FOUR NEW PRENYLATED FLAVONOIDS, GLYASPERINS A, B, C, AND D FROM THE ROOTS OF GLYCYRRHIZA ASPERA[1]

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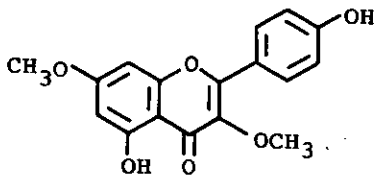
Abstract ——— Four new prenylated flavonoids, glyasperins A (**1**), B (**2**), C (**3**), and D (**4**), along with ten known compounds were isolated from the roots of Glycyrrhiza aspera. The structures of glyasperins A-D were elucidated by spectroscopic methods.

Licorice, the roots and rhizomes of various species of Glycyrrhiza (Leguminosae), has been used for a long time as one of the most important crude drugs. The commercial Chinese licorice imported to Japan is generally classified to three kinds, the northeastern licorice (Tohoku Kanzo in Japanese), the northwestern licorice (Seihoku Kanzao in Japanese) and Sin Jiang licorice (Shinkyo Kanzo in Japanese).[2] And nowadays the Sin Jiang licorice serves as the main resources of the crude drugs in China for its large amounts of production and good qualities.[3,4] Among Sin Jiang licorice, five Glycyrrhiza species have been reported , i.e. G. uralensis, G. glabra, G. inflata, G. eurycarpa,[5] and G. aspera.[3,4] In the continuous research of Chinese licorice,[6] we reexamined the phenolic consitituents of



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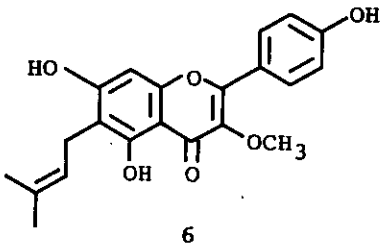

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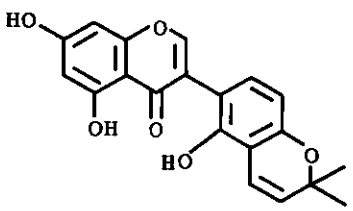

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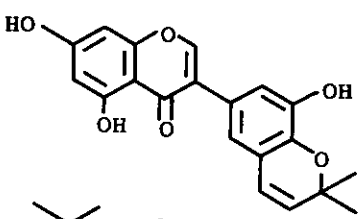

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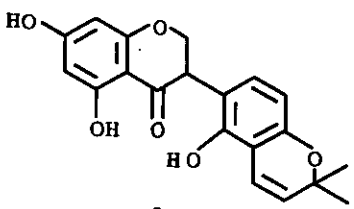

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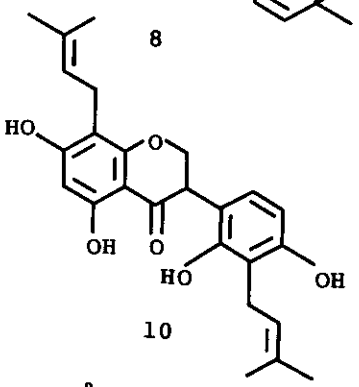

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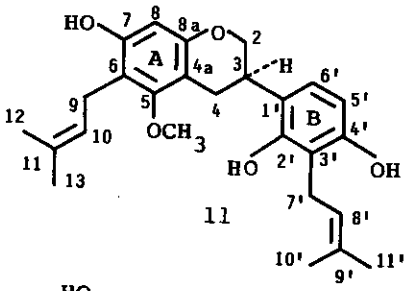

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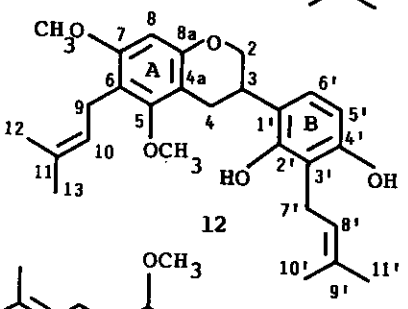

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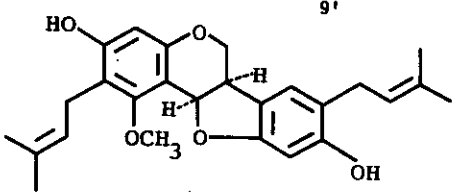

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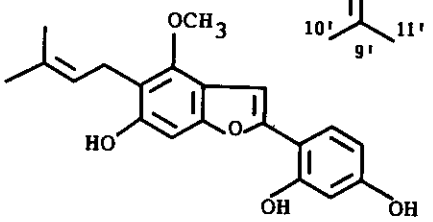

