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GLYCOSIDES OF MEGASTIGMANE AND OF THE SIMPLE ALCOHOLS FROM *ALANGIUM PREMNIFOLIUM*

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Key Word Index—*Alangium premnifolium*; Alangiaceae; leaves; megastigmane glycoside; alangionosides N and O; shimaurinosides A and B; 1,2-propanediol-1-*O*-xyloglucoside; (*S*)-2-pentanol-xyloglucoside.

Abstract—From the water-soluble fraction of a methanol extract of leaves of *Alangium premnifolium*, two new megastigmane glycosides, alangionosides N and O, along with three known megastigmane glycosides, dendranthemoside A and alangionosides A and B, were isolated. Shimaurinosides A and B, xylopyranosyl(1 → 6)glucopyranosides of simple alcohols were also found to be constituents of the water-soluble fraction. Structures were determined by spectroscopic analyses.

INTRODUCTION

Phytochemical investigations of the *n*-BuOH-soluble fraction of a methanol extract of leaves of *Alangium premnifolium* (Japanese name: Shima-urinoki) disclosed the presence of megastigmane glycosides, named alangionosides A–M [1–3]. In continuing work on the same species, constituents of the water-soluble fraction of the methanol extract were examined. As a result, along with three known megastigmane glycosides, alangionosides A (**1**) and B (**2**) [1], and dendranthemoside A (**3**) [4], two new megastigmane glycosides, named alangionosides N (**4**) and O (**5**) and glycosides of two simple alcohols, shimaurinosides A (**7**) and B (**8**), were isolated.

RESULTS AND DISCUSSION

The water-soluble fraction of the methanol extract was separated by Diaion HP-20 CC and the compounds purified by means of a combination of silica gel CC, ODS CC, droplet counter-current chromatography (DCCC) and preparative HPLC. Three known megastigmane glycosides, alangionosides A and B, and dendranthemoside A, were identified by comparison of their physical data with reported values [1, 4].

Alangionoside N (**4**), $[\alpha]_D$ − 36.4°, was obtained as an amorphous powder, whose molecular composition analysed for $C_{24}H_{42}H_{12}$ by HR-FAB-mass spectrometry. The ^{13}C NMR spectrum showed the presence of terminal β-xylopyranose and 6-glycosylated β-glucopyranose, and a further 13 signals for an aglycone moiety, which were essentially the same as those of dendranthemoside A (**3**) (Table 1). Since the absolute configurations of **3** was determined by X-ray analysis [5], the structure of alangionoside N was determined to be (3*S*,5*R*,6*R*,7*E*,9ξ)-megastigma-7-ene-3,6,9-triol 3-*O*-β-D-xylo-pyranosyl(1″-6′)-β-D-glucopyranoside, as shown in the formula.

Alangionoside O (**5**), $[\alpha]_D$ − 50.6°, was obtained as an amorphous powder. ^{13}C NMR spectroscopy revealed that it was also a megastigmane derivative with a β-D-xylopyranosyl(1 → 6)-β-D-glucopyranosyl residue. HR-FAB-mass spectrometry indicated that **5** had one more oxygen atom than **4**, which compensated for the lack of one methine signal and one more tertiary carbon signal with a hydroxyl group in the ^{13}C NMR spectrum of **5**. The relative relationship of substituents on the six-membered ring was determined by 2D-NMR. First, C-2 and C-4 were assigned on the basis that the correlation between H_3-13 and δ_C 42.3 (C-4) was observed in the ^{13}C–^1H long-range COSY spectrum. Second, the coupling pattern of H-3 (*tt*, $J = 4$, 12 Hz) indicated that the proton must be in the axial position and the cross-peaks between H_3-13 and H_2-4 observed in a NOESY experiment indicated that the 13-methyl group was in the equatorial position, and those between

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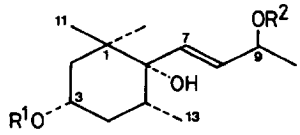
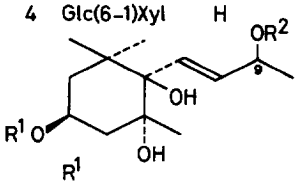
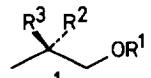


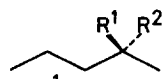
	R^1	R^2
1	H	Glc (9S)
2	H	Glc(6-1)Api (9S)
3	Glc	H (9S)
4	Glc(6-1)Xyl	H



