REVISED STRUCTURES OF ALBANINS D AND E, GERANYLATED FLAVONES FROM MORUS ALBA[1]

Toshio Fukai and Taro Nomura*
Faculty of Pharmaceutical Sciences, Toho University,
2-2-1, Miyama, Funabashi, Chiba 274, Japan

Abstract ---- The chemical shifts of the proton signals of the hydrogen-bonded hydroxyl groups of albanins D and E, isolated from Morus alba L. (Moraceae), were compared with those of the hydroxyl groups of 6- or 8-isoprenoid substituted flavones to doubt the location of the geranyl groups of albanins D and E. The proposed structures (3) and (**4**) for albanins D and E were revised to the structures (**1**) and (**2**), respectively, on the basis of the syntheses of 6-geranylated flavones (**1** and **2**) and 8-geranylated flavones (3 and **4**).

In the previous papers,[2,3] we reported that the chemical shifts of hydrogen-bonded hydroxyl groups of 6-isoprenoid substituted flavanones and isoflavones appeared more downfield than those of 6-nonsubstituted flavanones and isoflavones, respectively. In this paper, we report the observation on the chemical shifts of the hydrogen-bonded hydroxyl groups at the C-5 position of the 6- or 8-isoprenoid substituted flavones, and also describe the revision of the proposed structures (3 and **4**) for albanins D and E isolated from Morus alba L.[4,5]

We examined the ^{1}H nmr spectra (in acetone-d_6) of 19 kinds of the known 6- or 8-isoprenoid substituted flavones. The hydrogen-bonded hydroxyl groups of the 6-prenylated flavones were observed in the range of δ13.18 - 13.43, while the chemical shifts of hydroxyl groups of the 8-prenylated or geranylated flavones were classified into the two groups: 1) δ12.84 - 13.15 (data from the four compounds), 2) δ13.25 - 13.32 (albanins D and E from M. alba) (Table 1). In the case of pyranoflavones, the hydrogen-bonded hydroxyl groups of the angular type flavones were observed in the range of δ12.98 - 13.29, while the relevant proton signals of the linear type flavones in the range of δ13.26 - 13.57 (Table 2).

Table 1. Chemical shifts of 5-OH in acetone-d_6 at 23°C (400 MHz)

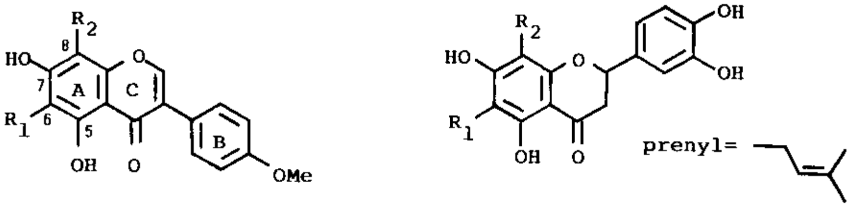
trivial name	chemical shift of 5-OH	prenylation shift**	isoprenoid group on A-ring	OH positions	others	ref.
albanin A	13.16		none	5,7,2',4'	3-prenyl	5
cudraflavone C	13.43[a]	-0.27	6-prenyl	5,7,2',4'	3-prenyl	13
kuwanon C	13.09	+0.07	8-prenyl	5,7,2',4'	3-prenyl	14
chrysin	12.91		none	5,7		15
no name	13.18[b]	-0.27	6-prenyl	5,7		16
no name	12.84[c]	+0.07	8-prenyl	5,7		16
kuwanon S	13.04		none	5,7,4'	3'-geranyl	14
gancaonin Q	13.31[d]	-0.27	6-prenyl	5,7,4'	3'-prenyl	17
gancaonin O	13.28		6-prenyl	5,7,3',4'		2
cudraflavone D	13.37		6-prenyl	5,7,2',4'	5'-prenyl	13
canniflavin B*	13.30		6-prenyl	5,7,4'	3'-OMe	18
canniflavone-1*	13.28		6-prenyl	5,7,4'	3'-OMe	19
brosimone H*	13.15		8-geranyl	5,2',4'	3-prenyl,7-OMe	7
apigenin (**5**)	13.02		none	5,7,4'		15
albanin D	13.25[e]	-0.23	(8-geranyl)	5,7,4'		5,6
licoflavone B[§]	13.28	-0.26	6-prenyl	5,7,4'		20,21
norartocarpetin (**6**)	13.15		none	5,7,2',4'		22
albanin E[+,*]	13.32	-0.17	(8-geranyl)	5,7,2',4'		5,6
albanin E[#]	13.09	+0.06	8-geranyl	5,7,2',4'		7,8

**: Induced shift by prenylation (geranylation) at C-6 or C-8 position. a: δ13.29 (90 MHz, 35°C). b: δ13.04 (90 MHz, 35°C). c: δ12.69 (90 MHz, 35°C). d: δ13.17 (90 MHz, 35°C). e: δ13.12 (100 MHz, ref. 6) *: Data from corresponding reference. §: isolated from Artocarpus venenosa (ref. 21), +: isolated from M. alba. (measured in DMSO-d_6-acetone-d_6=1:2). #: isolated from B. oblongifolia (courtesy of F. Ferrari).

Table 2. Chemichal shifts of 5-OH of pyranoflavone in acetone-d_6 at 23°C (400 MHz)

trivial name	chemical shift of 5-OH	shift value*	structure of A- and D-ring	OH positions	others	ref.
morusin (**12**)	13.25[a]	-0.09	angular	5,2',4'	3-prenyl	14
cudraflavone B (**13**)	13.57	-0.41	linear	5,2',4'	3-prenyl	14
brosimone G[§]	13.25	-0.09	angular	5,2',4'	5"-C-prenyl	7
oxydihydro-morusin (**14**)	13.29[b]		angular	5,2',4'	3-(3"-OH)-isoamyl	14
cyclomorusin (**15**)	12.98		angular	5,4'		14
cudraflavone A (**16**)	13.26[c]		linear	5,4'		14

