Indonesian Medicinal Plants. X.[1] Chemical Structures of Four New Triterpene-Glycosides, Gongganosides D, E, F, and G, and Two Secoiridoid-Glucosides from the Bark of *Bhesa paniculata* (Celastraceae)

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Four new triterpene-glycosides, named gongganosides D (4), E (5), F (6), and G (7), and two new secoiridoid-glucosides, (7*R*)-7-caffeoyloxysweroside (8) and (7*S*)-7-caffeoyloxysweroside (9), were isolated from the bark of the Indonesian medicinal plant *Bhesa paniculata* (Celastraceae). The chemical structures have been elucidated on the bases of their chemical and physicochemical properties.

Keywords Indonesian medicinal plant; *Bhesa paniculata*; Celastraceae; triterpene-glycoside; secoiridoid-glucoside; 27-oxoursolic acid

In our previous paper,[1] we reported the chemical structures of three quinovic acid-glycosides, gongganosides A (**1**), B (**2**), and C (**3**), isolated from the ethyl acetate-soluble portion of the bark of *Bhesa paniculata* ARN. (Celastraceae), an Indonesian medicinal plant. In a parallel study, we have been investigating the chemical constituents of the *n*-butanol-soluble portion of the bark.

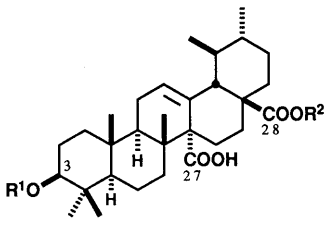
The *n*-butanol-soluble portion (13% from the bark), which was obtained by partitioning of the methanol extract from the bark,[1] was subjected to TSK gel G3000S, Sephadex LH-20 and silica gel column chromatography and subsequent high-performance liquid chromatography (HPLC) with a reversed-phase adsorbent to afford four new triterpene-glycosides, gongganosides D (**4**, 0.035%), E (**5**, 0.074%), F (**6**, 0.015%), and G (**7**, 0.011%), and two new secoiridoid-glucosides, (7*R*)-7-caffeoyloxysweroside (**8**, 0.0051%) and (7*S*)-7-caffeoyloxysweroside (**9**, 0.0088%), along with vogeloside (**13**, 0.15%),[2] epivogeloside (**14**, 0.12%),[2] sweroside (**16**, 0.33%),[3] and rubescine (0.0066%).[4]

In this paper, we describe in detail the structure elucidation of the triterpene-glycosides and the secoiridoid-glucosides.

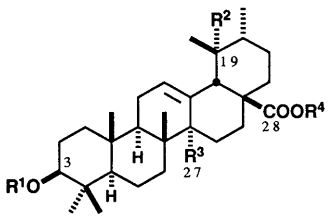
Gongganoside D (4) In the positive fast atom bombardment-mass (FAB-MS), gongganoside D (**4**) gave a quasi-molecular ion peak $(M+Na)^+$ at *m/z* 965, corresponding to $C_{48}H_{78}NaO_{18}$. The infrared (IR) spectrum of **4** indicated the presence of a hydroxyl (3400 cm^{-1}) group, a carboxyl (1696 cm^{-1}) group, and a carbon–carbon double bond (1652 cm^{-1}).

On enzymatic hydrolysis using crude hesperidinase, gongganoside D (**4**) furnished pomolic acid (**10**)[5] as the aglycone and a mixture of glucose and rhamnose (2 : 1). The absolute configurations of the monosaccharides were determined to be D and L, respectively, by gas-liquid chromatographic (GLC) analysis.[6]

The proton and carbon-13 nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) analysis including two dimensional techniques, *i.e.* ^{1}H–^{1}H correlation spectroscopy (COSY), ^{13}C–^{1}H COSY, correlation spectroscopy *via* long-range



	R^1	R^2
gongganoside A (**1**) :	β-D-xyl(1→3)-α-L-rha	H
gongganoside B (**2**) :	α-L-rha	β-D-glc
gongganoside C (**3**) :	β-D-xyl(1→3)-α-L-rha	β-D-glc

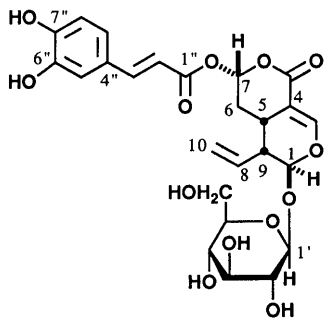


	R^2	R^3	R^4
gongganoside D (**4**) :	OH	CH_3	H
gongganoside E (**5**) :	OH	CH_3	β-D-glc
gongganoside F (**6**) :	H	CH_3	β-D-glc
gongganoside G (**7**) :	H	CHO	β-D-glc

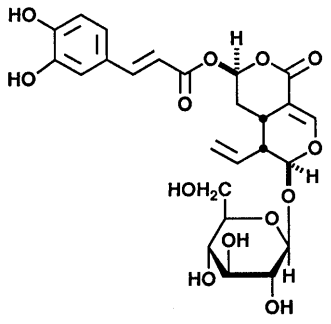
R^1 = α-L-rha(1→2)-β-D-glc(1→2)-β-D-glc

(rha = rhamnopyranose, glc = glucopyranose)

Fig. 1



(7*R*)-7-caffeoyloxysweroside (**8**)



(7*S*)-7-caffeoyloxysweroside (**9**)

Fig. 2

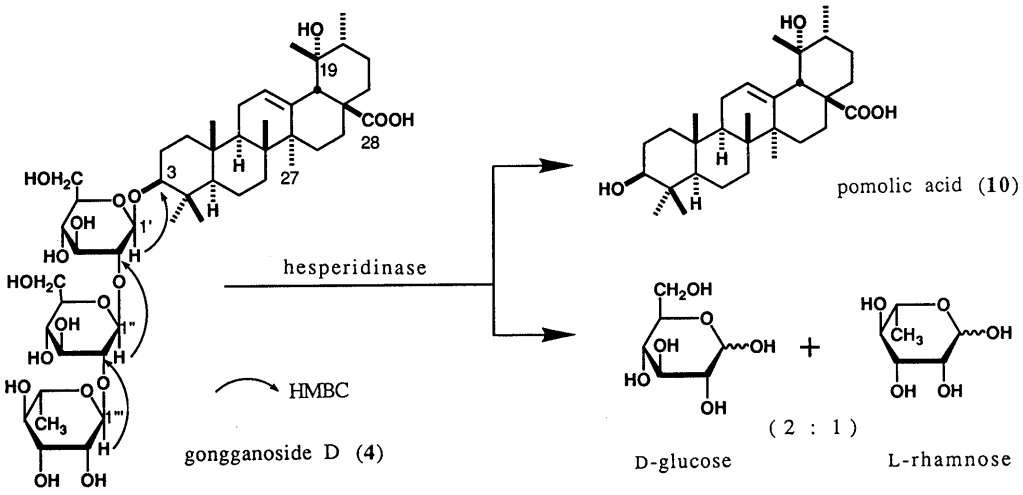


Chart 1

TABLE I. ^{13}C-NMR Data for Gongganosides D (**4**), E (**5**), F (**6**), and G (**7**) (in CD_3OD)