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Figure 1

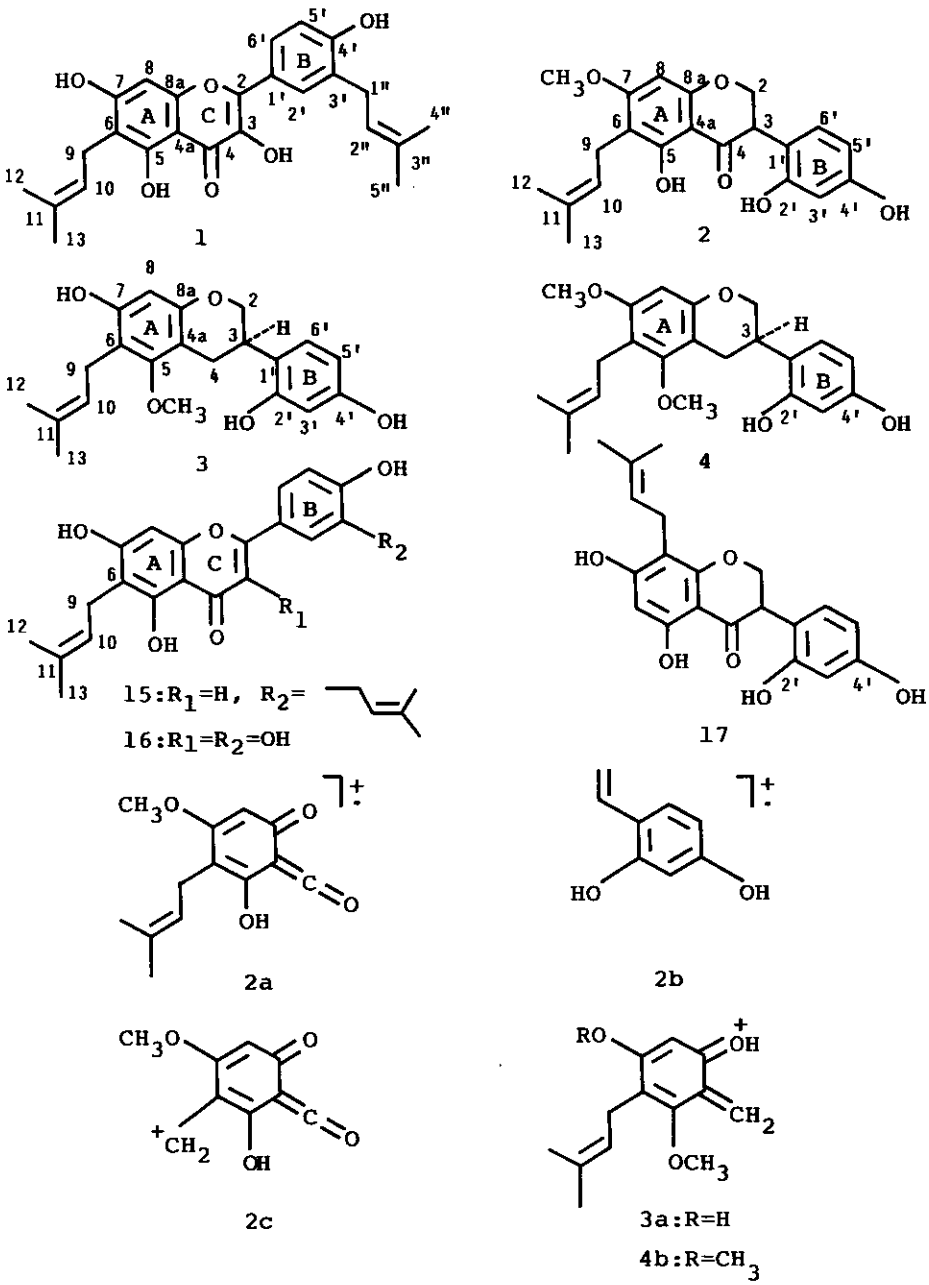


Figure 2

Table 1. ^{13}C Nmr data of **1**, **2** and related compounds (**15**, **16**, and **17**) in acetone-d_6, 100 MHz

