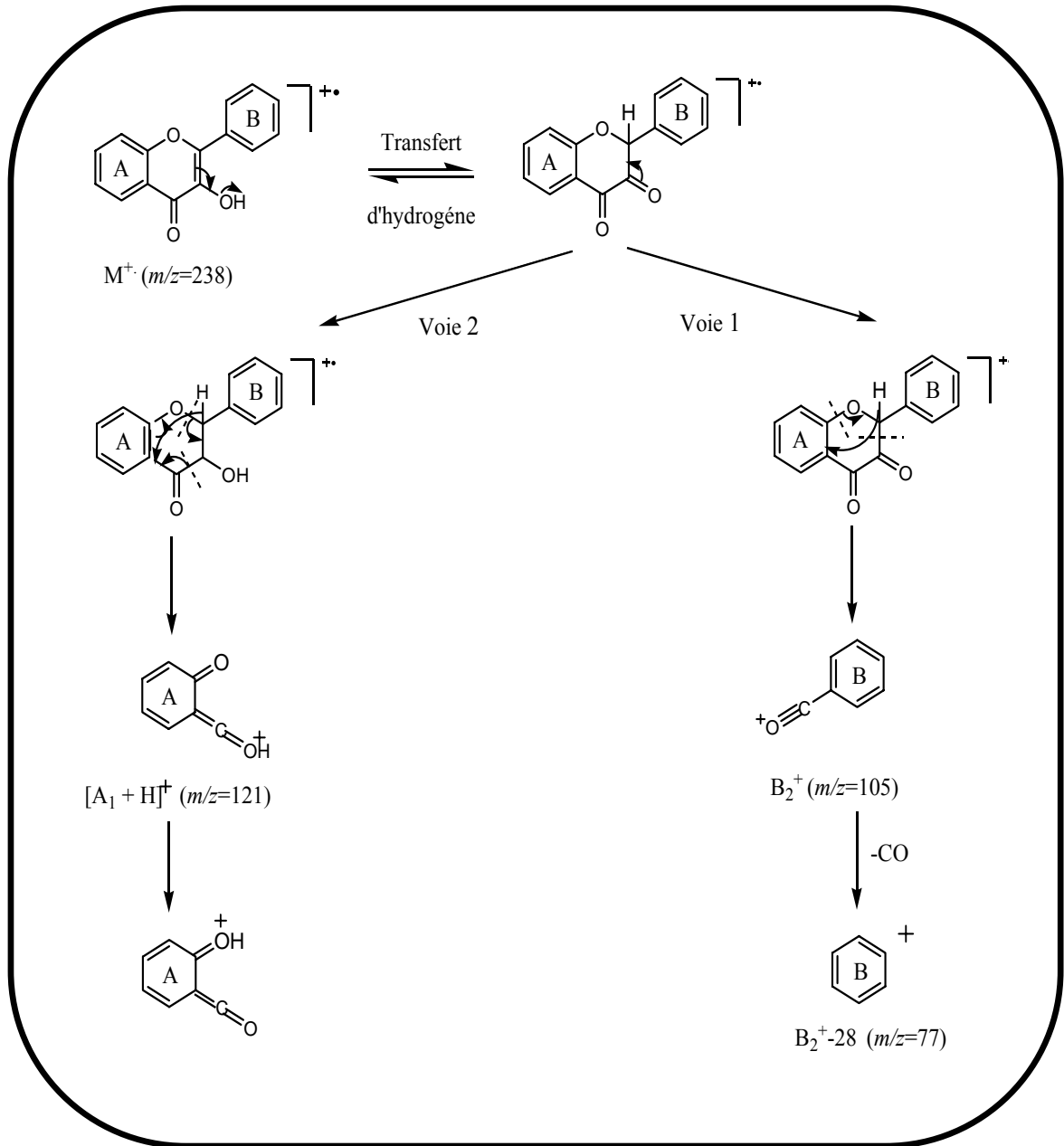
[71 70]

....(M-H)⁻ (M+H)⁺ (M+Ca)⁺ (M+Na)⁺



[69]

-16-



[69]

: -17-

: _____ -6-3

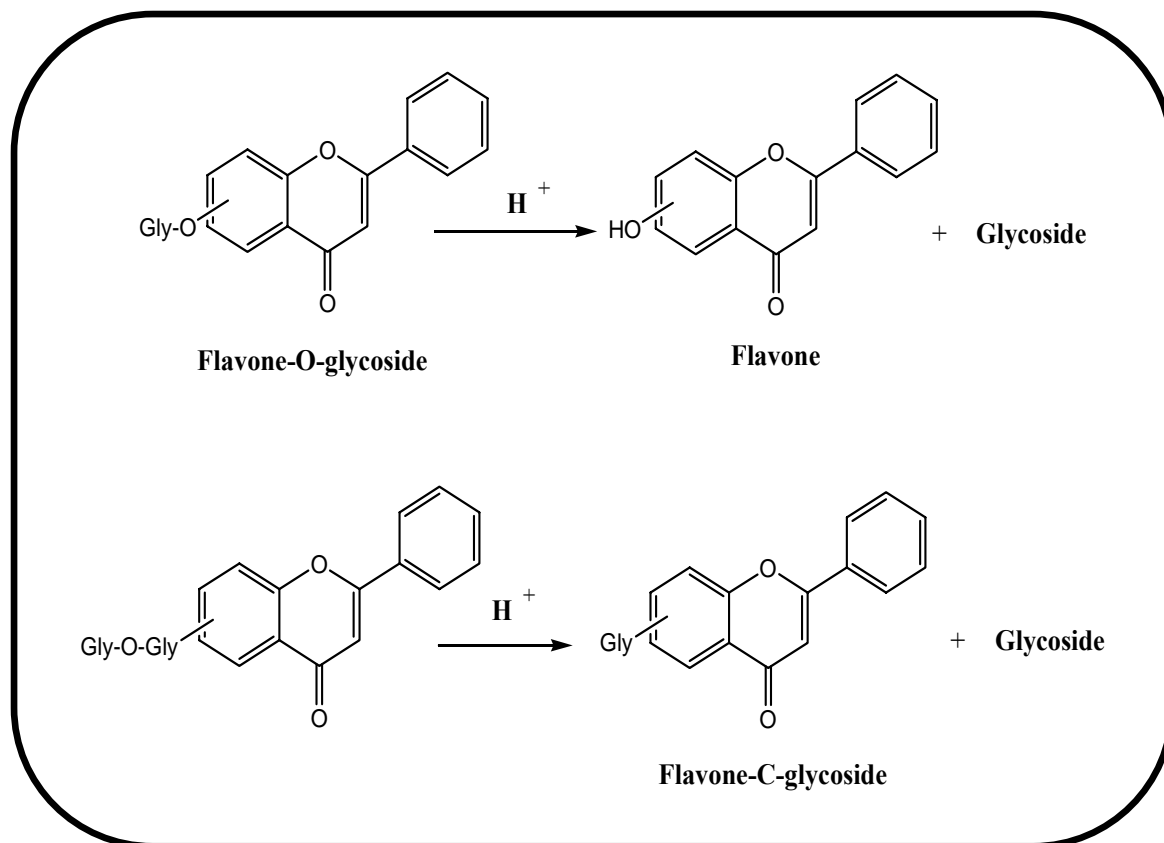
(C-O)

