^1H NMR SPECTRA OF PRENYLATED FLAVONOIDS AND PYRANOFLAVONOIDS[1]

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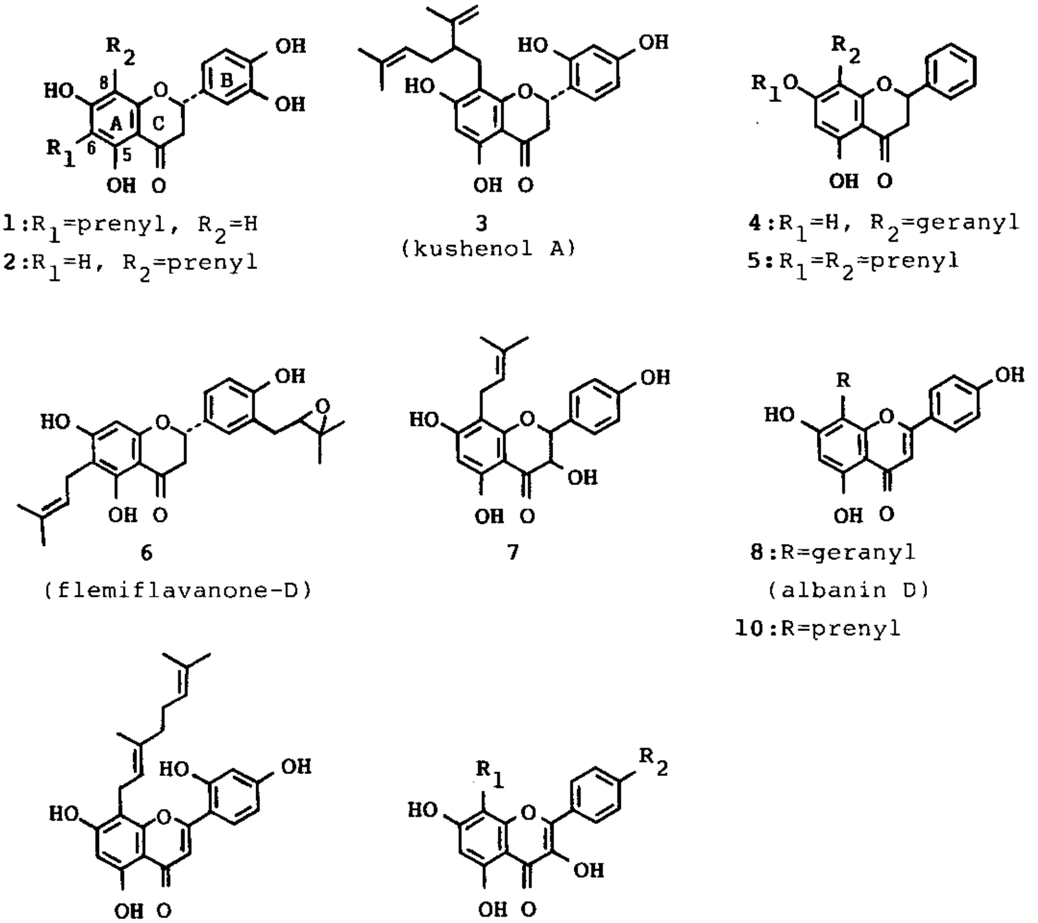
Abstract —— ^1H Nmr examination of prenylated flavonoids has shown that the presence of the prenyl group at C-3, C-6, or C-8 position of flavone can be deduced from the chemical shift of methylene protons of prenyl group measured in acetone-d_6. The chemical shifts of olefinic proton on pyran ring and A ring proton can be used to distinguish between linear type pyranoflavone and angular type pyranoflavone. The application of this ^1H nmr method to the identification of Atalantia flavone and Artocarpus flavones is discussed.