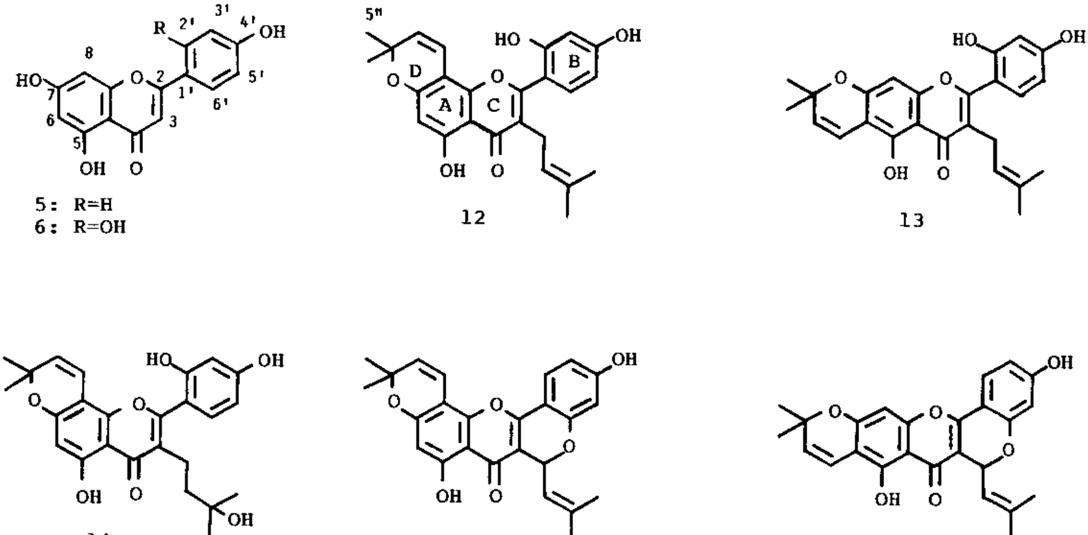
*: Difference of chemical shifts between the pyranoflavone and albanin A. §: Data from corresponding reference. a: δ13.20 (90 MHz, 35°C). b: δ13.24 (90 MHz, 35°C). c: δ13.21 (400 MHz, 50°C).



	5-OH		5-OH
R_1=R_2=H (biochanin A)	δ13.01	R_1=R_2=H (eriodictyol)	δ12.18
R_1=prenyl, R_2=H (gancaonin A)	δ13.29 (-0.28 ppm)*	R_1=prenyl, R_2=H	δ12.47 (-0.29 ppm)*
R_1=H, R_2=prenyl (gancaonin M)	δ12.95 (+0.06 ppm)*	R_1=H, R_2=prenyl	δ12.14 (+0.04 ppm)*

Figure 1. Chemichal Shifts of 5-OH proton of isoflavones and flavanones.

*: Induced shift by prenylation at 6- or 8-position.



5: R=H
6: R=OH

12

13

14

15

16

Figure 2.

On the other hand, the chemical shifts of hydrogen-bonded hydroxyl groups at the C-5 position of isoflavones and flavanones show the remarkable downfield shift (ca. -0.3 ppm) by prenylation at the C-6 position, while those of the hydroxyl groups show the slight upfield shift (ca. +0.05 ppm) by prenylation at the C-8 position (Figure 1).[2,3] In the case of some flavones, the similar shifts were observed by prenylation at the C-8 or C-6 positions (Table 1). In comparison between the chemical shifts of the hydroxyl groups of apigenin (**5**) and albanin D, the remarkable downfield shift (-0.23 ppm) were observed. The similar downfield shift (-0.17 ppm) was observed by comparing norartocarpetin (**6**) with albanin E (Table 1). The above downfield shift values (-0.23 and -0.17 ppm) are inconsistent with the slight upfield shift value (ca. +0.05 ppm) observed in some flavones prenylated at the C-8 position. To elucidate the inconsistency we synthesized 8-geranylapigenin (**3**) and its 6-isomer (**1**) as well as 8-geranylnorartocarpetin (**4**) and its 6-isomer (**2**) (Scheme 1). The location of the geranyl groups in the structures (**1**, **2**, **3**, and **4**) was confirmed by the ^{13}C nmr spectra (gated decoupling with NOE) and long-range selective proton decoupling (LSPD) experiment (Table 3). The synthetic flavones were identified with albanins D and E on the fact that the physical and spectral data (melting points, uv and ^{1}H nmr spectra) of synthesized flavones **1** and **2** were in agreement with the relevant data of albanins D and E,[6] respectively. From the above results, the proposed structures (**3**) and (**4**) for albanins D and E isolated from M. alba should be revised to the structures (**1**) and (**2**), respectively.

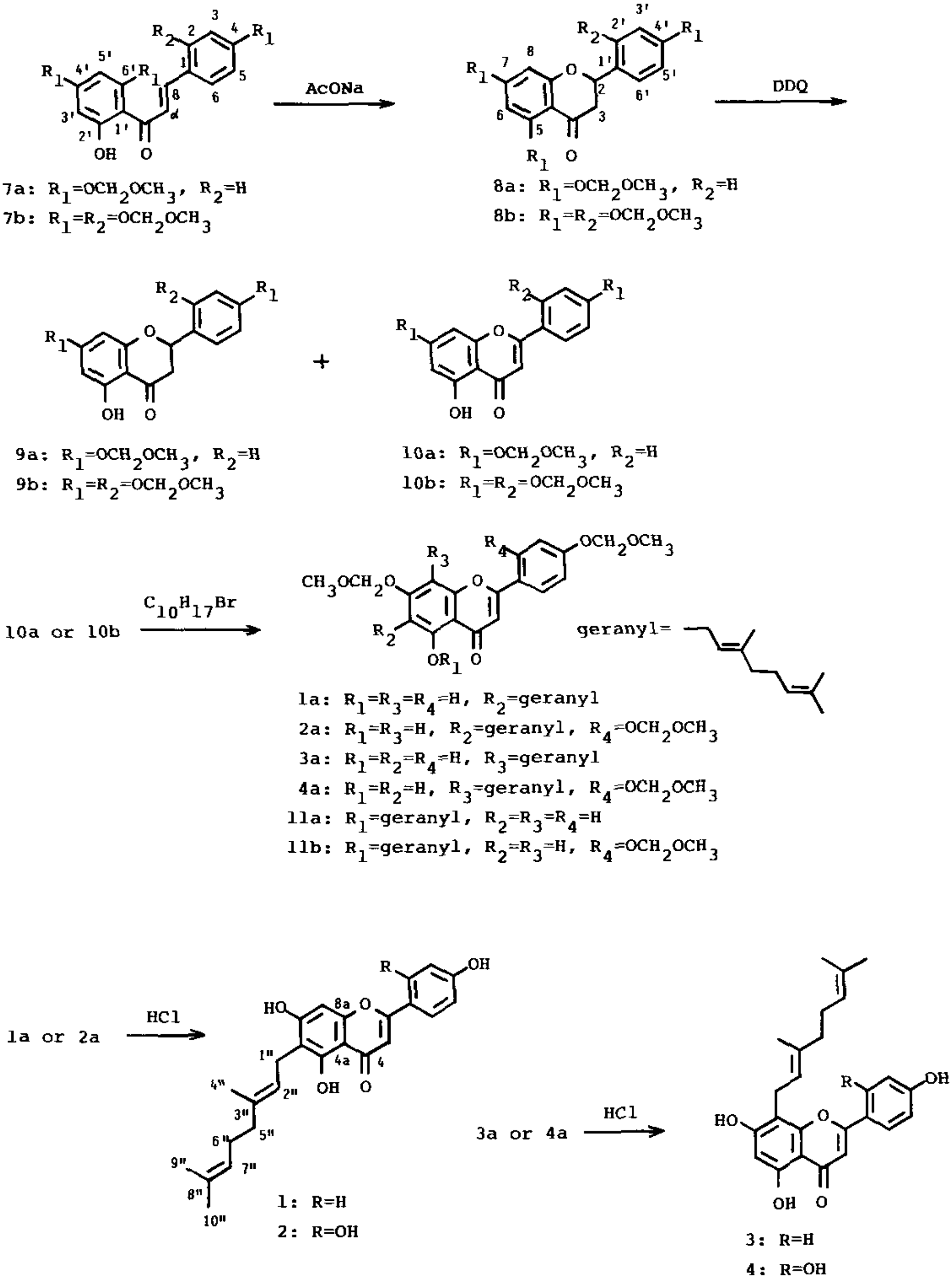
On the other hand, Ferrari et al. reported the isolation of 8-geranylnorartocarpetin from Brosimopsis oblongifolia (Moraceae) and described as "albanin E".[7] Albanin E from B. oblongifolia was identical with the synthetic **4** in comparison of the ^{1}H nmr spectra and tlc analysis.[8] As the structure of albanin E from M. alba was revised, the trivial name "albanin E" for the flavone isolated from B. oblongifolia should be changed to the other one.