(18)

[72]

-C

-O



: -18 -

HCl (2N)

(1)

(1)

. 120 15 ° 100

Ether)

/

(éthylque

.(n-butanol)

(Acétate d'éthyle)

()
(CCM) (UV)

HCl

(0,2M) NaH₂PO₄ Gel de terre silicieuse Merck F₂₅₄

° 100

(10 / 90 : /) :

5 °100

[63] R_f (14) (UV)

R_f :-14-

	R _f
α(L) rhamnose	0,88
D(+)-xylose	0,79
L(+)-arabinose	0,66
β-D(+)-glucose	0,53
D(+)-galactose	0,33

المراجع

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الفصل الثالث

الجزء العملي

Pulicaria crispa

-I _____:

2004

Pulicaria crispa

. 1800

-II _____:

(80/20 : MeOH /H₂O)

36

4

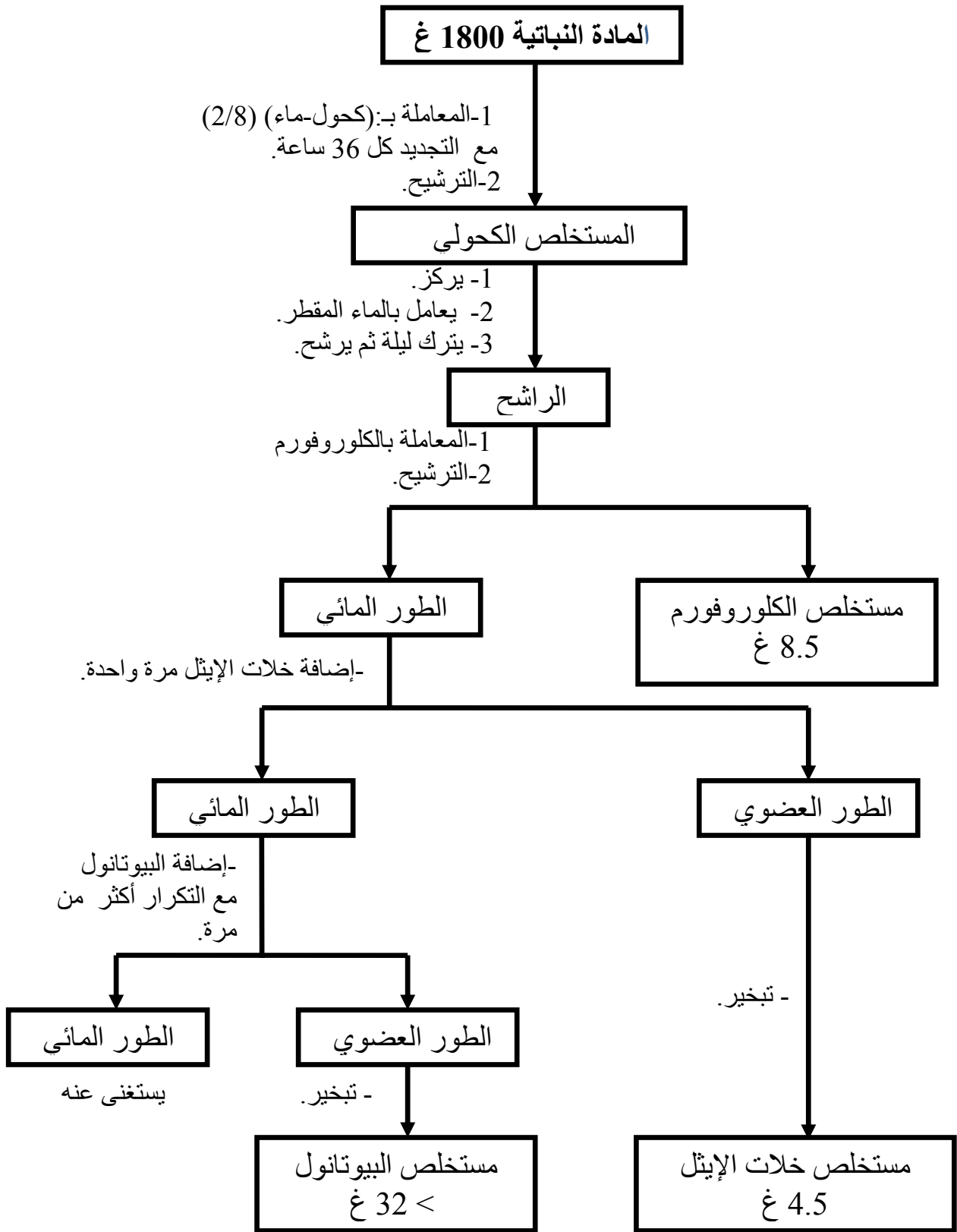
1.8

.()

3/1

()

.(1)



-1-

III- عمليات الفصل:

1- العمود الكروماتوغرافي:

-1-1 :

(2/3) (polyamide SC6)

30

-

-

UV

:(1)

-1-

نسبة الميثانول في المملص (%)	نسبة التولوين في المملص (%)	أرقام الكسور
0	100	5 – 1
2	98	10– 6
5	95	19–11
10	90	30 – 20
15	85	41 – 31
20	80	55 – 42
30	70	70 – 56
40	60	86 – 71
50	50	101 – 87
60	40	116 – 102
80	20	121 – 117
100	0	125–122

-2-1 :

:

(CCM)

❖

: DC6.6

3/3/4 : / / (S.I) -

1/3/3/13 : / / / (S.II) -

2/25/20/60 : / / / (S.III) -

: Whatman

(CP)

❖

. 30 : (AcOH) (S.IV) -

4/1/5 : B.A.W (S.V) -

. 15 : (AcOH) (S.VI) -

:(2)

:-2-

الكسور المحصل عليها من العمود	الكسور بعد الجمع
1	1
3-2	2
30-4	3
37-31	A
57-38	B
71-58	C
73-72	D
77-74	E
85-78	F
103-86	G
107-104	H
125-108	I

Pulicaria crisper

-3- B, C, D, E, F, G :

: -3-

الأوزان (غ)	الكسور المختارة
4.9009	B
0.257	C
0.2764	D
1.1229	F
0.8279	G
1.0341	E

:

G F (1) B :

30

(Whatman N°3)

C

D

H₂O/EtOH/BuOH/AcOH : 60/20/25/2

AcOEt /H₂O/AcOH : 8/0.5/0.5

:

(Whatman N°3)

B

B₄,B₃,B₂,B₁ :

30

B₄

B₄₁

H₂O /MeOH/MEC/Acétylacétone : 13/3/3/1

(cristaux)

C -

C₁, C₂....C₆

H₂O/EtOH/BuOH/AcOH : 60/20/25/2

C₃₂₄ C_P

D -

AcOEt /H₂O/AcOH : 8/0.5/0.5

D₂ D₅

D₁,D₂,....D₅

.D₄₂, D_{p1}, D_{p2} :