In our previous ^1H nmr studies on the isoprenoid substituted flavonoids[2] (isoflavone, flavone, flavanone, and flavonol), we reported that the signal of hydrogen-bonded hydroxyl proton (OH-5) of 6-isoprenoid substituted flavonoid appeared at more downfield (0.25-0.30 ppm) than that of the 6-nonsubstituted flavonoids having same B and C rings (measured in acetone-d_6). In contrast, the OH-5 signal of the 8-isoprenoid substituted flavonoid shows upfield shift (0.04-0.10 ppm) compared with that of the flavonoid having same B and C rings and no side chain.[3-6] The observation of the C-prenylation effects for the OH-5 signal is useful method for the characterization of 6- or 8-prenylated flavonoids, because the measurement



1:R_1=prenyl, R_2=H
2:R_1=H, R_2=prenyl

3
(kushenol A)

4:R_1=H, R_2=geranyl
5:R_1=R_2=prenyl

6
(flemiflavanone-D)

7

8:R=geranyl
(albanin D)
10:R=prenyl

9
(albanin E)

11:R_1=prenyl, R_2=H
(glepidotin A)
12:R_1=γ-hydroxyisoamyl,
R_2=OH

Figure 1. Revised structures of isoprenoid substituted flavonoids*

*: The structures were revised (or would be revised) to corresponding 6- or 8-isoprenoid substituted isomers (see Table 1).

Table 1. The revised structures of 6- or 8-isoprenoid substituted flavonoids[*]

	revised position of C_5-unit	chemical shift of OH-5[§]	trivial name	refrences and notes
1	8-prenyl	12.14 (A)		4,28
2	6-prenyl	12.47 (A)		4,28
3	6-lavandulyl	12.56 (A)	kushenol A	29,30
4	6-geranyl	12.40 (C)		31,32
5	6-prenyl	12.30 (C)		33
6	8-prenyl	11.98 (C)	flemiflavanone-D	34,35
7	6-prenyl	12.06 (A)		36,37
8	6-geranyl	13.25 (A)	albanin D	5,38
9	6-geranyl	13.32 (A)	albanin E	5,38
10	6-prenyl	13.30 (A)		12,39
11	6-prenyl	12.30 (A)	glepidotin A	6,40
12	6-(γ-hydroxy-isoamyl)	12.40 (A)		6,36

*: The structures reported in the earlier literature were shown in Figure 1.
§: (A); Measured in acetone-d_6, (C): measured in $CDCl_3$.

Table 2. Chemical shifts (δ) of methylene protons of prenyl (geranyl) group and A ring protons of 6- or 8-prenylated (geranylated) flavonoids in acetone-d_6[*]

	(6-prenylflavonoids)		(8-prenylflavonoids)	
(A ring)	CH_2	H-8	CH_2	H-6
isoflavone	3.36-3.38	6.49-6.57	3.45-3.46	6.36-6.43
flavone	3.35-3.37	6.57-6.63	3.56-3.58	6.33-6.35
flavonol	3.36-3.37	6.53-6.65	3.52-3.58	6.26-6.39
(methylene protons on B ring)				
ortho-OH and -H	3.30-3.43	(9 compounds)		
di*ortho*-OH	3.44-3.45	(6 compounds)		

*: The numbers of reference compounds are as follows; 6-prenylisoflavones (12 compounds), 8-prenylisoflavones (7), 6-prenylflavones (9), 8-prenylflavones (4), 6-prenylflavonols (4), and 8-prenylflavonols (4).

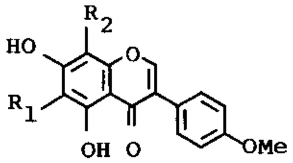
requires only a small amount (less than 500 micrograms) of sample. This method can also be used to confirm the structure postulated earlier for the prenylated flavonoid if the chemical shift of the OH-5 signal has been described. In the course of the ^1H nmr studies on the 6- or 8-isoprenoid substituted flavanones, flavones, and flavonols, twelve compounds (**1-12**) among fifty-seven are found to be necessary reinvestigated. These flavonoids were shown in Figure 1 and Table 1. Structures of the six flavonoids (**1**, **2**, **8**, **9**, **11**, and **12**) were revised by synthesis.[4-6]

In this paper, we report the chemical shifts of the other proton signals of the prenylated flavonoids and pyranoflavonoids for the confirmation of the location of isoprenoid residue.

