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WATER-SOLUBLE PHENOLIC GLYCOSIDES FROM LEAVES OF *ALANGIUM PREMNIFOLIUM*

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Key Word Index—*Alangium premnifolium*; Alangiaceae; leaves; guaiacylglycerol glucoside; syringoylglycerol glucoside; benzyl alcohol glycoside; henryoside glucoside; pyrocatechol diglucoside.

Abstract—From the water-soluble fraction of a methanol extract of leaves of *Alangium premnifolium*, guaiacylglycerol and syringoylglycerol glucosides, benzyl alcohol triglycosides, salicyl alcohol glycoside, a derivative of henryoside, 3,4-dihydroxyphenethyl alcohol glycoside and pyrocatechol diglucoside were isolated. Their structures were elucidated from spectroscopic evidence. Copyright © 1997 Elsevier Science Ltd

INTRODUCTION

Fifteen megastigmane glycosides were isolated from the *n*-BuOH-soluble fraction of a methanol extract of leaves of *Alangium premnifolium* [1–3]. Isolation work on the water-soluble fraction has yielded two new megastigmane glycosides and two glycosides of simple alcohols [4]. Continued phytochemical investigation of the fraction revealed eight new phenolic glycosides, along with three known phenolic glycosides. The present paper deals with structural elucidation of these compounds.

RESULTS AND DISCUSSION

The water-soluble fraction was separated by a combination of various chromatography techniques. Compounds **1–3**, out of the 11 phenolic glycosides, isolated were known and their structures were determined spectroscopically to be guaiacylglycerol 9-*O*-glucopyranoside (**1**) [5] and 8-*O*-glucopyranoside (**2**) [6], and benzyl alcohol *O*-(6′-*O*-*β*-D-xylopyranosyl)-*β*-D-glucopyranoside (**3**) [7], respectively.

Compound 4 (**4**), $[\alpha]_D$ −11.5°, was isolated as an amorphous powder whose molecular formula was determined to be $C_{17}H_{26}O_{11}$ from the observation of a quasi-$[M]^+$ by negative-ion high resolution FAB-mass spectrometry. The IR spectrum indicated the presence of hydroxyl groups (3300 cm^{-1}), an aromatic ring (1610 and 1515 cm^{-1}) and phenolic hydroxyl groups (1230 cm^{-1}); the UV absorption maximas indicated the presence of an aromatic moiety. The ^{13}C NMR spectrum showed the presence of four aromatic carbon signals and one primary and two secondary alcoholic carbon signals, together with six signals typical of *β*-glucopyranosides. Thus, the aromatic ring must have a symmetrical substitution and, as judged from the ^1H NMR spectrum, the structure of the aglycone portion was identified as syringoylglycerol. The position of the sugar linkage was expected to be the hydroxyl group at the 9-position (δ_C 72.5), compared with those of guaiacyl glycerol glucopyranosides (**1** (δ_C 72.5) and **2** (δ_C 62.7)) (see Table 1). The relative stereochemistry of the glycerol portion was expected to be of the *threo*-form from the coupling constant (J = 7 Hz) of the proton at the 7-position [5, 8, 9].

Compounds **5**, $[\alpha]_D$ +7.9°, and **6**, $[\alpha]_D$ −37.7°, were obtained as needles whose molecular formulae were the same as that of compound **4**; other spectroscopic evidence also indicated that these compounds must have similar structures to compound **4** (Table 1). In the ^{13}C NMR spectra, the 9-positions resonated at a higher field (δ_C 63.3 and 62.4, respectively) than that of compound **4** (δ_C 72.5), while each of the secondary alcohols appeared downfield at δ_C 87.5 and 86.7, respectively. Therefore, compounds **5** and **6** were expected to be isomers of **4** with regard to the position