EXPERIMENTAL

Abbreviations; s = singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet, br = broad. The general procedures and the instruments used are described in our previous papers.[3,9]

5,7,4'-Tris(methoxymethoxy)flavanone (8a)

A mixture of 2'-hydroxy-4,4',6'-tris(methoxymethoxy)chalcone (7a, 1 g, 2.5 mmol)[10] and sodium


AcONa
DDQ
7a: R1=OCH2OCH3, R2=H
7b: R1=R2=OCH2OCH3
8a: R1=OCH2OCH3, R2=H
8b: R1=R2=OCH2OCH3
+
9a: R1=OCH2OCH3, R2=H
9b: R1=R2=OCH2OCH3
10a: R1=OCH2OCH3, R2=H
10b: R1=R2=OCH2OCH3
10a or 10b
C10H17Br
geranyl=
1a: R1=R3=R4=H, R2=geranyl
2a: R1=R3=H, R2=geranyl, R4=OCH2OCH3
3a: R1=R2=R4=H, R3=geranyl
4a: R1=R2=H, R3=geranyl, R4=OCH2OCH3
11a: R1=geranyl, R2=R3=R4=H
11b: R1=geranyl, R2=R3=H, R4=OCH2OCH3
1a or 2a
HCl
1: R=H
2: R=OH
3a or 4a
HCl
3: R=H
4: R=OH

Scheme 1.

Table 3. ^{13}C Nmr data of synthetic flavones (**1** - **4**) in acetone-d_6 (100.4 MHz)§

C	**1**	**3**
2	164.79 (Sdt, ^{2}J=4, ^{3}J=6 Hz)*	165.07 (br S)
3	104.04 (D, ^{1}J=167 Hz)	103.89 (D, ^{1}J=168 Hz)
4	183.13 (S)	183.45 (S)
4a	105.24 (Sm)	105.41 (Sm)
5	160.21 (Std, $^{2}J_{5OH-C5}$=$^{3}J_{H1''-C5}$=4 Hz)	161.01 (St, ^{2}J=^{3}J=4 Hz)
6	112.39 (Sm)	99.36 (Dd, ^{1}J=160, $^{3}J_{5OH-C6}$=7 Hz)
7	162.44 (Std, ^{3}J=4, ^{2}J=2 Hz)	162.25 (br S)
8	94.10 (D, ^{1}J=164 Hz)	107.47 (br S)
8a	156.56 (Sd, ^{2}J=4 Hz)	156.08 (St, $^{3}J_{H1''-C8a}$=4 Hz)
1'	123.43 (Std, ^{3}J=8 and 3 Hz)	123.66 (Sm)
2',6'	129.14 (Dd, ^{1}=161, ^{3}J=7 Hz)	129.26 (Dd, ^{1}J=161, ^{3}J=7 Hz)
3',5'	116.84 (Dd, ^{1}J=162, ^{3}J=4 Hz)	116.89 (Dd, ^{1}J=161, ^{3}J=4 Hz)
4'	161.79 (Stt, ^{3}J=10, ^{2}J=4 Hz)	161.94 (Stt, ^{3}J=9, ^{2}J=2 Hz)
1"	21.95 (Td, ^{1}J=124, ^{2}J=4 Hz)	22.28 (Td, ^{1}J=129, ^{2}J=4 Hz)
2"	123.16 (Dm, ^{1}J=*ca.* 150 Hz)	123.62 (Dm, overlapped with C7")
3"	135.34 (Sm)	135.74 (br S)
4"	16.27 (Qm, ^{1}J=*ca.* 125 Hz)	16.55 (Qm, ^{1}J=*ca.* 124 Hz)
5"	40.52 (Tm, ^{1}J=*ca.* 125 Hz)	40.35 (Tm, ^{1}J=*ca.* 125 Hz)
6"	27.41 (Tm, ^{1}J=*ca.* 125 Hz)	27.33 (Tm, ^{1}J=*ca.* 126 Hz)
7"	125.15 (Dm, ^{1}J=*ca.* 150 Hz)	125.02 (Dm, overlapped with C2")
8"	131.56 (Sm)	131.66 (br S)
9"	17.69 (Qm, ^{1}J=*ca.* 125 Hz)	17.66 (Qm, ^{1}J=*ca.* 124 Hz)
10"	25.79 (Qm, ^{1}J=*ca.* 124 Hz)	25.73 (Qm, ^{1}J=*ca.* 124 Hz)