1. Prenylated flavanone and isoflavone

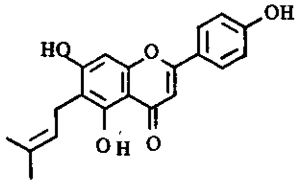
The chemical shifts of the methylene protons of prenyl group (H_2-1") of synthetic 6-prenyl-3',4',5,7-tetrahydroxyflavanone (**1'** = (±)-**1**)[4] and 8-prenyl-3',4',5,7-tetrahydroxyflavanone (**2'** = (±)-**2**)[4] were almost same (**1'**, δ 3.24; **2'**, δ 3.22) as well as those of aromatic proton on A ring (**1'**, δ 6.02; **2'**, δ 6.01) measured in acetone-d_6. The 6-prenylated and 8-prenylated flavanones could not be discriminated each other with those chemical shifts as well as with the chemical shifts of C-6 and C-8 carbon signals.[7]

The H_2-1" signal of 6-prenyl group of isoflavone (**13**)[8] was observed at δ 3.37, and that of 8-prenyl group of **14**[3] appeared at δ 3.45. The H-8 signal of **13** was observed at δ 6.50, and the H-6 signal of **14** appeared at δ 6.36. The chemical shifts of these signals of prenylated isoflavones were summarized in Table 2. These chemical shifts may discriminate between 6-prenylated and 8-prenylated isoflavones, but the additional observation of the OH-5 signal is more reliable for the structure determination of these compounds.[3] The downfield shift (0.08 ppm) of the H_2-1" signal of 8-prenyl group of **14** compared with that of 6-prenyl group of **13** presumably reflects a localization of π electron at C-8 position, rather than

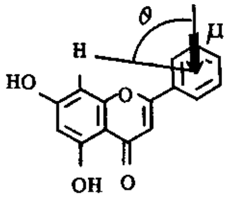


13:R_1=prenyl, R_2=H (gancaonin A)

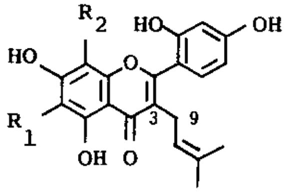
14:R_1=H, R_2=prenyl (gancaonin M)



15 (licoflavone B)

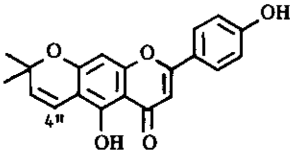


16

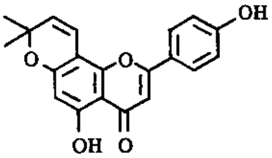


17:R_1=H, R_2=prenyl (kuwanon C)

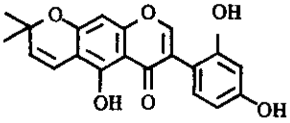
18:R_1=prenyl, R_2=H (cudraflavone C)



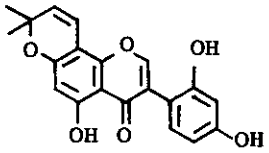
19 (carpachromene)



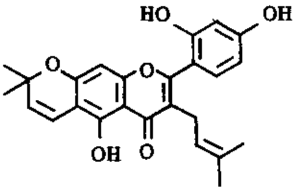
20 (atalantoflavone)



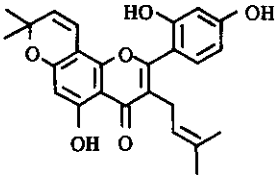
21 (parvisoflavone B)



22 (parvisoflavone A)



23 (cudraflavone B)



24 (morusin)

Figure 2

deshielding effect at the methylene protons as discussed below. In the ^{13}C nmr spectra of **13** and **14**, the chemical shifts of these prenyl groups (C-1" - C-5") show remarkable resemblance,[3] thus, the electron densities of these methylene protons may be almost same.[9] Therefore, the downfield shift of the H_2-1" signal of **14** may be caused by ring current effect. Changes in electron distribution may be detected experimentally by using ^{13}C nmr spectroscopy (160-200 ppm/π electron).[10] The C-8 carbon signal of **14** was observed at more upfield (4.06 ppm) in comparison between prenylated carbons of **14** (C-8) and **13** (C-6), therefore, the π electron density at C-8 carbon of **14** is higher (0.02-0.025 π electron) than the density at C-6 carbon of **13**. Thus, it is likely that the downfield shift of the H_2-1" signal of the 8-prenyl group is caused by the A ring current effect.

