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TRITERPENOID GLYCOSIDES FROM BARK OF *MELIOSMA LANCEOLATA*

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Key Word Index—*Meliosma lanceolata*; Sabiaceae; triterpenoid glycoside; bayogenin bisdesmosidic glycoside; 2β,3β,23-trihydroxyolean-12-en-28-oic acid; 28-*O*-glucosyl-bayogenin-3-*O*-4′-anhydro-4′,5′-didehydroglucuronide.

Abstract—From the bark of *Meliosma lanceolate*, nine triterpenoid glycosides including the 28-*O*-β-D-glucopyranosyl ester of bayogenin-3-*O*-β-D-glucuronopyranoside, its 4′-*O*-β-D-galactopyranoside and 4′-*O*-α-L-arabinopyranoside were isolated and the structures characterized along with that of 28-*O*-β-D-glucopyranosyl-bayogenin-3-*O*-β-D-4′-anhydro-4′,5′-didehydroglucuronopyranoside. Bisdesmosidic triosides of hederagenin were obtained as minor components.

INTRODUCTION

The genus *Meliosma* is distributed widely in East and South-East Asia. One of the species, *M. lanceolata* Bl., is indigenous to Malaysia and Indonesia, and is used locally for the treatment of ailments of the liver. This paper deals with the isolation and characterization of triterpenoid glycosides from the bark of the plant.

RESULTS AND DISCUSSION

When the methanol percolate of the bark was treated in the usual manner, including reversed-phase and normal-phase column chromatography, nine glycosides (**1**–**9**) were isolated. Among them, **5** was predominant.

Compound **1** showed a $[M+Na]^+$ peak at *m/z* 863.4404 ($C_{43}H_{68}O_{16}+Na$). The presence in the ^1H NMR spectrum of five tertiary methyl signals, but no secondary methyl signals, and of two doublet proton signals at δ 3.69 (*d*, 11 Hz) and 4.36 (*d*, 11 Hz) all originating from the aglycone moiety indicated that the aglycone was an oleanane-type triterpenoid with one primary carbinol. The presence of a trisubstituted olefinic linkage at C-12/C-13 was confirmed by the appropriate ^1H (δ 5.43, *br s*) and ^{13}C (δ 123.0 *d*, 144.1 *s*) signals. Two secondary hydroxyl groups were assigned to the 2β and 3β positions based on the presence of two doublet signals at δ 4.78 (*q*, $J=3$ Hz) and 4.35 (*d*, $J=3$ Hz). The primary carbinol was located to C-23, by comparison of the ^{13}C chemical shifts with those of the corresponding triterpenoids, and the aglycone was assigned as 2β,3β,23-trihydroxyolean-12-en-28-oic acid (bayogenin) [1–4].

In the ^1H NMR spectrum, two anomeric protons were observed at δ 6.30 and 5.24 (both 8 Hz doublet signals). The former suggested the presence of an ester-linked sugar at a carboxyl group, possibly C-28. The sugar was identified as glucose based on the ^1H and ^{13}C NMR, and ^1H–^1H COSY spectra. The sugar represented by the anomeric proton at δ 5.24 had no C-6 carbinyl proton signals based on the ^1H–^1H COSY investigation, and instead one carbomethoxyl signal was observed at δ 3.68. The signals from H-1′–H-5′ showed glucose-type coupling patterns and the second sugar was considered to be glucuronic acid methyl ester. The cross-peaks between the anomeric protons and C-28 or C-3 in HMBC measurements suggested that the glucose and glucuronic acid moieties were linked to C-28 and C-3, respectively.

Compound **2** gave rise to ^1H and ^{13}C NMR spectra that were similar to those of **1**, except for the presence of signals due to a carbomethoxyl residue. On methylation with CH_2N_2–ether, **2** was converted into **1**. Therefore, **2** was characterized to be demethylated **1**.