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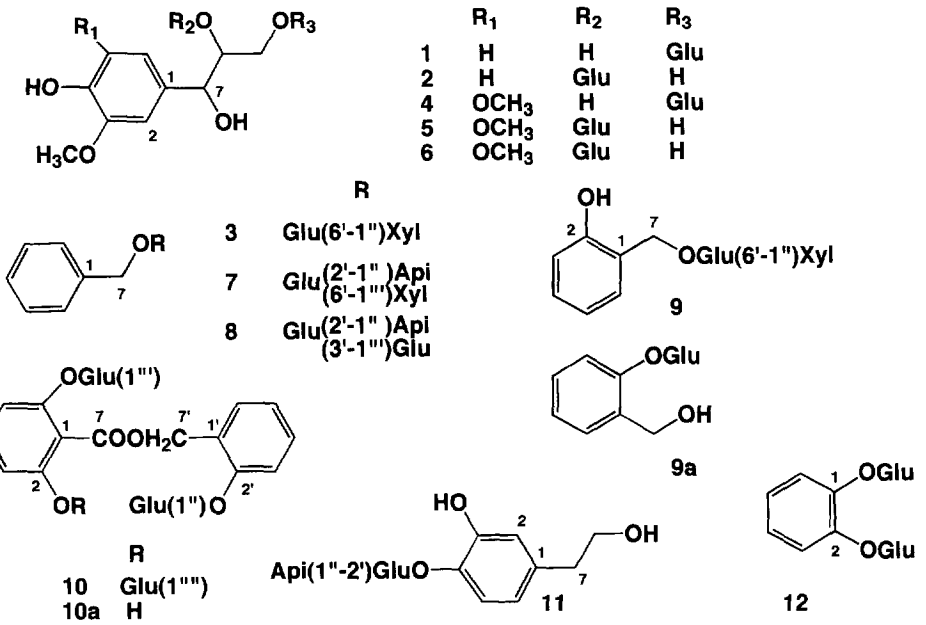

Table 1. ^{13}C NMR data for syringoylglycerol glucosides (**4**–**6**) (CD_3OD, 100 MHz)

C	4	5	6
1	133.8	132.8	132.4
2	105.5	105.4	105.7
3	149.0	149.3	149.2
4	135.9	136.3	136.4
5	149.0	149.3	149.2
6	105.5	105.4	105.7
7	75.7	75.1	75.0
8	75.6	87.5	86.7
9	72.5	63.3	62.4
$-OCH_3 \times 2$	56.8	56.9	56.8
1′	105.0	105.3	104.3
2′	75.2	75.6	75.0
3′	78.0	78.1	78.2
4′	71.6	71.5	71.6
5′	77.9	77.9	77.9
6′	62.7	62.6	62.7

of the sugar linkage. The positions of the sugar linkages were shown to be the hydroxyl groups at the 8-positions from ^{13}C–^1H COSY experiments, in which cross-peaks were observed between δ_C 75.1 and δ_H 4.69 (*d*, $J = 7$ Hz, H-7) for compound **5**, and δ_C 75.0 and δ_H 4.66 (*d*, $J = 8$ Hz, H-7) for compound **6**. The relative stereochemistry of the glycerol portion of both compounds must be of the *threo*-form, as judged from the coupling constants of the H-7 protons. Thus, the structures of compounds **5** and **6** were concluded to be syrigoylglycerol 7-O-β-glucopyranosides whose aglycones were enantiomers of each other.

Compound 7 (**7**) was obtained as an amorphous powder and ^{13}C and ^1H NMR indicated that it was a compound analogous to **3** with a disubstituted sugar and terminal β-apiofuranose and β-xylopyranose units [7] (Table 2). GC analysis showed that compound **7** contained one mole each of apiose, xylose and glucose, and this was supported by high resolution-FAB-mass spectrometry, which revealed the elemental composition of **7** to be $C_{23}H_{34}O_{14}$. On irradiation of the anomeric protons at δ_H 4.35 (*d*, $J = 7$ Hz) and 4.42 (*d*, $J = 8$ Hz) in NOE experiments, H-6′a, δ_H 3.76 (*dd*, $J = 6$ and 12 Hz), and one of the benzylic protons, δ_H 4.63 (*d*, $J = 12$ Hz), showed

Table 2. ^{13}C NMR data for benzyl alcohol glycosides (**3**, **7** and **8**) (CD_3OD, 100 MHz)

C	3	7	8
1	139.1	139.0	139.0
2	129.3	129.3	129.3
3	129.3	129.4	129.3
4	128.7	128.8	128.7
5	129.3	129.4	129.3
6	129.3	129.3	129.3
7	72.0	72.0	71.9
1′	103.4	102.2	104.5
2′	74.9	78.8	80.0
3′	78.0	78.5	87.0
4′	71.2	71.2	70.1
5′	77.8	77.7	77.6
6′	69.9	69.8	62.8
1″	105.6	110.7	111.1
2″	75.1	78.0	78.0
3″	77.1	80.7	80.4
4″	71.6	75.3	75.1
5″	66.9	66.0	65.4
1‴	–	105.6	102.2
2‴	–	74.9	75.4
3‴	–	76.9	78.2
4‴	–	71.6	71.6
5‴	–	66.9	78.2
6‴	–		62.6