C	1	15[a]	16[b]	C	2		17[c]
2	147.03		146.67	2	71.31	(Td)[§]	71.2
3	136.59		136.59	3	47.38	(Dd)	47.2
4	176.56		176.56	4	199.23	(Sm)	198.8
4a	104.01	105.22	104.04	4a	104.10	(Sdd)	103.7
5	158.95	160.24	158.96	5	162.94	(Sm)	163.4
6	111.72	112.33	111.81	6	109.85	(Sm)	96.5
7	162.72	162.42	162.78	7	165.95	(Sm)	164.7
8	93.83	94.07	93.91	8	91.51	(D)	108.1
8a	155.63	156.58	155.67	8a	161.34	(Sdd)	161.3
9	21.92	22.01	22.01	9	21.62	(Td)	
10	123.28	123.27	123.24	10	123.53	(Dm)	
11	131.66	131.59	131.65	11	131.26	(Sm)	
12	17.90	17.91	17.91	12	17.80	(Qm)	
13	25.88	25.88	25.88	13	25.86	(Qm)	
1'	123.46	123.45		1'	113.40	(Sm)	114.0
2'	129.06	128.85		2'	159.26	(Sddd)	158.8
3'	130.32	129.91		3'	103.88	(Dd)	103.8
4'	158.95	159.51		4'	157.39	(Sm)	157.0
5'	115.82	116.34		5'	107.57	(Dd)	107.9
6'	127.95	126.57		6'	131.50	(Dd)	131.6
1"	29.07	29.05		MeO	56.37	(Q)	
2"	123.21	123.04					
3"	133.10	133.28					
4"	17.91	17.91					
5"	25.90	25.91					

a, b: See refs 17 and 18. c: See ref. 21. [§]: Capital letters refer to the pattern resulting from directly bonded proton(s) and lowercase letters to long-range $^{13}C-^{1}H$ coupling.

the roots of G. aspera,[7] and reported here four new prenylated flavonoids, named glyasperins A (**1**), B (**2**), C (**3**), and D (**4**), along with ten known compounds, kumatakenin (**5**),[8] topazolin (**6**),[9] licoisoflavone B (**7**),[10] semilicoisoflavone B (**8**),[11] licoisoflavanone (**9**),[10] 3'-(γ,γ-dimethylallyl)-kievitone (**10**),[12] licoricidin (**11**),[13] licorisoflavan A (**12**),[14] 1-methoxyficifolinol (**13**),[11] and licocoumarone (**14**).[15]

Glyasperin A (**1**), yellow prisms, mp 164-165 °C, $C_{25}H_{26}O_6$, gave a green color with methanolic ferric chloride test. The uv spectra suggested its flavonol skeleton substituted with 4',5,7-trihydroxyl groups.[16] The ^{1}H nmr spectrum (acetone-d_6) showed the signals of two 3,3-dimethylallyl (prenyl) group protons, ABX type aromatic protons, an aromatic proton, and a hydrogen-bonded hydroxyl proton. Since the singlet signals of the aromatic proton and hydrogen-bonded hydroxyl proton appeared at δ 6.59 and

Table 2. ^{13}C Nmr data of **3**, **4**, **11**, and **12**, and one bond and long-range ^{13}C-^{1}H correlation data of **3** and **4**

C	**3** ppm	**3** C-H^{+} via ^{1}J	**3** C-H^{++} via ^{2}J, ^{3}J	**11** ppm	**4*** ppm	**12** ppm	**12** C-H^{+} via ^{1}J	**12** C-H^{++} via ^{2}J, ^{3}J
2	70.37 (Tm)[§]	3.96,4.19	H-4	70.54	70.48	70.51	3.96,4.21	H-4,4
3	32.26 (Dm)	3.39	H-2,2,4,4,6'	32.17	32.22	31.98	3.41	H-2,2
4	26.61 (Tm)	2.83,2.92	H-2	27.29	26.53	27.07	2.75,2.93	H-4,4
4a	108.38 (Sm)		H-4,4,8	108.40[a]	109.14	109.01		H-4,4
5	158.32 (Sm)		H-4,4,9,9,Me	158.31	157.87[b]	157.91		H-4,4,9,Me
6	114.39 (Sm)		H-8,9,7(OH),	114.40[a]	115.56	115.46		H-9,9
7	155.43 (Sm)		H-8,9,7(OH)	155.44	157.97[b]	157.83		Me-7
8	99.82 (D)	6.17		99.83	96.36	96.26	6.22	
8a	154.48 (Sm)		H-2,4,4,8	154.43	154.78	154.64		H-2,4,4,8
1'	119.80 (Sm)		H-3',2'(OH)	120.82	119.69	120.58		H-4,2'(OH)
2'	156.73 (Dm)		H-3',6'	154.13	156.78[c]	154.01[d]		H-6',7'
3'	103.58 (Dm)	6.46	H-5'	116.32	103.60	116.19		H-7',2',4'(OH)
4'	158.30 (Dm)		H-3',6'	155.32	158.05[c]	155.22[d]		H-7'
5'	107.72 (Dt)	6.35	H-3'	108.33	107.74	108.27	6.45	
6'	128.70 (Dd)	6.89		123.93	128.71	125.04	6.80	
9	23.33 (Dt)	3.28		23.32	23.24	23.15	3.25	
10	125.31 (Dm)	5.25	H-12,13	125.13	125.18	125.04	5.17	H-12,13
11	130.27 (Sm)		H-12,13	130.31	130.41	130.32		H-12,13
12	17.90 (Qm)	1.75	H-13	17.85	17.86	17.83	1.74	H-13
13	25.85 (Qm)	1.65	H-12	25.85	25.86	25.86	1.66	H-12
7'				23.23		23.24	3.47	
8'				125.29		123.78	5.26	H-10',11'
9'				131.82		131.78		H-10',11'
10'				17.95		17.94	1.78	H-11'
11'				25.88		25.83	1.63	H-10'
MeO	60.57 (Q)	3.70		60.57	60.73	60.60	3.67	
					55.89	55.75	3.73	