In the case of flavanone derivatives, the chemical shift of C-8 carbon of **1'** was similar with that of C-6 carbon of **2'** (nonsubstituted carbons). The chemical shift of C-6 carbon of **1'** was also similar to that of C-8 carbon of **2'** (prenylated carbons). Therefore, the π electron densities (effects of A ring current) are almost same at C-8 position of the 6-prenylated flavanone and C-6 position of the 8-prenylated flavanone as well as at C-6 position of the 6-prenylated flavanone and C-8 position of the 8-prenylated flavanone. Thus, the H_2-1" and aromatic proton signals of A rings of these 6- and 8-prenylflavanones may be observed at the same region, respectively.

2. Prenylated flavone and flavonol

The H_2-1" and H-8 signals of 6-prenylated (6-geranylated) flavones and flavonols were observed in the range of δ 3.35-3.37 and δ 6.53-6.65 (except 3-prenylflavones), respectively, as shown in Table 2. In contrast, the H-6 signals of 8-prenylated (8-geranylated) flavones and flavonols were observed in the range of δ 6.26-6.39, and the H_2-1" signals of these compounds except 3-prenylflavones appeared in the range of δ 3.52-3.58. The chemical shifts described above are sufficiently consistent to permit their use in the structure determination of 6-prenylated or 8-prenylated flavone (flavonol).

The A ring current effects for C-6 and C-8 positions of flavone and flavonol derivatives are probably similar to the effect for those of isoflavone derivatives, because the chemical shifts of C-6 and C-8 carbons are similar between these flavonoids having same substitution on A ring.[3,5] Considering the following result, the B ring current of flavone (flavonol) may cause the downfield shift of H-8 signal. The downfield shift (0.11 ppm) of H-8 signal of 6-prenylflavone (**15**)[5] was observed to compare with that of 6-prenylisoflavone (**13**). The value of the B ring current shift for the H-8 of flavones and flavonols was +0.11 ppm which given by the following equation.[11]

$\Delta\delta(\mathrm{ppm}) = \mu(1-\cos^2\theta)/r^3$ (see structure (**16**), in which $\mu = 27$, $\theta = 90°$, $r = $ ca. 6.3 Å)

The downfield shift (0.12 ppm) of the H_2-1" signal of 8-prenylflavone (**10**) compared with that of 8-prenylisoflavone (**14**) is also explained by the B ring current effect.

The prenylapigenin (**10**) isolated from Marshallia grandiflora is considered to be prenylated at C-8 position,[12] and the OH-5 signal of this compound appears at δ 13.30. By our previous ^{1}H nmr method (C-prenylation effect for OH-5),[5] the chemical shift indicates that the structure of the compound is 6-prenylapigenin (Table 1). The chemical shifts of the proton on A ring (δ 6.63) and H_2-1" signal (δ 3.37) also indicate that the structure of the compound is 6-prenylapigenin (**15**).

3. 3-Prenylflavone

Several 3-prenylated flavones have been isolated from Moraceae plant.[13] The chemical shifts of H_2-1" signal of 6-prenyl group or H-6 signal of these flavones were similar to those of 3-nonsubstituted flavones, respectively. However, the signals of H_2-1" of 8-prenyl group or H-8 of 3-prenylflavones appeared at more upfield than those of 3-nonsubstituted flavone, respectively, as described below. By comparison of H_2-1" signal (δ 3.36, 8-prenyl group) of 3,8-diprenylflavone (**17**)[14] with that of 3-nonsubstituted flavone (8-geranyl-2',4',5,7-tetrahydroxyflavone),[5] the upfield shift (0.22 ppm) of the signal of **17** was found. The chemical shift of H-6 signal (δ 6.32) of **17** was similar to that of the 3-nonsubstituted 8-geranylflavone (δ 6.33). By comparison of H-8 signal of 3,6-diprenylflavone (**18**) with that of 3-nonsubstituted flavone (6-geranyl-2',4',5,7-tetrahydroxyflavone),[5] the upfield shift (0.16 ppm) of the signal of **18** (H-8, δ 6.41)[15] was also found. The chemical shift of H_2-1" signal of 6-prenyl group (δ 3.37) of **18** was same as that of the 6-geranylflavone. The upfield shifts may be caused by B ring current, because the 3-prenyl substituent forces the B ring out-of-plane with the chromone ring (A and C rings).[16] The H-8 and H_2-1" of 8-prenyl group of the 3-prenylflavones exist above the B ring plane.