	4	5	6	7		4	5	6	7
C-1	39.7	39.9	40.0	39.9	C-30	16.6	16.6	21.6	21.4
C-2	27.0[a)]	27.1[a)]	27.0	27.0	Glc				
C-3	92.2	92.3	92.2	91.9	C-1′	105.7	105.7	105.7	105.7
C-4	40.4	40.5	40.5	40.5	C-2′	78.1	78.2	78.1	78.2
C-5	56.9	57.0	57.0	56.8	C-3′	78.8	78.9	78.8	78.8
C-6	19.4	19.5	19.3	19.2	C-4′	72.0	72.1	72.0	72.1
C-7	34.1	34.2	34.3	36.8	C-5′	77.7	77.8	77.8	77.8
C-8	41.0	41.3	40.9	42.1	C-6′	62.8	62.9	62.8	62.9
C-9	48.9	48.6	49.0	50.4	Glc				
C10	37.8	37.8	37.8	38.2	C-1″	102.0	102.0	102.0	102.0
C-11	24.7	24.7	24.4	24.5	C-2″	79.5	79.6	79.6	79.6
C-12	129.4	129.7	127.2	133.3	C-3″	79.2	79.3	79.2	79.3
C-13	139.9	139.6	139.1	132.6	C-4″	72.6	72.7	72.6	72.6
C-14	42.5	42.6	43.2	60.1	C-5″	78.1	78.2	78.1	78.2
C-15	29.6	29.7	29.3	21.6	C-6″	63.6	63.7	63.7	63.7
C-16	26.6[a)]	26.5[a)]	25.2	25.2	Rha				
C-17	49.8	49.4	49.4	49.6	C-1‴	101.9	102.0	102.0	102.0
C-18	55.0	54.9	54.1	54.4	C-2‴	72.1	72.2	72.2	72.2
C-19	73.5	73.6	40.4	37.5	C-3‴	72.1	72.1	72.1	72.1
C-20	43.0	42.9	40.2	40.5	C-4‴	74.1	74.2	74.1	74.2
C-21	27.2	27.2	31.7	31.0	C-5‴	69.4	69.5	69.4	69.5
C-22	38.9	38.3	37.4	37.2	C-6‴	18.3	18.3	18.3	18.3
C-23	28.7	28.8	28.8	28.6	Glc				
C-24	16.8[b)]	16.9[b)]	16.9[a)]	16.9	C-1⁗		95.8	95.6	95.6
C-25	15.9[b)]	16.0[b)]	16.1[a)]	16.9	C-2⁗		73.8	73.8	73.9
C-26	17.5	17.6	17.9	18.8	C-3⁗		78.3	78.2	78.2
C-27	24.8	24.7	24.0	208.8	C-4⁗		71.1	71.1	71.1
C-28	182.3	178.5	177.8	177.5	C-5⁗		78.5	78.5	78.6
C-29	27.1	27.1	17.7	17.9	C-6⁗		62.4	62.4	62.4

a, b) Assignments may be interchanged in each column.

coupling (COLOC), and heteronuclear multiple bond correlation (HMBC), led us to presume that **4** was a pomolic acid glycoside containing D-glucopyranose and L-rhamnopyranose.

In the ^{1}H-NMR spectrum (in pyridine-d_5) of **4**, two anomeric proton signals owing to D-glucopyranose were observed at δ 4.87 (1H, d, J=7.4 Hz, 1′-H) and δ 5.70 (1H, d, J=7.1 Hz, 1″-H). The coupling constants indicated β-orientation for the anomeric configurations, along with one anomeric proton signal owing to L-rhamnopyranose at δ 6.39 (1H, br s, 1‴-H). Furthermore, in the ^{13}C-NMR spectrum (in CD_3OD) of **4**, three anomeric carbon signals were observed at δ_C 105.7 (1′-C), δ_C 102.0 (1″-C), and δ_C 101.9 (J_{C-H}=170.7 Hz, 1‴-C). This J_{C-H} value indicated that the anomeric configuration of the terminal sugar (L-rhamnopyranose) is α.[7]

Further, HMBC experiments (in CD_3OD) on gongganoside D (**4**) showed the presence of characteristic cross-peaks between signals at δ 4.40 (1′-H) and δ_C 92.2 (3-C), between signals at δ 4.88 (1″-H) and δ_C 78.1 (2′-C), and between signals at δ 5.17 (1‴-H) and δ_C 79.5 (2″-C). In addition, **4** gave characteristic negative FAB-MS ions at m/z 941 $(M-H)^-$, 795 (**i**), 633 (**ii**), 471 (**iii**) (Fig. 3).

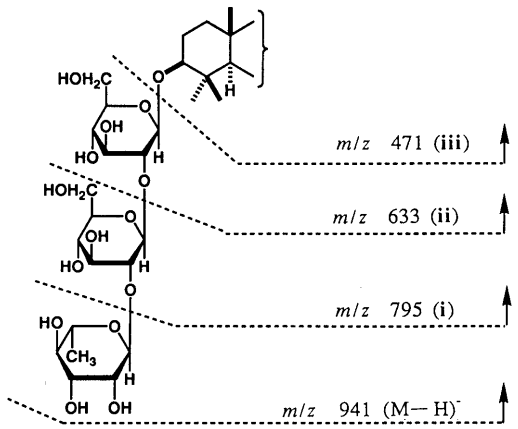


Fig. 3. Negative FAB-MS for Gongganoside D (**4**)

Based on the foregoing evidence, the chemical structure of gongganoside D (**4**) has been concluded to be pomolic acid 3-*O*-α-L-rhamnopyranosyl(1→2)-β-D-glucopyranosyl(1→2)-β-D-glucopyranoside.

Gongganoside E (5) In the positive FAB-MS, gongganoside E (**5**) gave a quasi-molecular ion peak $(M+Na)^+$ at m/z 1127, corresponding to $C_{54}H_{88}NaO_{23}$. The ^{1}H- and ^{13}C-NMR spectra of **5** showed signals characteristic of a pomolic acid glycoside containing rhamnopyranose and glucopyranose moieties (Table I). The IR spectrum of **5** showed significant absorption bands due to a hydroxyl (3390 cm^{-1}) group, an ester group (1726 cm^{-1}), and a carbon–carbon double bond (1636 cm^{-1}).

Alkaline hydrolysis of gongganoside E (**5**) with aqueous lithium hydroxide afforded gongganoside D (**4**) and D-glucose as determined by GLC analysis.[6] Furthermore, in the ^{13}C-NMR spectrum of **5**, an esterification shift[8] was observed for the signal of 28-C (−3.8 ppm) as compared with the signal of **4**. Thus, it has been presumed that gongganoside E (**5**) is a C-28 glucosyl ester of **4**.