E -

. E_P

(Whatman N°3)

F

-

30

F₁, F₂...F₇

H₂O/EtOH/BuOH/AcOH : 60/20/25/2

. F₄₂₁, F_{4p}, F_P, F_{P2} :

:

G

-

30

(Whatman N°3)

H₂O/EtOH/BuOH/AcOH : 60/20/25/2

الفصل الرابع

النتائج و المناقشة

التعيين :

(250.13 MHz) RMN ¹H

.(CD₃OD)

R_f

-1-

DC6.6 { Toluène/MeCOEt/MeOH 4 : 3 : 3 (I) -
H₂O/MeCOEt/EtOH/(Ac)₂CH₂ 13:3:3:1 (II) -
AcOH : 15% (VI) -

(III) ، (II) ، (I) R_f :-1-

R _f × 100			
(III)	(II)	(I)	
13.63	20	17.77	F _{4P}
13.75	21.11	18.88	F ₄₂₁
13.63	20	18.33	E _P
14.77	19.44	18.88	F _{p2}
11.93	22.22	20.55	C _P
13.06	22.22	17.77	D _P
14.77	22.77	18.88	D ₆
14.77	21.11	16.66	D _{P1}

$$:E \equiv F_{421} \equiv F_{4P}$$

I-التعيين :

: F_{4P}

: _____ -1-I

. : *

.(2) : (R_f) *

-2-

R _f × 100	
17.77	I
20.00	II
13.63	III

: _____ -2-I

: _____ -1-2-I

(UV) -3-

I (ن.م)	II (ن.م)	
375	259	MeOH
DO ↗ 447	272	NaOH
الطيف غير مستقر		NaOH+5min
448	273	AlCl ₃
431	269	AlCl ₃ +HCl
383	260	NaOAc
392	264	NaOAc+H ₃ BO ₃

: _____ -2-2-I

RMN ¹H -4-

رقم الهيدروجين	التكامل	التعددية (J.Hz)	الإزاحة (δ.ppm)
H-5'	1H	8.52 <i>d</i>	6.91
H-2'	1H	2.12 <i>d</i>	7.8
H-6'	1H	8-2 <i>dd</i>	7.7
H-8	1H	<i>s</i>	6.92
O-CH ₃	3H	<i>s</i>	3.91
H-1''	1H	7.42 <i>d</i>	5.13
H-6''a	1H	12-2 <i>dd</i>	3.96
H-6''b	1H	12.2-5.9 <i>dd</i>	3.74
H-4'', H-3'' H-2'', H-5''	4H	<i>m</i>	3.46-3.65

: _____ -3-2-I

: _____ ✓

: أصفر -

: (UV) -

I (ن.م)	(ن.م)	II (ن.م)	
378	-	263	MeOH
444	335	276	NaOH

-3-I _____ :

.()

$\lambda_1=374 \text{ nm (MeOH)}$ I UV -

.3

$\Delta\lambda_1 (\text{NaOH / MeOH}) = +72 \text{ nm}$:

4' OH (DO)

.(3, 4'-di-OH) 4' 3 OH

7-OR 7 335-320 nm -

.NaOAc (+1nm) II

$\Delta\lambda_1 (\text{AlCl}_3+\text{HCl / MeOH}) = +56 \text{ nm}$:

.5 OH

$\Delta\lambda_1 (\text{AlCl}_3+\text{HCl / AlCl}_3) = -17 \text{ nm}$:

(3',4'-di-OH) B

. $\Delta\lambda_1 (\text{NaOAc}+\text{H}_3\text{BO}_3/\text{MeOH}) = +17 \text{ nm}$:

:

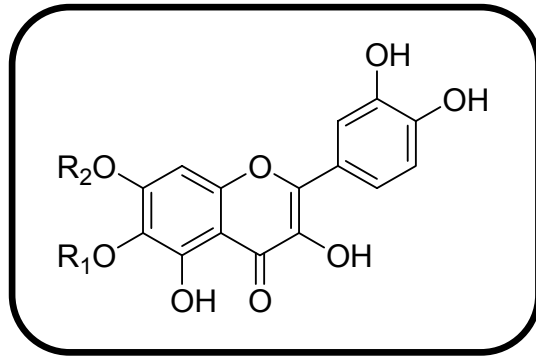
dd d :

*

. OH 4' 3' - - B *d*

) A -

8		6.92 ppm	(B	
				6
7-OR	7	3.91 ppm		-
.7	6	OMe		
		$\delta = 5.13 \text{ ppm} : d (J = 7.42 \text{ Hz})$		-
		C-O	-	
		(axial)	H-2''	
		($J = 12.1-2 \text{ Hz}$) 3.96 ppm	dd	
	H-6''b	H-6''a	($J = 12.1-2 \text{ Hz}$)	3.74 ppm
		3.56-3.64 ppm	إشارتين على شكل ثلاثي (t) بثابت تزاوج $J = 7 \text{ Hz}$	
		3.46 ppm	dd	بثابت تزاوج $J = 9-8.2 \text{ Hz}$ تلحق بالبروتونات
				H-4'' H-3''، H-2''
				أما البروتون H-5'' فظهر في المجال 3.55-3.65 ppm
	H-4''	H-3''		
	4''	(di-axial)	-	
				(axial)
				F_{4p} :



$R_1=Me$, $R_2= Sucre$

$R_2=Me$, $R_1= Sucre$

و للتأكد من الصيغة النهائية قمنا بإجراء الحلمهة الحمضية للمركب لمعرفة موضع ارتباط