*: The datum was obtained only from the completed decoupling spectrum. [§]: Capital letters refer to the pattern resulting from directly bonded proton(s) and lowercase letters to long-range ^{13}C-^{1}H coupling. a: Signals were reassigned by the comparison with those of **3** and **12** in which the signals were assigned by COLOC. b-d: The assignments may be interchangeable.

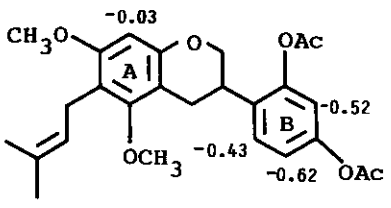
δ 12.44, respectively, the position substituted by prenyl group in the A ring was deduced to be located in C-6 atom rather than in C-8 atom.[19] Furthermore, comparing the ^{13}C nmr spectrum of **1** with those of gancaonin Q (**15**) [17] and gancaonin P (**16**),[18] the chemical shifts of the A and C rings of **1** were found to be in agreement with those of the relevent carbon atoms of **16**, and the chemical shifts of the carbon atoms of the B ring of **1** to be consistent with those of the relevent carbon atoms of **15** (Table 1), which indicated the prenyl group in the B ring of **1** was substituted in C-3' atom.

Thus, the structure of glyasperin A is characterized as formula (**1**).

Glyasperin B (**2**) was obtained as an amorphous powder, $C_{21}H_{22}O_6$, $[\alpha]_D^{20}$ -5.7°. The uv spectrum showed that the compound (**2**) was either an isoflavanone or a flavanone derivative.[16] The ^1H nmr spectrum exhibited the signals of an isoflavanone skeleton in which the methylene protons of C-2 appeared as a double doublet (δ 4.46) and a triplet (δ 4.61), and the methine proton of C-3 as a double doublet (δ 4.26), respectively. The ^1H nmr spectrum also showed the signals of the following protons: protons in a prenyl group, protons in a methoxyl group, ABX type aromatic protons, a singlet aromatic proton, and a hydrogen-bonded hydroxyl proton. The mass spectrum gave the fragment ions at m/z 234.0872 ($C_{13}H_{14}O_4$, **2a**), 179.0355 ($C_9H_7O_4$, **2c**), and 136 (**2b**), indicating that the prenyl and methoxyl groups were located in the A ring. In the ^{13}C nmr spectrum of **2**, the oxygenated carbon atoms were observed in the range of δ 157.39-165.95, showing that all the oxygenated aromatic carbons were located each other at meta position,[20] and the chemical shifts of the B ring of **2** were found to be in agreement with those of relevant carbon atoms of kievitone (**17**).[21] All the above evidence suggested that the compound (**2**) was 2',4',5-trihydroxy-7-methoxy-6-, or -8-prenylisoflavanone. The position of prenyl group in the A ring was determined by further observation of the ^{13}C nmr spectrum using gated decoupling with NOE technique. The signal at δ 91.51 appeared as a doublet, J=162.8 Hz revealed that the prenyl group was substituted in C-6.

Therefore, the structure of glyasperin B is established as formula (**2**).

Glyasperin C (**3**) was recrystallized from acetone to give colorless needles, mp 79-80 °C, $C_{21}H_{24}O_5$, $[\alpha]_D^{20}$ -15.6 °. The uv spectrum resembled that of licoricidin (**11**), an isoflavan derivative isolated from the same material. The ^1H nmr spectrum showed the signals of the following: protons in a prenyl group, protons in a methoxyl group, an aromatic proton, ABX type aromatic protons, a methine proton, and protons in two methylene groups. The mass spectrum gave the fragment ions at m/z 221.1171 ($C_{13}H_{17}O_3$, **3a**) and 136 (**2b**). The ^{13}C nmr spectrum of **3** was analyzed by using gated decoupling