C	**2**	**4**
2	162.61 (St, ^{2}J=^{3}J=4 Hz)	162.82 (St, ^{2}J=^{3}J=4 Hz)
3	108.59 (D, ^{1}J=170 Hz)	108.44 (D, ^{1}J=166 Hz)
4	183.51 (S)	183.81 (S)
4a	105.13 (S, overlapped with C3')	105.38 (Sm)
5	160.18 (Std, $^{2}J_{5OH-C5}$=$^{3}J_{H1''-C5}$=4 Hz)	161.00 (St, ^{2}J=^{3}J=4 Hz)
6	112.05 (Sm)	99.06 (Dd, ^{1}J=160, $^{3}J_{5OH-C6}$=6 Hz)
7	162.34 (Sm, overlapped with C4')	161.96 (Sm)
8	93.89 (D, ^{1}J=163 Hz)	107.23 (Sm)
8a	156.65 (Sd, ^{2}J=4 Hz)	156.21 (St, $^{3}J_{H1''-C8a}$=4 Hz)
1'	110.97 (Sm)	111.26 (Sdd, J=4 and 6 Hz)
2'	159.19 (Sdd, ^{2}J=3, ^{3}J=10 Hz)	159.23 (Sdd, ^{2}J=3, ^{3}J=10 Hz)
3'	104.39 (Dd, ^{1}J=158, ^{3}J=5 Hz)	104.41 (Dd, ^{1}J=158, ^{3}J=4 Hz)
4'	162.43 (Sm, overlapped with C7)	162.45 (Std, ^{2}J=3, ^{3}J=10 Hz)
5'	109.09 (Dd, ^{1}J=160, ^{3}J=5 Hz)	109.13 (Dd, ^{1}J=164, ^{3}J=5 Hz)
6'	130.86 (D, ^{1}J=160 Hz)	131.02 (D, ^{1}J=161 Hz)
1"	21.94 (Td, ^{1}J=128, ^{2}J=4 Hz)	22.30 (Td, ^{1}J=128, ^{2}J=4 Hz)
2"	123.30 (Dm, ^{1}J=*ca.* 150 Hz)	123.72 (Dm, ^{1}J=*ca.* 145 Hz)
3"	135.24 (Sm)	135.69 (Sm)
4"	16.26 (Qm, ^{1}J=*ca.* 125 Hz)	16.52 (Qm, ^{1}J=*ca.* 125 Hz)
5"	40.53 (Tm, ^{1}J=*ca.* 125 Hz)	40.39 (Tm, ^{1}J=*ca.* 125 Hz)
6"	27.44 (Tm, ^{1}J=*ca.* 125 Hz)	27.37 (Qm, ^{1}J=*ca.* 125 Hz)
7"	125.17 (Dm, ^{1}J=*ca.* 150 Hz)	125.07 (Dm, ^{1}J=*ca.* 145 Hz)
8"	131.56 (Sm)	131.66 (Sm)
9"	17.69 (Qm, ^{1}J=*ca.* 125 Hz)	17.68 (Qm, ^{1}J=*ca.* 125 Hz)
10"	25.79 (Qm, ^{1}J=*ca.* 125 Hz)	25.75 (Qm, ^{1}J=*ca.* 125 Hz)

§: The following results were observed with the LSPD experiments by irradiation of the 5-OH proton, **1**; C4a (Sm ⟶ St, ^{3}J=4 Hz), C5 (Std ⟶ St, $^{3}J_{H1''-C5}$=4 Hz), C6 (changed), **2**; C5 (Std ⟶ St, $^{3}J_{H1''-C5}$=4 Hz), C6 (changed), **3**; C4a (Sm ⟶ St, ^{3}J=4 Hz), C5 (St ⟶ Sd, $^{2}J_{H6-C5}$=4 Hz), C6 (Dd ⟶ D, ^{1}J=160 Hz), **4**; C4a (Sm ⟶ St, ^{3}J=4 Hz), C5 (St ⟶ Sd, $^{2}J_{H6-C5}$=4 Hz), C6 (Dd ⟶ D, ^{1}J=160 Hz).

*: Capital letters refer to pattern resulting from directly bonded proton(s) and lower case letters to long-range ^{13}C-^{1}H coupling.

acetate (1.7 g, 20.7 mmol) in methanol (20 ml) was refluxed for 2 h, and then treated as usual. The reaction product was chromatographed on silica gel with benzene containing increasing amount of acetone as an eluent to give **8a** (580 mg, 58%). Compound (**8a**) showed the following data: mp 102°C (colorless prisms, crystallized from *n*-hexane). Anal. Calcd for $C_{21}H_{24}O_8$: C, 62.37; H, 5.98. Found: C, 62.60; H, 6.03. EI-Ms, *m/z* (rel. int.): 405 $[M+1]^+$ (2%), 404 $[M]^+$ (8), 389 (6), 373 (5), 359 (10), 331 (5), 240 (6), 195 (10), 164 (12), 45 (100). ^{1}H Nmr ($CDCl_3$, 90 MHz): δ 2.73 (1H, dd, J = 4 and 16.5 Hz, C-3-H), 3.03 (1H, dd, J = 12 and 16.5 Hz, C-3-H), 3.48 (6H, s, $OCH_2OC\underline{H}_3$x2), 3.54 (3H, s, $OCH_2OC\underline{H}_3$), 5.15, 5.18, 5.27 (each 2H, s, $OC\underline{H}_2OCH_3$), 5.35 (1H, dd, J = 4 and 12 Hz, C-2-H), 6.35, 6.43 (each 1H, d, J = 2 Hz, C-6-H or C-8-H), 7.05 (2H, d, J = 9 Hz, C-3'-H and C-5'-H), 7.37 (2H, d, J = 9 Hz, C-2'-H and C-6'-H).

7,4'-Dimethoxymethylapigenin (10a)

A mixture of **8a** (624 mg, 1.5 mmol), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ, 360 mg, 1.6 mmol) and dry dioxane (0.5 ml) in dry benzene (10 ml) was refluxed for 5 h, and then treated as usual. The reaction product was chromatographed on silica gel with benzene as an eluent to give 7,4'-bis(methoxymethoxy)-5-hydroxyflavanone (**9a**, 75 mg, 13.5%) and **10a** (260 mg, 47%). Compound (**9a**) showed the following data: mp 88 - 89°C (colorless prisms, crystallized from methanol). $FeCl_3$ test: reddish brown. EI-Ms, *m/z* (rel. int.): 361 $[M+1]^+$ (17%), 360 $[M]^+$ (76), 329 (4), 315 (7), 254 (5), 241 (4), 223 (9), 196 (4), 182 (3), 164 (10), 151 (38), 147 (11), 121 (4), 45 (100). HR-Ms, *m/z*: 360.1196 $[M]^+$ ($C_{19}H_{20}O_7$ requires: 360.1209). ^{1}H Nmr ($CDCl_3$, 90 MHz): δ2.75 (1H, dd, J = 3.5 and 17 Hz, C-3-H), 3.09 (1H, dd, J = 12 and 17 Hz, C-3-H), 3.43, 3.47 (each 3H, s, $OCH_2OC\underline{H}_3$), 5.13, 5.17 (each 2H, s, $OC\underline{H}_2OCH_3$), 5.34 (1H, dd, J = 3.5 and 12 Hz, C-2-H), 6.15 (2H, s, C-6-H and C-8-H), 7.05 (2H, d, J = 9 Hz, C-3'-H and C-5'-H), 7.35 (2H, d, J = 9 Hz, C-2'-H and C-6'-H), 11.83 (1H, s, C-5-OH). Compound (**10a**) showed the following data: mp 152 - 153°C (pale yellow needles, crystallized from methanol). Anal. Calcd for $C_{19}H_{18}O_7$: C, 63.68; H, 5.09. Found: C, 63.27; H, 5.07. EI-Ms, *m/z* (rel. int.): 359 $[M+1]^+$ (10%), 358 $[M]^+$ (49), 343 (3), 327 (5), 326 (7), 45 (100). ^{1}H Nmr ($CDCl_3$, 90 MHz): δ 3.50 (6H, s, $OCH_2OC\underline{H}_3$x2), 5.23 (4H, s, $OC\underline{H}_2OCH_3$x2), 6.43 (1H, d, J = 2 Hz, C-6-H), 6.54 (1H, s, C-3-H), 6.62 (1H, d, J = 2 Hz, C-8-H), 7.11 (2H, d, J = 9 Hz, C-3'-H and C-5'-H), 7.78 (2H, d, J = 9 Hz, C-2'-H and C-6'-H), 12.62 (1H, s, C-5-OH).

