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TRITERPENOID SAPONINS FROM THE STEM BARK OF *SYMPLOCOS SPICATA*

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Key Word Index—*Symplocos spicata*; Symplocaceae; separation of analogous glycosides; structure elucidation; triterpenoid saponins; 3, 28-*O*-bisglucosides of 19α-hydroxyarjunolic and 19α-hydroxyasiatic acids.

Abstract—From the stem bark of *Symplocos spicata* a mixture of triterpenoid saponins was obtained. It behaved as a pure compound in TLC and HPLC, but heterogeneity was suspected on the basis of chemical and NMR spectral data. It was separated to give two analogous glycosides, which were identified as 3,28-*O*-bis-β-D-glucopyranosides of 19α-hydroxyarjunolic and 19α-hydroxyasiatic acids.

INTRODUCTION

Symplocos spicata is the plant source of an Ayurvedic crude drug 'Lodhara' in Travancore, Cochin, South India[1] and it is also known as an Indian folk medicine[2]. The constituents of barks and leaves of some *Symplocos* spp. including *S. spicata* were studied extensively, and a variety of alkaloids, lignan glycosides, flavonoids and other compounds were reported in the literature[2–6]. More recently an epicatechin glucoside[7] and two dihydrochalcone glucosides[8] have been reported. However, as far as the constituent saponins are concerned none of them has been identified despite the fact that their existence has long been presumed[2, 3].

This paper describes the first isolation from stem bark and structure elucidation of two new triterpenoid saponins which bear a very close resemblance in structure to each other, and a mixture of which behaved as a homogeneous saponin.

RESULTS AND DISCUSSIONS

A series of conventional extraction and separation procedures yielded a crystalline compound, tentatively named SYB-1A (**1**). Acetylation of **1** on heating with acetic anhydride–pyridine provided an acetate (**2**). Compounds **1** and **2** showed, respectively, a single spot on TLC and one peak on HPLC, and **2** in field desorption mass spectrometry exhibited the molecular ion at *m/z* 1248 and a cationized cluster ion $[M+Na]^+$ at 1271. From these, **1** was thought to be a homogeneous compound. However, **1** was hydrolysed with acid to afford glucose together with four kinds of aglycones, and the NMR spectra of **1** (^{13}C) and **2** (^1H) could not be regarded as those of pure glycosides.

When **1** was acetylated at room temperature, the product was shown by TLC to be a mixture of a minute amount of **2** and two kinds of more polar acetates. Subsequently, it was subjected to CC and prep. TLC, and the two polar acetates were isolated. They were homogeneous nona-acetates and deacetylated to regenerate the free glycosides, SYB-1A-O (**3**) and SYB-1A-U (**4**). Since **3** and **4** showed identical R_f values on TLC with that of **1**, they were considered to be the original constituents of **1**.

Compound **3** was acid-hydrolysed to give glucose and an aglycone (**5**) accompanied by trace amounts of by-products, probably artefacts yielded from **5**, but on hydrolysis with a snail enzyme D-glucose and pure (^{13}C NMR) **5** were afforded. Taking into account the elemental analytical data and the molecular ion observed in electron impact mass spectrometry, **5** was given the molecular formula $C_{30}H_{48}O_6$. Methylation of **5** with CH_2N_2 and acetylation on heating with acetic anhydride–pyridine yielded, a monomethyl ester and a triacetate (**6**) respectively. The electron impact mass spectra of **5** and **6** showed equally the characteristic fragment peaks (*m/z* 264, 246, 219, 201) due to the retro-Diels–Alder cleavage of olean-12-en- or urs-12-en-28-oic acid derivatives bearing one free hydroxyl group in the D or E ring[9]. The ^{13}C NMR spectrum of **5** was the same as that of 2α, 3β, 23-trihydroxyolean-12-en-28-oic acid (arjunolic acid) (**7**)[10] with regard to the signals assignable to C-2, C-3, C-12, C-13, C-23 and C-28. These data suggested that **5** was a derivative of **7** having one tertiary or hindered hydroxyl group in the D or E-ring. The ^1H NMR spectrum of **6** showed, in addition to the three signals attributable to the protons next to the acetyl groups and identical with those of 2, 3, 23-tri-*O*-acetate (**8**) [10] of **7**, a doublet which was in good agreement with that assigned to the 19β-(eq)-H of the methyl-ester triacetate of 19α-hydroxyarjunolic acid (**5**)[11]. Therefore, **5** is 2α, 3β, 19α, 23-tetrahydroxyolean-12-en-28-oic acid (19α-hydroxyarjunolic acid = arjungenin)[11].