	R^1	R^2
5	Glc(6-1)Xyl	H
5a	H	H
5b	Glc(OR^2)$_3$(6-1)Xyl(OR^2)$_3$	Ac
6	Glc	H (9*R*)
6a	Glc(OR^2)	Ac (9*R*)



	R^1	R^2	R^3
7	Glc(6-1)Xyl	H or OH	OH or H
7a	H	H(OH)	OH(H)
7b	Glc	OH	H
7c	Glc	H	OH



	R^1	R^2
8	OGlc(6-1)Xyl	H
8a	OH(H)	H(OH)
8b	OGlu	H
8c	H	OGlu

H-7 and H_3-11, -12 and -13 confirmed that the side-chain (C-7–C-10) was also in the equatorial orientation.

β-D-Glucopyranosylation-induced shift trends were applied to determine absolute configuration [1, 4, 5, 7].

Table 1. ^{13}C NMR spectral data for dendranthemoside A (**3**), alangionsoides N and O (**4** and **5**) and **5a** (CD_3OD, 100 MHz)

C	3	4	5	5a
1	40.5	40.5	40.8	40.7
2	42.7	42.7	44.5	46.5 (−2.0)*
3	75.7	75.9	73.3	65.3 (+8.0)
4	38.2	38.3	42.3	45.7 (−3.4)
5	35.5	35.5	77.8	77.8
6	78.3	78.3	79.1	79.0
7	133.8	133.9	131.1	131.3
8	135.6	135.5	136.2	136.2
9	69.3	69.3	69.6	70.0
10	24.2	24.2	24.3	24.2
11	25.1	25.2	27.6	27.5
12	25.9	25.9	26.4	26.2
13	16.5	16.5	27.3	27.1
1′	102.7	102.9	102.2	—
2′	75.2	75.1	75.1	—
3′	78.1	77.9	78.0	—
4′	71.8	71.6	71.5	—
5′	77.9	76.9	77.0	—
6′	62.9	69.7	69.6	—
1″	—	105.5	105.5	—
2″	—	74.9	75.0	—
3″	—	77.7	77.5	—
4″	—	71.2	71.2	—
5″	—	66.9	66.9	—

*$\Delta\ \delta_{5\text{-}5a}$.

Enzymatic hydrolysis of **5** with emulsin gave an aglycone (**5a**) and sugars. The high-field shifts by 2.0 and 3.4 ppm of the 2 and 4-positions, respectively and downfield shift by 8.0 ppm of the 3-position on glucosylation implied that the 3-position has the *S*-configuration and simultaneously, those of the 5- and 6-positions were deduced to be *R* and *S*, respectively. The planar structure and these absolute configurations were the same as those of kiwiionoside which was isolated from *Actinidia chinensis* and whose structure was solved by X-ray analysis (**6**) [6]. Although NMR spectroscopic data of the side-chain of alangionoside-*O*-heptaaceate (**5b**) were indistinguishable from those of kiwiionoside pentaacetate (**6b**) [6], the absolute configuration of the 9-position is still uncertain. Therefore, the structure was elucidated to be (3*S*,5*R*,6*S*,7*E*,9ξ)-megastigma-7-ene-3,5,6,9-tetrol, 3-*O*-β-D-xylopyranosyl(1″-6′)-β-D-glucopyranoside (5), as shown in the formula.

Shimaurinoside A (**7**), $[\alpha]_D$ − 42.2°, was recrystallized from MeOH to afford colourless needles. Negative ion HR-FAB-mass spectrometry of its elemental composition to be $C_{14}H_{26}O_{11}$. Eleven ^{13}C NMR signals out of the 14 were reasonably assigned to those of a β-D-xylopyranosyl(1→6)-β-D-glucopyranosyl moiety and the aglycone portion consisted of one methyl and primary and secondary alcoholic carbons, namely 1,2-propanediol (**7a**). When the ^{13}C NMR signals were compared with those of an authentic sample, the sugar moiety was found to be attached to the primary hydroxyl group. To determine the absolute configuration, synthesis of (*S*)- and (*R*)-1,2-propanediol-1-*O*-β-D-glucopyranosides (**7b** and **c**, respectively) was attempted. However, no significant differences were observed in the ^{13}C NMR between **7b** and **c** (Table 2).

