VARIATIONS IN THE CHEMICAL SHIFT OF BENZYLIC METHYLENE CARBON OF PRENYL GROUP ON HETEROCYCLIC PRENYLPHENOLS†

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Abstract —— ^{13}C Nmr examination of 377 kinds of heterocyclic prenyl(geranyl)phenols has shown that the chemical shift of the benzylic methylene signal of prenyl (geranyl) group (C1) was depended upon the substituents located at the adjacent positions. The prenyl (geranyl) groups could be classified into the six types and the chemical shifts of the C1 signal were observed in the restricted range specific to each type. The classification of the chemical shift of the C1 signal is useful for the structure determination of complex heterocyclic prenyl(geranyl)phenol. The chemical shifts of the C1 signals of these 377 heterocyclic prenyl(geranyl)phenols are listed up.

1. Introduction

A large number of isoprenoid-substituted phenols isolated from natural resources have been studied by many investigators with structural, biological, and pharmacological interests. In the course of our studies on the structures of isoprenoid-substituted phenols,[1,2] we noticed that the chemical shift of the carbon atom at the C-1 position (C1) of the 3-methyl-2-butenyl (prenyl) or (E)-3,7-dimethyl-2,6-octadienyl (geranyl) group was depended upon the substituents located at the adjacent positions.[3] To elucidate the observation, we examined the ^{13}C nmr spectra of about three hundred kinds of naturally occurring or synthetic prenyl(geranyl)phenols including about one hundred nonheterocyclic compounds, and reported that the prenyl (geranyl) groups could be classified into the six types according to the substituents located at the adjacent positions, and that the chemical shifts of the C1 signals were observed in the restricted range specific to each type (Type 1 – 6, Figure 1).[3] This classification of the chemical shift of the benzylic methylene signal (C1) of the prenyl (geranyl) group is useful

†This review is dedicated to the memory of the late Dr. Yoshio Ban, Professor Emeritus Hokkaido University.

for the structure determination of complex prenyl(geranyl)phenol. The structures of some naturally occurring heterocyclic prenylphenols were determined by the classification of the chemical shift of the C1 signal.[3–11] In this review, we describe the variations of the chemical shifts of one hundred seventy-eight kinds of natural occurring and synthetic heterocyclic prenylphenols with additional one hundred ninety-nine kinds of heterocyclic prenyl(geranyl)phenols reported since the previous paper.[3]

2. Classification of the prenyl (geranyl) group

The prenyl (geranyl) groups could be classified into the following six types and the chemical shifts of the C1 signals were observed in the restricted range as follows (Types 1–6, Figure 1).[3]

Type 1: When the di*ortho*-positions to the prenyl group were replaced by the oxygenated substituents, the chemical shift of the C1 signal was observed in the range of δ 20.7 – 24.0.

Type 2: In the ^{13}C nmr spectrum of 3-prenylated flavone, the chemical shift of the C1 signal of the prenyl group was observed in the range of δ 23.5 – 24.9.

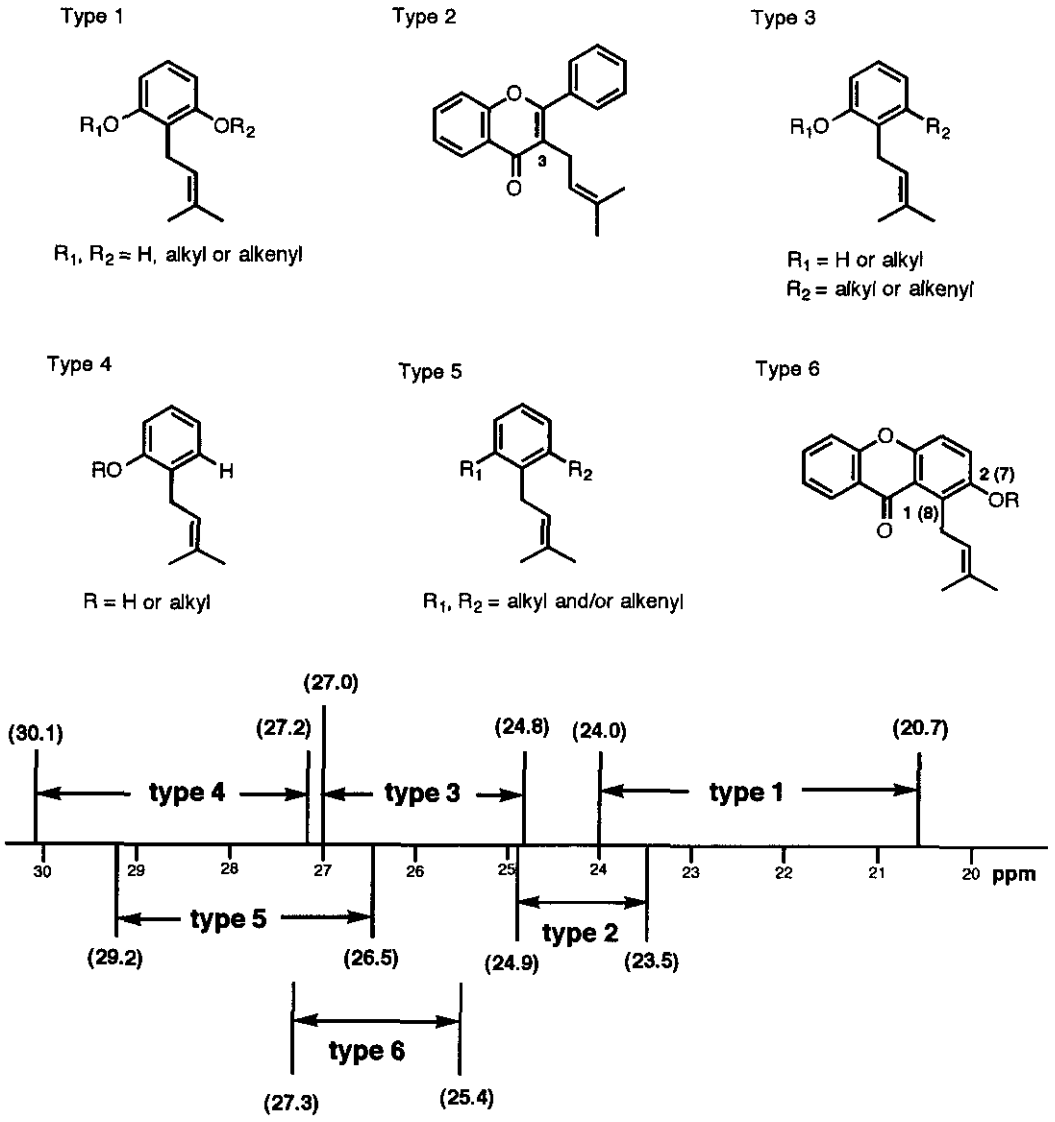
Type 3: When one of the *ortho*-positions to the prenyl group was replaced by an alkyl or alkenyl group, and another by an oxygenated substituent, the chemical shift of the C1 signal was observed in the range of δ 24.8 – 27.0.

Type 4: When one of the *ortho*-positions to the prenyl group was replaced by an oxygenated substituent and another was unsubstituted, the chemical shift of the C1 signal was observed in the range of δ 27.2 – 30.1.

Type 5: When di*ortho*-positions to the prenyl group were replaced by alkyl and/or alkenyl groups, the chemical shift of the C1 signal of the prenyl group was observed in the range of δ 26.5 – 29.2.

Type 6: In the ^{13}C nmr spectrum of 2-oxygenated 1-prenylxanthone (7-oxygenated 8-prenylxanthone), the chemical shift of the C1 signal was observed in the range of δ 25.4 – 27.3.

From the above results, the each group was distinguished by the chemical shift of the C1 signal of the prenyl group except between Type 4 and Type 5 (Figure 1). The group of Type 4, however, is distinguishable from Type 5 by the presence of long-range coupling between the methylene carbon and the adjacent aromatic proton to the prenyl group (^3J = 4 Hz). Furthermore, in the classification between the same skeletal compounds (flavone, flavanone, xanthone, etc.), the methylene signal of each group appeared at more narrow region. In the following sections, we will describe the details of the variations of the chemical shifts of benzylic methylene carbons of prenyl (geranyl) groups between the same skeletal compounds.



Figrure 1 Variations in the chemical shift of benzylic methylene carbon of prenyl (geranyl) group

3. *Flavones, flavonols, isoflavones, chromones, and aurones*

The chemical shifts of the C1 signals of prenyl (geranyl) groups of flavones, flavonols, isoflavones, chromones, and aurones were listed up in Table 1 and summarized as follows.

Type 1: The chemical shifts of the C1 signals of Type 1 prenyl groups located at the C-6 or C-8 position in the A ring were observed in the range of δ 21.6 – 22.6 (acetone-d_6), δ 21.2 – 22.7 ($CDCl_3$), and δ 20.8 - 21.9 (DMSO-d_6), while the C1 signals of the prenyl groups in the B ring were observed in the range of δ 23.2 – 23.8 (acetone-d_6) and δ 22.2 – 22.6 (DMSO-d_6).