Compound **3** showed in its ^{13}C NMR spectrum the signals assignable to C-3[12] and C-28[13] of **5** bearing an *O*-D-glucoside moiety and those due to

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anomeric carbons of two D-glucoside units, one of which was considered to be an ester glucoside[13]. The ^{1}H NMR spectrum of **3** also showed two anomeric proton signals of D-glucose moieties as doublets ($J = 7$ Hz) indicating their β-linkage with the aglycone. The acetate (**9**) of **3** obtained on refluxing acetic anhydride–pyridine was a deca-acetate, and the field desorption mass spectrum exhibited the molecular ion at m/z 1248, supporting the fact that **3** consisted of two moles of D-glucose and one mole of **5**.

When **3** was methylated by the Hakomori method[14], the ester glycosidic linkage at C-28 was cleaved and a compound was provided, which was characterized, by identification of the methanolysis products, as 2′, 3′, 4′, 6′, 2, 19, 23-*O*-heptamethyl ether 28-methyl ester (**10**) of the 3-*O*-β-D-glucopyranoside of **5**.

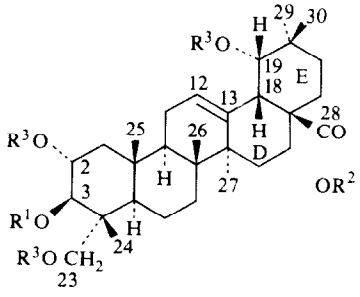
Consequently, **3** is 3-*O*-β-D-glucopyranosyl 2α, 3β, 23, 19α-tetrahydroxyolean-12-en-28-oic acid 28-*O*-β-D-glucopyranoside (19α-hydroxyarjunolic acid 3, 28-*O*-bisglucoside).

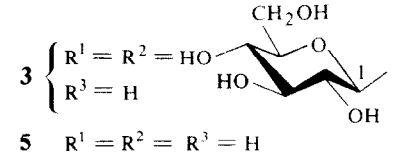
Compound **4** was hydrolysed with a snail enzyme to afford D-glucose and a homogeneous (^{13}C NMR) aglycone (**11**) which was identical with **5** on TLC but different in mp, optical rotation and ^{13}C NMR. Acetylation of **11** gave a triacetate (**12**) and further methylation with diazomethane provided its monomethyl ester.

Compounds **11** and **12** showed in electron impact mass spectrometry the molecular ions at m/z 504 and 630, respectively, and the same fragment ions as those from **5** and **6**, which were considered to be yielded by the retro-Diels–Alder cleavage. This suggested that **11** was possibly an ursane derivative corresponding to **5**. In the ^{13}C NMR spectrum of **11**, the signals attributed to C-2, C-3 and C-23 in that of **5** and those of C-12, C-13, C-18, C-19 and C-28 in that of 19α-hydorxyursolic acid (**13**)[15] were observed. Compound **12** showed in the ^{1}H NMR spectrum signals identical with those of 2β-, 3α-H and 23-H$_2$ of **6** and of 18β-H of triacetyl clethric acid methyl ester[15]. Accordingly, **11** must be 2α, 3β, 23, 19α-tetrahydroxyurs-12-en-28-oic acid [19α-hydroxy derivative of asiatic acid (**14**)[16]].