Compound **3** was less polar than **2** on TLC and retained UV absorption at 232 nm. Mass spectrometry gave a $[M+Na]^+$ peak at *m/z* 845.4313, suggesting a molecular formular, $C_{43}H_{66}O_{15}$, 18 mu smaller than **1**. Because the presence of the 28-*O*-glucosyl-bayogenin moiety was confirmed by the NMR spectra, the UV absorption at 232 nm was considered to be due to the sugar moiety at C-3, in which the anomeric proton was observed in the lower-field at δ 5.85, H-4 as a 3 Hz doublet signal (δ 6.48) but no H-5 signal was found. In the ^{13}C NMR spectrum the carbonyl carbon of C-6 in

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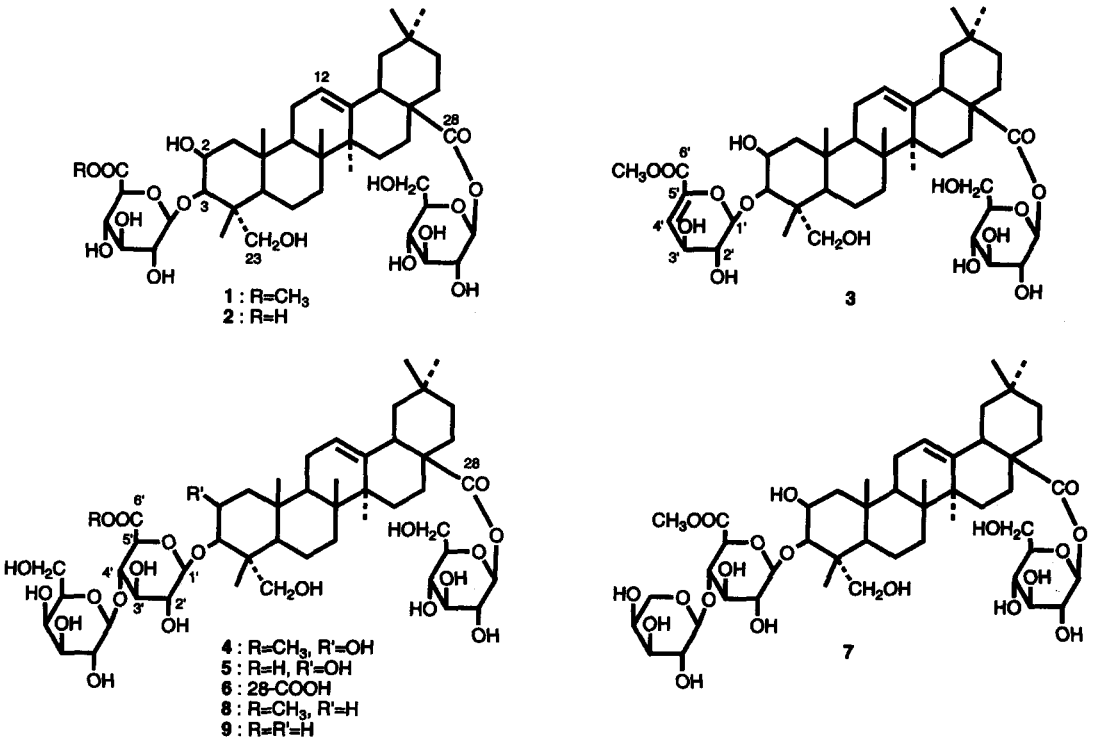

the glucuronic acid moiety was shifted to higher-field by *ca* 7 ppm, and two olefinic carbon signals at 114.3 ppm and 141.1 ppm could be assigned to C-4 and C-5 of the glucuronic acid unit, respectively. Thus, the structure was determined to be 28-*O*-glucopyranosyl-bayogenin - 3 - *O* - 4′ - anhydro - 4′,5′ - didehydroglucuronopyranoside. The 28-deglucosyl derivative of **3** has been reported from *Castanospermum* [1], and the NMR chemical shifts of the corresponding moieties in **3** were in good agreement with those in the literature.