Preparation of 8-geranylapigenin (3) and 6-geranylapigenin (1) from 10a

A mixture of **10a** (267 mg, 0.8 mmol), geranyl bromide (0.5 ml, 2.3 mmol), and KOH (0.3 g, 5.4 mmol) in methanol (50 ml) was allowed to stand for 4 h. After treated as usual, the reaction product was purified by preparative tlc (silica gel, solvent system: *n*-hexane-acetone=4:1, $CHCl_3$ only) to give 7,4'-dimethoxymethyl-8-geranylapigenin (**3a**, 9 mg, 2.4%), 7,4'-dimethoxymethyl-6-geranylapigenin (**1a**, 9 mg, 2.4%), 7,4'-dimethoxymethyl-5-*O*-geranylapigenin (**11a**, 18 mg, 5%), and starting material (**10a**, 120 mg, 45%). A mixture of **1a** (9 mg) and 3N HCl (0.5 ml) in methanol (5 ml) was refluxed for 15 min. The mixture was diluted with water (20 ml) and treated as usual. The reaction product was purified by preparative tlc (silica gel, benzene-acetone=5:1) to give **1** (3 mg, 41%). A mixture of **3a** (9 mg) and 3N HCl (0.5 ml) in methanol (5 ml) was refluxed for 15 min. The mixture was diluted with water (20 ml) and treated as usual. The reaction product was purified by preparative tlc (silica gel, benzene-acetone=5:1) to give **3** (5 mg, 68%). Compound (**3a**) showed the following data: mp 117 - 118°C (pale yellow needles, crystallized from methanol). $FeCl_3$ test: greenish brown. Gibbs test: negative. EI-Ms, *m/z* (rel. int.): 495 $[M+1]^+$ (7%), 494 $[M]^+$ (23), 449 (4), 425 (5), 393 (8), 381 (4), 371 (15), 358 (10), 339 (6), 327 (9), 45 (100). HR-Ms, *m/z*: 494.2296 $[M]^+$ ($C_{29}H_{34}O_7$ requires: 494.2304). ^{1}H Nmr ($CDCl_3$, 90 MHz): δ 1.52, 1.61 (each 3H, br s, C-8"-CH_3), 1.82 (3H, br s, C-3"-CH_3), 2.00 (4H, br s, C-5"-Hx2 and C-6"-Hx2), 3.51 (6H, s, $OCH_2OC\underline{H}_3$x2), 3.57 (2H, br d, J = 7 Hz, C-1"-Hx2), 5.0 - 5.3 (2H, m, C-2"-H and C-7"-H), 5.27 (4H, s, $OC\underline{H}_2OCH_3$x2), 6.58 (1H, br s, C-6-H), 6.59 (1H, s, C-3-H), 7.14 (2H, d, J = 9 Hz, C-3'-H and C-5'-H), 7.84 (2H, d, J = 9 Hz, C-2'-H and C-6'-H), 12.64 (1H, s, C-5-OH). Compound (**1a**) showed the following data: mp 85 - 87°C (pale yellow needles, crystallized from methanol). $FeCl_3$ test: green. Gibbs test: positive (navy blue). EI-Ms, *m/z* (rel. int.): 495 $[M+1]^+$ (10%), 494 $[M]^+$ (29), 479 (3), 449 (4), 425 (25), 393 (8), 383 (15), 371 (69), 327 (11), 283 (6), 45 (100). HR-Ms, *m/z* 494.2310 $[M]^+$ ($C_{29}H_{34}O_7$ requires: 494.2304). ^{1}H Nmr ($CDCl_3$, 90 MHz): δ 1.58, 1.64 (each 3H, br s, C-8"-CH_3), 1.81 (3H, br s, C-3"-CH_3), 2.00 (4H, br s, C-5"-Hx2 and C-6"-Hx2), 3.41 (2H, br d, J = 7 Hz, C-1"-Hx2), 3.50 (6H, s, $OCH_2OC\underline{H}_3$x2), 5.1 - 5.3 (2H, m, C-2"-H and C-7"-H), 5.24, 5.30 (each 2H, s, $OC\underline{H}_2OCH_3$), 6.57 (1H, s, C-3-H), 6.72 (1H, br s, C-8-H), 7.12 (2H, d, J = 9 Hz, C-3'-H and C-5'-H), 7.83 (2H, d, J = 9 Hz, C-2'-H and C-6'-H), 12.79 (1H, s, C-5-OH). Compound (**11a**) was obtained as a yellow oil and showed the following data. $FeCl_3$ test: negative. EI-Ms, *m/z* (rel. int.): 495 $[M+1]^+$ (4%), 494 $[M]^+$ (13), 479 (2), 449 (3), 426 (3), 425 (9), 412 (10), 393 (3), 371 (7), 367 (15), 359 (13), 358 (45), 327 (7), 326 (7), 69 (13), 45 (100). HR-Ms, *m/z* 494.2309 $[M]^+$ ($C_{29}H_{34}O_7$ requires: 494.2304). ^{1}H Nmr ($CDCl_3$, 90 MHz): δ 1.60, 1.67 (each 3H, br s, C-8"-CH_3), 1.77 (3H, br s, C-3"-CH_3), 2.18 (4H, br s, C-5"-Hx2 and C-6"-Hx2), 3.49, 3.52 (each 3H, s, $OCH_2OC\underline{H}_3$), 4.75 (2H, br d, J = 6.5 Hz, C-1"-Hx2), 5.0 - 5.25 (1H, m, C-7"-H), 5.25 (4H, s, $OC\underline{H}_2OCH_3$x2), 5.58 (1H, br t, J = 6.5 Hz, C-2"-H), 6.46 (1H, d, J = 2 Hz, C-6-H), 6.55 (1H, s, C-3-H), 6.74 (1H, d, J = 2 Hz, C-8-H), 7.11 (2H, d, J = 9 Hz, C-3'-H and C-5'-H), 7.81 (2H, d, J = 9 Hz, C-2'-H and C-6'-H). Compound (**3**) showed the following data: mp 147 - 150°C (pale yellow prisms, crystallized from acetone). $FeCl_3$ test: olive. Gibbs test: negative. EI-Ms, *m/z* (rel. int.): 407 $[M+1]^+$ (17%), 406 $[M]^+$ (60), 349 (6), 337 (80), 323 (21), 321 (16), 309 (8), 295 (18), 283 (100), 270 (29), 254 (2), 219 (10), 165 (17). HR-Ms, *m/z* 406.1785 ($C_{25}H_{26}O_5$ requires: 406.1780). Uv λ_{max}^{EtOH} nm (log ε): 205 (4.06), 220 (sh 3.93), 274 (3.75), 300 (3.64), 325 (3.67), 360 (infl. 3.46). Uv $\lambda_{max}^{EtOH+AlCl_3}$: 230 (sh 3.96), 282 (3.74), 308 (3.74), 346 (3.74), 395 (4.44). ^{1}H Nmr (acetone-d_6, 400 MHz): δ 1.49 (3H, br d, J = 0.7 Hz, C-8"-CH_3), 1.55 (3H, br d, J = 1 Hz, C-8"-CH_3), 1.84 (3H, br d, J = 1 Hz, C-3"-CH_3), 1.89 - 2.10 (4H, m, C-5"-Hx2 and C-6"-Hx2), 3.58 (2H, br d, J = 7 Hz, C-1"-Hx2), 5.03 (1H, br t, J = 7 Hz, C-7"-H), 5.32 (1H, br t, J = 7 Hz, C-2"-H), 6.35 (1H, br s, C-6-H), 6.64 (1H, s, C-3-H), 7.05 (2H, d, J = 9 Hz, C-3'-H and C-5'-H), 7.97 (2H, d, J = 9 Hz, C-2'-H and C-6'-H), 9.50 (2H, br s, OHx2), 12.97 (1H, s, C-5-OH). Compound (**1**) showed the following data: mp 205 - 207°C (pale yellow prisms, crystallized from acetone). $FeCl_3$ test: dark green. Gibbs test: positive. EI-Ms, *m/z* (rel. int.): 407 $[M+1]^+$ (12%), 406 $[M]^+$ (41), 363 (7), 349 (2), 337 (100), 323 (7), 322 (6), 321 (12), 309 (8), 295 (20), 284 (43), 283 (93), 270 (7), 254 (1), 165 (10). HR-Ms, *m/z* 406.1787 $[M]^+$ ($C_{25}H_{26}O_5$ requires: 406.1780). Uv λ_{max}^{EtOH} nm (log ε): 205 (4.13), 217 (4.17), 255 (sh 3.65), 275 (3.89), 305 (3.76), 335 (3.96). Uv $\lambda_{max}^{EtOH+AlCl_3}$: 205 (4.18), 219 (4.12), 260 (3.61), 285 (sh 3.86), 304 (3.89), 354 (3.97), 390 (sh 3.69). ^{1}H Nmr (acetone-d_6, 400 MHz): δ 1.55 (3H, br d, J = 0.5 Hz, C-8"-CH_3), 1.60 (3H, br d, J = 1 Hz, C-8"-CH_3), 1.80 (3H, br d, J = 1 Hz, C-3"-CH_3), 1.94 - 2.10 (4H, m, C-5"-Hx2 and C-6"-Hx2), 3.37 (2H, br d, J = 7 Hz, C-1"-Hx2), 5.08 (1H, br t, J = 7 Hz, C-7"-H), 5.33 (1H, br t, J = 7 Hz, C-2"-H), 6.61 (1H, br s, C-8-H), 6.62 (1H, s, C-3-H), 7.02 (2H, d, J = 9 Hz, C-3'-H and C-5'-H), 7.91 (2H, d, J = 9 Hz, C-2'-H and C-6'-H), 9.44 (2H, br s, OHx2), 13.29 (1H, s, C-5-OH).