In the ^{1}H-NMR spectrum (in pyridine-d_5) of **5**, the anomeric proton signal of the D-glucopyranosyl moiety esterified to the C-28 carboxyl group was observed at δ 6.35 (1H, d, J=7.8 Hz, 1‴-H), and the coupling constant indicated a β-glycosyl linkage.

Thus, the chemical structure of gongganoside E (**5**) has been concluded to be 28-*O*-β-D-glucopyranosylpomolic acid 3-*O*-α-L-rhamnopyranosyl(1→2)-β-D-glucopyranosyl(1→2)-β-D-glucopyranoside.

Gongganoside F (6) Gongganoside F (**6**) gave a quasi-molecular ion peak $(M+Na)^+$ at m/z 1111, which corresponded to $C_{54}H_{88}NaO_{22}$, in the positive FAB-MS. The IR spectrum of **6** showed a similar absorption pattern to that of gongganoside E (**5**).

On hydrolysis with 5% aqueous HCl, gongganoside F (**6**) provided an aglycone (**11**), which was identical with ursolic acid,[9] and a mixture of D-glucose and L-rhamnose (3 : 1) as determined by GLC analysis.[6]

By comparison of the ^{13}C-NMR data for gongganoside F (**6**) with that for gongganoside E (**5**), it has been clarified

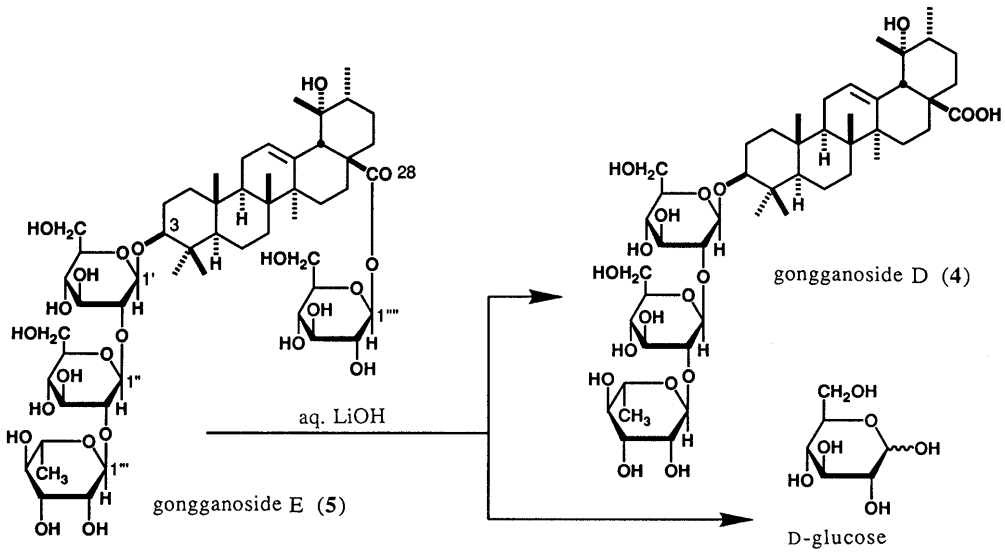


Chart 2

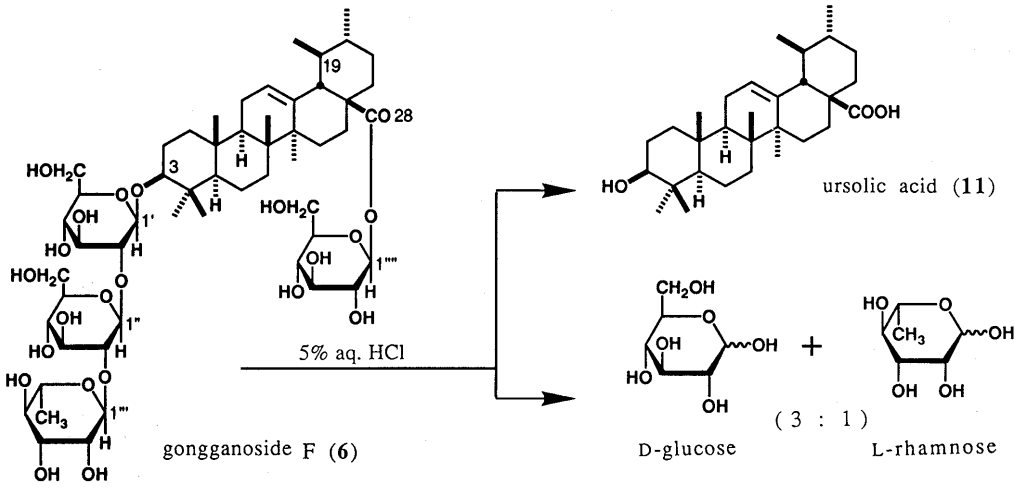


Chart 3

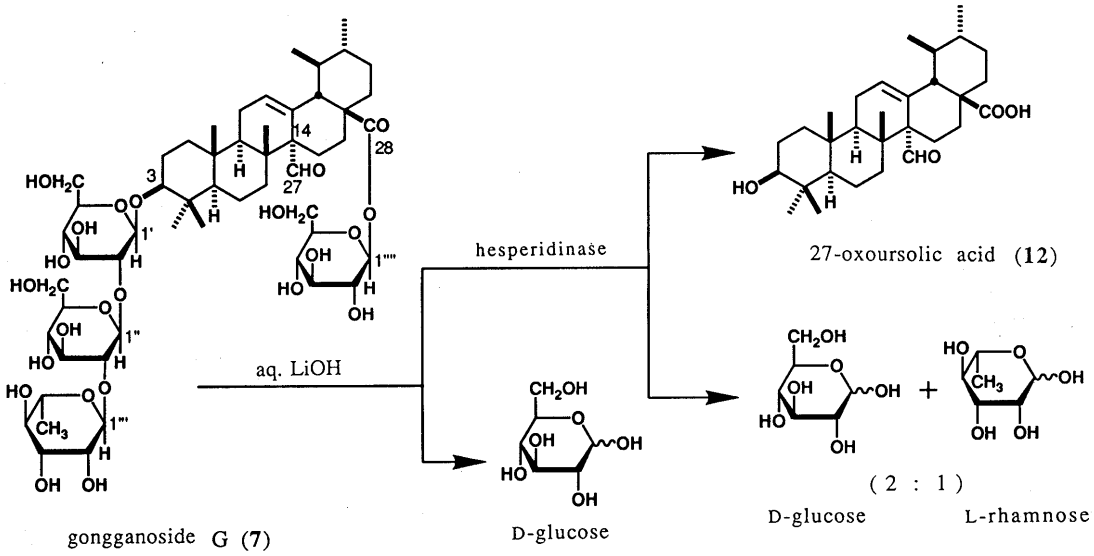


Chart 4

that **6** contains the same oligosaccharide sequence as **5** (Table I). Furthermore, the HMBC experiment (in CD_3OD) on **6** showed the presence of characteristic cross-peaks between the anomeric proton (δ 5.34) of D-glucopyranose and the carbonyl carbon (δ_C 177.8, 28-C) in the aglycone (**11**), and between the anomeric proton (δ 4.39, 1′-H) of another D-glucopyranose and the oxymethine carbon (δ_C 92.2, 3-C) in **11**.