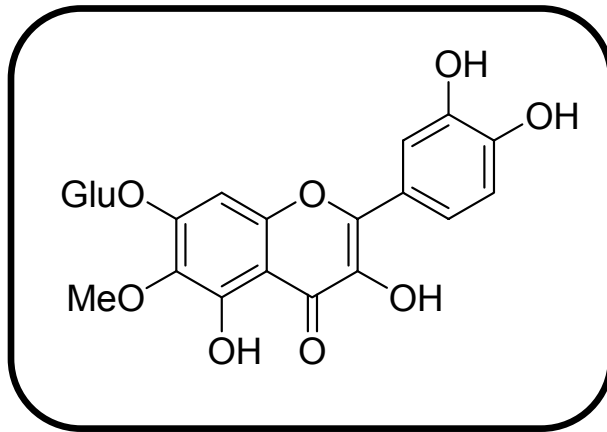
المستبدل السكري

335 nm

NaOH

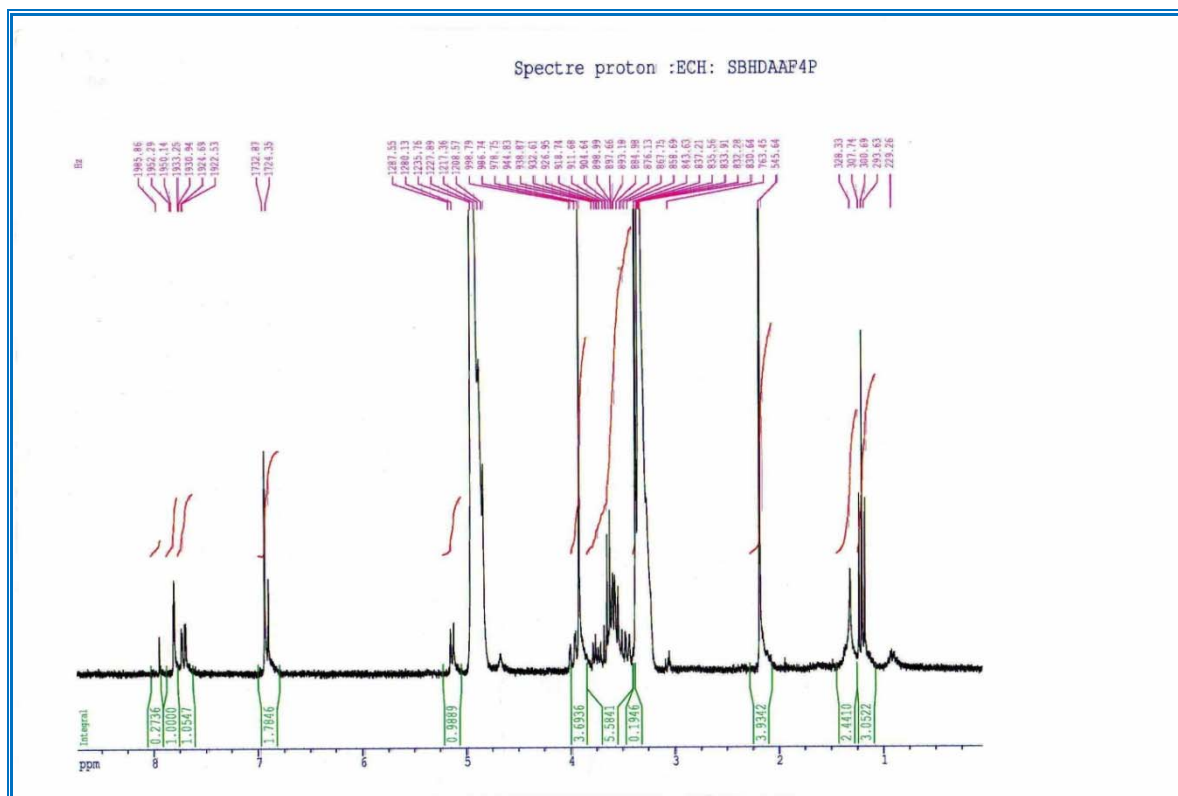
(7-OH) 7

: F_{4P}



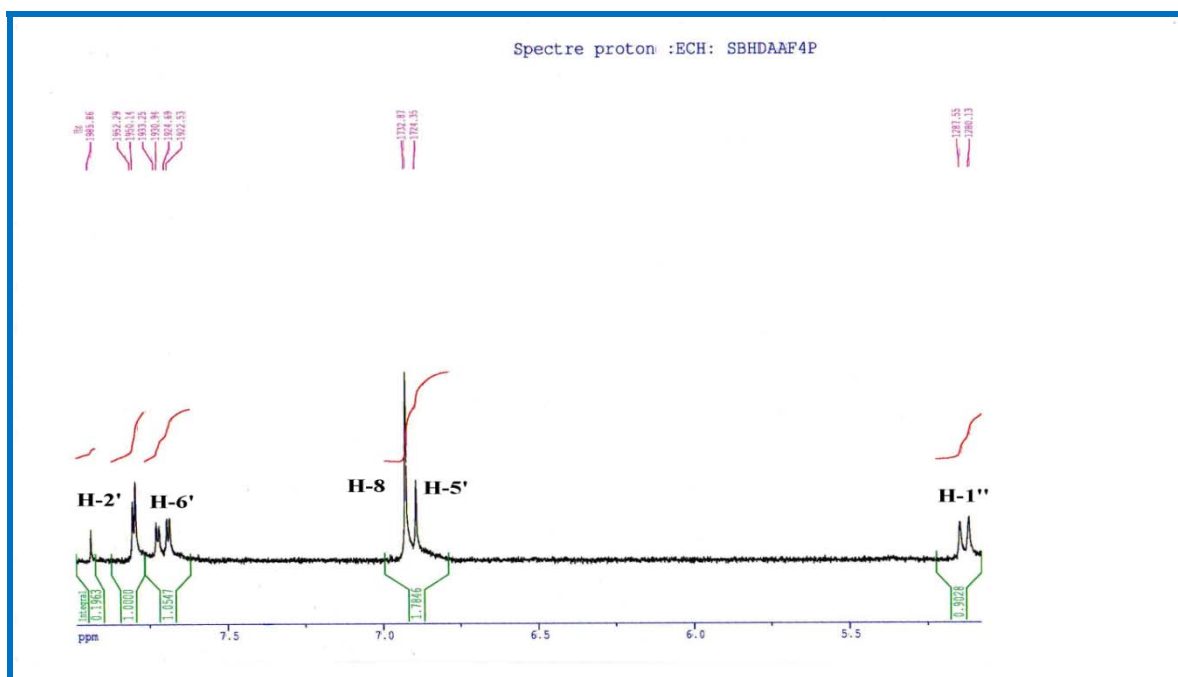
Patuletin 7-O-β-glucoside

الشكل (1) يبين طيف الرنين النووي المغناطيسي للبروتون للمركب F_{4P} والشكلين (2) و (3) توسيع للطيف في مختلف المجالات.