2'-Hydroxy-2,4,4',6'-tetrakis(methoxymethoxy)chalcone (7b)

A mixture of 2',4'-bis(methoxymethoxy)-6'-hydroxyacetophenone (1.1 g, 4.3 mmol),[11] 2,4-bis(methoxymethoxy)benzaldehyde (1.7 g, 7.5 mmol),[12] and KOH (2 g, 35.7 mmol) in methanol (5 ml) was allowed to stand for 3 h. The mixture was diluted with water (30 ml), neutralized with acetic acid, and treated as usual. The reaction product was chromatographed on silica gel with benzene containing increasing amount of acetone as an eluent to give **7b** (1.6 g, 80%). Compound (**7b**) showed the following data: mp 95 - 96°C (yellow needles, crystallized from methanol). $FeCl_3$ test: olive. Anal. Calcd for $C_{23}H_{28}O_{10}$: C, 59.48; H, 6.08. Found: C, 59.34; H, 6.10. EI-Ms, *m/z* (rel. int.): 465 $[M+1]^+$ (4%), 464 $[M]^+$ (16), 419 (13), 402 (11), 387 (12), 241 (8), 197 (10), 45 (100). ^1H Nmr ($CDCl_3$, 90 MHz): δ 3.48, 3.51 (each 6H, s, $OCH_2OC\underline{H}_3$x2), 5.18, 5.25 (each 4H, s, $OC\underline{H}_2OCH_3$x2), 6.20, 6.28 (each 1H, d, J = 2 Hz, C-3'-H or C-5'-H), 7.52 (1H, d, J = 8 Hz, C-6-H), 7.70 (1H, dd, J = 2 and 8 Hz, C-5-H), 7.82 (1H, d, J = 15 Hz, C-α-H), 7.84 (1H, d, J = 2 Hz, C-3-H), 8.15 (1H, d, J = 15 Hz, C-ß-H), 13.79 (1H, s, C-2'-OH).

5,7,2',4'-Tetrakis(methoxymethoxy)flavanone (**8b**)

A mixture of **7b** (0.9 g, 1.9 mmol) and sodium acetate (1.6 g, 19.5 mmol) in methanol (20 ml) was refluxed for 6 h, and treated as usual. The reaction product was chromatographed on silica gel with benzene containing increasing amount of acetone as an eluent to give **8b** (263 mg, 29%). Compound (**8b**) showed the following data: mp 95 - 96°C (colorless needles, crystallized from acetone). $FeCl_3$ test: negative. Anal. Calcd for $C_{23}H_{28}O_{10}$: C, 59.48; H, 6.08. Found: C, 59.34; H, 6.10. EI-Ms, *m/z* (rel. int.): 465 $[M+1]^+$ (2%), 464 $[M]^+$ (8), 419 (15), 402 (17), 387 (9), 241 (6), 224 (5), 179 (7), 45 (100). ^1H Nmr ($CDCl_3$, 90 MHz): δ 2.75 (1H, dd, J = 5 and 16 Hz, C-3-H), 3.03 (1H, dd, J = 13 and 16 Hz, C-3-H), 3.48 (9H, s, $OCH_2OC\underline{H}_3$x3), 3.55 (3H, s, $OCH_2OC\underline{H}_3$), 5.17 (6H, s, $OC\underline{H}_2OCH_3$x3), 5.27 (2H, s, $OC\underline{H}_2OCH_3$), 5.72 (1H, dd, J = 5 and 13 Hz, C-2-H), 6.37, 6.42 (each 1H, d, J = 2 Hz, C-6-H or C-8-H), 6.75 (1H, dd, J = 2.5 and 9 Hz, C-5'-H), 6.83 (1H, d, J = 2.5 Hz, C-3'-H), 7.45 (1H, d, J = 9 Hz, C-6'-H).