Table 2. ^{13}C NMR spectral data for shimaurinosides A and B (**7** and **8**) their aglycones (**7a** and **8a**) and synthetic glucosides from (S)- and (R)-1,2-propanediols (**7b** and **c**, respectively) and (*S*)- and (*R*)-2-pentanols (**8b** and **c**, respectively) (CD_3OD)

C	7	7a	7b	7c	8	8a	8b	8c
1	77.2	68.6	76.6	76.2	22.1 (−1.4)*	23.5	22.0 (−1.5)†	19.7 (−3.8)‡
2	67.7	69.2	67.8	67.4	78.0 (+9.7)	68.3	78.2 (+9.9)	75.1 (+6.8)
3	19.2	19.5	19.2	19.4	40.1 (−2.4)	42.5	40.0 (−2.5)	40.7 (−1.8)
4					19.6	20.0	19.6	19.7
5					14.6	14.6	14.6	14.5
1′	104.8		104.8	104.5	104.1		104.0	102.1
2′	75.0		75.3	75.1	75.3		75.3	75.4
3′	77.8		78.0	78.0	77.7		77.8	78.2
4′	71.6		71.7	71.6	71.5		71.8	71.8
5′	76.9		77.9	77.9	76.9		77.5	77.8
6′	70.0		62.7	62.7	69.8		62.9	62.9
1″	105.5				105.5			
2″	74.9				74.9			
3″	77.2				77.6			
4″	71.2				71.2			
5″	66.9				66.9			

*$\Delta\ \delta_{8-8a}$.
†$\Delta\ \delta_{8b-8a}$.
‡$\Delta\ \delta_{8c-8a}$.

Therefore, the absolute configuration of the 2-position remains to be determined.

Shimaurinoside B (**8**), $[\alpha]_D$ −48.9°, was obtained as colourless needles, whose elemental composition was determined to be $C_{16}H_{30}O_{10}$ by HR-FAB-mass spectrometry. The ^{13}C NMR spectrum indicated the presence of a β-D-xylopyranosyl(1→6)-β-D-β-D-glucopyranosyl moiety and the remaining five carbon signals consisted of two methyls, whose protons appeared as a doublet (3H, $J = 6$ Hz) and a triplet (3H, $J = 7$ Hz), respectively, in the ^1H NMR spectrum, two methylenes and a secondary alcohol. Therefore, the structure of shimaurinoside B was determined to be the xylogłucoside of 2-pentanol (**8a**). The significantly different upfield shifts between the 1- and 3-positions (−1.4 and −2.4 ppm, respectively) on glycosylation of 2-pentanol (**8a**) to **8** indicated that the absolute configuration is *S* [1, 7]. This was further confirmed by the synthesis of β-D-glucopyranosides of (*S*)- and (*R*)-2-pentanols (**8b** and **c**, respectively). The ^{13}C NMR chemical shifts of the aglycone portions revealed that the chiral centre in **8** has the *S*-configuration (Table 2).

EXPERIMENTAL

General. Mps: uncorr. ^1H and ^{13}C NMR were measured at 400 and 100 MHz, respectively, in CD_3OD, with TMS as int. standard. Reverse-phase CC (RPCC): Cosmosil (ODS), $\Phi = 50$ mm, $L = 25$ cm, MeOH–H_2O (1:9, 1 l)→(1:1, 1 l), frs of 10 g being collected. Droplet counter-current chromatography (DCCC): 500 columns ($\Phi = 2$ mm, $L = 40$ cm). The ascending method was used with $CHCl_3$–MeOH–H_2O–*n*-PrOH (9:12:8:2) and 5-g frs were collected and numbered according to elution order. (*R* and *S*)-2-Pentanols were purchased from Wako Pure Industries Ltd. (Osaka). *R* and *S*-1,2-propanediols were from Tokyo Chemical Industry Co., Ltd. (Tokyo).

Plant material. Leaves of *A. premnifolium* Ohwi were collected in Nakagami-gun, Okinawa, Japan, in August 1990. A voucher specimen is deposited at the Laboratory of Pharmacognosy, Institute of Pharmaceutical Sciences, Hiroshima University School of Medicine.