(CD₃OD) F₄P

: -1-

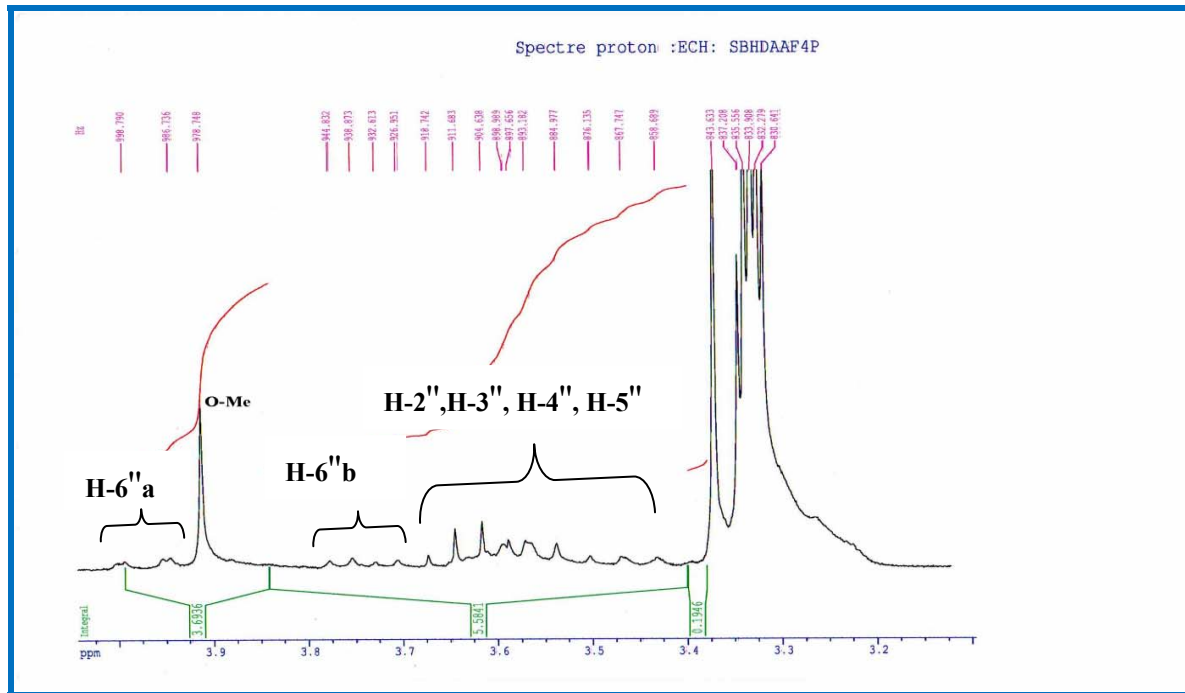


8-5 ppm

F₄P

RMN ¹H

: -2-



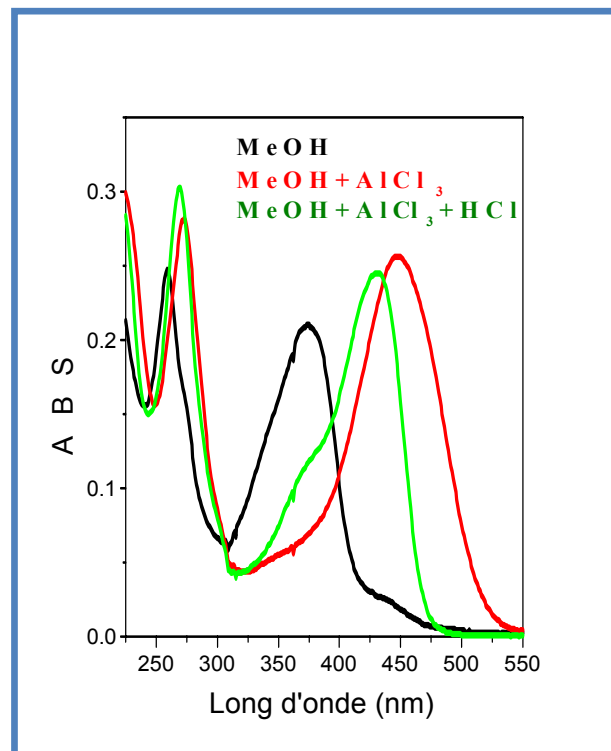
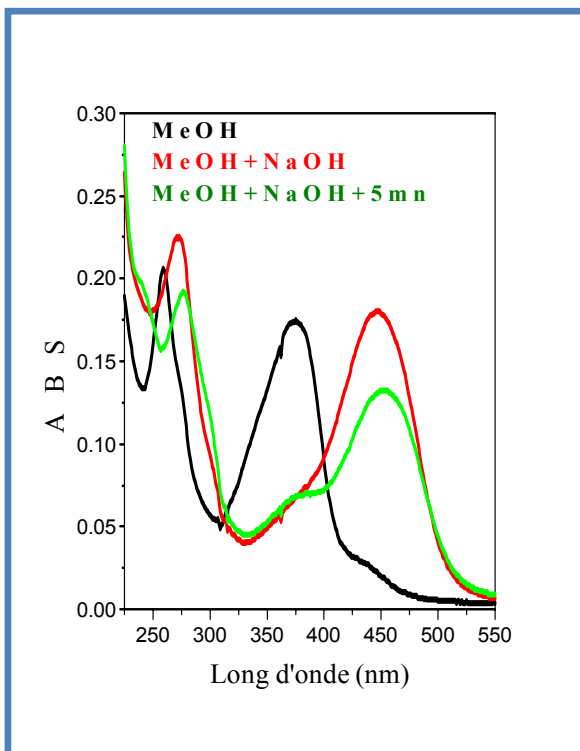
F_{4P}

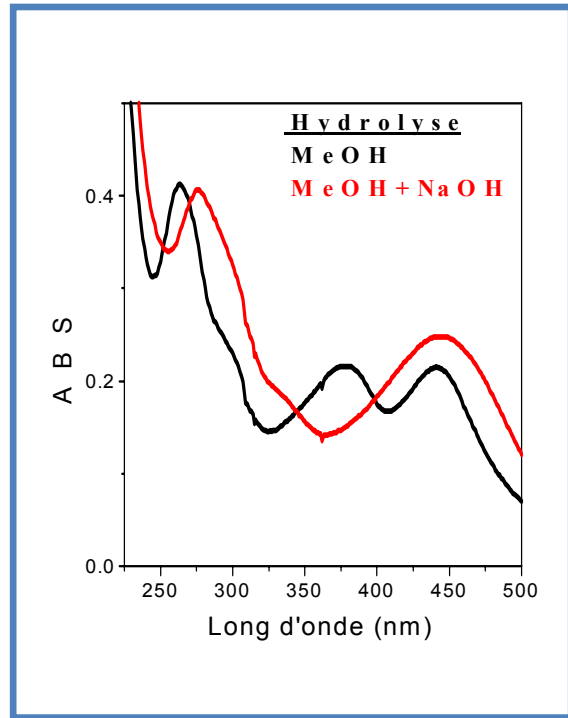
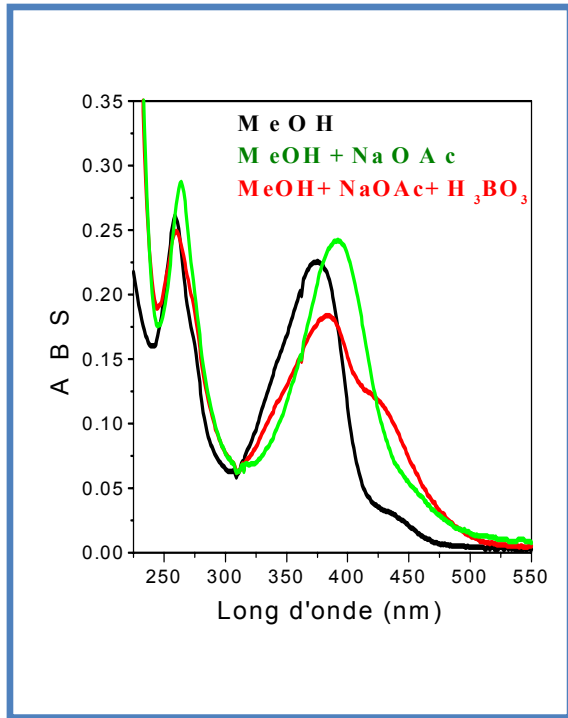
F_{4P}

RMN ¹H

: -2-

4-3 ppm





F_{4P}

(UV)

:-4-

$C_P \equiv D_P \equiv D_{P1} \equiv D_6 \equiv F_{P2}$

II- التعيين

:

C

II-1- _____ :

..... :

*

(5).