relaxation. Thus, it was evident that the β-xylopyranosyl moiety was bound to the hydroxyl group at the 6′-position. To determine the position of the other glycosidic linkage, compound **7** was acetylated and then the ^1H–^1H COSY spectrum of the octaacetate (**7a**) analysed. From the two protons at δ_H 3.59 and 3.84 (H-6′a and H-6′b), the connectivities to δ_H 3.64 (H-5′), 4.86 (H-4′), 5.16 (H-3′), 3.71 (H-2′) and then to 4.46 (H-1′) it was clearly demonstrated that H-2′ was not affected by acetylation. Therefore, the structure of compound **7** was elucidated to be benzyl alcohol *O*-(2′-*O*-β-apiofuranosyl, 6′-*O*-β-xylopyranosyl)-β-glucopyranoside.

Compound 8 (**8**), $C_{24}H_{36}O_{15}$, was an amorphous powder and its spectroscopic data were similar to those of compound **7** (Table 2). Glucose and apiose were detected by GC in the ratio of 2:1. Essentially the same rationale as described above was adopted to elucidate the structure of compound **8**. Acetylation gave a nona-acetate (**8a**). From the interaction between H-1″ and H-2′, observed in the difference NOE spectrum and the connectivities in the ^1H–^1H COSY spectrum from one (δ 4.36) of the anomeric protons of the two glucose moieties to δ 3.77 (H-2′), 3.96 (H-3′), 4.86 (H-4′), 3.59 (H-5′) and then to 4.17 (2H, H_2-6′), the structure of compound **8** was elucidated as benzyl alcohol *O*-(2′-*O*-β-apiofuranosyl, 3′-*O*-β-glucopyranosyl)-β-glucopyranoside.

Compound **9**, $[\alpha]_D$ −50.6°, was expected to be a phenolic glycoside from its characteristic absorption maxima in IR and UV spectra and elemental composition $C_{18}H_{26}O_{11}$ determined by high-resolution FAB-mass spectrometry. The ^{13}C and ^1H NMR spectra showed the presence of a β-D-xylopyranosyl(1 → 6) β-D-glucopyranosyl moiety and a benzene ring substituted with a hydroxyl group and a carbinol group. Therefore, compound **9** is a derivative of salicin. However, comparison of the ^{13}C NMR data with those of salicin led to the conclusion that glycosylation must have occurred on the alcoholic hydroxyl group; this is not the case for salicin (see C-7 of **9** and **9a** in Table 3).

Compound 10 (**10**) was obtained as an amorphous powder and its IR spectrum indicated the presence of benzene rings (1600 and 1490 cm^{-1}) and an ester linkage (1710 cm^{-1}) (Table 3). The ^{13}C and ^1H NMR spectra showed that one of the aromatic rings had a symmetrical substitution pattern, similar to an anacardic acid; the other was similar to salicin. In combination with the results of high-resolution FAB-mass spectrometry ($C_{32}H_{42}O_{20}$), compound **10** was expected be a derivative of henryoside (**10a**) and its structure was thus assigned as the 6′-*O*-β-glucopyranoside of henryoside [10, 11].

Compound **11** was obtained as needles, mp 173–174°, and its elemental composition was determined to be $C_{19}H_{28}O_{12}$. ^1H NMR showed the presence of three aromatic protons coupled in an ABX-system and the presence of a terminal β-apiofuranoside was shown by the ^{13}C NMR spectrum. One more sugar component was identified as glucose by GC. Further information obtained from the NMR spectra indicated that the aglycone portion must be 3,4-dihydroxyphenethyl alcohol. The position of the glucoside linkage was shown to be the hydroxyl group at the 3-position from the observation of NOE enhancement of the aromatic signal (δ_H 7.17; *d*, $J = 8$ Hz) on irradiation of the anomeric proton of the glucose. Acetylation of compound **11** gave an octaacetate (**11a**), whose glucose ring protons were assigned on the basis of the ^1H–^1H COSY spectrum. The downfield shifts of H-3′ (δ_H 5.23) and H-4′ (δ_H 5.08) on acetylation suggested that the β-apiofuranose moiety must be attached to the hydroxyl group at the 2′-position. Therefore, the structure of compound **11** was determined to be 3,4-dihydroxyphenethyl alcohol 3-*O*-(2′-*O*-β-apiofuranosyl)-β-glucopyranoside.