Extraction and isolation. Air-dried leaves were extracted with MeOH (30 l × 2). The MeOH extract was concd to *ca* 2.5 l and then 150 ml of H_2O and an appropriate volume of MeOH were added to adjust the solution to 95% aq. MeOH. This soln was extracted with 3 l of *n*-hexane (*n*-hexane extract: 200 g) and then concd. The concentrate was suspended in 1.5 l of H_2O, and then extracted with EtOAc (1 l × 2, 52.1 g) and *n*-BuOH (1.5 l and 1 l, 139 g). On concnt. of the aq. layer, 365 g of a H_2O-sol. fr. was obtained. This fr. (360 g) was separated by CC on Diaion HP-20, ($\Phi =$ 70 mm, $L = 650$ mm). Adsorbed materials were eluted with H_2O–MeOH with a step-wise increase of MeOH [5% (8 l), 10% (6 l), 20% (6 l), 40% (6 l), 60% (6 l) and 80% (6 l)]; 2-l frs were collected. The residue (18.1 g) of frs 4–6 was subjected to silica gel (500 g) CC with $CHCl_3$ (1.5 l), $CHCl_3$–MeOH (39:1, 3 l), (9:1, 6 l), (37:3, 6 l), (9:1, 6 l), (17:3, 6 l) and (4:1, 6 l); frs of 500 ml were collected. The residue (1.32 g) of the 15% MeOH eluate (frs 49–54) was separated by RPCC (361 mg, frs 36–39) and then by DCCC to give 60 mg of **7** in frs 10–12.

The residue (12.2 g) of the 20% MeOH eluate of Diaion HP-20 CC (frs 9–11) was subjected to silica gel CC (450 g) with the same solvent system as above. The residue (2.04 g) of the 15% MeOH eluate (frs 48–58) was separated by RPCC (168 mg in frs 125–142) and then DCCC to give 3 frs, **2** and **4** (49 mg in frs 30–37),

2 (60 mg in frs 21–24), and **3**, **1** and **8** (37 mg in frs 30–37). The first fr. was purified again by DCCC to give 12 mg of **4** (in frs 19–22) and 16 mg of **2** (in frs 25–29). The last fr. was purified by prep. HPLC to give 4 mg of **3**, 15 mg of **1** and 8 mg of **8**.

The residue (1.04 g) of the 20% MeOH eluate (frs 59–66) was sepd by RPCC (162 mg in frs 97–108) and then DCCC (118 mg in frs 9–13). It was finally purified by prep. HPLC to afford 64 mg of **5**.

Known compounds isolated. Alangionoside A (**1**), powder, $[\alpha]_D^{20}$ − 19.7° [MeOH *c* 0.91) [1]. Alangionoside B (**2**), powder, $[\alpha]_D^{20}$ − 42.0° (MeOH, *c* 1.62) [1]. Dendranthemoside A (**3**), colourless powder, $[\alpha]_D^{20}$ − 34.2° (MeOH, *c* 0.77) [4]. Physico-chemical data for these compounds were essentially the same as reported values.

Alangionoside N (**4**). Powder. $[\alpha]_D^{22}$ − 36.4° (MeOH, *c* 0.88). ^{1}H NMR (CD_3OD): δ 0.82 (3H, *d*, *J* = 7 Hz, H_3-13), 0.90 (3H, *s*, H_3-12), 0.99 (3H, *s*, H_3-11), 1.24 (3H, *d*, *J* = 6 Hz, H_3-10), 1.49 (H, *q*, *J* = 12 Hz, H-4ax), 1.56 (H, *ddd*, *J* = 2, 4, 12 Hz, H-2eq), 1.68 (H, *t*, *J* = 12 Hz, H-2ax), 1.82 (H, *br d*, *J* = 12 Hz, H-4eq), 1.97 (H, *dqd*, *J* = 4, 7, 12 Hz, H-5), 3.14 (H, *dd*, *J* = 8, 9 Hz, H-2′), 3.19 (H, *dd*, *J* = 10, 12 Hz, H-5″a), 3.20 (H, *dd*, *J* = 7, 9 Hz, H-2″), 3.44 (H, *m*, H-5′), 3.48 (H, *ddd*, *J* = 5, 9, 10 Hz, H-4″), 3.75 (H, *dd*, *J* = 6, 12 Hz, H-6′a), 3.86 (H, *dd*, *J* = 5, 12 Hz, H-5″b), 3.93 (H, *tt*, *J* = 4, 12 Hz, H-3), 4.06 (H, *dd*, *J* = 2, 12 Hz, H-6′b), 4.29 (H, *dquin*, *J* = 1, 6 Hz, H-9), 4.34 (H, *d*, *J* = 8 Hz, H-1′), 4.35 (H, *d*, *J* = 7 Hz, H-1″), 5.56 (H, *dd*, *J* = 1, 16 Hz, H-7), 5.72 (H, *dd*, *J* = 6, 16 Hz, H-8). ^{13}C NMR: see Table 1. HR-FAB-MS (negative): *m/z* 521.2588 $[M-H]^-$ ($C_{24}H_{41}O_{12}$ requires 521.2598).