Based on the foregoing evidence, the chemical structure of gongganoside F (**6**) has been concluded to be 28-*O*-β-D-glucopyranosylursolic acid 3-*O*-α-L-rhamnopyranosyl(1→2)-β-D-glucopyranosyl(1→2)-β-D-glucopyranoside.

Gongganoside G (7) The elemental composition of gongganoside G (**7**) was proved to be $C_{54}H_{86}O_{23}$ by high-resolution FAB-MS. The IR spectrum of **7** showed absorption bands due to a hydroxyl (3420 cm^{-1}) group, an ester (1726 cm^{-1}) group, and an aldehyde (1706 cm^{-1}) group. The ^1H- and ^{13}C-NMR spectra (in CD_3OD) of **7** showed the presence of the same oligosaccharide sequence as those of gongganosides E (**5**) and F (**6**), and the existence of one aldehyde (δ 9.84, s; δ_C 208.8, d) group in the triterpene-aglycone (Table I). Furthermore, in the COLOC experiment on gongganoside G (**7**), characteristic cross-peaks were observed between signal of the anomeric proton at 1′-C (δ 4.38) and the signal of the hydroxymethine carbon at 3-C (δ_C 91.9), and between the signal of the anomeric proton at 1‴′-C (δ 5.37) and the signal of the carbonyl carbon at 28-C (δ_C 177.5).

Treatment of gongganoside G (**7**) with aqueous LiOH afforded D-glucopyranose and a partial hydrolysate which was further hydrolyzed with hesperidinase to give an aglycone (**12**) and a mixture of D-glucose and L-rhamnose (2:1). All absolute configurations of monosaccharides were determined by GLC analysis.[6]

The COLOC experiment on the aglycone (**12**) exhibited a characteristic cross-peak between the signal assignable to the aldehyde proton at C-27 (δ 9.83) and the signal assignable to the quaternary carbon at C-14 (δ_C 58.8). Thus, the aglycone of gongganoside G (**7**) is a new triterpene, 27-oxoursolic acid.

Consequently, the chemical structure of gongganoside

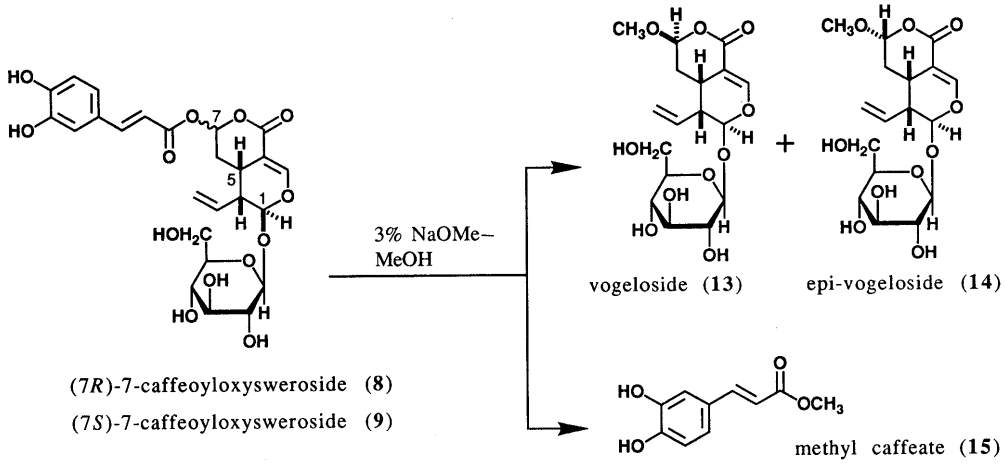


Chart 5

TABLE II. ^{13}C-NMR Data for **8**, **9**, and Sweroside (**16**) (in CD_3OD)

	8	9	16
C-1	97.9	98.7	97.9
C-3	154.6	155.2	153.9
C-4	104.7	104.6	106.0
C-5	25.2	23.0	28.4
C-6	30.4	29.0	25.9
C-7	94.5	93.8	69.7
C-8	132.9	133.1	133.3
C-9	43.6	43.4	43.7
C-10	121.4	121.4	120.8
C-11	166.5	166.1	168.5
C-1′	99.7	100.4	99.7
C-2′	74.7	74.7	74.7
C-3′	77.8	78.1	77.8
C-4′	71.5	71.5	71.5
C-5′	78.4	78.4	78.3
C-6′	62.7	62.6	62.5
C-1″	166.5	166.5	
C-2″	113.7	113.7	
C-3″	149.0	149.0	
C-4″	127.4	127.4	
C-5″	115.3	115.3	
C-6″	146.9	146.9	
C-7″	150.1	150.0	
C-8″	116.5	116.5	
C-9″	123.5	123.5	

G (**7**) has been determined as 28-*O*-β-D-glucopyranosyl-27-oxoursolic acid 3-*O*-α-L-rhamnopyranosyl(1→2)-β-D-glucopyranosyl(1→2)-β-D-glucopyranoside.

Secoiridoid Glucosides (8, 9) In the positive FAB-MS, both **8** and **9** gave the same quasi-molecular ion peak $(M+Na)^+$ at *m/z* 559, corresponding to $C_{25}H_{28}NaO_{13}$. Furthermore, the ultraviolet (UV) and IR spectra of **8** and **9** showed quite similar absorption patterns to each other.

The ^{1}H- and ^{13}C-NMR spectra (Table II) of **8** and **9** showed signals characteristic of a sweroside (**16**)[3] possessing a caffeoyl moiety. On alkaline hydrolysis with 3% NaOMe–MeOH, **8** and **9** each afforded methyl caffeate (**15**) and a mixture of vogeloside (**13**)[2] and epi-vogeloside (**14**)[2] in a ratio of *ca.* 1:1. In addition, the COLOC experiments on **8** and **9** indicated that the signal of the methine proton at C-7 (δ 6.63 for **8**, δ 6.70 for **9**) in the secoiridoid moiety correlates with the signal of the ester carbonyl carbon (δ_C 166.5 for **8**, δ_C 166.5 for **9**) in the caffeoyl moiety. From the above-mentioned facts, it has been presumed that **8** and **9** are diastereomeric in the orientation of the ester linkage at C-7.