The major glycoside **5**, showed polar behaviour but its ^{1}H and ^{13}C NMR signals were similar to those of the less polar **4**, except for the absence of the signals due to the carbomethoxyl group in **4**. As **5** was converted into **4** by CH_2N_2–ether, **4** was assigned to be the 6′ methyl ester derivative of **5**. The mass spectra of **4** and **5** gave $[M+Na]^+$ peaks at *m/z* 1025.4934 ($C_{49}H_{78}O_{21}$ + Na) and 1011.4782 ($C_{48}H_{76}O_{21}$ + Na), respectively. The NMR spectra suggested **4** and **5** to be triosides composed of glucose, galactose and glucuronic acid or its methyl ester. As ^{13}C signals due to the structures of **1** or **2** were assignable in the spectra of **4** and **5**, the glucose and glucuronic acid were attached to the 28-COOH and 3-OH groups of bayogenin, respectively. The location of the galactose residue was assigned to 4-OH of glucuronic acid, based on the lower-field shift of C-4 (+8.8 ppm) and the higher-field shifts of C-3 (−1.2 ppm) and C-5 (−1.2 ppm) of glucuronic acid. The identities of the component sugars were further confirmed by GC of methyl glucoside, methyl galactoside and methyl glucuronide 6-methyl ester obtained by methanolysis of **5**. In order to determine the absolute configuration of each sugar, the glucose at 28-COOH of **5** was first removed to form **6**, which was then methylated with CH_2N_2–ether to form a dimethyl ester of **6** (**5b**). On NaBH 4 reduction, **5b** was converted into the 28-methyl ester of 3-*O*-galactosyl-glucoside (**5c**). After hydrolysis of **5c**, the sugars and the glucose from 28-COOH were converted to their thiazolidine derivatives [5] and analysed by GC to confirm that all the sugars of **5** were in the D-form. The structure of **5** was thus represented as 28-*O*-*β*-D-glucopyranosyl-bayogenin-3-*O*-*β*-D-galactopyranosyl-(1→4)-*β*-D-glucuronopyranoside.

Compound **7** gave a $[M+Na]^+$ peak at *m/z* 995.4822, indicating it to be a trioside. In the ^{1}H NMR spectrum, three anomeric proton signals were observed at δ 6.31 (*d*, $J = 8$ Hz), 5.19 (*d*, $J = 8$ Hz) and 4.81 (*d*, $J = 9$ Hz), the first two of which were assignable to those of glucose at 28-COOH and glucuronic acid at 3-OH, respectively. On comparison of the NMR signals with those of **1** and **4**, the signals due to **1** in **6** were assignable. The third sugar, having an anomeric proton signal at δ 4.81 appeared to be arabinose, based on the analysis of the proton signals in the ^{1}H–^{1}H COSY spectrum. The C-4 signal of the glucuronic acid moiety was shifted to the lower-field by +7.5 ppm, and C-3 and C-5 to the higher-field by −2.0 ppm and −1.9 ppm, respectively, when compared with the corresponding signals of **1**, suggesting that the arabinose unit was linked to the 4-OH of glucuronic acid. In order to identify the sugars, as well as their configurations, **7** was treated in the same manner as **5** and confirmed to be composed of D-glucose, D-glucuronic acid and L-

arabinose. The structure of **7** was therefore determined to be 28-*O*-*β*-D-glucopyranosyl-bayogenin-3-*O*-*α*-L-arabinopyranosyl-(1→4)-*β*-D-glucuronopyranoside.

Based on the mass spectral data, **8** and **9** were 16 amu smaller than **4** and **5**, respectively. While the ^{13}C NMR spectra showed that **8** and **9** contained the same aglycone, the proton signals of H-3 in the aglycone were observed as a double-doublet pattern

Table 1. ^{13}C NMR spectral data for compounds **1–9** (δ in pyridine-d_5, 100 MHz)