7,2',4'-Trimethoxymethylnorartocarpetin (**10b**)

A mixture of **8b** (1.8 g, 3.9 mmol), DDQ (710 mg, 3.1 mmol), and dry dioxane (1 ml) in dry benzene (20 ml) was refluxed for 5 h, and treated as usual. The reaction product was chromatographed on silica gel with benzene as an eluent to give 5-hydroxy-7,2',4'-tris(methoxymethoxy)flavanone (**9b**, 318 mg, 20%) and **10b** (695 mg, 43%). Compound (**9b**) showed the following data: mp 69 - 70°C (colorless needles, crystallized from methanol). $FeCl_3$ test: reddish violet. Anal. Calcd for $C_{21}H_{24}O_9 \cdot \frac{1}{2}H_2O$: C, 58.74; H, 5.87. Found: C, 59.04; H, 5.70. EI-Ms, *m/z* (rel. int.): 421 $[M+1]^+$ (5%), 420 $[M]^+$ (22), 402 (20), 375 (31), 358 (14), 197 (8), 45 (100). ^1H Nmr ($CDCl_3$, 90 MHz): δ 2.78 (1H, dd, J = 4 and 15 Hz, C-3-H), 3.03 (1H, dd, J = 12 and 15 Hz, C-3-H), 3.47 (6H, s, $OCH_2OC\underline{H}_3$x2), 3.48 (3H, s, $OCH_2OC\underline{H}_3$), 5.17 (4H, s, $OC\underline{H}_2OCH_3$x2), 5.18 (2H, s, $OC\underline{H}_2OCH_3$), 5.70 (1H, dd, J = 4 and 12 Hz, C-2-H), 6.18 (2H, s, C-6-H and C-8-H), 6.72 (1H, dd, J = 2 and 9 Hz, C-5'-H), 6.82 (1H, d, J = 2 Hz, C-3'-H), 7.44 (1H, d, J = 9 Hz, C-6'-H), 11.84 (1H, s, C-5-OH). Compound (**10b**) showed the following data: mp 106 - 108°C (pale yellow prisms, crystallized from methanol). $FeCl_3$ test: reddish brown. Anal. Calcd for $C_{21}H_{22}O_9$: C, 60.29; H, 5.30. Found: C, 60.04; H, 5.32. EI-Ms, *m/z* (rel. int.): 419 $[M+1]^+$ (5%), 418 $[M]^+$ (19), 403 (3), 402 (3), 388 (2), 387 (3), 386 (3), 375 (5), 341 (5), 197 (2). ^1H Nmr ($CDCl_3$, 90 MHz): δ 3.50 (9H, s, $OCH_2OC\underline{H}_3$x3), 5.24 (4H, s, $OC\underline{H}_2OCH_3$x2), 5.28 (2H, s, $OC\underline{H}_2OCH_3$), 6.43 (1H, d, J = 2 Hz, C-6-H), 6.58 (1H, d, J = 2 Hz, C-8-H), 6.80 (1H, dd, J = 2 and 9 Hz, C-5'-H), 6.90 (1H, s, C-3-H), 6.90 (1H, d, J = 2 Hz, C-3'-H), 7.79 (1H, d, J = 9 Hz, C-6'-H), 12.68 (1H, s, C-5-OH).

Preparation of 8-geranylnorartocarpetin (**4**) and 6-geranylnorartocarpetin (**2**) from **10b**

A mixture of **10b** (765 mg, 1.8 mmol), geranyl bromide (1 ml, 4.6 mmol), and KOH (0.5 g, 8.9 mmol) in methanol (70 ml) was allowed to stand for 3 h. After treated as usual, the reaction product was chromatographed on silica gel with benzene containing increasing amount of acetone as an eluent. The fraction eluted with benzene (530 mg) was purified by preparative tlc (silica gel, *n*-hexane-acetone=4:1, $CHCl_3$ only) to give 8-geranyl-7,2',4'-trimethoxymethylnorartocarpetin (**4a**, 50 mg, 5%), 6-geranyl-7,2',4'-trimethoxymethylnorartocarpetin (**2a**, 31 mg, 3%), and the starting material (**10b**, 236 mg, 41%). The fraction eluted withe benzene-acetone (49:1) (310 mg) was purified by preparative tlc (silica gel, *n*-hexane-acetone=4:1) to give 5-*O*-geranyl-7,2',4'-trimethoxymethylnorartocarpetin (**11b**, 35 mg, 3.5%). A mixture of **4a** (16 mg) and 3N HCl (0.5 ml) in methanol (5 ml) was refluxed for 15 min. The mixture was diluted with water (20 ml) and treated as usual. The reaction product was purified with preparative tlc (silica gel, *n*-hexane-acetone=3:1) to give **4** (6 mg, 50%). A mixture of **2a** (20 mg) and 3N HCl (0.5 ml) in methanol (5 ml) was refluxed for 15 min. The mixture was diluted with water (20 ml) and treated as usual. The reaction product was purified by preparative tlc (*n*-hexane-acetone=2:1) to give **2** (4 mg, 27%). Compound (**4a**) showed the following data: mp 101 - 103°C (pale yellow needles, crystallized from acetone-methanol). $FeCl_3$ test: green. Gibbs test: negative. Anal. Calcd for $C_{31}H_{38}O_9\cdot\frac{1}{2}H_2O$: C, 66.06; H, 6.97. Found: C, 66.18; H, 6.91. EI-Ms, *m/z* (rel. int.): 555 $[M+1]^+$ (4%), 554 $[M]^+$ (11), 509 (14), 486 (6), 485 (16), 471 (7), 453 (13), 432 (17), 431 (63), 418 (18), 399 (11), 387 (23), 386 (13), 355 (9), 343 (8), 311 (4), 45 (100). ^1H Nmr ($CDCl_3$, 90 MHz): δ1.54, 1.61 (each 3H, br s, C-8"-CH_3), 1.79 (3H, br s, C-3"-CH_3), 1.99 (4H, br s, C-5"-Hx2 and C-6"-Hx2), 3.48 (3H, s, $OCH_2OC\underline{H}_3$), 3.51 (6H, s, $OCH_2OC\underline{H}_3$ x2), 3.55 (2H, br d, J = 6 Hz, C-1"-Hx2), 5.00 - 5.40 (2H, m, C-2"-H and C-7"-H), 5.22, 5.26, 5.29 (each 2H, s, $OC\underline{H}_2OCH_3$), 6.58 (1H, br s, C-6-H), 6.80 (1H, dd, J = 2 and 9 Hz, C-5'-H), 6.95 (1H, s, C-3-H), 6.98 (1H, d, J = 2 Hz, C-3'-H), 7.82 (1H, d, J = 9 Hz, C-6'-H), 12.72 (1H, s, C-5-OH). Compound (**2a**) showed the following data: mp 78 - 81°C (pale yellow needles, crystallized from methanol). $FeCl_3$ test: green. Gibbs test: positive. Anal. Calcd for $C_{31}H_{38}O_9$: C, 67.13; H, 6.91. Found: C, 66.87; H, 6.94. EI-Ms, *m/z* (rel. int.): 555 $[M+1]^+$ (12%), 554 $[M]^+$ (40), 509 (5), 486 (11), 485 (36), 471 (2), 457 (7), 453 (5), 443 (12), 432 (20), 431 (67), 418 (4), 417 (8), 399 (8), 387 (8), 386 (2), 355 (4), 343 (2), 311 (3), 45 (100). ^1H Nmr ($CDCl_3$, 90 MHz): δ1.58, 1.65 (each 3H, br s, C-8"-CH_3), 1.81 (3H, br s, C-3"-CH_3), 2.00 (4H, br s, C-5"-Hx2 and C-6"-Hx2), 3.42 (2H, br d, J = 7 Hz, C-1"-Hx2), 3.50 (9H, s, $OCH_2OC\underline{H}_3$x3), 5.0 - 5.4 (2H, m, C-2"-H and C-7"-H), 5.21 (2H, s, $OC\underline{H}_2OCH_3$), 5.28 (4H, s, $OC\underline{H}_2OCH_3$x2), 6.67 (1H, br s, C-8-H), 6.80 (1H, dd, J = 2 and 9 Hz, C-5'-H), 6.93 (1H, d, J = 2 Hz, C-3'-H), 6.94 (1H, s, C-3-H), 7.81 (1H, d, J = 9 Hz, C-6'-H), 12.87 (1H, s, C-5-OH). Compound (**11b**) was obtained as pale yellow oil and showed the following data. $FeCl_3$ test: negative. EI-Ms, *m/z* (rel. int.): 555 $[M+1]^+$ (3%), 554 $[M]^+$ (7), 485 (7), 472 (5), 457 (4), 418 (48), 403 (7), 387 (7), 386 (9), 341 (13), 149 (6), 139 (6), 137 (17), 121 (10), 93 (50), 69 (68), 45 (100). HR-Ms, *m/z* 554.2521 $[M]^+$ ($C_{31}H_{39}O_9$ requires: 554.2516). ^1H Nmr ($CDCl_3$, 90 MHz): δ1.60, 1.67 (each 3H, br s, C-8"-CH_3), 1.77 (3H, br s, C-3"-CH_3), 2.18 (4H, br s, C-5"-Hx2 and C-6"-Hx2), 3.50 (9H, s, $OCH_2OC\underline{H}_3$x3), 4.72 (2H, br d, J = 6 Hz, C-1"-Hx2), 4.95 - 5.20 (1H, m, C-7"-H), 5.20, 5.23, 5.27 (each 2H, s, $OC\underline{H}_2OCH_3$), 5.60 (1H, br t, J = 6 Hz, C-2"-H), 6.43 (1H, d, J = 2.5 Hz, C-6-H), 6.69 (1H, d, J = 2.5 Hz, C-8-H), 6.75 (1H, dd, J = 2.5 and 9 Hz, C-5'-H), 6.87 (1H, s, C-3-H), 6.92 (1H, d, J = 2.5 Hz, C-3'-H), 7.76 (1H, d, J = 9 Hz, C-6'-H). Compound (**4**) showed the following data: mp 260 - 263°C (pale yellow needles, crystallized from benzene-acetone). $FeCl_3$ test: olive. EI-Ms, *m/z* (rel. int.): 423 $[M+1]^+$ (12%), 422 $[M]^+$ (42), 379 (1), 365 (5), 353 (47), 339 (15), 337 (13), 325 (4), 311 (10), 299 (100), 286 (22), 219 (14), 165 (17). HR-Ms, *m/z* 422.1723 $[M]^+$ ($C_{25}H_{26}O_6$ requires: 422.1729). Uv λ_{max}^{EtOH} nm (log ε): 205 (4.24), 252 (3.71), 271