Type 2: The chemical shifts of the C1 signals of the prenyl groups at the C-3 position of flavone skeleton were observed in the range of δ 24.4 – 24.7 (acetone-d_6), δ 24.1 – 24.4 ($CDCl_3$), and δ 23.4 – 24.1 (DMSO-d_6).

Type 3: The chemical shifts of the C1 signals were observed in the range of δ 25.8 – 27.3 (acetone-d_6), δ 25.8 – 26.2 ($CDCl_3$), and δ 25.2 (DMSO-d_6).

Type 4: The chemical shifts of the C1 signals were observed in the range of δ 28.6 – 29.5 (acetone-d_6), δ 28.9 – 29.2 ($CDCl_3$), and δ 27.4 – 28.2 (DMSO-d_6).

Type 5: The chemical shifts of the C1 signals were observed in the range of δ 28.0 – 29.2 ($CDCl_3$) and δ 27.3 – 28.4 (DMSO-d_6).

As described in section 2, the prenyl group of Type 4 could not be distinguished from the group of Type 5 by the chemical shifts. The group of Type 4, however, could be distinguished from that of Type 5 by nondecoupling spectrum because the long-range coupling between the methylene carbon and an aromatic proton was observed in Type 4 (observed as triplet of triplet or double doublet of triplet signal), or by observation of NOE between the methine and/or methylene protons of the prenyl group and the aromatic proton.

The C1 signal of the prenyl group in $CDCl_3$ solution showed upfield shift (+ 0.5 ppm) compared with in the acetone-d_6 solution (**81** and **84**), while the C1 signal showed in DMSO-d_6 (**6**, **9**, **17**, **37**, **39**, and **76**) solution showed upfield shift (+ 0.4 – 1.4 ppm).

Pumilaisoflavone C (**92**) isolated from *Tephrosia pumila* has been assigned as 3',5'-dimethoxy-6,2'-diprenyl-5,7,4'-trihydroxyisoflavone.[12] The chemical shifts of the C1 signals of the compound have been reported as δ 21.4 and δ 23.4 in $CDCl_3$. From the classification of the chemical shift, these groups were Type 1 (di*ortho*-oxygen functions) but not Type 3 (carbon and oxygen functions, 2'-prenyl). Considering the ^1H and ^{13}C nmr data described in the literature,[12,13] the compound seems to be 2',5'-dimethoxy-6,3'-diprenyl-5,7,4'-trihydroxy-isoflavone. The more detailed reinvestigation should be carried out to confirm the structure.

4. Flavanones, 3-hydroxyflavanones (dihydroflavonols), and isoflavanones

The chemical shifts of the C1 signals of prenyl (geranyl) groups of flavanones, 3-hydroxyflavanones (dihydroflavonols), and isoflavanones were listed up in Table 2 and summarized as follows.

Type 1: The chemical shifts of the C1 signals of Type 1 prenyl groups, which located at the C-6 or C-8 position in the A ring, were observed in the range of δ 21.4 – 22.8 (acetone-d_6), δ 20.8 – 22.8 ($CDCl_3$), and δ 20.5 - 22.3 (DMSO-d_6), while the chemical shifts of C1 signals of the prenyl groups in the B ring were observed in the range of δ 23.3 – 24.6 (acetone-d_6) and δ 23.0 – 23.3 (DMSO-d_6). When the di*ortho*-positions to the geranyl groups were replaced by the acetoxyl group (Type 1'), the C1 signals of the geranyl groups were observed at δ

23.1 ($CDCl_3$) [bonannione A triacetate (**168**, 6-geranyl-5,7,4'-triacetoxyflavanone) and bonanniol A tetraacetate (**215**, 6-geranyl-3,5,7,4'-tetraacetoxydihydroflavonol)]. In 5-unsubstituted 7-hydroxyflavanone, the C1 signal of the prenyl group located at the C-8 position was observed at δ 23.3 ($CDCl_3$, Type 1") [euchrenone a_8 (**189**, 7,2'-dihydroxy-8-prenyl-4'-methoxyflavanone)].

Type 3: The chemical shifts of the C1 signals of Type 3 prenyl groups were observed in the range of δ 24.9 – 25.6 (acetone-d_6).

Type 4: The chemical shifts of the C1 signals of Type 4 prenyl groups were observed in the range of δ 27.6 – 29.1 (acetone-d_6), δ 27.6 – 29.8 ($CDCl_3$), and δ 26.9 – 29.1 (DMSO-d_6).

5. Flavans, isoflavans, and pterocarpans

The chemical shifts of the C1 signals of prenyl (geranyl) groups of flavans, isoflavans, and pterocarpans were listed up in Table 3 and summarized as follows.

Type 1: The chemical shifts of the C1 signals of Type 1 prenyl groups of 3-hydroxyflavan (catechin) derivatives were observed in the range of δ 22.6 – 22.8 (acetone-d_6) and δ 22.0 – 22.7 ($CDCl_3$). The C1 signals of prenyl groups of isoflavans as well as pterocarpans were observed in the range of δ 23. 1– 23.6 (acetone-d_6) and δ 22.5 – 23.2 ($CDCl_3$).

Type 3: The chemical shifts of the C1 signals of Type 3 prenyl groups of flavans were observed in the range of δ 25.1 – 25.6 ($CDCl_3$).

Type 4: The chemical shifts of the C1 signals of Type 4 prenyl groups were observed in the range of δ 28.7 – 28.8 (acetone-d_6) and δ 28.6 – 29.3 ($CDCl_3$).

6. Xanthones

The chemical shifts of the C1 signals of prenyl (geranyl) groups of xanthones were listed up in Table 4 and summarized as follows.

Type 1: The chemical shifts of the C1 signals of prenyl (geranyl) groups located at the C-2 or the C-4 position of the 1,3-dioxygenated xanthones were observed in the range of δ 21.6 – 22.8 (acetone-d_6), δ 21.2 – 23.3 ($CDCl_3$), and δ 20.7 – 21.2 (DMSO-d_6). The C1 signals of the prenyl groups located at the C-5 position of 8-unhydroxylated xanthones were observed in the range of δ 23.0 – 23.1 (acetone-d_6).

Type 4: The C1 signals of Type 4 prenyl groups were observed in the range of δ 28.8 – 29.0 (acetone-d_6), δ 27.4 – 28.2 ($CDCl_3$), and δ 28.3 – 28.6 (DMSO-d_6).

Type 6: The C1 signals of prenyl (geranyl) groups located at the C-8 position of 7-hydroxyxanthones (the C-1

position of 2-hydroxyxanthone) were observed in the range of δ 26.0 – 27.3 (acetone-d_6), δ 25.6 – 26.8 ($CDCl_3$), and δ 25.3 – 25.8 (DMSO-d_6). The group may be implicit in Type 3.

The C1 signals of prenyl groups located at the C-8 positions of 7-unhydroxylated xanthones were observed at δ 29.3 [subelliptenone A (**333**, 2-(1,1-dimethylallyl)-7,8-diprenyl-1,4,5,6-tetrahydroxyxanthone)] and at δ 34.2 [caloxanthone B (**345**, 1,6-dihydroxy-8-prenyl-(4',5'-dihydro-4',4',5'-trimethylfurano(2',3':3,4)xanthone)]. The prenyl group of the former compound could be classified into Type 5, while that of the later (*ortho*-carbon function and *ortho*-unsubstituted) could not be classified into any group.

7. 2-Arylbenzofurans, coumaronochromones, 3-arylcoumarins, coumestans, and coumarins

The chemical shifts of the C1 signals of prenyl (geranyl) groups of 2-arylbenzofurans, coumaronochromones, 3-arylcoumarins, coumestans, and coumarins were listed up in Table 5 and summarized as follows.

Type 1: The C1 signals of Type 1 prenyl (geranyl) groups were observed in the range of δ 22.0 – 24.0 (acetone-d_6), δ 21.6 – 23.5 ($CDCl_3$), and δ 21.0 – 22.3 (DMSO-d_6).

Type 3: The C1 signals of Type 3 prenyl groups were observed in the range of δ 25.8 – 26.7 ($CDCl_3$).

8. Conclusion

^{13}C Nmr examination of three hundred seventy-seven kinds of heterocyclic prenyl(geranyl)phenols has shown that the benzylic methylene carbons (C1) appear at various regions depending upon the substituent groups at *ortho*-positions of the prenyl (geranyl) groups. In the previous paper,[3] the prenyl (geranyl) groups could be classified into the six types, and the chemical shifts of the C1 signals were observed in the restricted range specific to each type (Figure 1). Boundaries of the each group, which classified with the C1 chemical shifts, became ambiguous with the addition of the examined compounds. It was caused by a solvent effect to the methylene signal. Nevertheless, the boundaries were clearly when the chemical shifts were compared in the same solvent (Figure 2). Furthermore, in the classification between the same skeletal compounds (flavone, flavanone, xanthone, etc.), the methylene signals of each group appeared at more narrow region. This classification of the chemical shift of the benzylic methylene carbon of the prenyl (geranyl) group is useful for the structure determination of complex heterocyclic prenyl(geranyl)phenols.