Alangionoside O (**5**). Powder. $[\alpha]_D^{22}$ − 50.6° (MeOH, *c* 1.09). ^{1}H NMR (CD_3OD): δ 0.85 (3H, *s*, H_3-12ax), 1.15 (3H, *s*, H_3-13), 1.22 (3H, *s*, H_3-11eq), 1.27 (3H, *d*, *J* = 6 Hz, H_3-10), 1.59 (H, *ddd*, *J* = 2, 4, 12 Hz, H-2eq), 1.75 (H, *t*, *J* = 12 Hz, H-2ax), 1.76 (H, *t*, *J* = 12 Hz, H-4ax), 1.95 (H, *ddd*, *J* = 2, 4, 12 Hz, H-4eq), 3.15 (H, *dd*, *J* = 8, 9 Hz, H-1′), 3.19 (H, *dd*, *J* = 10, 11 Hz, H-5″a), 3.20 (H, *dd*, *J* = 7, 9 Hz, H-2″), 3.44 (H, *m*, H-5′), 3.48 (H, *ddd*, *J* = 5, 9, 10 Hz, H-4″), 3.77 (H, *dd*, *J* = 6, 12 Hz, H-6′a). 3.87 (H, *dd*, *J* = 5, 11 Hz, H-5′b), 4.06 (H, *dd*, *J* = 2, 12 Hz, H-6′b), 4.19 (H, *tt*, *J* = 4, 12 Hz, H-3), 4.41 (H, *d*, *J* = 8 Hz, H-1′), 5.79 (H, *dd*, *J* = 6, 16 Hz, H-8), 6.06 (H, *dd*, *J* = 1, 16 Hz, H-7). ^{13}C NMR: see Table 1. HR-FAB-MS (negative): *m/z* 537.2538 $[M-H]^-$ ($C_{24}H_{41}O_{13}$ requires 537.2547).

Shimaurinoside A (**7**). Needles (MeOH), mp 111–113°. $[\alpha]_D^{22}$ − 42.2° (MeOH, *c* 1.02). ^{1}H NMR (CD_3OD): δ 1.14 (3H, *d*, *J* = 6 Hz, H_3-3), 3.19 (H, *dd*, *J* = 10, 11 Hz, H-5″a), 3.20 (H, *dd*, *J* = 8, 9 Hz, H-2′), 3.22 (H, *dd*, *J* = 7, 9 Hz, H-2″), 3.34 (H, *t*, *J* = 9 Hz, H-3′), 3.37 (H, *t*, *J* = 9 Hz, H-4′), 3.48 (H, *ddd*, *J* = 5, 9, 12 Hz, H-4″), 3.65 (2H, *d*, *J* = 5 Hz, H-1), 3.68 (H, *dd*, *J* = 7, 12 Hz, H-6′a), 3.86 (H, *dd*, *J* = 5, 11 Hz, H-5″b), 3.93 (H, *tq*, *J* = 5, 6 Hz, H-2), 4.13 (H, *dd*, *J* = 2, 12 Hz, H-6′b), 4.28 (H, *d*, *J* = 8 Hz, H-1′), 4.30 (H, *d*, *J* = 7 Hz, H-1″). ^{13}C NMR: see Table 2. HR-FAB-MS (negative): *m/z* 369.1416 $[M-H]^-$ ($C_{14}H_{25}O_{11}$ requires 369.1397).

Shimaurinoside B (**8**). Needles, mp 177–180°, $[\alpha]_D^{20}$ − 48.9° (MeOH, *c* 0.61). ^{1}H NMR (CD_3OD): δ 0.92 (3H, *t*, *J* = 7 Hz, H_3-5), 1.22 (3H, *d*, *J* = 6 Hz, H_3-1), 1.35–1.65 (4H, *m*, H_2-3 and H_2-4), 3.14 (H, *dd*, *J* = 8, 9 Hz, H-2′), 3.18 (H, *dd*, *J* = 10, 11 Hz, H-5″a), 3.20 (H, *dd*, *J* = 8, 9 Hz, H-2″), 3.33 (H, *dd*, *J* = 8, 9 Hz, H-3′), 3.34 (H, *dd*, *J* = 7, 8 Hz, H-4′), 3.42 (H, *m*, H-5′), 3.48 (H, *ddd*, *J* = 5, 9, 10 Hz, H-4″), 3.83 (H, *sextet*, *J* = 6 Hz, H-2), 3.74 (H, *dd*, *J* = 5, 12 Hz, H-6′a), 3.86 (H, *dd*, *J* = 5, 11 Hz, H-5″b), 4.05 (H, *dd*, *J* = 2, 12 Hz, H-1′), 4.32 (H, *d*, *J* = 8 Hz, H-1″), 4.34 (H, *d*, *J* = 8 Hz, H-1′). ^{13}C NMR: see Table 2. HR-FAB-MS (negative): *m/z* 381.1736 $[M-H]^-$ ($C_{16}H_{29}O_{10}$ requires 381.1761).