C	1*	2	3*	4*	5	6	7*	8	9
1	44.3	45.5	44.7	44.3	45.0	44.3	44.3	38.6	38.6
2	71.0	68.5	70.7	70.9	69.3	70.3	70.9	25.8	25.6
3	82.8	84.1	81.9	83.1	84.0	83.4	83.0	82.7	83.3
4	42.9	42.3a	42.9	42.8	42.6	42.8	42.8	43.4	43.3
5	47.6	48.3	47.5	47.7	48.0	47.8	47.6	47.5	47.6
6	17.9	18.3	17.6	17.9	18.2	18.0	17.9	18.1	18.2
7	32.8	33.0	32.8	32.8	33.0	33.0	32.8	32.8	32.8
8	40.0	40.1	40.0	40.0	40.1	39.9	40.0	39.9	39.9
9	48.5	48.5	48.5	48.5	48.6	48.5	48.5	48.1	48.1
10	36.9	37.3	36.9	36.9	37.1	37.0	36.9	36.8	36.9
11	23.9	24.1	23.9	23.9	24.1	24.0	23.9	23.8	23.8
12	123.0	122.9	123.0	123.0	123.0	122.8	122.9	122.8	122.9
13	144.1	144.0	144.1	144.1	143.8	144.7	144.1	144.1	144.1
14	42.2	42.2a	42.3	42.3	42.3	42.3	42.2	42.1	42.1
15	28.2	28.1	28.2	28.2	28.2	28.2	28.2	28.2	28.2
16	23.3	23.4	23.4	23.4	23.4	23.7	23.3	23.4	23.4
17	46.9	47.0	47.0	46.9	47.0	46.6	46.9	46.9	46.9
18	41.7	41.7	41.7	41.7	41.7	42.0	41.7	41.7	41.7
19	46.1	46.1	46.1	46.1	46.1	46.3	46.1	46.1	46.1
20	30.7	30.7	30.7	30.7	30.7	30.9	30.7	30.7	30.7
21	34.0	34.0	34.0	34.0	34.0	34.2	34.0	33.9	34.0
22	32.5	32.5	32.5	32.5	32.5	32.4	32.5	32.5	32.5
23	64.5	65.8	64.9	65.0	65.7	65.4	64.9	64.5	64.5
24	14.9	14.7	14.7	14.8	14.8	14.9	14.8	13.4	13.5
25	17.2	17.8	17.2	17.2	17.6	17.3	17.2	16.1	16.1
26	17.5	17.8	17.6	17.5	17.8	17.5	17.5	17.5	17.5
27	26.1	26.1	26.1	26.1	26.1	26.2	26.1	26.0	26.1
28	176.3	176.5	176.3	176.3	176.4	180.1	176.3	176.3	176.4
29	33.0	33.0	33.0	33.0	33.0	33.2	33.0	33.0	33.0
30	23.6	23.6	23.6	23.6	23.6	23.7	23.6	23.6	23.6
28-*O*-glc.									
1	95.7	95.7	95.7	95.7	95.7		95.7	95.7	95.7
2	74.1	74.1	74.1	74.1	74.1		74.1	74.1	74.1
3	78.8	78.8	78.8	78.8	78.9		78.8	78.8	78.9
4	71.1	71.2	71.2	71.1	71.1		71.2	71.2	71.2
5	79.2	79.2	79.2	79.2	79.2		79.2	79.2	79.2
6	62.2	62.2	62.2	62.2	62.2		62.2	62.2	62.3
3-*O*-glcA (or glcA(Me))									
1	106.4	103.7	104.1	106.1	104.0	105.1a	106.1	105.9	103.3
2	75.1	75.2	71.9	74.5	75.0a	74.3b	74.7	74.8	75.0
3	77.7	78.0	68.2	75.9	76.8	76.6	75.7	76.0	76.0
4	73.0	73.2	114.3	82.3	82.0	82.8	80.5	82.9	83.3
5	77.0	75.5	141.1	74.9	74.3a	75.5b	75.1	75.1	72.4
6	170.6	172.7	163.2	169.7	173.0	173.0	169.7	169.7	174.0
Me	51.9		51.9	52.3			52.3	52.3	
outer sugar									
1				105.6	106.0	105.7a	105.1	105.7	106.2
2				71.8	72.6	72.5	71.5	71.9	72.4
3				74.9	74.9a	74.9b	74.2	75.0	75.0
4				69.9	69.9	69.9	69.2	69.9	69.8
5				77.2	77.2	77.2	67.4	77.2	77.2
6				61.9	62.0	62.0		61.9	61.9

*Signal assignments were based on ^{13}C–^{1}H COSY and/or HMBC spectra.

[a,b]Assignments may be interchangeable.

Table 2. ^{1}H NMR spectral data for compounds **1–9** (δ (ppm) in pyridine-d_5, 400 MHz)