Compound **4** showed in the ^{1}H NMR spectrum two anomeric proton signals as doublets ($J = 7$ Hz), and in the ^{13}C NMR spectrum signals identical with those of two anomeric carbons of the D-glucose moieties in **3**. Thus, taking the same R_f values of **4** and **3** on TLC into account, **4** was presumed to be the 3, 28-*O*-bis-β-D-glucopyranoside of **11**.

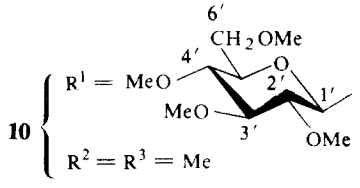
Methylation of **4** in the same way as for **3** provided product **15**. It was methanolysed and then acetylated to give methyl 2, 3, 4, 6-tetra-*O*-methyl-α-D-glucopyranoside and two kinds of aglycones (**16** and **17**). Both compounds exhibited in electron impact mass spectrometry their molecular ions equally at m/z 570,



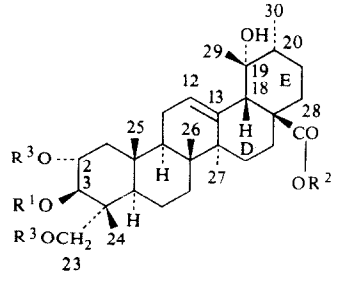


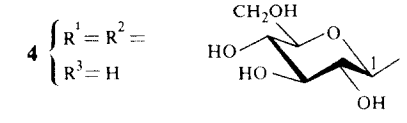
3 $R^1 = R^2 =$ HO, $R^3 =$ H

5 $R^1 = R^2 = R^3 =$ H



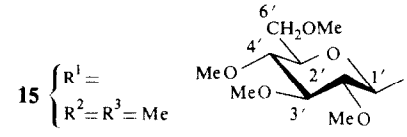
10 $R^1 =$ MeO, $R^2 = R^3 =$ Me



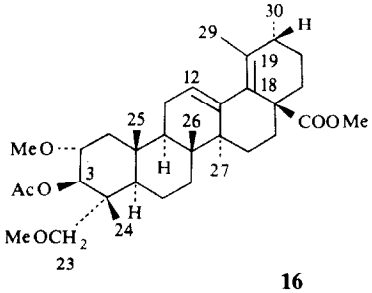


4 $R^1 = R^2 =$, $R^3 =$ H

11 $R^1 = R^2 = R^3 =$ H



15 $R^1 =$, $R^2 = R^3 =$ Me



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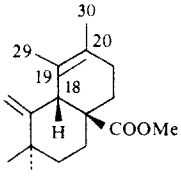

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and showed in the ^{1}H NMR spectra a doublet (J = 10 Hz) at δ 5.00 assignable to the 3α(ax)-H next to an acetyl group. However, in the ^{1}H NMR spectrum of **16** a singlet (3H) at 1.72 and a doublet (3H, J = 6 *Hz*) *at* 1.07 were observed, while **17** showed a singlet (6H) at 1.62. Compounds **16** and **17** were then regarded as urs-12, 18-diene and urs-12, 19-diene derivatives, respectively, secondarily produced by elimination of the 19-hydroxyl group, and hence **15** should be the 2′, 3′, 4′, 6′, 2, 23-*O*-hexamethyl ether 28-methyl ester of 3-*O*-β-D-glucopyranoside of **11**.

Now, it follows that **4** is 3-*O*-β-D-glucopyranosyl 2α, 3β, 19α, 23-tetrahydroxyurs-12-en-28-oic acid 28-*O*-β-D-glucopyranoside (19α-hydroxyasiatic acid 3, 28-*O*-bisglucoside). The 28-*O*-β-D-glucopyranoside of **5** was isolated from *Terminalia arjuna* (Combretaceae) and named arjunglucoside I[11], but **3** and the analogous bisglucoside **4** are, to our knowledge isolated for the first time as natural products. The co-occurrence of **3** and **4** and their isolation as a seemingly homogeneous compound may suggest that similar cases are also conceivable. Purity control of a compound by examination of ^{1}H NMR and ^{13}C NMR spectra, as well as by chemical means and preparative separation of such a mixture by partial acetylation followed by preparative TLC, are worthy of note.