(R_f):

*

-5-

$R_f \times 100$	
20.55	I
22.22	II
11.93	III

:

II-2-

II-2-1- مطيافية الأشعة فوق البنفسجية :

-6- (UV)

I (ن.م)	II (ن.م)	
374	259	MeOH
437	265	NaOH
الطيف غير مستقر		NaOH+5min
442	270	AlCl ₃
431	270	AlCl ₃ +HCl
424-383	259	NaOAc

393	264	NaOAc+H ₃ BO ₃
-----	-----	--------------------------------------

II-2-2- مطيافية الرنين النووي المغناطيسي للبروتون :

*** الجدول -7- نتائج RMN(¹H) ***

رقم الهيدروجين	التكامل	التعددية (J.Hz)	الإزاحة (δ.ppm)
H5'	1H	8.52 <i>d</i>	6.91
H2'	1H	2.12 <i>d</i>	7.8
H6'	1H	8-2 <i>dd</i>	7.7
H8	1H	<i>s</i>	6.92
O-CH ₃	3H	<i>s</i>	3.91
H-1''	1H	7.34 <i>d</i>	5.13
H-6''a	1H	12.1-2.1 <i>dd</i>	3.96
H-6''b	1H	11.8-5.7 <i>dd</i>	3.74
H-4'', H-3''	2H	7 <i>t</i> 8 <i>t</i>	3.56-3.64
H-2''	1H	9-9 <i>t</i>	3.46
H-5''	1H	<i>m</i>	3.55-3.65

-3-2-II

:

: _____ ✓

: أصفر -

: (UV) -

(م.ن) I		(م.ن) II	
375	-	263	MeOH
438	330	280	NaOH

: -3-II

.()

$\lambda_I=374 \text{ nm (MeOH)}$ I UV -

.3 OH

$\Delta\lambda_I (\text{NaOH/MeOH}) = +63 \text{ nm}$:

4' OH (DO↓)

. A

7-OR 7 OH 335-320 nm -

.NaOAc II

OH $\Delta\lambda_I (\text{AlCl}_3+\text{HCl} / \text{MeOH}) = +57 \text{ nm}$:

.3 OH 5

$\Delta\lambda_I (\text{NaOAc}+\text{H}_3\text{BO}_3/\text{MeOH}) = +18 \text{ nm}$: -

ثنائي الهيدروكسيل على الحلقة.

:
d dd d : *
 4' 3' - - B ثنائية
 .4' OR
) A -
 6.92 ppm خاصة بالبروتون 8 (B
 6 A
 4' 7 3.91 ppm -
 .7-OMe 4'-OSucre 7-OSucre 4'-OMe : OR
 δ= 5.13 ppm : *d* (*J* = 7.34) -
 C-O -
 (axial) H-2''
 .(β-galactose β-glucose)
 (*J*= .12.1-2.1 Hz.) 3.97 ppm *dd*
 H-6''b H-6a'' (*J*=11.8 -5.7.Hz) 3.74 ppm
 3.56-3.64 ppm إشارتين على شكل ثلاثي (*t*) بثابت تزواج *J* = 7 Hz
 . H-4'' H-3'' *J* = 8

$J = 9. \text{ Hz}$ تعلق بالبروتون $H-2''$.

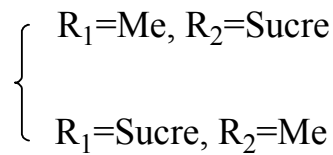
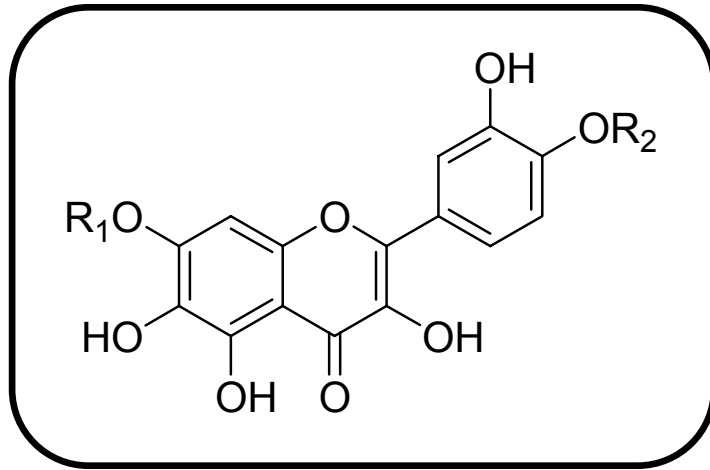
أما البروتون $H-5''$ فظهر في المجال 3.50-3.7 ppm.

$H-4''$ $H-3''$

$H-4''$ (axial-axial) -

(axial)

ومنه فصيغة المركب C_p تكون من الشكل :



وللتأكد من الصيغة النهائية قمنا بإجراء التحليل الحمضية للمركب لمعرفة نوع السكر وكذا

NaOH

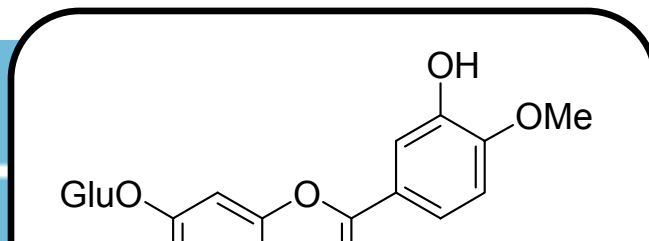
وضع ارتباطه

7

333 nm

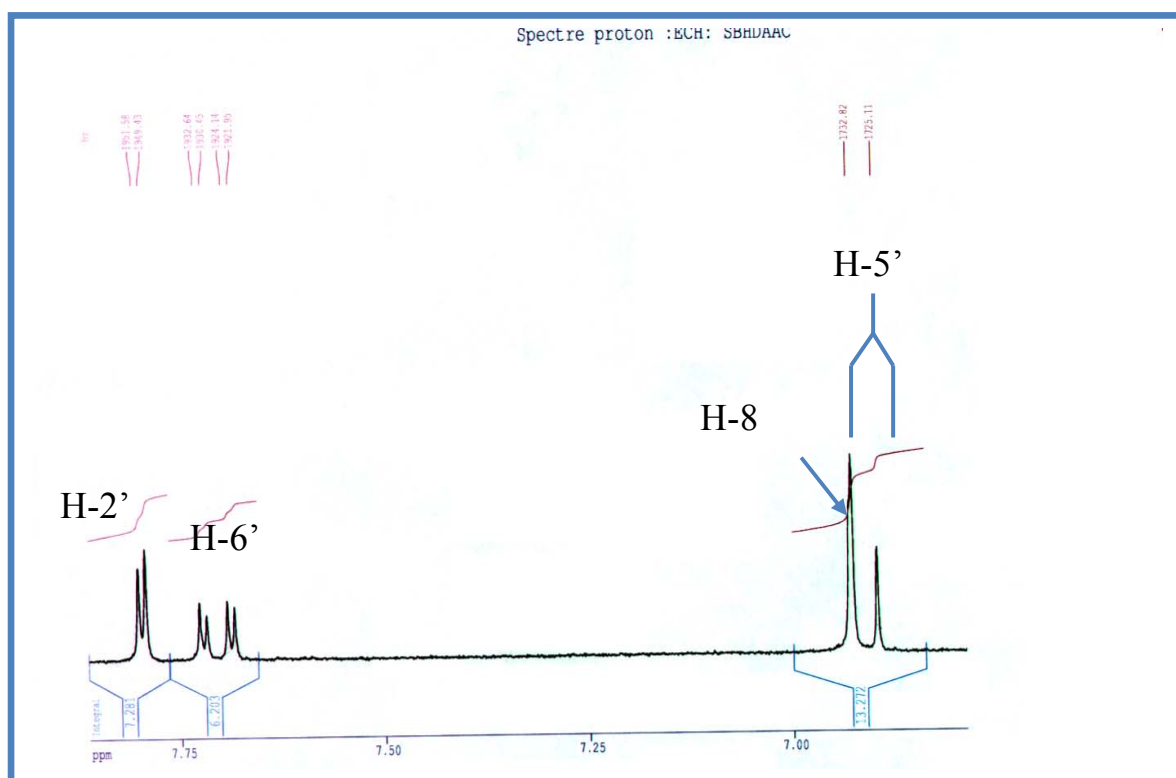
(7-OH)