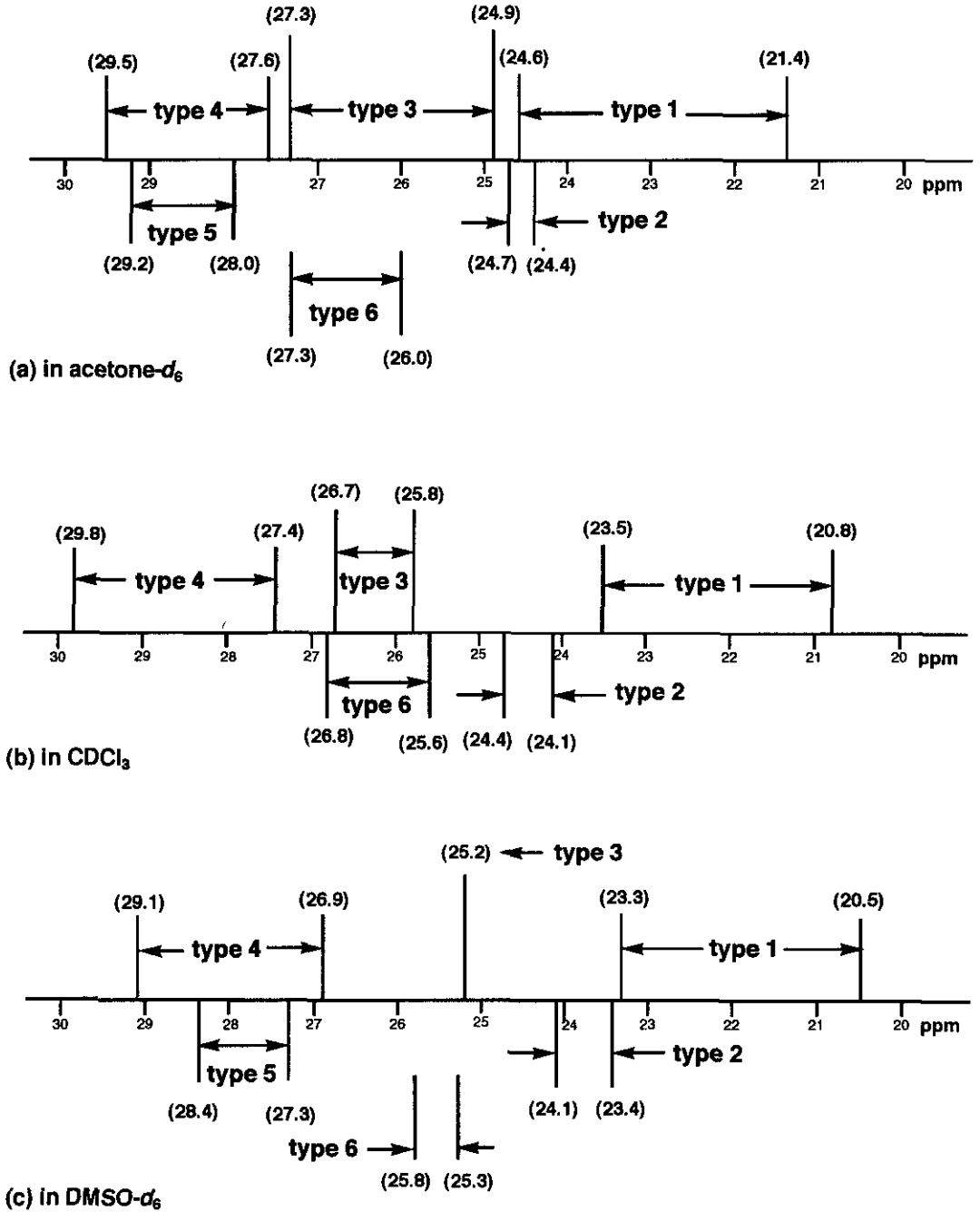
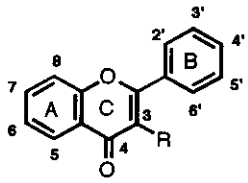
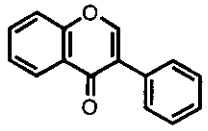


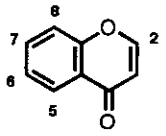
Figure 2 Variations in the chemical shift of benzylic methylene carbon of prenyl (geranyl) group of heterocyclic compounds [measured in (a) acetone-d_6, (b) $CDCl_3$, and (c) DMSO-d_6]



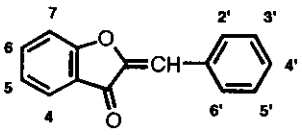
R = H: flavone
R = OH: flavonol



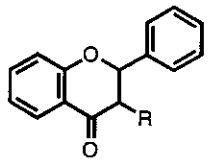
isoflavone



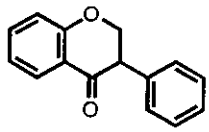
chromone



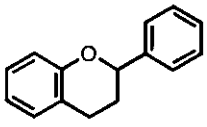
aurone



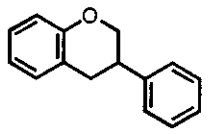
R = H: flavanone
R = OH: dihydroflavonol
(3-hydroxyflavanone)



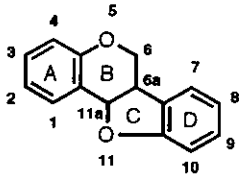
isoflavanone



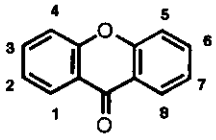
flavan



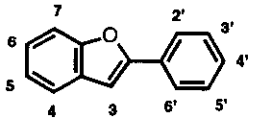
isoflavan



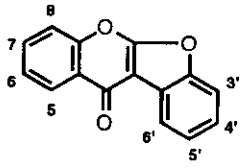
pterocarpan



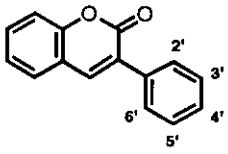
xanthone



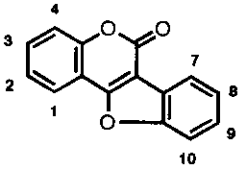
2-arylbenzofuran



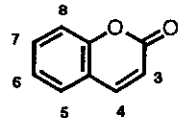
coumaronochromone



3-arylcoumarin

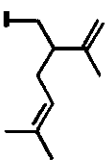


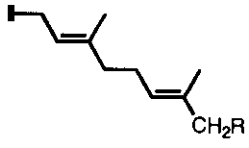
coumestan



coumarin

lavandulyl:





R = H: geranyl (G)

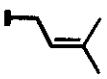
R =  : farnesyl (F)

Figure 3 Skeltal structures of heterocyclic compounds

Table 1[a] Chemical shifts of methylene carbons of prenyl groups of flavones, flavonols, isoflavones, chromones, and aurones

trivial name	OH position	others	prenyl position	type	chemical shift	sol.	ref.
- flavone -							
no name (**1**)	5, 7		6	1	22.0	A	ud
no name (**2**)	5, 7, 4'		6	1	22.1	A	14)
albanin D (**3**)	5, 7, 4'		6 (G)	1	22.0	A	15)
albanin E (**4**)	5, 7, 2', 4'		6 (G)	1	21.9	A	15)
gancaonin O (**5**)	5, 7, 3', 4'		6	1	22.0	A	16)
cyclocommunin (**6**) (isocyclomulberrin)	5, 7, 4'	3-CH(CH=CMe$_2$)O-2'	6	1	22.2 20.9	A D	17) 18)
artonin F (**7**)	5, 2', 4'	7,8-Dmp 3-CH$_2$CH(CMe$_2$-O-5')-6'	6	1	21.9	A	19)
artocarpesin (**8**)	5, 7, 2', 4'		6	1	21.7	A	14)
cannflavin A (**9**) (canniflavone-2)	5, 7, 4'	3'-OMe	6 (G)	1	22.0 21.6	A D	20) 21)
artonin G (**10**)	5, 7, 2', 4'	3-CH$_2$CH(CMe$_2$-O-5')-6'	6 3'	1 1	22.1 23.2	A	22)
no name (**11**)	5, 7, 4'		8 (G)	1	22.3	A	15)
no name (**12**)	5, 7		8	1	22.4	A	ud
artonin A (**13**)	5, 2', 4'	7,6-Dmp 3-CH$_2$CH(CMe$_2$-O-5')-6'	8	1	22.0	A	23)
artonin B (**14**)	5, 2', 4', 5'	7,6-Dmp 3-CH$_2$CH(CMe=CH$_2$)-6'	8	1	22.1	A	23)
brosimone L (**15**)	5, 7, 2', 4'		8 (G)	1	22.3	A	15)
licoflavone C (**16**)	5, 7, 4'		8	1	22.4	A	24)
cyclomulberrin (**17**)	5, 7, 4'	3-CH(CH=CMe$_2$)O-2'	8	1	22.5 21.1	A D	17) 18)
dihydroisocyclo-artomunin (**18**)	5, 7, 4'	5'-OMe 3-CH(CH=CMe$_2$)O-2'	8	1	22.5	A	17)
laxifolin (**19**)	5, 4'	7,8-Dmp	6	1	21.7	C	25)
dihydrocyclo-artomunin (**20**)	5, 4', 5'	7-OMe 3-CH(CH=CMe$_2$)O-2'	8	1	21.9	C	26)
isolaxifolin (**21**)	5, 4'	7,6-Dmp	8	1	21.6	C	25)
brosimone L trimethoxy-methyl ether (**22**)	5	7, 2', 4'-OCH$_2$OCH$_3$	8 (G)	1	21.9	C	ud
cudraflavone D (**23**)	5, 7, 2', 4'		6 5'	1 4	21.2 27.4	D	27)