Compound 12 (**12**) was obtained as needles. Although the ^{13}C NMR spectrum showed the presence of only three sp^2 carbon signals, one of which must have an oxygen function and six signals typical of a β-glucopyranoside, negative-ion high-resolution FAB-mass spectrometry revealed its molecular formula to be $C_{18}H_{26}O_{12}$. Therefore, compound **12** was expected to consist of two units of β-glucopyranose and a symmetrically substituted benzene ring as an aglycone. The observation of three sp^2 carbon signals, one of which bears a hydroxyl substituent, indicated the aglycone to be pyrocatechol. Therefore, the structure of compound 12 was determined to be the 1,2-di-*O*-β-glucopyranoside of pyrocatechol.

EXPERIMENTAL

General. Mps: uncorr. ^1H and ^{13}C NMR: 400 and 100 MHz, respectively. Highly porous synthetic resin: Diaion HP-20 (Mitsubishi Chemical Co. Ltd), 80 mm i.d. × 600 mm, H_2O–MeOH (4:1) → MeOH, frs of 2 l collected. Silica gel: Kieselgel 60 (Merck), 70–230 mesh, $CHCl_3$ → $CHCl_3$–MeOH, frs of 500 ml being collected. RPCC: ODS [Cosmosil, ODS 75 C_{18}–OPN (Nakarai Tesque, Kyoto), Φ = 40 mm i.d. × 250 mm, frs of 10 g collected. DCCC: 500 columns (Tokyo Rikakikai) Φ = 2 mm i.d. × 40 cm, $CHCl_3$–MeOH–H_2O–*n*-PrOH (9:12:8:2); frs of 5 g collected. HPLC: ODS (Inertsil, GL Science) 20 mm i.d. × 250 mm, H_2O–MeOH, flow rate 6 ml min^{-1}, detection at 254 nm. GC: FID detector, column (Shimadzu CPB-20) 0.22 mm × 25 m, 0.25 μm film thickness; carrier gas, N_2 at 1.5 kg cm^{-2}. Salicin was from Nakarai Tesque, Inc. Standard apiose for GC analysis was obtained from alangionoside B [1].

Extraction and isolation. Leaves of *A. premnifolium* Ohwi were the same as those used previously [1]. A MeOH extract of leaves of *A. premnifolium* (5.72 kg) was concd to 3 l and then 150 ml of H_2O was added to make a 95% aq. MeOH soln. The soln was extracted with 3 l of *n*-hexane and the MeOH layer concd to give a residue. This residue was suspended in H_2O (1.5 l) and then extracted with EtOAc (1 l × 2)

Table 3. ^{13}C NMR Data for compounds **9**–**12**, and salicin (**9a**) and henryoside (**10a**) (CD_3OD, 100 MHz)

C	9	9a	10		10a*	11	12†
1	125.2	132.3	117.4		111.7	136.4	147.3
2	156.7	157.2	156.5		158.4	119.4	147.3
3	116.4	117.2	111.6		107.8	145.3	118.2
4	130.2	129.9	132.8		134.2	148.6	122.7
5	120.6	123.8	111.6		110.5	117.4	122.7
6	131.3	130.0	156.5		160.1	121.3	118.7
7	68.1	61.1	168.4		170.1	39.7	–
8						64.3	
1′	103.6	103.5	126.9		126.9	103.6	101.6
2′	75.1	75.2	156.8		156.8	83.6	73.3
3′	77.7	78.3	116.9		116.8	77.7	76.9
4′	71.6	71.5	130.8		130.9	71.2	69.6
5′	77.2	78.1	123.8		123.7	77.6	76.2
6′	69.8	62.6	131.0		130.8	62.4	60.6
7′			63.7		63.7		
1″	105.5	–	102.9		102.7	112.6	101.6
2″	75.0	–	74.9		74.9	78.1	73.3
3″	77.9	–	78.3		78.3	79.7	76.9
4″	71.2	–	71.2		71.2	74.9	69.6
5″	66.9	–	77.9		77.9	65.0	76.2
6″	–	–	62.6		62.6	–	60.6
1‴, 1⁗	–	–	103.2	103.2	103.1	–	–
2‴, 2⁗	–	–	75.0	75.0	74.9	–	–
3‴, 3⁗	–		78.3	78.3	78.3	–	–
4‴, 4⁗	–	–	71.3	71.3	71.3	–	–
5‴, 5⁗	–	–	78.0	78.0	78.1	–	–
6‴,6⁗	–	–	62.5	62.5	62.5	–	–