H	1	2	3	4	5	6	7	8	9
2	4.78 *q* (3)	4.79 *q* (3)	4.83 *q* (3)	4.73 *q* (3)	4.67 *q* (3)	4.77 *br s*	4.75 *q* (3)		
3	4.35 *d* (3)	4.13 *d* (3)	4.48 *d* (3)	4.28 *d* (3)			4.29 *d* (3)	4.21 *dd* (10, 4)	
12	5.43 *br s*	5.43 *br s*	5.43 *br s*	5.43 *br s*	5.44 *br s*	5.48 *br s*	5.43 *br s*	5.42 *br s*	5.42 *br s*
18	3.19 *dd* (13, 4)	3.19 *dd* (13, 4)	3.19 *dd* (13, 4)	3.19 *dd* (13, 4)	3.18 *dd* (13, 4)	3.28 *dd* (13, 4)	3.19 *dd* (13, 4)	3.18 *dd* (13, 4)	3.18 *dd* (13, 4)
23	3.69 *d* (11)	3.66 *d* (11)	3.70 *d* (11)	3.67 *d* (11)	3.64 *d* (10)	3.68 *d* (11)	3.67 *d* (11)	3.68 *d* (10)	
	4.36 *d* (11)	4.09 *d* (11)	4.08 *d* (11)	4.32 *d* (11)			4.33 *d* (11)		4.28 *d* (10)
24	1.35 *s*	1.24 *s*	1.31 *s*	1.34 *s*	1.24 *s*	1.28 *s*	1.35 *s*	0.94 *s*	0.94 *s*
25	1.59 *s*	1.58 *s*	1.58 *s*	1.58 *s*	1.61 *s*	1.57 *s*	1.59 *s*	0.93 *s*	0.94 *s*
26	1.17 *s*	1.14 *s*	1.16 *s*	1.16 *s*	1.12 *s*	1.07 *s*	1.17 *s*	1.11 *s*	1.12 *s*
27	1.23 *s*	1.20 *s*	1.21 *s*	1.23 *s*	1.20 *s*	1.34 *s*	1.23 *s*	1.20 *s*	1.24 *s*
29	0.88 *s*	0.89 *s*	0.89 *s*	0.88 *s*	0.89 *s*	1.00 *s*	0.88 *s*	0.88 *s*	0.88 *s*
30	0.88 *s*	0.87 *s*	0.89 *s*	0.88 *s*	0.87 *s*	0.90 *s*	0.88 *s*	0.88 *s*	0.88 *s*
28-*O*-Glc									
1	6.30 *d* (8)	6.29 *d* (8)	6.31 *d* (8)	6.31 *d* (8)	6.29 (8)		6.31 *d* (8)	6.31 *d* (8)	6.30 *d* (8)
2	4.18 *dd* (8, 9)	4.18 *dd* (8, 9)	4.18 *dd* (8, 9)	4.18 *dd* (8, 9)	4.16 *dd* (8, 9)		4.18 *dd* (8, 9)	4.18 *dd* (8, 9)	
3	4.26 *t* (9)	4.27 *t* (9)	4.26 *t* (9)	4.26 *t* (9)	4.26 *t* (9)		4.26 *t* (9)	4.26 *t* (9)	
4	4.33 *t* (9)	4.33 *t* (9)	4.33 *t* (9)	4.33 *t* (9)	4.32 *t* (9)		4.33 *t* (9)	4.33 *t* (9)	
5	4.01 *m*	4.01 *m*	4.01 *m*	4.01 *m*	4.01 *m*		4.02 *m*	4.01 *m*	
6	4.45 *dd* (11, 2)	4.45 *br d* (12)	4.44 *dd* (11, 2)	4.35–4.36	4.44 *br d* (11)		4.45 *br d* (11)	4.30–4.45	
	4.38 *dd* (11, 4)	4.38 *dd* (12, 4)	4.37 *dd* (11, 4)	4.35–4.36	4.38 *dd* (11, 4)		4.38 *dd* (11, 4)	4.30–4.45	
3-*O*-Glc.A (or GlcA(Me))									
1	5.24 *d* (8)	4.93 *d* (7)	5.85 *d* (6)	5.20 *d* (8)	4.93 *d* (8)	5.15 *d* (8)	5.19 *d* (8)	5.12 *d* (8)	5.10 *d* (8)
2	4.01 *t* (8)	3.86 *dd* (7, 8)	4.42 *br d* (6)	3.97 *t* (8)	3.93 *t* (8)		3.96 *t* (8)	4.05 *t* (8)	
3	4.14 *t* (8)	4.18 *t* (8)	4.70 *t* (3)	4.15 *t* (8)	4.16 *t* (8)		4.10 *t* (8)	4.16 *t* (8)	
4	4.38 *dd* (10, 8)	4.03 *dd* (10, 8)	6.48 *d* (3)	4.38 *dd* (10, 8)			4.39 *dd* (10, 8)	4.30–4.45	
5	4.46 *d* (10)	4.23 *d* (10)		4.46 *d* (10)			4.40 *d* (10)	4.37 *d* (10)	
COOMe	3.68 *s*		3.66 *s*	3.81 *s*			3.80 *s*	3.83 *s*	
Outer sugar									
1				4.90 *d* (8)	4.93 *d* (8)	5.14 *d* (7)	4.81 *d* (9)	4.89 *d* (8)	5.03 *d* (8)
2				4.38 *dd* (8, 9)			4.39 *t* (9)	4.40 *dd* (8, 9)	
3				4.06 *dd* (9, 3)	4.04 *dd* (9, 3)		4.06 *dd* (9, 3)	4.06 *dd* (9, 3)	
4				4.44 *d* (3)			4.23 *br s*	4.43 *d* (3)	
5				4.07 *m*			3.73 *dd* (12, 2)	4.07 *m*	
							4.27 *dd* (12, 3)		
6				4.35–4.46				4.30–4.45	