cycloaltilisin (**24**)	5, 7, 5'	4'-OMe, 3-CH(CH=CMe_2)O-2'	8	1	21.2	D	18)
cycloheterophyllin (**25**)	5, 4', 5'	7,6-Dmp 3-CH(CH=CMe_2)O-2'	8	1	20.9 21.0	D	28) 23)
artonin J (**26**)	5, 7, 2', 4'	3-CH_2CH(CMe_2-O-5')-6'	3'	1	22.5	D	29)
artonin T (**27**)	5, 2', 4'	7-OMe, 3-CH_2CH(CMe_2-O-5')-6'	3'	1	22.5	D	30)
albanin A (**28**)	5, 7, 2', 4'		3	2	24.4	A	31)
brosimone H (**29**)	5, 7, 2', 4'		3	2	24.6	A	31)
			8 (G)	1	21.9		
cudraflavone B (**30**)	5, 2', 4'	7,6-Dmp	3	2	24.6	A	32)
					24.4	A	33)
cudraflavone C (**31**)	5, 7, 2', 4'		3	2	24.6	A	27)
			6	1	22.0		
artonin H (**32**)	5, 7, 2', 4', 5'		3 (G)	2	24.4	A	22)
			6	1	22.0		
artonin V (**33**)	5, 7, 2', 4', 5'		3	2	24.6	A	34)
			8	1	22.1		
kuwanon C (**34**) (mulberrin)	5, 7, 2', 4'		3	2	24.9	P	35)
					23.5	D	35)
					23.9	D	36)
			8	1	22.3	P	
					21.1	D	
					21.3	D	
kuwanon C 3Me (**35**)	5	7, 2', 4'-OMe	3	2	23.6	D	37)
			8	1	21.0		
kuwanon T (**36**)	5, 7, 2', 4'		3	2	23.6	D	38)
			3'	1	22.2		
morusin (**37**) (mulberrochromene)	5, 2', 4'	7,8-Dmp	3	2	24.8	P	35)
					23.7	D	
					24.6	A	
					23.9	D	36)
morusin 2Ac (**38**)	5	7,8-Dmp, 2', 4'-OAc	3	2	24.3	P	35)
artonin E (**39**)	5, 2', 4', 5'	7,8-Dmp	3	2	23.6	D	19)
					24.7	A	34)
rubraflavone A (**40**)	7, 2', 4'		3 (G)	2	24.1	D	36)
artocarpin (**41**)	5, 2', 4'	7-OMe, 6-CH=CHCHMe_2	3	2	23.6	D	39)
artocarpin 2Me (**42**)	5	7, 2', 4'-OMe, 7-OMe, 6-CH=CHCHMe_2	3	2	23.4	D	39)
cudraflavone B 2Me (**43**)	5	7,6-Dmp, 2', 4'-OMe	3	2	24.1	C	33)
cudraflavone B 3Me (**44**)		7,6-Dmp, 5, 2', 4'-OMe	3	2	24.4	C	33)
kanzonol E (**45**)	7	4',3'-Dmp	6	4	28.7	A	ud
prenyllicoflavone A (**46**) (licoflavone B)	7, 4'		6	4	28.7	A	40)
			3'	4	29.1		24)

licoflavone A (**47**)	7, 4'		3'	4	28.6	A	41)
					28.9	M	24)
gancaonin Q (**48**)	5, 7, 4'		6	1	22.0	A	6)
			3'	4	29.1		
kuwanon S (**49**)	5, 7, 4'		3' (G)	4	28.9	A	38)
- flavonol -							
licoflavonol (**50**)	3, 5, 7, 4'		6	1	22.1	A	ud
topazolin (**51**)	5, 7, 4'	3-OMe	6	1	22.1	A	ud
no name (**52**)	5, 7, 3', 4'	3-OMe	6	1	22.2	A	ud
gancaonin P (**53**)	3, 5, 7, 3', 4'		6	1	22.0	A	16)
broussoflavonol B (**54**)	5, 7, 3', 4'	3-OMe	6	1	22.2	A	42)
			8	1	22.6		
glyasperin A (**55**)	3, 5, 7, 4'		6	1	21.9	A	43)
			3'	4	29.1		
petalostemumol G (**56**)	3, 5, 7, 3', 4'		8	1	22.0	A	44)
			2'	3	26.8		
			6'		32.5		
petalostemumol G 4Me (**57**)	5	3, 7, 3', 4'-OMe	8	1	21.8	A	44)
			2'	3	25.8		
			6'		33.1		
no name (**58**)	5	3, 7-OCH_2OCH_3	6	1	21.6	C	45)
no name (**59**)	5	3, 7, 4'-OCH_2OCH_3	6	1	21.6	C	45)
no name (**60**)	5	3, 7, 3', 4'-OCH_2OCH_3	6	1	21.7	C	45)
no name (**61**)	5	3, 7-OCH_2OCH_3	8	1	21.9	C	45)
no name (**62**)	5	3, 7, 4'-OCH_2OCH_3	8	1	21.9	C	45)
no name (**63**)	5	3, 7, 3', 4'-OCH_2OCH_3	8	1	21.9	C	45)
rhynchospermin (**64**)	3, 5, 3'	7, 4'-OMe	8	1	21.7	C+D	46)
isorhynchospermin (**65**)	3, 5, 3'	7, 4'-OMe	6	1	21.2	C+D	47)
macarangin (**66**)	3, 5, 7, 4'		6 (G)	1	22.1	M	48)
glepidotin A (**67**)	3, 5, 7		6	1	21.2	D	49)
broussoflavonol A (**68**)	5, 3', 4'	3-OMe, 7,6-Dmp	8	1	21.1	D	42)
					22.1	A	
anhydroicaritin (**69**)	3, 5, 7	4'-OMe	8	1	21.8	D+P	ud
podoverine A (**70**)	5, 7, 3', 4'	3-OMe	2'	3	26.9	A	50)
					26.8	M	
broussoflavonol C (**71**)	3, 5, 7, 3', 4'	8-$CMe_2CH{=}CH_2$	5'	3	26.2	C	4)
			6'	5	29.2		
			5'	3	25.2	D	3)
			6'	5	28.4		
broussoflavonol C 4Me (**72**)	5	3, 7, 3', 4'-OMe	5'	3	25.8	C	4)
		8-$CMe_2CH{=}CH_2$	6'	5	29.1		

broussoflavonol D (**73**)	3, 5, 7, 3'	8-$CMe_2CH{=}CH_2$, 4',5'-Dmp	6'	5	28.0 27.3	C D	4) 3)
broussoflavonol 3Me (**74**)	5	3, 7, 3'-OMe, 4',5'-Dmp 8-$CMe_2CH{=}CH_2$	6'	5	28.3	C	4)
broussoflavonol E (**75**)	3, 5, 7, 3'	8-$CMe_2CH{=}CH_2$, 4',5'-Dmp(2H)	6'	5	27.9	D	3)
- isoflavone -							
gancaonin A (**76**)	5, 7	4'-OMe	6	1	22.1 21.2	A D	16) 51)
gancaonin N (**77**)	5, 7, 2'	4'-OMe	6	1	22.1	A	16)
osajin (**78**)	5, 4'	7,8-Dmp	6	1	21.8	A	14)
pomiferin (**79**)	5, 3', 4'	7,8-Dmp	6	1	21.8	A	14)
6, 8-diprenylorobol (**80**)	5, 7, 3', 4'		6, 8	1	21.6	A	52)
auriculasin (**81**) (cudraisoflavone A)	5, 3', 4'	7,6-Dmp	8	1	21.8 21.3	A C	14) 52)
gancaonin M (**82**)	5, 7	4'-OMe	8	1	22.1	A	16)
glyasperin J (**83**)	5, 7, 4'	2',3'-Dmp	8	1	22.1	A	53)
senegalensin (**84**)	5, 4'	6-$CH_2CH(C(OH)Me_2)O$-7	8	1	22.4 21.9	A C	54)
gancaonin L (**85**)	5, 7, 3', 4'		8	1	22.1	A	16)
warangalone (**86**) (scandenone)	5, 4'	7,6-Dmp	8	1	21.8 21.2	A C	14) 52)
isopiscerythramine (**87**)	5, 7, 3'	4'-NH_2, 5'-OMe	8 2'	1 3	22.0 26.6	A	9)
piscerythrone (**88**)	5, 7, 2', 4'	5'-OMe	3'	1	23.8	A	10)
glicoricone (**89**)	7, 2', 4'	6'-OMe	5'	1	23.5	A	55)
licoricone (**90**)	7, 6'	2', 4'-OMe	3'	1	23.4	A	ud
erysenegalensein D (**91**)	5, 7, 2', 4'	8-$CH_2CH(OH)CMe{=}CH_2$	6	1	21.7	C	56)
pumilaisoflavone C (**92**)	5, 7, 4'	3', 5'-OMe (?)	6 2'	1 3	21.4 23.4	C	12)
euchrenone b_{15} (**93**)	5, 7, 4'	2'-OMe	6, 8	1	21.7	C	57)
8-prenylluteone (**94**)	5, 7, 2', 4'		6, 8	1	21.7	C	52)
eriotriochin (**95**)	5, 4'	6-$CH_2CH(CMe_2OCH_2CH_2OH)$-O-7	8	1	21.9	C	58)
ulexone A (**96**)	5, 7	4',3'-Dmp	8	1	21.6	C	59) 60)
prebarbigerone (**97**)		7, 2', 4', 5'-OMe	8	1	22.3	C	61)
pre-5-methoxy-durmillone (**98**)	7	5, 6-OMe, 3'-OCH_2O-4'	8	1	22.1	C	61)
erysenegalensein E (**99**)	5, 7, 4'	8-$CH_2CH(OH)CMe{=}CH_2$	6	1	21.6	C+M	56)
gancaonin G (**100**)	5, 4'	7-OMe	6	1	21.1	D	62)