: C



C_P

: (5)

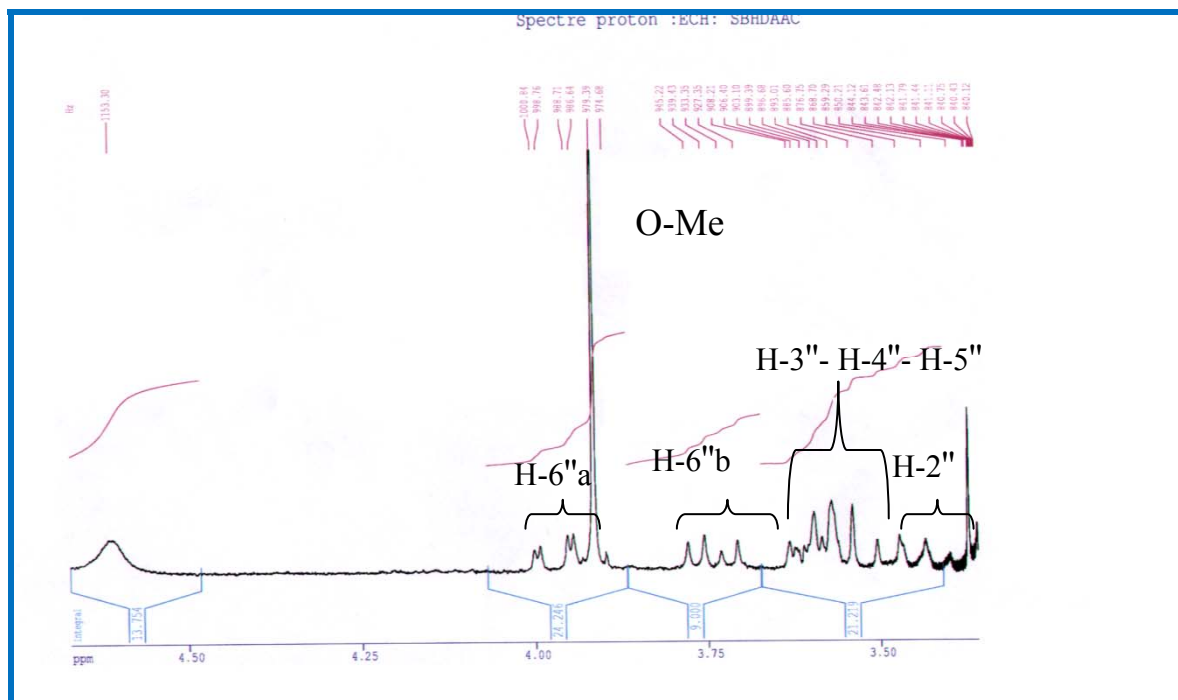


5-8 ppm

C_P

RMN ¹H

: (6)

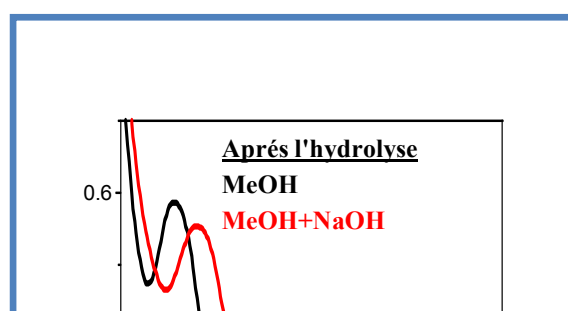
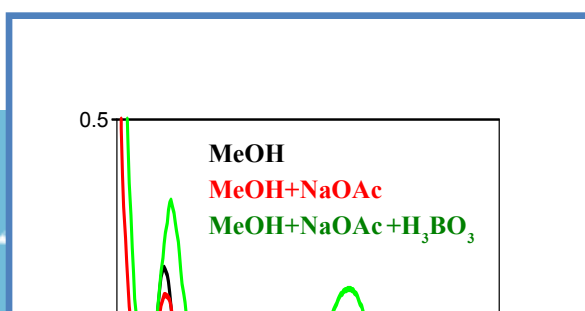
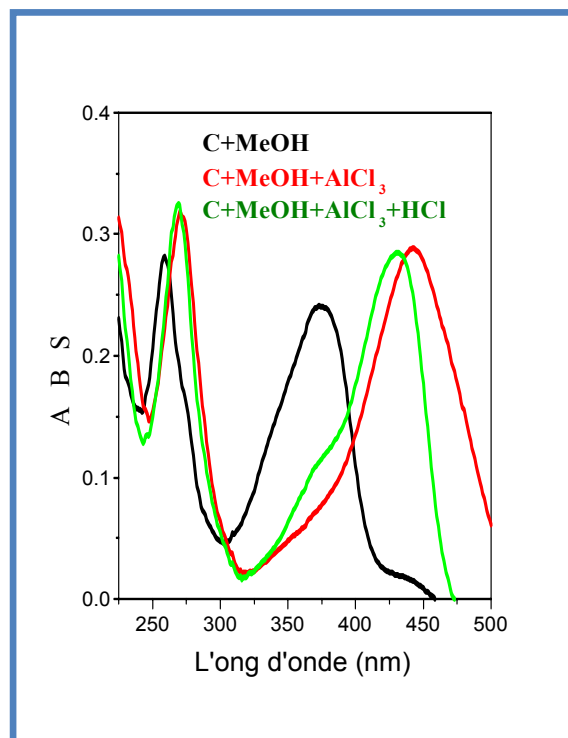
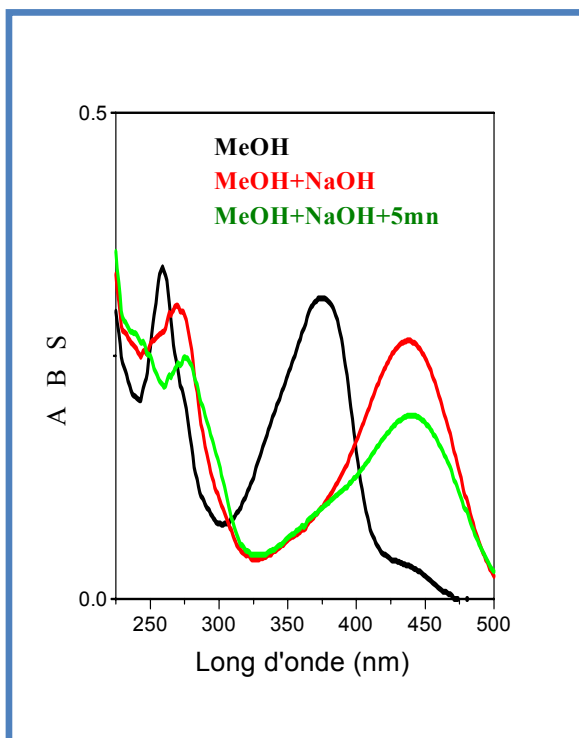