Coupling constants (J in Hz) given in parentheses.

($J = 10.4$ Hz) and the aglycone of **8** and **9** was determined to be hederagenin. The sugar moiety was confirmed to be the same as those of **4** and **5**, based on the ^{13}C NMR spectra.

The structures of nine glycosides have been characterized. It should be noted that quite similar glycosides composed of bayogenin and glucuronc acid [2] or 4′-anhydro-4′,5′-didehydroglucuronic acid [1] are present in *Castanospermum australe* (Fabaceae), although the 28-COOH was free.

EXPERIMENTAL

General. Mps uncorr; ^1H NMR and ^{13}C NMR: 400 and 100 MHz, respectively, in pyridine-d_5 with TMS as int. standard; UV: MeOH; GC: FID; column, Shimadzu DB-1 (0.25 mm × 30 m); column temp. 250°, injector temp. 300°, detector temp. 300°; carrier gas, He 20 cm sec^{-1}, make-up gas He 50 ml min^{-1}, split ratio 1/110. TLC and silica gel CC: the solvent systems used were (1) $CHCl_3$–MeOH–H_2O (7:3:1, bottom layer; 10:5:1), (2) EtOAc–MeOH–H_2O (8:2:1), (3) 25% MeCN (for RP TLC). Spray reagent for TLC: 10% H_2SO_4.

Plant material. Barks of *M. lanceolata* were collected on Sumatra Island in August 1990 (Herbarium numbe 4042 AT. F., stored at Fukuyama University).

Extraction and isolation of compounds **1–9**. Dried powdered bark (1.7 kg) was percolated with MeOH. The MeOH soln was concd, diluted with H_2O and the deposit removed. The soln was further concd and passed through a polystyrene column (MCI-gel HP-20, Mitsubishi) eluted with H_2O and 25%, 50%, 75%, and 100% MeOH. The 75% MeOH eluate (21.1 g) was further chromatographed on an RP column (YMC-gel) and a silica gel column, repeatedly, to yield nine glycosides: **1** (11 mg), **2** (21 mg), **3** (18 mg), **4** (10 mg), **5** (1.13 g), **6** (22 mg), **7** (5 mg), **8** (5 mg), **9** (12 mg).

28-O-β-D-*Glucopyranosyl-bayogenin*-3-O-6′-O-*methyl*-β-D-*glucuronopyranoside* (**1**). A solid, $[\alpha]_D^{22}$ +20.5° (MeOH; *c* 0.56), FAB-MS *m/z*: 863.4404, $C_{43}H_{68}O_{16}$ + Na requires 863.4405.

28-O-β-D-*Glucopyranosyl-bayogenin*-3-O-β-D-*glucuronopyranoside* (**2**). A solid, $[\alpha]_D^{22}$ +14.7° (MeOH; *c* 1.09), FAB-MS *m/z*: 871.4073, $C_{42}H_{65}O_{16}$ + 2Na requires 871.4068.

28-O-β-D-*Glucopyranosyl-bayogenin*-3-O-6′-O-*methyl*-4′-*anhydro*-4′,5′-*didehydro*-β-D-*glucuronopyranoside* (**3**). A solid, $[\alpha]_D^{22}$ +12.3° (MeOH; *c* 0.93), FAB-MS *m/z*: 845.3213, $C_{43}H_{66}O_{15}$ + Na requires 845.4299. UV λ_{max} nm (log ε): 233 (3.78)

28-O-β-D-*Glucopyranosyl-bayogenin*-3-O-β-D-*galactopyranosyl*-(1→4)-6′-O-*methyl*-β-D-*glucuronopyranoside* (**4**). Prisms, mp 220–230°, $[\alpha]_D^{26}$ +27.2° (MeOH; *c* 0.53), FAB-MS *m/z*: 1025.4934, $C_{49}H_{78}O_{21}$ + Na requires 1025.4933.