EXPERIMENTAL

All mps were uncorr. Optical rotations were taken at 15–21° using a 1 dm cell. TLC was carried out on Si gel with solvent systems, unless otherwise stated, as follows: (a) $CHCl_3$–MeOH–H_2O (40:20:1) and (b) $CHCl_3$–MeOH–H_2O (70:30:3). IR spectra were run as KBr disks. ^{1}H NMR spectra were recorded at 100 MHz in $CDCl_3$ soln. unless otherwise specified using TMS as int. standard. ^{13}C NMR spectra were taken at 25.05 MHz in C_5D_5N soln with TMS employing the FT mode. The EI- and FDMS were produced on double focusing mass spectrometers and recorded electrically. The former were taken with an accelerating potential of 4.5–6.5 kV and an ionizing potential of 75 eV, and the latter at +3.5 kV for the field anode and −5 kV for the slotted cathode plate, an ion source pressure of *ca* 10^{-7} Torr and emitter heating current of 15–16 mA.

Plant material. Stem bark was collected in March from Coimbatone, south India (a herbarium specimen of the plant is on file in the Department of Medicinal Chemistry, Banaras Hindu University).

Isolation of SYB-1A (**1**). Cut material (6.2 kg) was soaked with 90% EtOH, filtered and the filtrate evaporated at 40°. The extractives were shaken with C_6H_6 and H_2O, the aq. layer was extracted with *n*-BuOH and the extracts evaporated *in vacuo* to dryness. The residue was chromatographed on a Si gel column ($CHCl_3$–MeOH–H_2O, 13:7:2) to give a solid, which was crystallized from EtOH–Me_2CO to yield **1** (1.2 g).

SYB-1A (**1**). Colourless needles, mp 217–220°(dec.), $[\alpha]_D$ +9.6° (MeOH; *c* 1.4). IR ν_{max} cm^{-1}: 3400 (OH), 1730 (ester). Homogeneous on TLC [R_f 0.07 (solvent a), 0.25 (solvent b)] and on HPLC (column, Radial-Pak A; solvent MeOH and 90% MeOH). On refluxing with 10% HCl in 70% MeOH for 30 min, glucose (PPC) together with two major (R_f 0.72, 0.63) and two minor aglycones (R_f 0.74, 0.67) (TLC; solvent a) were obtained.

SYB-1A acetate (**2**). Compound **1** was acetylated with Ac_2O–pyridine at 80° for 3 hr to yield **2** as a powder (from *n*-hexane), mp 83–85°. FDMS *m/z*: 1248 [M]$^+$, 1271 [M + Na]$^+$. Homogeneous on TLC [*n*-hexane–AcOEt, 1:1; $CHCl_3$–MeOH, 100:1; $CHCl_3$–Me_2CO, 10:1; CH_2Cl_2–Me_2CO, 10:1) (R_f 0.25)] and on HPLC (column, Radial-Pak A: solvent MeOH–$CHCl_3$–H_2O, 8:1:1).

Separation of **1** *providing SYB-1A-O* (**3**) *and SYB-1A-U* (**4**). Compound **1** (600 mg) was acetylated with Ac_2O–pyridine (6 ml each) at room temp. for 3 hr. The product, showing three spots [R_f 0.25 (minor), 0.18, 0.17] on TLC (CH_2Cl_2–Me_2CO, 10:1), was chromatographed on Si gel (solvent as above) to give a mixture of two major constituents, which was then separated by prep. TLC (solvent as above) to afford the two acetates, R_f 0.17, mp 148–151° (184 mg), and R_f 0.18, mp 145–148° (107 mg), both being homogeneous (TLC) nona-acetates [^{1}H NMR: δ 1.88–2.24 (27H, OAc × 9)]. The former (R_f 0.17) was refluxed with 0.4% $NaHCO_3$ in MeOH for 40 min. The hydrolysate was filtered, neutralized with dil. HCl and passed through Sephadex LH-20 (eluent, MeOH) and Si gel (eluent $CHCl_3$–MeOH–H_2O, 70:30:3) columns to give the free compound, SYB-1A-O (**3**) (48 mg). In the same way the less polar acetate (R_f 0.18) was saponified to yield SYB-1A-U (**4**) (28 mg).