6-prenylisocaviunin (**101**)[b]	5, 7	8, 2', 4', 5'-OMe (?)	6	1	21.0	D	63)
luteone (**102**)	5, 7, 2', 4'		6	1	21.2	D	64)
gancaonin B (**103**)	5, 7, 3'	4'-OMe	6	1	21.1	D	51)
gancaonin H (**104**)	5, 7, 3'	4',5'-Dmp	6	1	21.0	D	62)
wighteone (**105**)	5, 7, 4'		6	1	21.1	D	64)
					21.9	D	65)
angustone B (**106**)	5, 7, 2'	4',3'-Dmp	6	1	21.2	D	64)
6,8-diprenylgenistein (**107**)	5, 7, 4'		6, 8	1	21.4	D	66)
angustone A (**108**)	5, 7, 2', 4'		6	1	21.2	D	64)
			3'	1	22.6		
isoangustone A (**109**)	5, 7, 3', 4'		6	1	21.0	D	67)
			5'	4	28.2		
auriculatin (**110**)	5, 2', 4'	7,6-Dmp	8	1	20.8	D	66)
lupiwighteone (**111**)	5, 7, 4'		8	1	21.0	D	51)
licoisoflavone A (**112**)	5, 7, 2', 4'		3'	1	22.6	D	64)
angustone C (**113**)	5, 2', 4'	7,6-Dmp	3'	1	22.6	D	64)
erythbigenin (**114**)	5, 7, 3', 4'	5'-OMe	2', 6'	3	27.0/27.1	A	68)
erythbigenin 3Me (**115**)	5	7, 3', 4', 5'-OMe	2', 6'	3	27.3	A	68)
piscidone (**116**)	5, 7, 3', 4'	5'-OMe	2'	3	26.8	A	10)
erythgenin (**117**)	5, 7, 4', 5'	3'-OMe	2'	3	27.0	A	10)
erythbigenone A[c] (**118**)	5, 7, 4'	5'-OMe, 2'-$CH_2C(OH)CMe_2O$-3'	6'	3	26.9	A	69)
erythbigenone B[c] (**119**)	5, 7, 4'	5'-OMe 2'-$CH_2C(OH)CMe_2O$-3'	6'	3	27.0	A	69)
erythbigenol A[c] (**120**)	5, 7, 4'	5'-OMe 2'-$CH_2CH(C(OH)Me_2)O$-3'	6'	3	26.6	A	69)
erythbigenol B[c] (**121**)	5, 7, 4'	5'-OMe 2'-$CH_2CH(C(OH)Me_2)O$-3'	6'	3	26.6	A	69)
piscerythramine (**122**)	5, 7, 3'	4'-NH_2, 5'-OMe	2', 6'	3	26.9/27.1	A	9)
piscerythoxazole (**123**)	7	5'-OMe, 4'-N=CH-O-3'	2'	3	27.3	A	9)
neobavaisoflavone (**124**)	7, 4'		3'	4	29.0	A	70)
glisoflavone (**125**)	7, 3', 4'	5-OMe	5'	4	29.1	A	71)
neobavaisoflavone 2Me (**126**)		7, 4'-OMe	3'	4	29.2	C	70)
neobavaisoflavone 2Ac (**127**)		7, 4'-OAc	3'	4	28.9	C	70)
- chromone -							
sophorachromone A (**128**)	5, 7		8 (G)	1	22.6	A	72)
heteropeucenin (**129**)	5, 7	2-Me	8	1	22.2	A	72)
no name (**130**)	5, 7	2-O-C_7H_7O	8	1	22.0	A	73)

peucenin 7-methyl ether (**131**)	5	2-Me, 7-OMe	6	1	21.5	C	74)
cneorum-chromone-H 7-methyl ether (**132**)	5	2-Me, 7-OMe	6, 8	1	22.6/22.7	C	75)
- aurone -							
antiarone B (**133**)	4, 6, 3', 4'		5	1	21.8	A	76)
			2'	3	25.8		
antiarone A (**134**)	4, 6, 3', 4'		2'	3	25.8	A	76)
			5'	4	28.7		
broussoaurone A (**135**)	6, 3', 4'		5	4	29.5	A	77)

[a]Abbreviations in the Tables are the followings: G = geranyl, F = farnesyl, Dmp = 2,2-dimethylpyrano, Dmp(2H) = 3,4-dihydro-2,2-dimethylpyrano, 2Me = dimethyl ether, 2Ac = diacetate, A = acetone-d_6, B = benzene-d_6, C = $CDCl_3$, D = DMSO-d_6, M = CD_3OD, P = pyridine-d_5, AN = CD_3CN, ud = unpublished data, and nr = not reported. [b]The chemical shifts of methoxyl groups of compound **101** have been reported as δ 55.1, 56.7, 60.1, and 61.4 and indicate that the methoxyl groups (δ 60.1 and 61.4) must be di*ortho*-substituted ones.[188]. [c]atropisomers.

Table 2 Chemical shifts of methylene carbons of prenyl groups of flavanones, 3-hydroxyflavanone (dihydroflavonol), and isoflavanone

trivial name	OH position	others	prenyl position	type	chemical shift	sol.	ref.
- flavanone -							
no name (**136**)	5, 7, 4'		6	1	22.1	A	78)
no name (**137**)	5, 7, 3', 4'		6	1	21.7	A	79)
nymphaeol-A (**138**)	5, 7, 3', 4'		6 (G)	1	21.4	A	80)
sophoraflavanone D (**139**)	5, 7, 2', 4', 6'		6 (G)	1	21.8	A	81)
cudraflavanone A (**140**)	5, 7, 2'	4',5'-Dmp	6	1	21.6	A	82)
					20.7	D	
					21.6	M	
exiguaflavanone D (**141**)	5, 7, 2', 6'	4'-OMe, 8-lavandulyl	6	1	21.8	A	83)
kushenol B (**142**)	5, 7, 2', 4'	8-lavandulyl	6	1	21.8	A	84)
exiguaflavanone J (**143**)	5, 7, 2', 4', 6'	8-lavandulyl	6	1	22.6	A	85)
kushenol E (**144**)	5, 7, 2', 4'		6	1	21.8	A	86)
			8	1	22.5		
kenusanone B (**145**)	5, 7, 2', 4', 6'		6	1	21.9	A	81)
			8	1	22.6		