In the nuclear Overhauser and exchange spectroscopy (NOESY) spectrum of **8**, a correlation was observed between the signals of the methine proton at C-7 and the methine proton at C-5, while **9** showed no correlation between 7-H and 5-H. Consequently, the absolute configurations at C-7 of **8** and **9** are *R* and S, respectively.

Thus, the chemical structures of the two secoiridoid-glucosides have been elucidated as (7*R*)-7-caffeoyloxysweroside (**8**) and (7*S*)-7-caffeoyloxysweroside (**9**).

In conclusion, we have isolated three new quinovic acid-glycosides named gongganosides A (**1**), B (**2**), and C (**3**),[1] four new triterpene-glycosides named gongganosides D (**4**), E (**5**), F (**6**), and G (**7**), and two new secoiridoid-glucosides, (7*R*)-7-caffeoyloxysweroside (**8**) and (7*S*)-7-caffeoyloxysweroside (**9**), from the bark of *Bhesa paniculata* (Celastraceae), a medicinal plant in Indonesia.

Experimental

The instruments used to obtain physical data and the experimental conditions for chromatography were the same as in our previous paper.[1]

Isolation of Gongganosides D (4), E (5), F (6), and G (7), and Secoiridoid-Glucosides (8, 9) As was noted earlier,[1] the MeOH extract (700 g) of the bark of *Bhesa paniculata* ARN. (Celastraceae) collected in Sumatra Island, Indonesia in August 1990, was treated with a mixture of EtOAc and H_2O (1:1). The water phase was treated with *n*-BuOH and the solvent from both phases was evaporated off under reduced pressure to give the *n*-BuOH extract (281 g, 13%) and the H_2O extract (318 g, 15%). The *n*-BuOH extract was subjected to TSK gel G3000S column chromatography (eluting with $H_2O \rightarrow$EtOH), SiO_2 column chromatography [eluting with $CHCl_3$:MeOH:H_2O=7:3:1 (lower phase)→$CHCl_3$:MeOH:H_2O=65:35:10 (lower phase)], Sephadex LH-20 column chromatography (eluting with MeOH), reversed-phase column chromatography (Cosmosil 75C_{18}-OPN, eluting with MeOH:H_2O=3:7→MeOH:H_2O=9:1), and reversed-phase HPLC (Wakosil-II5C_{18} HG, eluting with MeOH:H_2O=7:3) to afford gongganoside D (**4**, 770 mg, 0.035%, from the bark), E (**5**, 1.62 g 0.074%), F (**6**, 330 mg, 0.015%), G (**7**, 242 mg, 0.011%), (7*R*)-7-caffeoyloxysweroside (**8**, 112 mg, 0.0051%), (7*S*)-7-caffeoyloxysweroside (**9**, 194 mg, 0.0088%), vogeloside (**13**, 3.30 g, 0.15%),[2] epi-vogeloside (**14**, 2.64 g, 0.12%),[2] sweroside (**16**, 7.26 g, 0.33%),[3] and rubescine (145 mg, 0.0066%).[4]

Gongganoside D (**4**): A white amorphous solid, $[\alpha]_D$ −17.0° (*c*=1.1 in MeOH at 23 °C). IR (KBr) cm^{-1}: 3400, 2934, 1696, 1652, 1453, 1076.

^{1}H-NMR (CD_3OD) δ: 0.79 (3H, s, 26-H_3), 0.87 (3H, s, 24-H_3), 0.93 (3H, d, J=6.7 Hz, 30-H_3), 0.95 (3H, s, 25-H_3), 1.11 (3H, s, 23-H_3), 1.18 (3H, s, 29-H_3), 1.33 (3H, s, 27-H_3), 2.49 (1H, s, H-18), 4.40 (1H, d, J=7.7 Hz, 1′-H), 5.17 (1H, br s, 1‴-H), 5.28 (1H, br s, 12-H); (pyridine-d_5) δ: 0.72 (3H, s), 0.97 (3H, s), 1.03 (3H, s), 1.06 (3H, d, J=6.6 Hz, 30-H_3), 1.26 (3H, s, 23-H_3), 1.39 (3H, s, 27-H_3), 1.67 (3H, s, 29-H_3), 1.72 (3H, d, J=6.0 Hz, 6‴-H_3), 2.97 (1H, s, 18-H), 3.24 (1H, dd, J=3.8, 11.0 Hz, 3-H), 4.87 (1H, d, J=7.4 Hz, 1′-H), 4.99 (1H, br s, 12-H), 5.70 (1H, d, J=7.1 Hz, 1″-H), 6.39 (1H, br s, 1‴-H). ^{13}C-NMR (CD_3OD): as given in Table I; (pyridine-d_5) δ_C: 15.0 (25-C), 16.3 (30-C), 16.4 (24-C), 16.8 (26-C), 18.2 (6‴-C), 18.6 (6-C), 23.6 (11-C), 24.3 (27-C), 26.0 (16-C), 26.1 (2-C), 26.6 (21-C), 26.8 (29-C), 28.0 (23-C), 28.9 (15-C), 33.1 (7-C), 36.5 (10-C), 38.2 (22-C), 38.4 (1-C), 39.3 (4-C), 39.9 (8-C), 41.7 (14-C), 42.0 (20-C), 47.3 (9-C), 48.0 (17-C), 54.3 (18-C), 55.6 (5-C), 62.3 (6′-C), 63.1 (6″-C), 69.0 (5‴-C), 71.6 (4′-C), 72.0 (3‴-C), 72.2 (2‴-C), 72.3 (totally 2C, 19-C, 4″-C), 74.0 (4‴-C), 77.6 (totally 2C, 5′-C, 5″-C), 78.3 (2′-C), 78.4 (3′-C), 78.8 (3″-C), 79.0 (2″-C), 89.7 (3-C), 101.5 (1‴-C), 101.7 (1″-C), 104.9 (1′-C), 127.6 (12-C), 139.6 (13-C), 180.8 (28-C). Positive FAB-MS m/z: 965 $(M+Na)^+$. High-resolution positive FAB-MS m/z: Calcd for $C_{48}H_{78}NaO_{18}$: 965.5086. Found: 965.5062 $(M+Na)^+$. Negative FAB-MS m/z: 941 $(M-H)^-$, 795 (**i**), 633 (**ii**), 471 (**iii**).