SYB-1A-O (**3**). Colourless needles (from *n*-BuOH–H_2O), mp 246–249° (dec.), $[\alpha]_D$ +7.4° (MeOH; *c* 1.4). R_f 0.25 (TLC; solvent b). IR ν_{max} cm^{-1}: 3350 (OH), 1752 (ester). ^{1}H NMR (C_5D_5N + D_2O): δ 5.17, 6.24 (1H each, *d*, J = 7 Hz, H-1 of glucose). ^{13}C NMR: δ 63.7 (*t*, C-23), 67.0 (*d*, C-2), 80.7 (*d*, C-19), 88.3 (*d*, C-3), 95.5 (*d*, C-1 of glucose), 105.4 (*d*, C-1 of glucose), 123.5 (*d*, C-12), 143.9 (*s*, C-13), 176.8 (*s*, C-28). (Found: C, 56.93; H, 8.29. $C_{42}H_{68}O_{16}$ requires: C, 57.13; H, 8.45%).

SYB-1A-O deca-acetate (**9**). Prepared by acetylation of **3** with Ac_2O–pyridine at 80° for 5 hr. Powder (from *n*-hexane), mp 142–146°, R_f 0.25 (TLC; CH_2Cl_2–Me_2CO, 10:1). FDMS *m/z*: 1248 [M]$^+$. ^{1}H NMR: δ 2.0–2.2 (30 H, OAc × 10), 4.54 (1H, *d*, J = 8 Hz, H − 1 of glucose), 5.56 (1H, *d*, J = 8 Hz, H-1 of ester-glycosidic glucose).

Hydrolysis of **3** *with snail enzyme.* Compound **3** (40 mg) in 0.5% AcOH(20 ml) was incubated with a crude snail enzyme (gastric juice of *Achatina fulica*) (40 mg) at 37° for 4 days, and the mixture shaken with AcOEt–*n*-BuOH (2:1). The bottom layer, showing only one spot of glucose on PPC, was evaporated *in vacuo* and the residue chromatographed on a Sephadex LH-20 column (eluent, MeOH) to give D-glucose as a syrup, $[\alpha]_D$ +52.2° (H_2O; *c* 1.6). The upper layer was evaporated and chromatographed on Si gel (eluent, $CHCl_3$–MeOH–H_2O, 90:10:0.5) to provide an aglycone (**5**) as colorless prisms (from AcOEt–MeOH) (15 mg), mp 290–293°, $[\alpha]_D$ +53.3° (MeOH; *c* 0.9), R_f 0.63 (TLC; solvent a). IR ν_{max} cm^{-1}: 3400(OH), 1700 (COOH). EIMS *m/z*: 504 [M]$^+$ 264, 246, 219, 201. ^{13}C NMR: δ 66.3 (*t*, C-23), 68.7 (*d*, C-2), 78.1 (*d*, C-3), 123.1(*d*, C-12), 144.5 (*s*, C-13), 180.5 (*s*, C-28). (Found: C, 70.87; H, 9.62. Calc. for $C_{30}H_{48}O_6$: C, 71.39; H, 9.59%). Compound **5** was acetylated with Ac_2O–pyridine at 80° for 1.5 hr to give an acetate (**6**), colourless needles (from *n*-hexane–Me_2CO), mp 208–210°, ^{1}H NMR: δ 0.70 (3H, *s*, H-26), 0.88 (3H, *s*, H-24), 0.97 (6H, *s*, H-29, H-30), 1.08 (3H, *s*, H-25), 1.24 (3H, *s*, H-27), 1.99, 2.03, 2.10 (3H each, *s*, OAc × 3), 3.09 (1H, *s*, H-18). 3.33 (1H, *d*, J = 3 Hz, H-19β), 3.58, 3.83 (1H each, *d*, J = 12 Hz, H-23), 5.05 (1H, *d*, J = 10 Hz, H-3α), 5.20 (1H, *m*, H-2β), 5.41 (1H, *m*, H-12). EIMS *m/z*: 630 [M]$^+$, 264, 246, 219, 201. Methylation of **5** with CH_2N_2 gave a monomethyl ester, powder (from *n*-hexane $CHCl_3$), mp 151–153°. ^{1}H NMR: δ 3.62 (3H, *s*, COOMe).