*Data for henryoside previously isolated [11].
†In DMSO-d_6.

and *n*-BuOH (1.5 l and 1 l), successively. The H_2O layer was evapd to dryness to give 365 g of a H_2O-sol. fr. This fr. was subjected to Diaion HP-20 CC, giving 3 frs in yields of 18.1 g (5–10% MeOH), 12.5 g (20% MeOH) and 22.6 g (40% MeOH). The first fr. was chromatographed on silica gel (500 g, Φ = 55 mm i.d. × 44 cm) with $CHCl_3$ (1.5 l), $CHCl_3$–MeOH (39:1, 3 l; 19:1, 6 l; 37:3, 6 l; 9:1, 6 l; 17:3, 6 l; 4:1, 6 l; 3:1, 3 l; and 7:3, 3 l), and $CHCl_3$–MeOH–H_2O (30:12:1, 3 l; and 15:6:1, 3 l). The pooled fr. (1.32 g in frs 43–48) was purified by RPCC (10% MeOH → 50% MeOH, 361 mg in frs 36–39), DCCC (223 mg in frs 14–18) and finally HPLC (5% MeOH), giving **2** (6 mg), **1** (79 mg) and **4** (61 mg). The pooled fr. (1.34 g in frs 55–64) was purified by RPCC (10% MeOH → 50% MeOH, 99 mg in frs 61–69) and then DCCC, giving 25 mg of **12** in a crystalline state. From the pooled fr. (1.99 g in frs 77–86), **5** (20 mg) and **6** (28 mg) were obtained by RPCC (10% MeOH → 50% MeOH, 246 mg in frs 43–50), DCCC (103 mg in frs 17–24) and then HPLC (5% MeOH).

Two other frs obtained from Diaion HP-20 CC were sepd in a similar manner as previous compounds by a combination of silica gel CC, RPCC, DCCC and HPLC, giving six compounds on CC in the following yields: **3** (125 mg), **9** (35 mg), **10** (73 mg) and **11** (29 mg) from the second fr. and **7** (32 mg) and **8** (9 mg) from the last fr.

Known compounds isolated. Guaicylglycerol 9-O-β-D-glucopyranoside (**1**), $[\alpha]_D^{29}$ −6.5° (MeOH, *c* 1.38) [5]. Guaicylglycerol 8-*O*-β-D-glucopyranoside (**2**), $[\alpha]_D^{29}$ −16.5° (MeOH, *c* 0.37) [6]. Benzyl alcohol O-(6′-O-β-D-xylopyranosyl)-β-D-glucopyranoside (**3**), mp 187–189°, $[\alpha]_D^{21}$ −70.6° (MeOH, *c* 0.60). ^{13}C NMR (CD_3OD): Table 2 [7].

Compound **4**. Amorphous powder. $[\alpha]_D^{29}$ −11.9° (MeOH, *c* 1.39). IR ν_{max}^{KBr} cm^{-1}: 3300, 2875, 1610, 1515, 1460, 1325, 1230, 1175, 1120, 1070, 1045. UV λ_{max}^{MeOH} nm (log ε): 210 (4.18), 231 (3.75), 271 (2.99). ^1H NMR (CD_3OD): δ 3.23 (1H, *dd*, *J* = 8 and 9 Hz, H-2′), 3.62 (1H, *dd*, *J* = 7 and 10 Hz, H-9a), 3.66 (1H, *dd*, *J* = 5 and 12 Hz, H-6′a), 3.84 (6H, *s*, -OCH_3 × 2), 3.84 (1H, *dd*, *J* = 2 and 12 H, H-6′b), 3.90 (1H, *dt*, *J* = 3 and 7 Hz, H-8), 4.05 (1H, *dd*, *J* = 3 and 10 Hz, H-9b), 4.30 (1H, *d*, *J* = 8 Hz, H-1′), 4.57 (1H, *d*, *J* = 7 Hz, H-7), 6.70 (2H, *s*, H_2-2 and 6). ^{13}C NMR (CD_3OD): Table 1. HR-FAB-MS (negative centroid) *m/z*: 405.1417 $[M-H]^-$ ($C_{17}H_{25}O_{11}$ requires 405.1397).