Enzymatic hydrolysis of alangionoside-O (**5**). Crude hesperidinase (20 mg) was added ×4 at 12 hr intervals to a soln of **5** (20 mg). 12 hr after the final addition, the hydrolysate was purified by silica gel CC [Φ = 15 mm, *L* = 250 mm, $CHCl_3$ (100 ml), $CHCl_3$–MeOH (19:1, 100 ml), $CHCl_3$–MeOH (9:1, 100 ml), $CHCl_3$–MeOH (17:3, 100 ml), $CHCl_3$–MeOH (4:1, 100 ml) and $CHCl_3$–MeOH (7:3, 100 ml), frs of 15 g being collected] to give an aglycone (**5a**) (8.0 mg, 87%) in frs 34–41. Aglycone, needles (MeOH), mp 183–185°. $[\alpha]_D^{20}$ − 33.8° (MeOH, *c* 0.53). ^{1}H NMR (CD_3OD): δ 0.84 (3H, *s*, H_3–12ax), 1.14 (3H, *s*, H_3-13), 1.20 (3H, *s*, H_3-11eq), 1.27 (3H, *d*, *J* = 6 Hz, H_3-10), 1.44 (H, *ddd*, *J* = 2, 4, 12 Hz, H-2eq), 1.64 (H, *t*, *J* = 12 Hz, H-2ax), 1.73 (H, *dd*, *J* = 11, 12 Hz, H-4ax), 1.78 (H, *ddd*, *J* = 2, 5, 12 Hz, H-4eq), 4.04 (H, *dddd*, *J* = 4, 5, 11, 12 Hz, H-3), 4.34 (H, *dquin*, *J* = 1, 6 Hz, H-9), 5.78 (H, *dd*, *J* = 6, 12 Hz, H-8), 6.06 (H, *dd*, *J* = 1, 16 Hz, H-7). ^{13}C NMR: see Table 1. FAB-MS (negative) *m/z*: 243 $[M-H]^-$; HR-EIMS *m/z* (rel. int.): 208.1464 (100) $[M-H_2O\times2]^+$, $C_{13}H_{20}O_2$ requires 208.1463, 125.0928 (78) $[M-H_2O\times2-C_5H_7O]^+$ requires 125.0967.

Alangionoside-O-heptaacetate (**5b**). Compound **5** (10 mg) was acetylated with a mixt. of Ac_2O and pyridine (0.25 ml each) at 20° for 18 hr. The reagents were evapd to dryness and then purified by recrystallization from MeOH to afford 14 mg (90%) of the heptaacetate. Needles, mp 230–232°. $[\alpha]_D^{26}$ − 26.1° ($CHCl_3$, *c* 0.92). ^{1}H NMR ($CDCl_3$): δ 0.84 (3H, *s*, H_3-12ax), 1.15 (3H, *s*, H_3-13), 1.23 (3H, *s*, H_3-11eq), 1.35 (3H, *d*, *J* = 7 Hz, H_3-10), 1.60 (H, *ddd*, *J* = 2, 5, 10 Hz, H-2eq), 1.67 (H, *t*, *J* = 12 Hz, H-2ax), 1.68 (H, *dd*, *J* = 10, 13 Hz, H-4ax), 1.88 (H, *ddd*, *J* = 2, 4, 13 Hz, H-4eq), 1.989, 2.028, 2.038, 2.042, 2.050, 2.054, 2.081 (3H each, each *s*, $C\underline{H}_3CO$–7), 3.36 (H, *dd*, *J* = 8, 12 Hz, H-5″a), 3.68 (2H, *m*, H-5′ and 6′a), 3.78 (2H, *m*, H-4′ and 5″b), 4.15 (H, *m*, H-3), 4.15 (H, *dd*, *J* = 5, 12 Hz, H-6′b), 4.61 (H, *d*, *J* = 7 Hz, H-1″), 4.63 (H, *d*, *J* = 8 Hz, H-1′), 4.87 (H, *dd*, *J* = 7, 8 Hz, H-2″), 4.91 (H, *dd*, *J* = 8, 10 Hz, H-4′), 4.93 (H, *dd*, *J* = 8, 10 Hz, H-2′), 5.16 (H, *t*, *J* = 8 Hz, H-3″), 5.18 (H, *t*, *J* = 10 Hz, H-3′), 5.38 (H, *dquin*, *J* = 1, 7 Hz, H-9), 5.72 (H, *dd*, *J* = 7, 16 Hz, H-8), 6.15 (H, *dd*,