4. Pyranoflavonoid

The difference of the chemical shift was also found between the A ring protons of linear type and angular type pyranoflavones. Further, the H-4" (olefinic proton on pyran ring) signal of angular type pyranoflavone appears at more downfield than that of linear type pyranoflavone as described below. The H-8 signal of linear type pyranoflavone (**19**) was observed at δ 6.49, and H-4" signal appeared at δ 6.67. The chemical shifts of H-6 and H-4" signals of angular type pyranoflavone (**20**) have been reported at δ 6.19 and δ 6.93, respectively.[17]

In addition, the downfield shift of H-8 signal of **19** (0.08 ppm) compared with that of linear type pyranoisoflavone (**21**, H-8; δ 6.41)[18] was found as described in the case of prenylflavone. The downfield shift of H-4" signal of **20** (0.19 ppm) compared with that of angular type pyranoisoflavone (**22**, H-4"; δ 6.74)[18] was also found. In contrast, the signal of H-4" of **19** (δ 6.67) was similar to that of **21** (δ 6.69). There is not much difference between the chemical shift of H-6 signal of **20** (δ 6.19) and that of **22** (δ 6.22).

The H-8 signal of linear type 3-prenylated pyranoflavone (**23**)[19] was observed at δ 6.27, and H-4" signal of 23 appeared at δ 6.69. The H-6 and H-4" signals of angular type pyranoflavone (**24**)[20] were observed at δ 6.16 and δ 6.61, respectively. The upfield shifts of H-8 of **23** and H-4" of **24** compared with relevant signals of 3-nonsubstituted pyranoflavones (**19**, **20**) were also observed, respectively.

5. Prenyl group of C-3 and B ring

The methylene proton (H_2-9) signals of 3-prenyl groups were observed in the range of δ 3.08-3.16 (13 compounds). On the other hand, the methylene proton signals of prenyl groups on B ring of flavones and isoflavones were observed in the range of δ 3.30-3.45. The prenyl groups could be classified into following two types according to number(s) of hydroxyl group(s) at the adjacent positions. When the both *ortho*-positions to the prenyl group were replaced by hydroxyl groups, the signals of the methylene protons were observed in the range of δ 3.44-3.45. On the other hand, when one of the *ortho*-positions to the prenyl group was replaced by a hydroxyl group, and another was nonsubstituted, the signals of the methylene protons were observed in the range of δ 3.30-3.43 (Table 2).

6. Erroneous structure of pyranoflavones

The structure of pyranoflavone isolated from *Atalantia ceylanica* has been reported as linear type flavone (**19**)[21] by comparison with the synthetic carpachromene (**19**).[22] The signals of an aromatic proton on A ring and H-4" of the naturally occurring flavone appear at δ 6.15 and δ 6.89, respectively. These chemical shifts indicate that the structure of the pyranoflavone is angular structure (**20**) which has been isolated from *Atalantia racemosa* by Banerji *et al.*[17]

Artobilochromen has been isolated from *Artocarpus nobilis*, and the structure has been reported as formula (**25**).[23] Although artobilochromen is considered to be prenylated at C-3' position (di*ortho*-substituted prenyl group), the H_2-1" signal of the prenyl group appears at δ 3.16 (in acetone-d_6). The chemical shift of the compound indicates that the prenyl