sophoraflavanone J (**146**)	5, 7, 2'	5'-CH($C_6H_5O_2$)CH(C_6H_5O)O-4'	6, 8	1	22.4	A	87)
lonchocarpol A (**147**)	5, 7, 4'		6	1	21.8	A	88)
			8	1	22.5		
			6	1	21.3	C	89)
			8	1	21.9		
antiarone H (**148**)	5, 7, 3'	4'-OMe	6	1	21.7	A	90)
			2'	3	25.2		
nymphaeol-C (**149**)	5, 7, 3', 4'		6	1	21.5	A	80)
			2' (G)	3	25.1		
leachianone G (**150**)	5, 7, 2', 4'		8	1	22.4	A	91)
kenusanone I (**151**)	5, 2', 4'	7-OMe	8	1	22.2	A	92)
sophoraflavanone B (**152**)	5, 7, 4'		8	1	22.7	A	78)
exiguaflavanone K (**153**)	5, 7, 4'	3'-OMe	8	1	22.4	A	85)
sophoraflavanone E (**154**)	5, 7, 2', 4', 6'		8 (G)	1	22.2	A	81)
euchrenone a_5 (**155**)	7	4',3'-Dmp	8	1	22.8	A	ud
no name (**156**)	5, 7, 3', 4'		8	1	22.3	A	79)
sophoraflavanone A (**157**)	5, 7, 4'		8 (G)	1	22.7	A	93)
					21.2	D	72)
sophoraflavanone H (**158**)	5, 7, 2'	5'-CH($C_6H_5O_2$)CH(C_6H_5O)O-4'	8	1	22.3	A	87)
kenusanone D (**159**)	5, 7, 2', 6'	4'-OMe	8	1	22.4	A	94)
kenusanone E (**160**)	5, 2', 6'	7, 4'-OMe	8	1	22.2	A	94)
maackiaflavanone (**161**)	5, 2', 4'	7-OMe	8	1	21.9	A	95)
			5'	4	28.2		
antiarone G (**162**)	5, 7, 4'	3'-OMe	8	1	22.3	A	90)
			2'	3	25.6		
lupinenol (**163**)	5, 4'	8-CH=C(CMe_2OH)O-7	6	1	22.5	B	88)
lonchocarpol C (**164**)	5, 4'	8-CH_2CH(C(OH)Me_2)O-7	6	1	22.1	C	89)
no name (**165**)	5, 7, 3', 4'		6 (F)	1	21.3	C	96)
bonannione A (**166**)	5, 7, 4'		6 (G)	1	21.1	C	97)
(mimulone)					20.6	D	98)
bonannione A 2Ac (**167**)	5	7, 4'-OAc	6 (G)	1	21.9	C	97)
bonannione A 3Ac (**168**)		5, 7, 4'-OAc	6 (G)	1'	23.1	C	97)
6-prenylpinocembrin (**169**)	5, 7		6	1	21.8	C	99)
no name (**170**)	5, 7, 2', 4'	5'-$CMe_2CH=CH_2$	6	1	21.7	C	99)
amoradin (**171**)	5, 4'	7-OMe	6	1	21.2	C	100)
			8	1	21.7		
amoradicin (**172**)	5, 3', 4'	7-OMe	6	1	22.3	C	100)
			8	1	22.8		
orotinin (**173**)	5, 2', 6'	7,6-Dmp	8	1	21.5	C	101)
orotinin 5-methyl ether (**174**)	2', 6'	5-OMe, 7,6-Dmp	8	1	21.0	C	101)
glabrol (**175**)	7, 4'		8	1	22.3	C	41)
			3'	4	29.7		

no name (**176**)	5, 7	4'-OMe	8	1	21.7	C	102)
heteroflavanone B (**177**)	5	7, 2', 4', 6'-OMe	8	1	22.1	C	103)
pongapinone B (**178**)		5, 7-OMe 3'-O-CH_2-O-4'	8	1	21.9	C	104)
heteroflavanone C (**179**)	5, 7	2', 4', 6'-OMe	8	1	22.2	C	105)
minimiflorin (**180**)	5, 2'	7,6-Dmp	8	1	21.5	C	101)
no name (**181**)		5-OMe, 7-O-prenyl	8	1	22.2	C	106)
no name (**182**)		5, 7-OMe	8	1	21.9	C	106)
7-methylglabranin (**183**)	5	7-OMe	8	1	21.7	C	107)
mundulin (**184**)	5	7,6-Dmp	8	1	21.3	C	108)
mundulin Ac (**185**)		5-OAc, 7,6-Dmp	8	1	21.9	C	108)
lupinifolin (**186**)	5, 4'	7,6-Dmp	8	1	21.3	C	108)
lupinifolin 2Ac (**187**)		5, 4'-OAc, 7,6-Dmp	8	1	21.9	C	108)
3'-methoxylupinifolin (**188**)	5, 4'	3'-OMe, 7,6-Dmp	8	1	21.3	C	25)
euchrenone a_8 (**189**)	7, 2'	4'-OMe	8	1"	23.3	C	109)
			5'	4	29.1		
3-O-methyldiplacone (**190**)	5, 7, 4'	3'-OMe	6 (G)	1	20.6	D	98)
diplacone (**191**)	5, 7, 3', 4'		6 (G)	1	20.6	D	98)
isobavachin (**192**)	7, 4'		8	1	21.7	D	110)
euchrestaflavanone C (**193**)	5, 7, 2'	4',5'-Dmp	8	1	21.3	D	93)
flemiflavanone-D (**194**)	5, 7, 4'	3'-CH_2C H CMe$_2$ O	8	1	21.7	D	111)
euchrestaflavanone A (**195**)	5, 7, 4'		8	1	21.3	D	112)
			3'	4	28.2		93)
			8	1	22.3	A	87)
			3'	4	29.1		
euchrestaflavanone B (**196**)	5, 7, 2', 4'		8	1	21.3	D	93)
			5'	4	27.5		
gancaonin E (**197**)	5, 7, 3', 4'		8	1	22.3	D	51)
			5'	4	29.1		
nymphaeol-B (**198**)	5, 7, 3', 4'		2' (G)	3	25.1	A	80)
antiarone F (**199**)	5, 7	3', 4'-OMe	2'	3	25.6	A	90)
antiarone I (**200**)	5, 7, 3'	4'-OMe	2'	3	24.9	A	90)
			5'	4	28.6		
sigmoidin A (**201**)	5, 7, 3', 4'		2'	3	25.4	A	90)
			5'	4	29.1		
(-)-sigmoidin E (**202**)	5, 7	4',5'-Dmp	3'	4	29.1	A	113)
abyssinone V (**203**)	5, 7, 4'		3', 5'	4	29.7	C	113)
abyssinone IV (**204**)	7, 4'		3', 5'	4	29.6	C	70)
sigmoidin B (**205**)	5, 7, 3', 4'		5'	4	29.0	C	114)
shinflavanone (**206**)	4'	7,8-Dmp	3'	4	29.8	C	41)
3'-prenylnaringenin (**207**)	5, 7, 4'		3'	4	28.1	D	115)

no name (**208**)	5, 7, 3'	4'-OMe	5'	4	28.2	D	116)
no name (**209**)		5, 7, 3'-OAc, 4'-OMe	5'	4	28.5	D	117)
kuwanon E (**210**)	5, 7, 2', 4'		5' (G)	4	28.3	M	118)
					27.3	D	
- 3-hydroxyflavanone (dihydroflavonol) -							
kushenol L (**211**)	3, 5, 7, 2', 4'		6	1	21.8	A	119)
			8	1	22.2		
3-hydroxyglabrol (**212**)	3, 7, 4'		8	1	22.1	A	120)
			3'	4	28.6		
kushenol M (**213**)	3, 5, 7, 2', 4'	6 or 8-lavandulyl	6 or 8	1	21.7	A	119)
kenusanone C (**214**)	3, 5, 7, 2', 6'	4'-OMe	6 (G)	1	21.9	A	94)
			8	1	22.4		
bonanniol A 4Ac (**215**)		3, 5, 7, 4'-OAc	6 (G)	1'	23.1	C	97)
bonanniol B 3Ac (**216**)		3, 7, 4'-OAc, 5-OMe	6 (G)	1	22.8	C	97)
mundulinol (**217**)	3, 5	7,6-Dmp	8	1	20.8	C	108)
mundulinol 2Ac (**218**)		3, 5-OAc, 7,6-Dmp	8	1	21.5	C	108)
lupinifolinol (**219**)	3, 5, 4'	7,6-Dmp	8	1	20.9	C	108)
lupinifolinol 3Ac (**220**)		3, 5, 4'-OAc, 7,6-Dmp	8	1	21.3	C	108)
bonanniol A (**221**)	3, 5, 7, 4'		6 (G)	1	20.6	D	97)
bonanniol B (**222**)	3, 7, 4'	5-OMe	6 (G)	1	21.6	D	97)
diplacol (**223**)	3, 5, 7, 3', 4'		6 (G)	1	20.6	D	98)
petalostemumol (**224**)	3, 5, 7, 3', 4'		8	1	20.5	D	44)
			2'	3	25.1		
			6'		31.3		
petalostemumol 3Me (**225**)	3, 5	7, 3', 4'-OMe	8	1	20.8	D	44)
			2'	3	25.5		
			6'		32.3		
petalostemumol 2Me (**226**)	3, 5, 3'	7, 4'-OMe	8	1	21.7	D	44)
			2'	3	26.7		
			6'		33.2		
- isoflavanone -							
no name (**227**)	5, 7, 2', 4'		6	1	21.8	A	121)
			3'	1	23.4		
kievitone (**228**)	5, 7, 2', 4'		8	1	22.1	A	122)
glyasperin B (**229**)	5, 2', 4'	7-OMe	6	1	21.6	A	43)
glyasperin K (**230**)	5, 2'	7, 4'-OMe	6	1	21.6	A	123)
kanzonol G (**231**)	5, 2', 4'	7-OMe	6	1	21.6	A	5)
			3'	1	23.3		
glyasperin J (**232**)	5, 7, 4'	2',3'-Dmp	8	1	22.1	A	53)