$J = 1$, 16 Hz, H-7). ^{13}C NMR ($CDCl_3$): δ 20.6–21.4 ($\underline{C}H_3CO$–), 20.8 (C-10), 25.5 (C-12), 26.5 (C-11), 27.1 (C-13), 39.5 (C-1), 41.3 (C-4), 43.1 (C-2), 61.8 (C-5″), 67.4 (C-6′), 68.8 (C-4′), 69.1, 70.6, 71.0, 71.3 (C-9), 71.6, 72.2, 73.5 (C-3), 76.6 (C-6), 77.9 (C-5), 98.5 (C-1′), 100.2 (C-1″), 131.1 (C-8), 132.6 (C-7), 169.3, 169.5, 169.6, 169.9, 170.1, 170.3, 170.5 ($CH_3\underline{C}O$– × 7). EI-MS *m/z* (rel. int.): 547 [xyl(OAc)$_3$glu(OAc)$_3$ oxonium ion]$^+$ (4), 368 (10), 317 (11), 251 [xyl(OAc)$_3$ oxonium ion]$^+$ (100), 208 [aglycone − H_2O − AcOH]$^+$ (66), 199 (69), 157 [aglycone − H_2O − AcOH − C_4H_5]$^+$ (90), 139 (97). FAB-MS (*m*-nitrobenzyl alcohol) *m/z*: 855 [M + Na]$^+$, 547 [xyl(OAc)$_3$glu(OAc)$_3$ oxonium ion]$^+$, 259 [xyl(OAc)$_3$ oxonium ion]$^+$ (+NaI), 871 [M + K]$^+$ + (+KI).

Synthesis of (S)- *and* (R)-1,2-*propanediol* - 1-O-β-D-*glucopyronosides* (**7b** and **c**). (*S*)-1,2-Propanediol (0.76 g, 10.4 mmol) was coupled with α-1-bromo-2,3,4,6-tetra-*O*-acetyl-D-glucopyranose (bromoacetylglucose) (3.27 g, 7.9 mmol) in the presence of Ag_2CO_3 (3.55 g, 12.1 mmol) in dry benzene (100 ml) for 12 hr at 25°. After alkaline hydrolysis, the residue was subjected to DCCC (frs 22–27, 705 mg) and then to RPCC [5% MeOH (1 l) in $H_2O \rightarrow$ 30% MeOH (1 l) in H_2O, frs 31–35, 250 mg]. Recrystallization from MeOH–EtOAc gave 150 mg of needles (**7b**), mp 131–132°. $[\alpha]_D^{26}$ − 18.7° (MeOH, *c* 1.71). ^1H NMR (CD_3OD): δ 1.13 (3H, *d*, $J = 7$ Hz, H_3-3), 3.21 (H, *dd*, $J = 7$, 9 Hz, H-2′), 3.35 (H, *dd*, $J = 8$, 10 Hz, H-1a), 3.66 (H, *dd*, $J = 5$, 12 Hz, H-6′a), 3.86 (H, *dd*, $J = 3$, 10 Hz, H-1b), 3.86 (H, *dd*, $J = 2$, 12 Hz, H-6′b), 3.95 (H, *dqd*, $J = 3$, 7, 8 Hz, H-2), 4.27 (H, *d*, $J = 7$ Hz, H-1′). ^{13}C NMR: see Table 2. HR-FAB-MS (negative) *m/z*: 237.1018 [M − H]$^-$ ($C_9H_{17}O_8$ requires 237.0974).