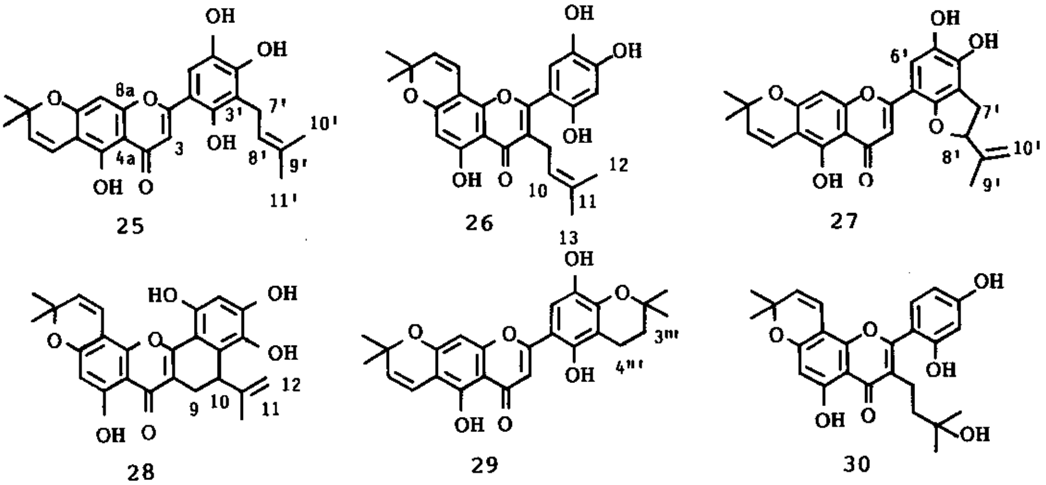


Figure 3

group exists at C-3 position. The ^{1}H and ^{13}C nmr data of artobilochromen are similar to those of artonin E[25] (KB-3,[26] **26**) obtained from *Artocarpus communis* (see Table 3). Thus, they are same compounds, and the formula (**25**) must be revised to the structure of artonin E (**26**).

(-)-Dihydrofuranoartobilochromen *a* has been also isolated from *A. nobilis* by Kumar *et al.*, and the structure of the compound was characterized as formula (**27**).[23] (±)-Dihydrofuranoartobilochromen *a* has been derived from artobilochromen by the treatment with DDQ. The spectroscopic data of (-)-dihydrofuranoartobilochromen *a* is similar to that of artobiloxanthone (**28**)[24] isolated from *A. nobilis* (see Table 3). Thus, the (-)-dihydrofuranoartobilochromen *a* is presumably (-)-artobiloxanthone.[27] Further, artobilochromen has been converted to chromanoartobilochromen *b* (**29**, isolated from the same plant) with acidic condition, thus, the structure of the compound (**29**) must be reinvestigated. The chemical shifts of A ring proton and protons of C$_5$ units of the compound (**29**) resemble those of oxydihydromorusin (**30**)[14] (Table 3). Thus, the compound (**29**) may be 3-isoprenoid substituted angular type pyranoflavone.

Table 3. ^{13}C Nmr and ^{1}H nmr data of **25–30**

C	**26**[a]	(C)	**25**[b]
2	161.6		161.4
3	119.9	(1')	120.3
4	181.8		182.4
4a	104.2		104.6
5	160.9	(7)	162.2
6	98.7	(8)	99.1
7	158.4	(8a)	158.9
8	100.4	(6)	100.7
8a	151.7	(5)	152.2
9	23.6	(7')	23.8
10	121.4	(8')	121.9
11	131.2	(9')	131.7
12	17.3	(10')	17.4
13	25.4	(11')	25.5
2"-Me	27.6		27.6
2"	78.0		78.2
3"	127.5		127.9
4"	114.1		114.6
1'	109.3	(3')	109.8
2'	148.7		149.2
3'	103.9	(3)	104.3
4'	148.5		149.0
5'	138.0		138.5
6'	116.1		116.5