3'-prenylkievitone (**233**)	5, 7, 2', 4'		8	1	22.1	A	121)
			3'	1	23.3		
sophoraisoflavanone C (**234**)	5, 7, 4'		6	1	20.6	D	124)
			3' (G)	4	27.2		
sophoraisoflavanone D (**235**)	5, 7, 2', 4'		6	1	20.6	D	124)
			5'	4	26.9		
isosophoranone (**236**)	5, 7, 4'	2'-OMe	6	1	20.7	D	110)
			3'	1	23.3		
sophoraisoflavanone B (**237**)	5, 7, 2'	4'-OMe	6	1	20.7	D	125)
			5'	4	27.2		
kenusanone F (**238**)	3, 5, 7, 4'	2'-OMe	3'	1	24.6	A	92)
echinoisoflavanone (**239**)	3, 5, 7	2', 4'-OMe	3'	1	24.3	A	126)
sophoraisoflavanone A (**240**)	5, 7, 4'	2'-OMe	3'	1	24.3	A	81)
					23.0	D	110)
2, 3-dihydroauriculatin (**241**)	5, 2', 4'	7,6-Dmp	8	1	20.8	D	66)
prostratol A (**242**)	7, 2' 4'		5' (G)	4	28.1	A	11)
prostratol B (**243**)	7, 2', 4'		6	4	28.1	A	11)
			5'	4	28.2		
prostratol C (**244**)	7, 2'	4'-OMe	5'	4	28.4	A	11)
sigmoidin J (**245**)	7, 4'	2', 5'-OMe	6	4	28.1	A	127)
kenusanone A (**246**)	5, 7, 2', 4'		5'	4	27.6	A	128)
sigmoidin I (**247**)	7, 4'	2'-OMe	5'	4	27.6	C	129)
no name (**248**)	5, 7, 3'	4'-OMe	5'	4	28.1	D	116)

Table 3. Chemical shifts of methylene carbons of prenyl groups of flavans, isoflavans, and pterocarpans

trivial name	OH position	others	prenyl position	type	chemical shift	sol.	ref.
- flavan -							
kazinol B (**249**)	7, 3'	4',5'-Dmp	2'	3	25.3	C	130)
kazinol B 2Me (**250**)		7, 3'-OMe, 4',5'-Dmp	2'	3	25.4	C	130)
kazinol E (**251**)	7, 3', 4'	6-$CMe_2CH{=}CH_2$	5'	3	25.6	C	131)
			6'	5	27.2		
broussoflavan A (**252**)	7, 3'	4'-$OCMe_2CH(OH)CH(OH)$-5'	2'	3	25.8	C+M	77)
kazinol A (**253**)	7, 3', 4'		2'	3	25.1	C	130)
			5'	4	29.3		
kazinol A 3Me (**254**)		7, 3', 4'-OMe	2'	3	25.1	C	130)
			5'	4	28.6		
kazinol H (**255**)	7, 3'	4',5'-Dmp, 6-$CMe_2CH{=}CH_2$	6'	5	26.5	C	131)
6-prenyl-(+)-catechin (**256**)	3, 5, 7, 3', 4'		6	1	22.8	A	132)

6-prenyl-(+)-catechin 4Me (**257**)	3	5, 7, 3', 4'-OMe	6	1	22.7	C	132)
8-prenyl-(+)-catechin (**258**)	3, 5, 7, 3', 4'		8	1	22.6	A	132)
8-prenyl-(+)-catechin 4Me (**259**)	3	5, 7, 3', 4'-OMe	8	1	22.0	C	132)
- isoflavan -							
glyasperin C (**260**)	7, 2', 4'	5-OMe	6	1	23.3	A	43)
glyasperin D (**261**)	2', 4'	5, 7-OMe	6	1	23.2	A	43)
licorisoflavan A (**262**)	2', 4'	5, 7-OMe	6	1	23.3	A	43)
			3'	1	23.2		
glyasperin I (**263**)	7, 4'	2', 5-OMe	6	1	23.4	A	53)
licoricidin (**264**)	7, 2', 4'	5-OMe	6	1	23.3	A	35)
			3'	1	23.2		
			6	1	22.4	D	133)
			3'	1	22.5		
kanzonol H (**265**)	2', 4'	5-OMe, 7,6-Dmp(2H)	3'	1	23.4	A	5)
glyasperin G (**266**)	2', 4'	5-OMe, 6-CH=CH-O-7	3'	1	23.3	A	53)
gancaonin Z (**267**)	7, 2'	4'-OMe	3'	1	23.1	A	134)
kanzonol M (**268**)	2', 7	5, 4'-OMe, 8-CHO	3'	1	23.2	A	135)
kanzonol N (**269**)	7, 2', 4'	5-OMe, 8-CHO	3'	1	23.6	A	135)
kanzonol R (**270**)	7, 2'	5, 4'-OMe	3'	1	23.4	A	135)
(-)-4'-O-methylpre-glabridin (**271**)	7, 2'	4'-OMe	8	1	22.5	C	136)
phaseollidin isoflavan (**272**)	7, 2', 4'		3'	1	22.8	C	137)
glyinflanin I (**273**)	7, 4'	2',3'-Dmp	6	4	28.7	A	138)
no name (**274**) (isoflav-3-ene)[a]	7, 2, 4'	5-OMe, $\Delta^{3,4}$	5	1	23.0	A	ud
- pterocarpan -							
kanzonol P (**275**)	9	1, 3-OMe	2	1	23.6	A	135)
kanzonol F (**276**)	3	1-OMe, 9,8-Dmp	2	1	23.4	A	5)
1-methoxyficifolinol (**277**)	3, 9	1-OMe	2	1	23.3	A	5)
			8	4	28.8		67)
phaseollidin (**278**)	3, 9		10	1	23.1	C	139)
					23.5	A	87)
cristacarpin (**279**)	3	9-OMe	10	1	22.7	C	139)
striatine (**280**)	3, 9	2-$CMe_2CH=CH_2$	10	1	23.2	nr	140)
erythrabyssin II (**281**)	3, 9		2	4	29.0	C	70)
			10	1	23.2		
erycristin (**282**)	3	9-OMe	2	4	29.1	C	141)
			10	1	23.0		

erycristagallin (**283**)	3, 9	$\Delta^{6a,11a}$	2	4	27.1	D	142)
(pterocarpene)[b]			10	1	nr		

[a]3,4-dehydroisoflavan. [b]6a,11a-dehydropterocarpan.

Table 4 Chemical shifts of methylene carbons of prenyl groups of xanthones

trivial name	OH position	others	prenyl position	type	chemical shift	sol.	ref.
- xanthone -							
no name (**284**)	1, 3, 8	7-OMe	2	1	21.9	A	143)
no name (**285**)	1, 3, 7, 8		2	1	21.8	A	143)
morusignin B (**286**)	1, 3, 5, 8		2	1	22.0	A	144)
					21.9	A	143)
morusignin D (**287**)	1, 3, 6	5-OMe	2	1	22.0	A	144)
gerontoxanthone I (**288**)	1, 3, 5, 6	4-$CMe_2CH{=}CH_2$	2	1	22.8	A	145)
morusignin H (**289**)	1, 5	4-$CH_2CH(C(OH)Me_2)$O-3	2	1	22.4	A	146)
morusignin F (**290**)	1, 5, 8	4-$CH_2CH(C(OH)Me_2)$O-3	2	1	22.3	A	146)
gartanin (**291**)	1, 3, 5, 8		2, 4	1	22.1/22.3	A	144)
					21.6/ 22.0	C	143)
morusignin E (**292**)	1, 5, 8	2-$CH_2CH(C(OH)Me_2)$O-3	4	1	22.5	A	146)
morusignin G (**293**)	1, 5	2-$CH_2CH(C(OH)Me_2)$O-3	4	1	22.6	A	146)
morusignin A (**294**)	1, 3, 5, 8		4	1	22.1	A	144)
xanthone V_1 (**295**)	1, 5, 6	3,2-Dmp	4	1	21.6	A	147)
xanthone V_2 (**296**)	1, 5, 6	7-OMe, 3,2-Dmp	4	1	21.7	A	147)
cudraxanthone J (**297**)	1, 3	8-$CH_2CH(C(OH)Me_2)$O-7	4	1	22.2	A	148)
cudraxanthone H (**298**)	1, 3, 7		4	1	22.1	A	148)
(gerontoxanthone H)			8	6	26.2		
			4	1	22.5	A	145)
			8	6	26.7		
cudraxanthone L (**299**)	1, 3, 6, 7	2-$CMe_2CH{=}CH_2$	5	1	23.0	A	149)
cudraxanthone M (**300**)	1, 6, 7	2-CMe_2CHMe-O-3	5	1	23.1	A	149)
caloxanthone A (**301**)	1, 6, 7	3,2-Dmp	5	1	23.0	A	8)
artonin Q (**302**)	1	3,2-Dmp, 7-$CMe{=}CH_2$ 5-$COCH_2C(OH)COOMe$-6	4	1	22.0	A	30)
garcinone D (**303**)	1, 3, 6	7-OMe, 8-$CH_2CH_2C(OH)Me_2$	2	1	22.0	C	150)
trapezifolixanthone (**304**)	1, 5	3,2-Dmp	4	1	21.7	C	151)
gerontoxanthone C (**305**)	1, 5, 6	2-CMe_2CHMe-O-3	4	1	22.2	nr	152)