The (*R*)-1,2-propanediol (0.79 g, 10.4 mmol) was treated with bromoacetylglucose in a similar manner to the S enantiomer and work-up gave the glucoside as an amorphous powder (**7b**, 105 mg). $[\alpha]_D^{26}$ − 32.9° (MeOH, *c* 2.13). ^1H NMR (CD_3OD): δ 1.15 (3H, *d*, $J = 7$ Hz, H_3-3), 3.21 (H, *dd*, $J = 8$, 9 Hz, H-2′), 3.56 (H, *dd*, $J = 4$, 10 Hz, H-1a), 3.66 (H, *dd*, $J = 5$, 12 Hz, H-6′a), 3.71 (H, *dd*, $J = 7$, 10 Hz, H-1b), 3.86 (H, *dd*, $J = 2$, 12 Hz, H-6′b), 4.28 (H, *d*, $J = 8$ Hz, H-1′). ^{13}C NMR: see Table 2. HR-FAB-MS (negative) *m/z*: 237.0947 [M − H]$^-$ ($C_9H_{17}O_7$ requires 237.0974).

Synthesis of (S)-2-*pentanol*-2-O-β-D-*glucopyranoside* (**8b**). 2-(*S*)-Pentanol (0.81 g, 9.2 mmol), bromoacetylglucose (5.26 g, 12.8 mmol) and Ag_2CO_3 (3.49 g, 12.7 mmol) were stirred for 22 hr and 55 ml of dry benzene at 20°, followed by refluxing for 4 hr. Insol. materials were filtered off, and then the diluted filtrate was washed with 5% $NaHCO_3$ (100 ml) and H_2O (100 ml), successively. The dried benzene layer was evapd and then the residue was treated with 0.1 M NaOH in MeOH (100 ml) for 20 min. The MeOH soln was neutralized with Amberlite IR-120B (H^+) and then evapd. The residue was purified by DCCC to give 784 mg of a crude crystalline material (in frs 55–70), a portion (238 mg) of which was recrystallized from MeOH–EtOAc to afford 99 mg of needles. (*S*)-2-Pentanol-2-*O*-β-D-glucopyranoside. mp 140–141°. $[\alpha]_D^{26}$ − 32.0° (MeOH, *c* 1.78). ^1H NMR (CD_3OD): δ 0.92 (3H, *t*, $J = 7$ Hz, H_3-5), 1.22 (3H, *d*, $J = 6$ Hz, H_3-1), 1.35–1.48 (3H, *m*, H-3a and H_2-4), 1.53–1.63 (H, *m*, H-3b), 3.14 (H, *dd*, $J = 8$, 9 Hz, H-2′), 3.34 (H, *t*, $J = 9$ Hz, H-3′), 3.66 (H, *dd*, $J = 5$, 12 Hz, H-6′a), 3.82 (H, *sextet*, $J = 6$ Hz, H-2), 3.85 (H, *dd*, $J = 2$, 12 Hz, H-6′b), 4.32 (H, *d*, $J = 8$ Hz, H-1′). ^{13}C NMR (CD_3OD): see Table 2. HR-FAB-MS (negative *m/z*: 249.1325 [M − H]$^-$ ($C_{11}H_{22}O_6$ requires 249.1338).

Synthesis of (R)-2-*Pentanol*-2-O-β-D-*glucopyranoside* (**8c**). (*R*)-2-Pentanol (0.81 g) was treated in a similar manner to the *S*-isomer to give crude crystals (486 mg). Recrystallization from the same solvents as described above gave 210 mg of needles, mp 117–119°. $[\alpha]_D^{26}$ − 45.8° (MeOH, *c* 1.79). ^1H NMR (CD_3OD): δ 0.91 (3H, *t*, $J = 7$ Hz, H_3-5), 1.16 (3H, *d*, $J = 6$ Hz, H_3-1), 1.34–1.47 (3H, *m*, H-3a and H_2-4), 1.54–1.66 (H, *m*, H-3b), 3.14 (H, *dd*, $J = 8$, 9 Hz, H-2′), 3.35 (H, *t*, $J = 9$ Hz, H-4′), 3.67 (H, *dd*, $J = 5$, 12 Hz, H-6′a), 3.85 (H, *dd*, $J = 2$, 12 Hz, H-6′b), 3.89 (H, *sextet*, $J = 6$ Hz, H-2), 4.32 (H, *d*, $J = 8$ Hz, H-1′). ^{13}C NMR (CD_3OD): see Table 2. HR-FAB-MS (negative *m/z*: 249.1339 [M − H]$^-$ ($C_{11}H_{21}O_6$ requires 249.1338).

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