4a

Figure 3 Acetylation shifts of **4a**

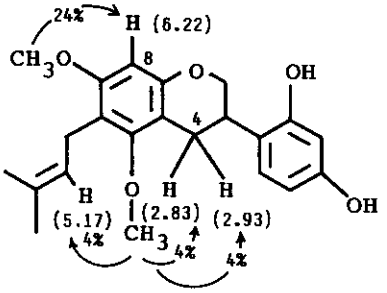


Figure 4 NOE values of **4**

with NOE, heteronuclear shift correlation spectroscopy (C,H-COSY), and correlation spectroscopy via long-range coupling (COLOC), and by comparing with that of licoricidin (**11**) as shown in Table 2. The A and C rings of this compound, including the methoxyl and prenyl groups, exhibited the similar chemical shifts as those of the relevent carbon atoms of **11**, which indicated that the A ring of **3** was substituted by 7-hydroxyl, 5-methoxyl, and 6-prenyl groups. In the ^{1}H nmr spectrum of **3**, the singals of ABX aromatic protons were observed, which showed that the B ring was either substituted by 2',4'- or by 3',4'-dihydroxyl groups. In the ^{13}C nmr spectrum, the oxgenated carbons in the B ring appeared at δ 156.73 and δ 158.30, so that the substituted pattern in the B ring of **3** was concluded to be 2',4'-dihydroxyphenyl moiety.[20] The absolute configuration of **3** was assigned to be 3-(R) by its CD spectrum in which the positive Cotton effect was exhibited at 289 nm.[22]

Thus, the structure of glyasperin C is represented by formula (**3**).

Glyasperin D (**4**) was recrystallized from acetone to give colorless prisms, mp 111-114 °C, $C_{22}H_{26}O_5$, $[\alpha]_D^{20}$ -13.4 °. The uv, ^{1}H, and ^{13}C nmr spectra showed that the compound (**4**) was a monomethyl ether of **3**. The mass spectrum gave the fragment ions at m/z 235 (**4b**) and 136 (**2b**). Comparing the ^{13}C nmr spectrum of **4** with that of **3**, the chemical shifts of the B ring in two compounds were found to be almost the same, which revealed that the substituted pattern in the B ring of **4** was also 2',4'-dihydroxyphenyl moiety. The position substituted by methoxyl group was also supported by

the observation of the acetylation shifts (Figure 3) and NOE experiments (Figure 4). Comparing the ^{1}H nmr spectra of **4** and its diacetylated product (**4a**), the chemical shifts of the B ring showed remarkable downfield shifts. The absolute configuration of **4** was assigned to be 3-(R) for its CD spectrum exhibited the same type of Cotton effect as that of **3**.

Consequently, the structure of glyasperin D is concluded to be formula (**4**). The compound (**12**) was obtained as colorless prisms, mp 65-67°C, $[\alpha]_D^{20}$+5.7°. The structure of **12** (except the stereochemistry at the C-3) was determined to be 3',6-diprenyl-2',4'-dihydroxy-5,7-dimethoxyisoflavan by analyses of its spectral data and comparison with those of **3**, **4**, and **11**. The same structure named licorisoflavan A by Shizuri *et al.*[14] has been reported in a abstract form and no details have been further published.

EXPERIMENTAL

The general procedures followed as described in the previous paper.[6] The optical rotations and CD spectra were measured on JASCO DIP-4 and JASCO J-720 instruments, respectively. The other instruments were used as described in the previous paper.[6] For preparative tlc (silica gel), Wagogel B-5F was used.

Plant Material

The roots of *Glycyrrhiza aspera* were collected in Manasi County, Xin Jiang Autonomous Region of China, in the August, 1986. The morphological and histological studies of the crude drugs were published in the previous paper.[23] The voucher specimen has been deposited in the drug museum of the Department of Pharmacognosy, School of Pharmaceutical Sciences, Beijing Medical University, P. R. China.

Isolation of Phenolic Compounds from Glycyrrhiza aspera Roots

Powdered roots of *G. aspera* (2 kg) were extracted by ethanol (50 l) for three days using continuous extractor at 20°C. The ethanol extract (300 g) was dissolved in methanol (1.5 l) and the dissolved portion (240 g) was absorbed on Amberlite XAD-2 resin (500 g), and then washed successively with n-hexane (6 l), benzene (7 l), benzene-acetone=8:1 (4.5 l), 6:1 (1 l), 4:1 (2 l), 2:1 (5 l), 1:1 (2 l), 1:2 (7 l), acetone (2 l), methanol (3 l). The benzene portion (33.6 g) was subjected to a silica gel (260 g) column chromatography (column A) and eluted with n-hexane (fr.1-2), n-hexane-benzene=5:1→1:7 (fr.3-9), benzene