Methylation of **3** *by the Hakomori method.* Compound **3** (50 mg) was treated with NaH (120 mg) and MeI (2 ml) in DMSO (10 ml). The reaction mixture was diluted with H_2O,

extracted with $CHCl_3$ and the $CHCl_3$ layer washed, dried and evaporated. The residue was chromatographed on Si gel (eluent, *n*-hexane–AcOEt, 2:1) to give a methylated product (**10**). FDMS *m/z*: 778 $[M]^+$. ^1H NMR: δ 0.63–1.21 (18H, tert. Me × 6), 3.23–3.60 (21H, OMe × 7), 3.62 (3H, *s*, COOMe), 4.21 (1H, *d*, *J* = 7 Hz, H-1′ of glucose), 5.40 (1H, *m*, H-12).

Methanolysis of **10**. Compound **10** was refluxed with 7% HCl in MeOH for 30 min. The mixture was neutralized with Amberlite A-45 and filtered. The filtrate was evaporated and the residue treated with Ac_2O–pyridine at 80°. The product was chromatographed on Si gel (*n*-hexane–AcOEt, 4:1 – 1:1) to give a syrup, which was identified as methyl 2, 3, 4, 6-tetra-*O*-methyl-α-D-glucopyranoside (TLC; *n*-hexane–AcOEt, 2:1), and a powder (from *n*-hexane–$CHCl_3$), mp 103–105°. EIMS *m/z*: 602 $[M]^+$. ^1H NMR: δ 0.64–1.22 (18H, tert. Me × 6), 2.08 (3H, *s*, OAc), 2.69, 3.06 (1H each *d*, *J* = 9 Hz, H-23), 3.23–3.29 (9H, OMe × 3), 3.60 (3H, *s*, COOMe), 5.00 (1H, *d*, *J* = 10 Hz, H-3α), 5.40 (1H, *m*, H-12).

SYB-1A-U (**4**). Colourless needles (from MeOH), mp 236–239° (dec.), $[\alpha]_D$ + 3.9° (MeOH; *c* 1.3), R_f 0.26 (TLC; solvent b). IR ν_{max} cm^{-1}: 3350 (OH), 1730 (ester). ^1H NMR ($C_5D_5N + D_2O$): δ 5.18 (1H, *d*, *J* = 7 Hz, H-1 of glucose), 6.20 (1H, *d*, *J* = 7 Hz, H-1 of ester glycosidic glucose). ^{13}C NMR: δ 54.2 (*d*, C-18), 63.7 (*t*, C-23), 67.0 (*t*, C-2), 72.4 (*s*, C-19), 88.3 (*d*, C-3), 95.5 (*d*, C-1 of glucose), 105.4 (*d*, C-1 of glucose), 128.0 (*d*, C-12), 138.8 (*s*, C-13), 176.5 (*s*, C-28). (Found: C, 54.87; H, 8.31. $C_{42}H_{68}O_{16}\cdot 5H_2O$ requires: C, 54.88; H, 8.55%).