	26[c]		**25**[d]
H-6	6.15 (d,J=0.7 Hz)	(H-8)	6.16 (s)
H-3"	5.66 (d,J=10 Hz)		5.67 (d,J=10 Hz)
H-4"	6.61 (dd,J=0.7 and 10 Hz)		6.65 (d,J=10 Hz)
Me-2"	1.44 (6H,s)		1.46 (s)
H-3'	6.60 (s)	(H-6')	6.60 (s)
H-6'	6.88 (s)	(H-3)	6.88 (s)
H_2-9	3.16 (br d,J=7 Hz)		3.16 (d,J=7 Hz)
H-10	5.14 (m)		5.14 (t,J=7 Hz)
Me-11	1.47 (br s)		1.46 (s)
	1.58 (br s)		1.59 (s)
OH-5	13.25 (s)		13.22 (s)

	30[e]		**29**[d]
H-6	6.16 (s)	(H-8)	6.14 (s)
H_2-9	2.50 (m)	(H_2-4"')	2.50 (m)
H_2-10	1.64 (m)	(H_2-3"')	1.70 (m)
Me-11	1.09 (s)	(Me-2"')	1.10 (s)
H-3"	5.65 (d,J=10 Hz)		5.65 (d,J=10 Hz)
H-4"	6.60 (d,J=10 Hz)		6.61 (d,J=10 Hz)
Me-2"	1.45 (s)		1.46 (s)
OH-5	13.29 (s)		13.22 (s)

	28[e]		**27**[d]
H-6	6.13 (s)	(H-8)	6.12 (s)
Me-2"	1.44 (s)		1.46 (s)
	1.47 (s)		1.48 (s)
H-3"	5.67 (d,J=10 Hz)		5.67 (d,J=10 Hz)
H-4"	6.93 (d,J=10 Hz)		6.93 (d,J=10 Hz)
H-9	2.45 (dd,J=8 and 16 Hz)	(H-7')	2.44 (dd,J=8 and 16 Hz)
	3.42 (dd,J=2 and 16 Hz)		3.44 (d,J=16 Hz)
H-10	4.01 (br d,J=8 Hz)	(H-8')	4.00 (d, J=8 Hz)
H-12	4.30 (br s)	(H-10')	4.64 (s)
	4.60 (br s)		4.66 (s)
Me-11	1.78 (br s)	(Me-9')	1.80 (s)
H-3'	6.59 (s)	(H-6')	6.60 (s)
OH-5	13.38 (s)		13.32 (s)

a: Measured in dmso-d_6, data from reference 25.
b: Measured in acetone-d_6, data from reference 24.
c: Measured in acetone-d_6, data from reference 25.
d: Measured in acetone-d_6, data from reference 23.
e: Measured in acetone-d_6.

EXPERIMENTAL

^{1}H Nmr data of the prenylated flavonoids and pyranoflavonoids isolated or prepared in our laboratory were recorded at 23 °C in acetone-d_6 (internal standard, TMS) using JEOL-NM-GX-400 or JEOL-NM-EX-400 nmr spectrometer.

REFERENCES AND NOTES

1. Part 6 in the series 'NMR Spectra of Isoprenoid Substituted Phenols.' Part 5; see reference 6.
2. In this paper, isoprenoid means prenyl (3-methyl-2-butenyl), geranyl, γ-hydroxyisoamyl, isoamyl, lavandulyl, and *p*-menthene groups.
3. T. Fukai, Q.-H. Wang, M. Takayama, and T. Nomura, *Heterocycles*, 1990, **31**, 373.
4. T. Fukai and T. Nomura, *Heterocycles*, 1990, **31**, 1861.
5. T. Fukai and T. Nomura, *Heterocycles*, 1991, **32**, 499.
6. T. Fukai and T. Nomura, *Heterocycles*, 1992, **34**, 1213.
7. Y. Shirataki, I. Yokoe, M. Endo, and M. Komatsu, *Chem. Pharm. Bull.*, 1985, **33**, 444.
8. T. Fukai, Q.-H. Wang, and T. Nomura, *Heterocycles*, 1989, **29**, 1369.
9. The similarity of the chemical shifts indicates that the electron densities of these methylene carbons are almost same as well as those of C-2" - C-5" (reference 10). Therefore, it is likely that the electron densities of these methylene protons are almost same.
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