Gongganoside E (**5**): A white amorphous solid, $[\alpha]_D$ −26.6° (c=1.1 in pyridine at 21 °C). IR (KBr) cm^{-1}: 3390, 2926, 1726, 1636, 1455, 1070. ^{1}H-NMR (CD_3OD) δ: 0.77 (3H, s, 26-H_3), 0.87 (3H, s, 24-H_3), 0.93 (3H, d, J=6.6 Hz, 30-H_3), 0.96 (3H, s, 25-H_3), 1.11 (3H, s, 23-H_3), 1.19 (3H, s, 29-H_3), 1.32 (3H, s, 27-H_3), 2.51 (1H, s, 18-H), 4.40 (1H, d, J=7.7 Hz, 1′-H), 5.17 (1H, d, J=1.5 Hz, 1‴-H), 5.30 (1H, br s, 12-H), 5.32 (1H, d, J=7.9 Hz, 1⁗-H); (pyridine-d_5) δ: 0.87 (3H, s), 1.08 (3H, d, J=6.6 Hz, 30-H_3), 1.11 (3H, s), 1.18 (3H, s), 1.36 (3H, s, 23-H_3), 1.41 (3H, s, 27-H_3), 1.70 (3H, s, 29-H_3), 1.78 (3H, d, J=5.9 Hz, 6‴-H_3), 2.92 (1H, s, 18-H), 3.30 (1H, dd, J=4.2, 11.0 Hz, 3-H), 4.93 (1H, d, J=7.3 Hz, 1′-H), 5.55 (1H, br s, 12-H), 5.83 (1H, d, J=7.1 Hz, 1″-H), 6.35 (1H, d, J=7.8 Hz, 1⁗-H), 6.39 (1H, br s, 1‴-H). ^{13}C-NMR (CD_3OD) : as given in Table I; (pyridine-d_5) δ_C: 15.6 (25-C), 16.8 (30-C), 16.7 (24-C), 17.3 (26-C), 19.0 (6-C), 18.7 (6‴-C), 24.0 (11-C), 24.5 (27-C), 26.1 (16-C), 26.5 (2-C), 27.0 (21-C), 27.0 (29-C), 28.4 (23-C), 29.3 (15-C), 33.5 (7-C), 36.9 (10-C), 37.7 (22-C), 38.8 (1-C), 39.6 (4-C), 40.5 (8-C), 42.1 (14-C), 42.1 (20-C), 47.7 (9-C), 48.6 (17-C), 54.4 (18-C), 56.0 (5-C), 62.3 (6⁗-C), 62.7 (6′-C), 63.4 (6″-C), 69.5 (5‴-C), 71.2 (4⁗-C), 71.8 (4′-C), 72.4 (3‴-C), 72.6 (totally 2C, 2‴-C, 19-C), 72.8 (4″-C), 74.0 (2⁗-C), 74.3 (4‴-C), 77.5 (5′-C), 77.9 (5″-C), 78.4 (5⁗-C), 78.9 (totally 2C, 2′-C, 3⁗-C), 79.2 (3″-C), 79.4 (totally 2C, 3′-C, 2″-C), 89.8 (3-C), 95.8 (1⁗-C), 102.0 (totally 2C, 1″-C, 1‴-C), 105.1 (1′-C), 128.4 (12-C), 139.3 (13-C), 177.0 (28-C). Positive FAB-MS m/z: 1127 $(M+Na)^+$. High-resolution positive FAB-MS m/z: Calcd for $C_{54}H_{88}NaO_{23}$: 1127.5614. Found: 1127.5586 $(M+Na)^+$. Negative FAB-MS m/z: 1103 $(M-H)^-$, 941, 795, 633, 471.

Gongganoside F (**6**): A white amorphous solid, $[\alpha]_D$ −15.6° (c=1.1 in MeOH at 21 °C). IR (KBr) cm^{-1}: 3420, 2926, 1728, 1633, 1452, 1078. ^{1}H-NMR (CD_3OD) δ: 0.82 (3H, s, 26-H_3), 0.86 (3H, s, 24-H_3), 0.88 (3H, d, J=6.4 Hz, 29-H_3), 0.96 (totally 6H, br s, 25-H_3, 30-H_3), 1.10 (totally 6H, s, 23-H_3, 27-H_3), 2.22 (1H, d, J=11.1 Hz, H-18), 4.39 (1H, d, J=7.6 Hz, 1′-H), 5.17 (1H, br s, 1‴-H), 5.23 (1H, br s, 12-H), 5.34 (1H, d, J=7.9 Hz, 1⁗-H); (pyridine-d_5) δ: 0.81 (3H, s), 0.87 (3H, d, J=7.3 Hz, 30-H_3), 0.92 (3H, d, J=6.3 Hz, 29-H_3), 1.07 (3H, s), 1.11 (3H, s), 1.18 (3H, s, 23-H_3), 1.34 (3H, s, 27-H_3), 1.77 (3H, d, J=6.1 Hz, 6‴-H_3), 2.49 (1H, d, J=11.2 Hz, 18-H), 3.31 (1H, dd, J=3.9, 11.3 Hz, 3-H), 4.93 (1H, d, J=7.5 Hz, 1′-H), 5.41 (1H, br s, 12-H), 5.82 (1H, d, J=7.3 Hz, 1″-H), 6.25 (1H, d, J=7.9 Hz, 1⁗-H), 6.38 (1H, br s, 1‴-H). ^{13}C-NMR (CD_3OD) : as given in Table I; (pyridine-d_5) δ_C: 15.6 (25-C), 16.8 (24-C), 17.3 (29-C), 17.5 (26-C), 18.4 (6‴-C), 18.9 (6-C), 21.2 (30-C), 23.6 (27-C), 23.7 (11-C), 24.6 (16-C), 26.0 (2-C), 28.4 (23-C), 28.6 (15-C), 30.7 (21-C), 33.5 (7-C), 36.8 (22-C), 36.9 (10-C), 38.9 (1-C), 39.0 (20-C), 39.3 (19-C), 39.5 (4-C), 40.0 (8-C), 42.4 (14-C), 48.2 (9-C), 49.6 (17-C), 53.2 (18-C), 55.9 (5-C), 62.2 (6⁗-C), 62.7 (6′-C), 63.3 (6″-C), 69.4 (5‴-C), 71.1 (4⁗-C), 71.9 (4′-C), 72.3 (3‴-C), 72.6 (2‴-C), 72.8 (4″-C), 74.0 (2⁗-C), 74.2 (4‴-C), 77.5 (5′-C), 77.8 (5″-C), 78.4 (5⁗-C), 78.8 (3⁗-C), 78.9 (2′-C), 79.1 (3″-C), 79.4 (totally 2C, 3′-C, 2″-C), 89.7 (3-C), 95.6 (1⁗-C), 102.0 (totally 2C, 1″-C, 1‴-C), 105.1 (1′-C), 126.0 (12-C), 138.9 (13-C), 176.1 (28-C). Positive FAB-MS m/z: 1111 $(M+Na)^+$. High-resolution positive FAB-MS m/z: Calcd for $C_{54}H_{88}NaO_{22}$: 1111.5665. Found: 1111.5651 $(M+Na)^+$. Negative FAB-MS m/z: 1087 $(M-H)^-$, 925, 779, 617, 455.