Hydrolysis of **4** *with enzyme*. In the same manner as for **3**, compound **4** (20 mg) was treated with a crude snail enzyme to give D-glucose and an aglycone (**11**) (10 mg), as colourless needles (from AcOEt–MeOH), mp 284–286°, $[\alpha]_D$ + 18.6° (MeOH; *c* 0.7), R_f 0.63 (TLC; solvent a). IR ν_{max} cm^{-1}: 3400 (OH), 1690 (COOH). EIMS *m/z*: 504 $[M]^+$, 264, 246, 219, 201. ^{13}C NMR: δ 54.4 (*d*, C-18), 66.4 (*t*, C-23), 68.7 (*d*, C-2), 72.5 (*s*, C-19), 78.1 (*d*, C-3), 127.6 (*d*, C-12), 139.6 (*s*, C-13), 180.2 (*s*, C-28). Acetylation of **11** as **5** gave triacetate (**12**), colourless needles (from *n*-hexane–Me_2CO), mp 210–213°. EIMS *m/z*: 630 $[M]^+$, 264, 246, 219, 201. ^1H NMR: δ0.72 (3H, *s*, H-26), 0.88 (3H, *s*, H-24), 0.94 (3H, *d*, *J* = 6 Hz, H-30), 1.09 (3H, *s*, H-25), 1.26 (3H, *s*, H-27), 1.26 (3H, *s*, H-29), 1.99, 2.04, 2.10 (3H each, *s*, OAc × 3), 2.54 (1H, *s*, H-18β), 3.57, 3.84 (1H each, *d*, *J* = 12 Hz, H-23), 5.05 (1H, *d*, *J* = 10 Hz, H-3α), 5.20 (1H, *m*, H-2β), 5.33 (1H, *m*, H-12). Methylation of **13** with CH_2N_2 afforded its monomethyl ester. ^1H NMR: δ 1.99, 2.04, 2.10 (3H each, *s*, OAc × 3), 3.60 (3H, *s*, COOMe).

Methylation of **4** *by the Hakomori method*. Carried out in the same way as for **3** to give a methylate (**15**). EIMS *m/z*: 764 $[M]^+$. ^1H NMR: δ 0.65–1.24 (18H, tert.Me × 6), 3.26–3.58 (18H, OMe × 6), 3.61 (3H, *s*, COOMe), 4.21 (1H, *d*, *J* = 7 Hz, H-1′ of glucose).

Methanolysis of **15**. Conducted and the product was acetylated in the same manner as for **10** to yield methyl 2, 3, 4, 6-tetra-*O*-methyl-α-D-glucopyranoside and a powder (from *n*-hexane–Me_2CO). The latter showed a single spot on TLC (*n*-hexane–EtOAc, 2:1) but two spots (R_f 0.30, 0.25) on high performance TLC (plate, RP-18; solvent 95% MeOH) and was separated by HPLC (column, Radial-Pak A; solvent 95% MeOH) to give two compounds **16** and **17**. Compound **16** was a powder (from *n*-hexane–Me_2CO), mp 80–84°. EIMS *m/z*: 570 $[M]^+$. ^1H NMR: δ 0.75 (3H, *s*, H-26), 0.80 (3H, *s*, H-24), 0.97 (3H, *s*, H-25), 1.04 (3H, *s*, H-27), 1.07 (3H, *d*, *J* = 6 Hz, H-30), 1.72 (3H, *s*, H-29), 2.10 (3H, *s*, OAc), 2.71, 3.06 (1H each, *d*, *J* = 10 Hz, H-23), 3.24, 3.32 (3H each, *s*, OMe × 2), 3.60 (3H, *s*, COOMe), 5.00 (1H, *d*, *J* = 10 Hz, H-3α), 5.36 (1H, *m*, H-12). Compound **17** was also a powder (from *n*-hexane–Me_2CO), mp 118–123°. EIMS *m/z*: 570 $[M]^+$. ^1H NMR: δ 0.74 (3H, *s*, H-26), 0.81 (3H, *s*, H-24), 0.96 (3H, *s*, H-25), 1.03 (3H, *s*, H-27), 1.62 (6H, *s*, H-29, H-30), 2.09 (3H, *s*, OAc), 2.70, 3.05 (1H each, *d*, *J* = 9 Hz, H-23), 3.23, 3.30 (3H each, *s*, OMe × 2), 3.62 (3H, *s*, COOMe), 5.00 (1H, *d*, *J* = 10 Hz, H-3α).

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