(fr.10-12), benzene-ethyl ether=20:1→1:5 (fr.13-27), and benzene-acetone=8:1→1:2 (fr.28-33). The fractions (500 ml each) were monitored by tlc. The fraction 9 (eluent, n-hexane-benzene=1:7, yield 0.39 g) was purified by preparative tlc (solvent system n-hexane-ethyl ether=4:1, multiple developments, x3) to give licorisoflavan A (**12**, 0.25 g). The fraction 12 (eluent, benzene, 4.37 g) was crystallized from benzene to give licoricidin (**11**, 1.15 g), and the mother liquor was subjected to a silica gel (80 g) column chromatography (column B) and eluted with chloroform (fr.1-10). The fraction 2 (0.82 g) was purified by preparative tlc (solvent system, $CHCl_3$-AcOEt=15:1, x2, n-hexane-acetone=4:1, x4) to give glyasperin A (**1**, 1.5mg). All other fractions were combined and the combined fractions were subjected to a silica gel (80 g) column chromatography (column C) and eluted with n-hexane-AcOEt=100:1→7:1 (fr.1-14) to give 1-methoxyficifolinol (**13**, 2 mg) from the fraction 2, and licoisoflavanone (**9**, 0.29 g) from the fraction 5. The fraction 4 (n-hexane-AcOEt=60:1, 0.89 g) was purified by preparative tlc (solvent system, n-hexane-AcOEt=5:1, x4, n-hexane-AcOEt=3:1, x3) to give 3'-(γ,γ-dimethylallyl)-kievitone (**10**, 20 mg). The fraction 7 (n-hexane-AcOEt=30:1, 0.18 g) was purified by preparative tlc (solvent system, n-hexane-AcOEt=5:1, x5) to give licoisoflavone B (**7**, 7 mg). The fraction 15 of column A (eluent, benzene-ethyl ether=10:1, 1.96 g) was subjected to a silica gel (100 g) column chromatography (column D) and eluted with n-hexane-acetone=100:1→2:1 (fr.1-19) to give kumatakenin (**5**, 5 mg) from the fraction 5. The fraction 6 (0.75 g) was purified by preparative tlc (solvent system, $CHCl_3$-AcOEt=6:1, x3, $CHCl_3$-acetone=20:1, x4) to give glyasperin D (**4**, 0.1 g). The fraction 8 (0.5 g) was purified by preparative tlc (solvent system, n-hexane-AcOEt=6:1, x3, $CHCl_3$-AcOEt=5:1, x3, benzene-ethyl ether=6:1, x3, $CHCl_3$-acetone=20:1, x4, n-hexane-AcOEt=3:1, x4) to give topazolin (**6**, 10 mg) and glyasperin B (**2**, 10 mg). The fractions 10 and 11 (0.46 g) were purified by preparative tlc (solvent system, n-hexane-AcOEt=3:1, x3) to give semilicoisoflavone B (**8**, 0.1 g). The fraction 12 (0.13 g) was purified by preparative tlc (solvent system, CHC_3-AcOEt=5:1, x3) to give licocoumarone (**14**, 20 mg). The fraction 19 (0.95 g) of column A was purified by preparative tlc (solvent system, $CHCl_3$-AcOEt=20:1, x4, n-hexane-AcOEt=3:1) to give glyasperin C (**3**, 0.12 g). The known compounds were identified by direct comparison with the authentic specimen or by comparing their spectral and physical data with corresponding publications.

Glyasperin A (1)

Compound (**1**) was recrystallized from n-hexane-acetone to give yellow prisms, mp 164-165 °C. $FeCl_3$ test: green. Uv ν_{max}^{MeOH} nm (log ε): 253 (4.21), 270 (4.20), 302 (3.96), 335 (sh 4.09), 370 (4.24). Uv $\nu_{max}^{MeOH+NaOAc}$ nm (log ε): 272 (4.23), 303 (4.00), 316 (4.00), 430 (4.29). Uv $\nu_{max}^{MeOH+NaOMe}$ nm (log ε): 282 (4.22), 324 (4.00), 430 (4.29, change to 3.96 after two minutes), Uv $\nu_{max}^{MeOH+AlCl_3}$ nm (log ε): 266 (4.31), 307 (sh 3.49), 368 (3.91), 434 (4.37). EI-Ms (probe) 70 eV, m/z (rel. int.): 423 $[M+1]^+$ (14), 422 $[M]^+$ (60), 407 (8), 405 (8), 380 (17), 379 (62), 368 (20), 367 (100), 351 (5), 323 (15), 311 (18), 168 (3). HR-Ms, m/z,

422.1709 $[M]^+$ ($C_{25}H_{26}O_6$ requires: 422.1657). ^1H Nmr (acetone-d_6): δ 1.65 (3H, br d, J=0.9 Hz, CH_3), 1.75, 1.76, 1.79 (each 3H, br s, CH_3), 3.37 (2H, br d, J=7.2 Hz, C-9-Hx2), 3.41 (2H, br d, J=7.5 Hz, C-1"-Hx2), 5.29 (1H, br t, J=7.2 Hz, C-10-H), 5.39 (1H, br t, J=7.5 Hz, C-2"-H), 6.59 (1H, s, C-8-H), 7.00 (1H, d, J=8.6 Hz, C-5'-H), 7.79 (1H, dd, J=2.4 and 8.6 Hz, C-6'-H), 8.06 (1H, d, J=2.2 Hz, C-2'-H), 9.31 (1H. br s, OH), 12.44 (1H, s, C-5-OH).