28-O-β-D-*Glucopyranosyl-bayogenin*-3-O-β-D-*galactopyranosyl*-(1→4)-β-D-*glucuronopyranoside* (**5**). Prisms, mp 290–300° (dec.), $[\alpha]_D^{27}$ +20.7° (MeOH; *c* 1.19), FAB-MS *m/z*: 1011.4782, $C_{48}H_{76}O_{21}$ + Na requires 1011.4777. On Methylation of **5** with CH_2N_2 in ether, **4** was obtained, and identified by TLC and ^1H NMR. Compound **5** (40 mg) was dissolved in 20% EtOH and shaken at 38° with cellulase (practical grade type I, Sigma) (40 mg) for 4 hr, the mixt. was diluted with H_2O and extracted with *n*-BuOH. The BuOH was evapd *in vacuo* and the residue was identified as **6** by NMR. The H_2O layer was concd and subjected to YMC-gel column. The H_2O eluate (3.4 mg) was identified as D-glucose by the procedure described below.

Bayogenin-3-O-β-D-*galactopyranosyl*-(1→4)-β-D-*glucuronopyranoside* (**6**). Prisms, mp 270–280° (dec.), $[\alpha]_D^{21}$ +13.3° (MeOH; *c* 0.06), FAB-MS *m/z*: 871.4066, $C_{42}H_{65}O_{16}$ + 2Na requires 871.4068.

28-O-β-D-*Glucopyranosyl-bayogenin*-3-O-α-L-*arabinopyranosyl*-(1→4)-6′-O-*methyl*-β-D-glucuronopyranoside (**7**). A solid, $[\alpha]_D^{26}$ +28.1° (MeOH; *c* 0.26), FAB-MS *m/z*: 995.4822, $C_{48}H_{76}O_{20}$ + Na requires 995.4828.

28-O-β-D-*Glucopyranosyl-hederagenin*-3-O-β-D-*galactopyranosyl*-(1→4)-6′-O-*methyl*-β-D-*glucuronopyranoside* (**8**). A solid $[\alpha]_D^{26}$ +28.1° (MeOH; *c* 0.26), FAB-MS *m/z*: 1009.4987, $C_{49}H_{78}O_{20}$ + Na requires 1009.4984.

28-O-β-D-*Glucopyranosyl-hederagenin*-3-O-β-D-*galactopyranosyl*-(1→4)-β-D-*glucuronopyranoside* (**9**). A solid $[\alpha]_D^{21}$ +6.61° (MeOH; *c* 0.59), FAB-MS *m/z*: 995.4845, $C_{48}H_{76}O_{19}$ requires 995.4828.

Absolute configuration of sugars. Compound **6** (obtained from **5**; see above) was methylated with CH_2N_2 in Et_2O to form **6** methylate (**5b**) ($[\alpha]_D^{22}$ +29.5° (MeOH; *c* 0.61), FAB-MS *m/z*: 877.4565, $C_{44}H_{70}O_{16}$ + Na requires 877.4561). Compound **5b** (12.2 mg) was then reduced with $NaBH_4$ (20 mg) in MeOH in 1 hr. The product was purified by CC to yield 28-*O*-methyl-bayogenin-3-*O*-galactosyl-(1→4)-glucoside (**5c**, 12 mg). Compound **5c** was hydrolysed with 1 M HCl at 90° for 1 hr, deacidified with Ag_2CO_3, treated with L-cysteine methyl ester hydrochloride to form the thiazolidine derivatives which after trimethylsilyation was examined by GC (R_t of thiazolidine derivatives from **5c**; 11.14 and 11.66 min). Glucose obtained from C-28 of **5** by cellulase hydrolysis was also examined in the same manner (R_t 11.14). **7** was treated in the same manner for **5c** (R_t 7.12, 11.12 and 11.53). The thiazolidine derivatives of specimen sugars were also prepared: D-glucose, 11.14; D-galactose, 11.65; D-arabinose, 7.49; L-glucose, 11.49; L-galactose, 12.21; L-arabinose, 7.11; D-glucuronic acid methyl ester, 11.52.

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