(3.83), 288 (3.57), 355 (3.84). Uv $\lambda_{max}^{EtOH+AlCl_3}$: 237 (sh 3.81), 258 (sh 3.74), 279 (3.84), 298 (3.66), 361 (3.84), 397 (3.75). ^1H Nmr (acetone-d_6, 400 MHz): δ1.50 (3H, br d, J = 0.7 Hz, C-8"-CH_3), 1.56 (3H, br d, J = 1 Hz, C-8"-CH_3), 1.82 (3H, br d, J = 1 Hz, C-3"-CH_3), 1.90 - 2.10 (4H, m, C-5"-Hx2 and C-6"-Hx2), 3.56 (2H, br d, J = 7 Hz, C-1"-Hx2), 5.04 (1H, br t, J = 7 Hz, C-7"-H), 5.30 (1H, br t, J = 7 Hz, C-2"-H), 6.33 (1H, br s, C-6-H), 6.58 (1H, dd, J = 2 and 8.5 Hz, C-5'-H), 6.62 (1H, d, J = 2 Hz, C-3'-H), 7.08 (1H, s, C-3-H), 7.88 (1H, d, J = 8.5 Hz, C-6'-H), 9.58 (3H, br s, OHx2), 13.09 (1H, s, C-5-OH). Compound (**2**) showed the following data: mp 174 - 177°C (pale yellow prisms, crystallized from benzene-acetone). $FeCl_3$ test: dark green. EI-Ms, m/z (rel. int.): 423 $[M+1]^+$ (11%), 422 $[M]^+$ (35), 379 (4), 353 (55), 337 (15), 325 (5), 311 (13), 299 (100), 286 (7), 219 (4), 165 (15). HR-Ms, m/z 422.1728 $[M]^+$ ($C_{25}H_{26}O_6$ requires: 422.1729). Uv λ_{max}^{EtOH} nm (log ε): 205 (sh 4.13), 213 (4.16), 252 (3.72), 271 (3.78), 285 (sh 3.60), 351 (3.94). Uv $\lambda_{max}^{EtOH+AlCl_3}$: 205 (sh 4.15), 215 (4.17), 260 (3.68), 281 (3.76), 292 (3.75), 369 (3.92), 390 (sh 3.85). ^1H Nmr (DMSO-d_6-acetone-d_6=1:2, 400 MHz): δ1.56 (3H, br s, C-8"-CH_3), 1.61 (3H, br d, J = 1 Hz, C-8"-CH_3), 1.78 (3H, br d, J = 1 Hz, C-3"-CH_3), 1.90 - 2.10 (4H, m, C-5"-Hx2 and C-6"-Hx2), 3.30 (2H, br d, J = 7 Hz, C-1"-Hx2), 5.08 (1H, br t, J = 7 Hz, C-7"-H), 5.27 (1H, br t, J = 7 Hz, C-2"-H), 6.47 (1H, dd, J = 2 and 9 Hz, C-5'-H), 6.55 (1H, br s, C-8-H), 6.59 (1H, d, J = 2 Hz, C-3'-H), 7.77 (1H, d, J = 9 Hz, C-6'-H), 10.02 (1H, br s, OH), 10.65 (2H, br s, OHx2), 13.40 (1H, s, C-5-OH); (acetone-d_6, 400 MHz): δ13.40 (1H, s, C-5-OH).

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