Gongganoside G (**7**): A white amorphous solid, $[\alpha]_D$ +40.7° (c=0.95 in MeOH at 18 °C). IR (KBr) cm^{-1}: 3420, 2926, 1726, 1706, 1635, 1453, 1075. ^{1}H-NMR (CD_3OD) δ: 0.84 (3H, s, 24-H_3), 0.88 (totally 6H, br s, 26-H_3, 29-H_3), 0.97 (totally 6H, br s, 25-H_3, 30-H_3), 1.06 (3H, s, 23-H_3), 2.28 (1H, d, J=10.9 Hz, H-18), 4.38 (1H, d, J=7.7 Hz, 1′-H), 5.16 (1H, d, J=1.4 Hz, 1‴-H), 5.37 (1H, d, J=7.9 Hz, 1⁗-H) , 5.81 (1H, br s, 12-H), 9.84 (1H, s, 14-CHO); (pyridine-d_5) δ: 0.73 (totally 6H, br s, 25-H_3, 30-H_3), 0.90 (3H, d, J=6.8 Hz, 29-H_3), 0.98 (3H, s), 1.06 (3H, s), 1.18 (3H, s, 23-H_3), 1.72 (3H, d, J=5.7 Hz, 6‴-H_3), 2.48 (1H, d, J=11.0 Hz, 18-H), 3.56 (1H, dd, J=4.1, 11.2 Hz, 3-H), 4.85 (1H, d, J=7.1 Hz, 1′-H), 5.75 (1H, d, J=7.2 Hz, 1″-H), 5.93 (1H, br s, 12-H), 6.25 (1H, d, J=7.8 Hz, 1⁗-H), 6.33 (1H, br s, 1‴-H), 10.16 (1H, s, 14-CHO). ^{13}C-NMR (CD_3OD): as given in Table I; (pyridine-d_5) δ_C: 16.2 (25-C), 16.6 (24-C), 17.6 (29-C), 18.2 (6-C), 18.5 (26-C), 18.8 (6‴-C), 20.1 (15-C), 21.0 (30-C), 23.6 (11-C), 24.7 (16-C), 26.3 (2-C), 28.1 (23-C), 30.0 (21-C), 36.0 (22-C), 36.3 (7-C), 36.5 (19-C), 37.0 (10-C), 38.5 (1-C), 38.7 (20-C), 39.4 (4-C), 41.4 (8-C), 47.8 (17-C), 49.3 (9-C), 53.5 (18-C), 55.7 (5-C), 59.2 (14-C), 62.1 (6⁗-C), 62.6 (6′-C), 63.3 (6″-C), 69.4 (5‴-C), 71.0 (4⁗-C), 71.8 (4′-C), 72.3 (3‴-C), 72.5 (2‴-C), 72.7 (4″-C), 74.0 (2⁗-C), 74.2 (4‴-C), 77.4 (5′-C), 77.8 (5″-C), 78.4 (5⁗-C), 78.8 (3⁗-C), 78.9 (2′-C), 79.2 (totally 2C, 3′-C, 3″-C), 79.3 (2″-C), 89.2 (3-C), 95.6 (1⁗-C), 101.9 (totally 2C, 1″-C, 1‴-C), 105.0 (1′-C), 132.0 (totally 2C, 12-C, 13-C), 175.9 (28-C), 207.2 (27-C). Positive FAB-MS m/z: 1125 $(M+Na)^+$. High-resolution positive FAB-MS m/z: Calcd for $C_{54}H_{86}NaO_{23}$: 1125.5458. Found: 1125.5463 $(M+Na)^+$. Negative FAB-MS m/z: 1101 $(M-H)^-$, 939, 793, 631, 469.

(7*R*)-7-Caffeoyloxysweroside (**8**): A white amorphous solid, $[\alpha]_D$ −180.4° (c=1.2 in MeOH at 19 °C). IR (KBr) cm^{-1}: 3420, 1713, 1628, 1265, 1155, 1097, 1065, 1045, 1003. UV (MeOH) nm (log ε): 223 (4.11), 246 (4.19), 337 (4.09). ^{1}H-NMR (CD_3OD) δ: 1.71 (1H, ddd, J=10.4, 10.4, 13.1 Hz, 6a-H), 2.10 (1H, ddd, J=3.0, 3.0, 13.1 Hz, 6b-H), 2.75 (1H, dd, J=5.8, 8.9 Hz, 9-H), 3.66 (1H, dd, J=5.5, 11.9 Hz, 6′a-H), 3.90 (1H, br d, J=*ca.* 11.9 Hz, 6′b-H), 4.68 (1H, d, J=7.8 Hz, 1′-H), 5.32 (1H, d, J=10.1 Hz, 10a-H), 5.56 (1H, m, 8-H), 5.60 (1H, s, 1-H), 6.28 (1H, d, J=15.8 Hz, 2″-H), 6.63 (1H, dd, J=3.0, 10.4 Hz, 7-H), 6.78 (1H, d, J=8.3 Hz, 8″-H), 6.98 (1H, d, J=8.3 Hz, 9″-H), 7.07 (1H, s, 5″-H), 7.65 (1H, d, J=15.8 Hz, 3″-H), 7.65 (1H, s, 3-H). ^{13}C-NMR: as given in Table II. Positive FAB-MS m/z: 559 $(M+Na)^+$. High-resolution positive FAB-MS m/z: Calcd for $C_{25}H_{28}NaO_{13}$: 559.1428. Found: 559.1412 $(M+Na)^+$.

(7*S*)-7-Caffeoyloxysweroside (**9**): A white amorphous solid, $[\alpha]_D$ +29.8° (c=1.1 in MeOH at 21 °C). IR (KBr) cm^{-1}: 3420, 1713, 1617, 1272, 1211, 1155, 1102, 1077, 1038, 1017. UV (MeOH) nm (log e): 222 (4.11), 247 (4.22), 335 (4.18). ^{1}H-NMR (CD_3OD) δ: 2.74 (1H, dd, J=5.6, 9.2 Hz, 9-H), 3.68 (1H, dd, J=4.7, 12.0 Hz, 6′a-H), 3.90 (1H, br d, J=*ca.* 12.0 Hz, 6′b-H), 4.72 (1H, d, J=7.7 Hz, 1′-H), 5.31 (1H, d, J=9.9 Hz, 10a-H), 5.33 (1H, d, J=17.5 Hz, 10b-H), 5.56 (1H, m, 8-H), 5.60 (1H, s, 1-H), 6.31 (1H, d, J=15.9 Hz, 2″-H), 6.70 (1H, br s, 7-H), 6.78 (1H, d, J=8.2 Hz, 8″-H), 7.00 (1H, d, J=8.2 Hz, 9″-H), 7.07 (1H, s, 5″-H), 7.63 (1H, d, J=15.9 Hz, 3″-H), 7.67 (1H, s, 3-H). ^{13}C-NMR: as given in Table II. Positive FAB-MS m/z: 559 $(M+Na)^+$. High-resolution positive FAB-MS m/z: Calcd for $C_{25}H_{28}NaO_{13}$: 559.1428. Found: 559.1431 $(M+Na)^+$.