Glyasperin B (2)

Compound (2) was obtained as an amorphous powder, $[\alpha]_D^{20}$ -5.7° (c=0.21, $CHCl_3$). Uv ν_{max}^{MeOH} nm (log ε): 289 (4.13), 333 (sh 3.52). Uv $\nu_{max}^{MeOH+NaOMe}$ nm (log ε): 292 (4.19), 341 (3.61). EI-Ms, m/z: 371 $[M+1]^+$ (16), 370 $[M]^+$ (48), 355 (7), 339 (7), 338 (8), 337 (8), 323 (10), 315 (11), 314 (10), 297 (7), 276 (9), 261 (7), 245 (8), 235 (41), 234 (22), 233 (20), 221 (16), 191 (8), 180 (14), 179 (100), 167 (8), 136 (14), 77 (10), 69 (13). HR-Ms, m/z: 370.1465 $[M]^+$ ($C_{21}H_{22}O_6$ requires 370.1419). ^1H Nmr (acetone-d_6): δ 1.63, 1.74 (each 3H, br s, C-11-CH_3), 3.22 (2H, br d, J=7.1 Hz, C-9-Hx2), 5.17 (1H, br t, J=7.1 Hz, C-10-H), 3.98 (3H, s, OCH_3), 4.26 (1H, dd, J=5.3 and 10.4 Hz, C-3-H), 4.46 (1H, dd, J=5.3 and 10.6 Hz, C-2-H), 4.61 (1H, t, J=10.6 Hz, C-2-H), 6.12 (1H, s, C-8-H), 6.29 (1H, dd, J=2.4 and 8.4 Hz, C-5'-H), 6.54 (1H, d, J=2.4 Hz, C-3'-H), 6.98 (1H, d, J=8.4 Hz, C-6'-H), 12.51 (1H, s, C-5-OH).

Glyasperin C (3)

Compound (3) was recrystallized from acetone to give colorless needles, mp 79-80°C, $[\alpha]_D^{20}$ -15.6°(c=0.42, MeOH). Uv ν_{max}^{MeOH} nm (log ε): 282 (4.85). EI-Ms, m/z: 357 $[M+1]^+$ (6), 356 $[M]^+$ (27), 341 (5), 302 (5), 301 (25), 233 (5), 222 (15), 221 (100), 220 (19), 205 (9), 197 (9), 177 (12), 166 (5), 165 (33), 137 (13), 136 (20), 135 (10), 79 (7), 69 (10). HR-Ms, m/z: 356.1624 $[M]^+$ ($C_{21}H_{24}O_5$ requires 356.1629). ^1H Nmr (acetone-d_6): δ 1.65, 1.75 (each 3H, br s, C-11-CH_3), 2.83 (1H, dd, J=10.8 and 15.9 Hz, C-4-H), 2.92 (1H, ddd, J=2.3, 5.4 and 15.9 Hz, C-4-H), 3.28 (2H, m, C-9-Hx2), 3.39 (1H, m, C-3-H), 3.70 (3H, s, OCH_3), 3.96 (1H, t, J=10.2 Hz, C-2-H), 4.19 (1H, ddd, J=2.4, 3.3 and 10.3 Hz, C-2-H), 5.25 (1H, br t, J=7.3 Hz, C-10-H), 6.17 (1H, s, C-8-H), 6.35 (1H, dd, J=2.4 and 8.2 Hz, C-5'-H), 6.46 (1H, d, J=2.4 Hz, C-3'-H), 6.89 (1H, d, J=8.2 Hz, C-6'-H), 8.08, 8.10 and 8.40 (each 1H, s, OH). CD (c=1.26 $x10^{-4}$ mol/l, MeOH): $[\theta]_{299}$ 0, $[\theta]_{289}$ +1.26 $x10^6$, $[\theta]_{285}$ 0, $[\theta]_{275}$ -1.95 $x10^6$, $[\theta]_{253}$ -1.65 $x10^5$, $[\theta]_{239}$ -2.65 $x10^6$.