C_p

RMN ¹H

:(7)

1-4 ppm





C_p (UV) : (8)

-III

: *Pulicaria crispa*

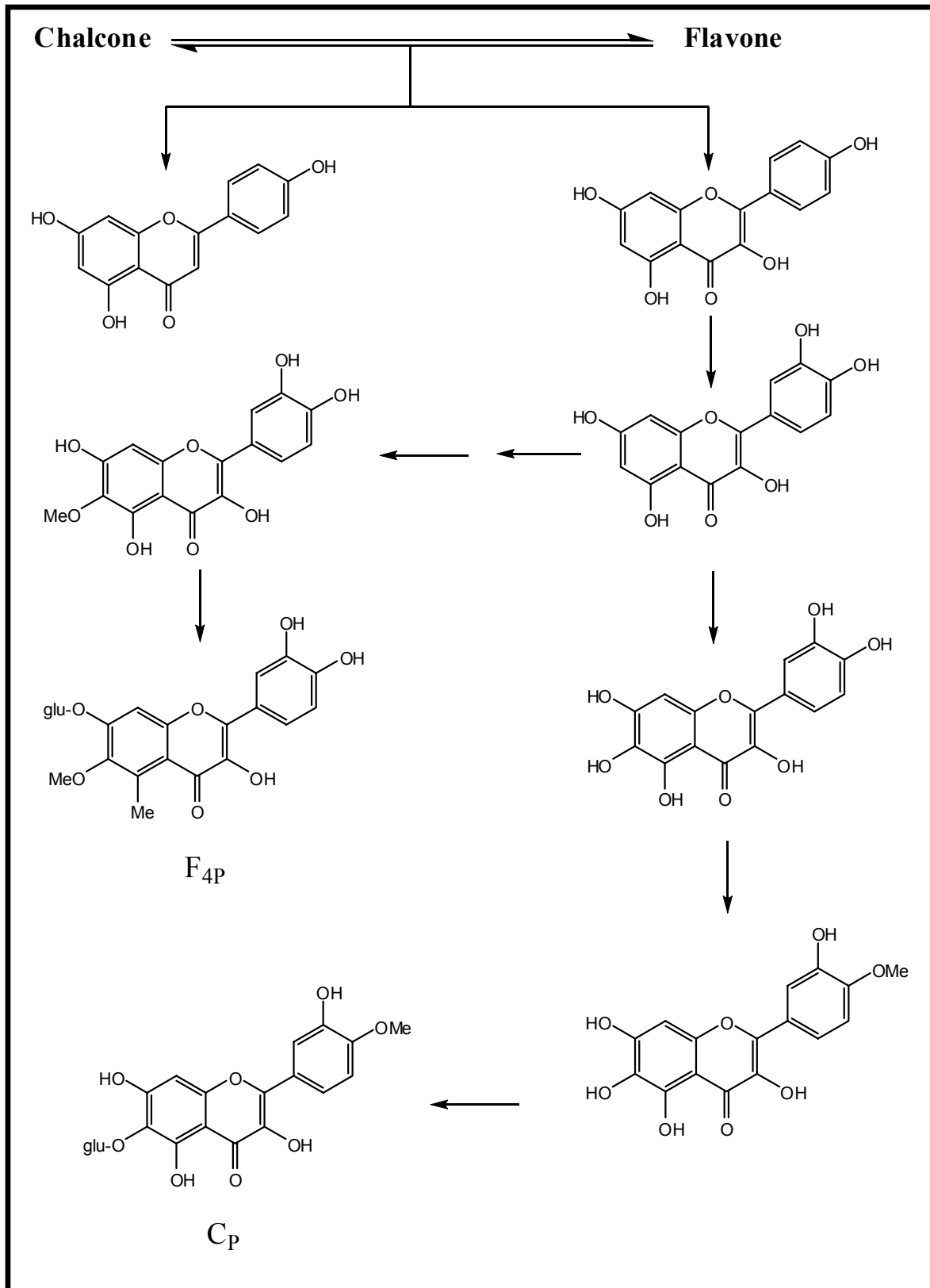
Pulicaria crispa

Quercetine

:(12)

** Patuletin 7-glucoside

** Quercetagetin 4'-methyl ether 7-glucoside



:-9-

Pulicaria crispa

الخاتمة

Pulicaria crisper (Forsk)

.RMN ¹H

UV

*Patuletin 7-O-β-D-glucoside

*Quercetagein 4'-methyl ether 7-O-β-D-glucoside

المخلص

Pulicaria crista (Forsk)

CC)

.(CCM

CP

RMN ¹H

UV

:

*Patuletin 7-*O*-β-D-glucoside

*Quercetagetin 4'-methyl ether 7-*O*-β-D-glucoside

Résumé

L'objectif principal de ce travail est d'identifier des métabolites secondaires (flavonoïdes) de la plante *Pulicaria crispa* (Forsk) appartenant à la famille des composées (Asteraceae).

L'utilisation des différentes méthodes de séparation chromatographiques (colonne, papier couche mince) a permis d'isoler deux composés flavonique, et grâce à l'hydrolyse acide et aux méthodes spectroscopiques usuelles (UV et RMN ¹H), les structures de ces flavonoïdes ont été établies comme suivant :

*Patuletin 7-*O*-β-D-glucoside

*Quercetagetin 4'-methyl ether 7-*O*-β-D-glucoside

Abstract

The principal aim of the present work consisted to identify the secondary metabolites (flavonoids) of *Pulicaria crispa* (Forsk) belonging to the compositae (Asteraceae) family.

The use of the different chromatographic methods (column, paper, thin layer) permitted the isolation of two flavonoids and with using acid hydrolysis and usual spectroscopic methods (UV, ¹H NMR), the structures of this compounds were established as:

*Patuletin 7-*O*-β-D-glucoside

*Quercetagetin 4'-methyl ether 7-*O*-β-D-glucoside