garcinone E (**306**)	1, 3, 6, 7		2	1	21.5	C	153)
			5	1	22.6		
			8	6	25.8		
calothwaitesixanthone (**307**)	1, 3	7,8-Dmp	2	1	21.5	C	154)
no name (**308**)	1, 3, 5	6,7-Dmp, 4-$CMe_2CH{=}CH_2$	2	1	22.0	C	155)
no name (**309**)	1, 5	6,7-Dmp, 4-CMe_2CHMe-O-3	2	1	22.0	C	155)
no name (**310**)	1, 3, 7		2 (G), 4	1	21.6/21.8	C	150)
no name (**311**)	1	3, 7-OMe	2 (G), 4	1	22.6	C	150)
no name (**312**)		1, 3, 7-OMe	2 (G), 4	1	23.3	C	150)
no name (**313**)	1, 3, 8	5-OMe	2	1	20.8	D	143)
no name (**314**)		1, 3, 7, 8-OMe	2	1	22.8	D	143)
tovophyllin A (**315**)	1, 3, 6	7,8-Dmp	2, 5	1	21.2/22.5	C	150)
cudraxanthone F (**316**)	1, 3, 6	5-OMe	2	1	21.5	C	156)
			7	4	28.1		
gartanin Me (**317**)	1, 3, 8	5-OMe	2, 4	1	21.6/21.9	C	143)
gartanin 3Me (**318**)	1	3, 5, 8-OMe	2, 4	1	22.6/22.7	C	143)
no name (**319**)	1, 5, 8	3-OMe	2	1	20.7	D	143)
garcinone B (**320**)	1, 3, 6	7,8-Dmp	2	1	21.0	D	157)
garcinone C (**321**)	1, 3, 6, 7	8-$CH_2CH_2C(OH)Me_2$	2	1	21.1	D	157)
mangostin (**322**)	1, 3, 6	7-OMe	2	1	21.0	D	157)
			8	6	25.8		
γ-mangostin (**323**)	1, 3, 6, 7		2	1	21.2	D	157)
			8	6	25.5		
			2	1	20.9	D	153)
			8	6	25.3		
			2	1	22.3	M	158)
			8	6	26.0		
no name (**324**)	1, 3, 5		4 (G)	1	21.1	D	159)
gerontoxanthone E (**325**)	1, 6	5-OMe, 2-CMe_2CHMe-O-3	7	4	29.0	A	145)
gerontoxanthone G (**326**)	1, 5, 6	2-CMe_2CHMe-O-3	7	4	28.8	A	145)
subelliptenone B (**327**)	1, 2, 5, 6	4-$CMe_2CH{=}CH_2$	7	4	28.8	A	7)
shamixanthone (**328**)	1	6-Me	4	4	27.4	C	160)
		8-$CH(OH)CH(CMe{=}CH_2)CH_2$-O-7			27.5	C	161)
cudraxanthone E (**329**)	1, 3, 6	5-OMe, 2-$CMe_2CH{=}CH_2$	7	4	28.2	C	156)
no name (**330**)	1, 4, 5		3	4	28.5	D	159)
garciniaxanthone C (**331**)	1, 4, 5		3	4	28.3	D	162)
			6	4	28.6		
garciniaxanthone A (**332**)	1, 4, 5	2-$CMe_2CH{=}CH_2$	6	4	28.3	D	162)
subelliptenone A (**333**)	1, 4, 5, 6	2-$CMe_2CH{=}CH_2$	7	5	25.3	A	159)
			8		29.3		
rubraxanthone (**334**)	1, 3, 6	7-OMe	8 (G)	6	27.3	A	163)
					25.4	D	164)
cudraxanthone I (**335**)	1, 7	3,4-Dmp	8	6	26.0	A	148)

isocowanin (**336**)	1, 3, 6	7-OMe	8 (G)	6	27.3	A	163)
			4	1	22.1		
no name (**337**)	1, 6	7-OMe, 3,2-Dmp	8	6	26.5	C	165)
no name (**338**)	1	6, 7-OMe, 3,2-Dmp	8	6	26.0	C	165)
cudraxanthone C (**339**)	1, 3, 6	7-OMe, 4-$CMe_2CH{=}CH_2$	8	6	26.5	C	166)
rubraxanthone 3Me (**340**)		1, 3, 6, 7-OMe	8 (G)	6	26.1	C	163)
isocowanin 3Me (**341**)		1, 3, 6, 7-OMe	8 (G)	6	26.0	C	163)
			4	1	21.3 or 21.4		
no name (**342**)	1	3, 6, 7-OMe	8 (G)	6	25.9	C	164)
cratoxylone (**343**)	1, 3, 6	7-OMe, 2-$CH_2CH_2C(OH)Me_2$	8	6	26.8	C	150)
calabaxanthone (**344**)	1	3,2-Dmp, 7-OMe	8	6	25.6	C	151)
					25.8	C	165)
caloxanthone B (**345**)	1, 6	5-OMe, 4-CMe_2CHMe-O-3	8		34.2	A	8)
zeyloxanthonone (**346**)	1, 3	8-diprenyl, 5,6-2H, 7-CO	2	1	21.6	C	167)

Table 5 Chemical shifts of methylene carbons of prenyl groups of 2-arylbenzofurans, coumaronochromones, 3-arylcoumarins, coumestans, and coumarins.

trivial name	OH position	others	prenyl position	type	chemical shift	sol.	ref.
- 2-arylbenzofuran -							
mulberrofuran L (**347**)	6, 3', 5'		7 (G)	1	23.3	A	168)
moracin C (**348**)	6, 3', 5'		4'	1	23.2	A	ud
mulberrofuran B (**349**)	3', 5'	6-OMe	7 (G)	1	23.3	A	168)
					22.9	C	
albafuran B (**350**)	6, 3', 5'		4' (G)	1	21.3	AN	169)
mulberrofuran D (**351**)	6, 3', 5'		7 (G)	1	23.1	C	170)
			2'	3	26.4		
mulberrofuran D 3Me (**352**)		6, 3', 5'-OMe	7 (G)	1	22.9	C	168)
			2'	3	26.7		
licocoumarone (**353**)	6, 2', 4'	4-OMe	5	1	22.3	D	171)
					23.4	A	ud
gancaonin I (**354**)	2', 4'	4, 6-OMe	5	1	22.3	D	62)
mulberrofuran N (**355**)	6, 3'	5'-OMe	2', 6'	3	27.0	A	172)
mulberrofuran A (**356**)	6, 5'	3'-OMe	2' (G)	3	25.8	C	173)
albafuran A (**357**)	6, 3', 5'		2' (G)	3	25.0	D	174)
moracin N (**358**)	6, 3', 5'		5	4	28.6	A	175)

- coumaronochromone -							
lupinalbin B (**359**)	5, 7, 4'		6	1	21.0	D	176)
millettin (**360**)	5, 4'	7,6-Dmp	8	1	21.0	nr	177)
euchretin A (**361**)	5, 7, 5'	4',3'-Dmp	6, 8	1	22.6/22.7	A	178)
euchretin A 3Me (**362**)		5, 7, 5'-OMe, 4',3'-Dmp	6, 8	1	24.0	A	178)
euchretin B 4Me (**363**)		5, 7, 4', 5'-OMe	8	1	22.1	C	179)
			3'	1	23.5		
- 3-arylcoumarin -							
gancaonin W (**364**)	7, 2', 4'	5-OMe	3'	1	23.4	A	180)
glycycoumarin (**365**)	7, 2', 4'	5-OMe	6	1	23.4	A	180)
					22.2	D	171)
scandenin 2Me (**366**)		4, 5, 4'-OMe, 7,8-Dmp	6	1	21.8	nr	177)
lonchocarpic acid 2Me (**367**)		4, 5, 4'-OMe, 7,6-Dmp	8	1	21.3	nr	177)
- coumestan -							
glycyrol (**368**)	3, 9	1-OMe	2	1	22.0	D	62)
3-*O*-methylglycyrol (**369**)	9	1, 3-OMe	2	1	22.2	D	181)
sigmoidin K (**370**)	3, 9		2	4	27.2	D	127)
			10	1	22.3		
- coumarin -							
no name (**371**)	5, 7		8 (G)	1	22.0	A	182)
toddaculin (**372**)		5, 7-OMe	6	1	22.5	C	183)
osthol (**373**)		7-OMe	8	1	21.6	C	184)
O-methylcedrelopsin (**374**)		6, 7-OMe	8	1	22.7	C	183)
no name (**375**)	7	3-$CMe_2CH{=}CH_2$	8	1	22.1	C	185)
ramosinin (**376**)		7-OMe, 3-$CMe_2CH{=}CH_2$	8	1	21.9	C	185)
osthenol (**377**)	7		8	1	22.0	C	186)

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