Enzymatic Hydrolysis of Gongganoside D (4) A solution of **4** (26 mg) in K_2HPO_4–KH_2PO_4 buffer (pH 5.0, 5.0 ml) was treated with crude hesperidinase (4 mg, from *Aspergillus niger*, Sigma Chemical Co.) and the whole was stirred at 50 °C for 24 h, then allowed to cool. The solvent was evaporated off under reduced pressure, and the residue was purified by column chromatography [SiO_2 2 g, $CHCl_3$: MeOH : H_2O = 7 : 3 : 1 (lower phase)] to afford an aglycone (**10**, 8 mg, 64%) and a mixture of glucose and rhamnose. The aglycone (**10**) was identical with an authentic sample of pomolic acid,[5] based on comparisons of IR, ^{1}H- and ^{13}C-NMR data. The sugar mixture was subjected to GLC analysis, which revealed the presence of D-glucose and L-rhamnose in 2 : 1 ratio.

GLC analysis for determination of the absolute configurations of monosaccharides was carried out by means of the procedure described in the literature.[6] GLC conditions were as described in the previous paper.[1]

Alkaline Hydrolysis of Gongganoside E (5) Giving 4 LiOH (6 mg) was added to a solution of gongganoside E (**5**, 24 mg) in water (3.0 ml). The reaction mixture was heated with stirring at 40 °C for 10 h, then cooled to ambient temperature, and the solvent was removed on a rotary evaporator to give a product (21 mg). The product was purified by column chromatography (SiO_2 3 g, CH_2Cl_2 : MeOH = 3 : 1) to afford a hydrolysate (15 mg, 73%), which was identical with gongganoside D (**4**), based on comparisons of IR, ^{1}H- and ^{13}C-NMR data, and D-glucose,

which was determined by the GLC analysis.[6]

Acidic Hydrolysis of Gongganoside F (6) Gongganoside F (**6**, 24 mg) was treated with 5% aqueous HCl (6.0 ml) at 80 °C for 10 h, then allowed to cool. The solvent was removed under reduced pressure to give a product (10 mg), which was purified by column chromatography [SiO_2 2 g, $CHCl_3$: MeOH : H_2O = 7 : 3 : 1 (lower phase)] to afford a sugar mixture and **11** (8 mg, 83%), which was identical with an authentic sample of ursolic acid[9] based on comparisons of IR, ^{1}H- and ^{13}C-NMR data. The sugar mixture was subjected to GLC analysis[6] to reveal D-glucose and L-rhamnose in 3 : 1 ratio.

Partial Hydrolysis of Gongganoside G (7) Followed by Enzymatic Hydrolysis A mixture of **7** (33 mg) in water–dioxane (2 : 1, 3.0 ml) and LiOH (6 mg) was heated at 80 °C for 10 h with stirring, then allowed to cool. The solvent was evaporated off under reduced pressure to give a product, which was purified by column chromatography (SiO_2 3 g, CH_2Cl_2 : MeOH = 3 : 1) to afford a hydrolysate (27 mg) and D-glucose (identified by GLC analysis[6]). A stirred solution of the hydrolysate (27 mg) in K_2HPO_4–KH_2PO_4 buffer (10 ml) at 50 °C was treated with crude hesperidinase (3 mg) for 48 h. After cooling, the mixture was concentrated under reduced pressure to give a product, which was purified by column chromatography [SiO_2 3 g, $CHCl_3$: MeOH : H_2O = 7 : 3 : 1 (lower phase)] to afford 27-oxoursolic acid (**12**, 6 mg, 44%) and a mixture of glucose and rhamnose. The sugar mixture was subjected to GLC analysis,[6] which revealed the composition to be D-glucose and L-rhamnose in 2 : 1 ratio.

27-Oxoursolic Acid (**12**): A white amorphous solid, $[\alpha]_D$ +28.7° (c = 0.33 in $CHCl_3$ at 12 °C). IR (KBr) cm^{-1}: 3430, 2927, 1726, 1699, 1651, 1384. ^{1}H-NMR ($CDCl_3$: CD_3OD = 4 : 1) δ: 0.76 (3H, s, 24-H_3), 0.85 (3H, d, J = 4.8 Hz, 29-H_3), 0.88 (3H, s, 26-H_3), 0.89 (3H, d, J = 4.8 Hz, 30-H_3), 0.94 (3H, s, 25-H_3), 1.26 (3H, s, 23-H_3), 3.15 (1H, dd, J = 7.3, 9.0 Hz, 3-H), 5.81 (1H, br s, 12-H), 9.83 (1H, s, 14-CHO). ^{13}C-NMR ($CDCl_3$: CD_3OD = 4 : 1) δ_C: 15.3 (25-C), 15.9 (24-C), 17.2 (29-C), 17.6 (26-C), 18.0 (6-C), 20.1 (30-C), 20.6 (15-C), 23.2 (11-C), 23.9 (16-C), 26.4 (23-C), 27.6 (2-C), 29.4 (21-C), 29.8 (7-C), 35.8 (22-C), 36.0 (19-C), 37.1 (totally 2C, 10-C, 1-C), 38.4 (20-C), 38.5 (4-C), 38.6 (8-C), 40.7 (17-C), 52.9 (totally 2C, 9-C,18-C), 55.1 (5-C), 58.8 (14-C), 78.2 (3-C), 131.2 (12-C), 131.9 (13-C), 180.2 (28-COOH), 207.7 (27-C). Positive FAB-MS m/z: 470 (M^+). High-resolution positive FAB-MS m/z: Calcd for $C_{30}H_{46}O_4$: 470.3396. Found: 470.3393 (M^+).

Alkaline Treatment of (7*R*)-7-Caffeoyloxysweroside (8) A solution of **8** (30 mg) in 3% NaOMe–MeOH (3.0 ml) was stirred at 30 °C for 1 h. The reaction mixture was neutralized with Dowex 50 × 8 (H^+ form) and the resin was filtered off. The solvent was evaporated off under reduced pressure from the filtrate to give a product (21 mg). Purification of the product by HPLC (Cosmosil 5C_{18}-AR, MeOH : H_2O = 1 : 2) afforded **13** (5 mg), **14** (4 mg), and **15** (3 mg), which were identified as vogeloside (**13**),[2] epi-vogeloside (**14**)[2] and methyl caffeate (**15**) by comparisons of IR, ^{1}H-NMR data and by HPLC (Cosmosil 5C_{18}-AR, MeOH : H_2O = 1 : 2) analysis.

Alkaline Treatment of (7*S*)-7-Caffeoyloxysweroside (9) A solution of **9** (27 mg) in 3% NaOMe–MeOH (3.0 ml) was stirred at 30 °C for 1 h. The reaction mixture was worked up through the same procedure as described for **8**, giving vogeloside (**13**, 4 mg), epi-vogeloside (**14**, 3 mg), and methyl caffeate (**15**, 3 mg).

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