Glyasperin D (4)

Compound (4) was recrystallized from acetone to give clorless prisms, mp 111-114°C, $[\alpha]_D^{20}$ -13.4°(c=0.21, MeOH). Uv ν_{max}^{MeOH} nm (log ε): 282 (4.80). EI-Ms, m/z: 371 $[M+1]^+$ (24), 370 $[M]^+$ (100), 368 (27), 355 (42), 354 (36), 339 (12), 323 (5), 302 (5), 269 (3), 247 (4),

235 (44), 219 (9), 191 (7), 167 (20), 136 (10), 123 (13). HR-Ms, m/z: 370.1745 $[M]^+$ ($C_{22}H_{26}O_5$ requires 370.1789). ^{1}H Nmr (acetone-d_6): δ 1.63 (3H, br d, J=1.1 Hz, C-11-CH_3), 1.75 (3H, br s, C-11-CH_3), 2.83 (1H, dd, J=10.7 and 16.0 Hz, C-4-H), 2.93 (1H, ddd, J=3.5, 6.5 and 16.1 Hz, C-4-H), 3.25 (2H, m, C-9-Hx2), 3.40 (1H, m, C-3-H), 3.70, 3.76 (each 3H, s, OCH_3), 3.99 (1H, t, J=10.1 Hz, C-2-H), 4.24 (1H, ddd, J=2.0, 3.1 and 10.2 Hz, C-2-H), 5.17 (1H, br t, J=7.2 Hz, C-10-H), 6.22 (1H, s, C-8-H), 6.34 (1H, dd, J=2.5 and 8.4 Hz, C-5'-H), 6.47 (1H, d, J=2.5 Hz, C-3'-H), 6,98 (1H, d, J=8.4 Hz, C-6'-H), 8.10 and 8.40 (each 1H, s, OH). CD (c=1.1 x10^{-4} mol/l, MeOH): $[\theta]_{294}$ 0, $[\theta]_{288}$ +9.63 x10^5, $[\theta]_{283}$ 0, $[\theta]_{274}$ -1.73 x10^6, $[\theta]_{257}$ -2.71 x10^5, $[\theta]_{238}$ -3.80 x10^6.

Diacetate of Glyasperin C (**4a**)

A mixture of **4** (5 mg), acetic anhydride (0.1 ml), and pyridine (0.1 ml), was kept at room temperature over night, and treated as usual. Compound (**4a**) was obtained as an amorphous powder. ^{1}H Nmr (acetone-d_6): δ 1.64, 1.74 (each 3H, br s, C-11-CH_3), 2.26, 2.31 (each 3H, s, OAc), 2.82 (1H, dd, J=11.6 and 16.1 Hz, C-4-H), 2.95 (1H, ddd, J=2.2, 5.5 and 16.1 Hz, C-4-H), 3.25 (2H, m, C-9-Hx2), 3.27 (1H,m, C-3-H), 3.69, 3.77 (each 3H, s, OCH_3), 4.03 (1H, t, J=10.3 Hz, C-2-H), 4.18 (1H, ddd, J=2.2, 3.5 and 10.3 Hz, C-2-H), 5.17 (1H, br t, J=7.2 Hz, C-10-H), 6.25 (1H, s, C-8-H), 6.99 (1H, d, J=2.4 Hz,C-3'-H), 7.05 (1H, dd, J=2.4 and 8.6 Hz, C-5'-H), 7.41 (1H, d, J=8.6 Hz, C-6'-H).

Licorisoflavan A (**12**)

Compound (**12**) was recrystallized from acetone to give colorless prisms, mp 65-67°C, $[\alpha]_D^{20}$ +5.7° (c=0.265, MeOH). Uv ν_{max}^{MeOH} nm (log ϵ): 282 (4.81). EI-Ms, m/z: 439 $[M+1]^+$ (33), 438 $[M]^+$ (100), 424 (8), 423 (24), 404 (8), 247 (7), 236 (16), 235 (97), 234 (5), 219 (10), 205 (7), 204 (14), 203 (13), 191 (20), 189 (10), 168 (6), 167 (32), 161 (11), 149 (15), 148 (14), 147 (15), 137 (5), 136 (5), 135 (14), 69 (13). ^{1}H-Nmr (acetone-d_6): δ 1.63 (3H, br d, J=0.6 Hz, CH_3), 1.66 (3H, br d, J=0.7 Hz, CH_3), 1.74, 1.78 (each 3H, br s, CH_3), 2.75 (1H, dd, J=10.9 and 15.9 Hz, C-4-H), 2.93 (1H, ddd, J=2.1, 4.9 and 15.9 Hz, C-4-H), 3.25 (2H, m, C-9-Hx2), 3.41 (1H, m, C-3-H), 3.47 (2H, d, J=7.2 Hz, C-7'-H), 3.67, 3.73 (each 3H, s, OCH_3), 3.96 (1H, t, J=10.2 Hz, C-2-H), 4.21 (1H, ddd, J=2.0, 3.3 and 10.9 Hz, C-2-H), 5.17 (1H, br t, J=7.4 Hz, C-10-H), 5.26 (1H, br t, J=7.2 Hz, C-8'-H), 6.22 (1H, s, C-8-H), 6.45 (1H, d, J=8.4 Hz, C-5'-H), 6.80 (1H, d, J=8.4 Hz, C-6'-H), 7.90, 8.12 (each 1H, br s, OH).

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