Compound **5**. Needles, mp 204–206° (MeOH). $[\alpha]_D^{29}$ +7.9°(MeOH, *c* 0.63). IR ν_{max}^{KBr} cm^{-1}: 3350, 2900, 1615, 1520, 1465, 1380, 1325, 1235, 1160, 1120, 1080, 1030. UV λ_{max}^{MeOH} nm (log ε): 211 (4.11), 230 (3.72), 271

(3.03). ^{1}H NMR (CD_3OD): δ 3.32 (1H, *dd*, J = 7 and 9 Hz, H-2′), 3.40 (1H, *dd*, J = 5 and 12 Hz, H-9a), 3.56 (1H, *dd*, J = 4 and 12 Hz, H-9b), 3.65 (1H, *dd*, J = 6 and 12 Hz, H-6′a), 3.82 (1H, *m*, H-8), 3.84 (1H, *dd*, J = 2 and 12 Hz, H-6′b), 3.85 (6H, *s*, -OCH_3 × 2), 4.37 (1H, *d*, J = 7 Hz, H-1′), 4.69 (1H, *d*, J = 7 Hz, H-7), 6.70 (2H, *s*, H-2 and 6). ^{13}C NMR (CD_3OD): Table 1. HR-FAB-MS (negative centroid) *m/z*: 405.1417 $[M-H]^-$ ($C_{17}H_{25}O_{11}$ requires 405.1397).

Compound **6**. Needles, mp 204–205° (MeOH). $[\alpha]_D^{29}$ −37.7° (MeOH, *c* 0.48). IR ν_{max}^{KBr} cm^{-1}: 3350, 2900, 1610, 1515, 1460, 1325, 1220, 1155, 1110, 1070, 1020. UV λ_{max}^{MeOH} nm (log ε): 212 (4.18), 231 (3.80), 271 (3.11). ^{1}H NMR (CD_3OD): δ 3.32 (1H, *dd*, J = 8 and 9 Hz, H-2′), 3.32 (1H, *dd*, J = 7 and 12 Hz, H-9a), 3.40 (1H, *m*, H-5′), 3.50 (1H, *dd*, J = 3 and 12 Hz, H-9b), 3.69 (1H, *dd*, J = 5 and 12 Hz, H-6′a), 3.85 (1H, *m*, H-8), 3.85 (6H, *s*, -OCH_3 × 2), 3.89 (1H, *dd*, J = 2 and 12 Hz, H-6′b), 4.52 (1H, *d*, J = 8 Hz, H-1′), 4.66 (1H, *d*, J = 8 Hz, H-9), 6.71 (2H, *s*, H_2-2 and 6). ^{13}C NMR (CD_3OD): Table 1. HR-FAB-MS (negative centroid) *m/z*: 405.1363 $[M-H]^-$ ($C_{17}H_{25}O_{11}$ requires 405.1397).

Compound **7**. Amorphous powder. $[\alpha]_D^{23}$ −87.2° (MeOH, *c* 2.11). IR ν_{max}^{KBr} cm^{-1}: 3350, 2900, 1625, 1455, 1040. UV λ_{max}^{MeOH} nm (log ε): 213 (3.35), 252 (2.33), 258 (2.38), 263 (2.30). ^{1}H NMR (CD_3OD): δ 3.19 (H, *dd*, J = 10 and 11 Hz, H-5‴a), 3.23 (H, *dd*, J = 8 and 9 Hz, H-2‴), 3.50 (H, *d*, J = 11 Hz, H-5″a), 3.56 (H, *d*, J = 11 Hz, H-5″b), 3.63 (H, *d*, J = 10 Hz, H-4″a), 3.76 (H, *dd*, J = 6 and 12 Hz, H-6′a), 3.87 (H, *dd*, J = 5 and 11 Hz, H-5‴b), 3.93 (H, *d*, J = 10 Hz, H-4″b), 3.94 (H, *d*, J = 2 Hz, H-2″) 4.11 (H, *dd*, J = 2 and 12 Hz, H-6′b), 4.35 (H, *d*, J = 7 Hz, H-1‴), 4.42 (H, *d*, J = 8 Hz, H-1′), 4.63 (H, *d*, J = 12 Hz, H-7a), 4.89 (H, *d*, J = 12 Hz, H-7b), 5.38 (H, *d*, J = 2 Hz, H-1″), 7.31 (H, *br t*, J = 8 Hz, H-4), 7.33 (2H, *br t*, J = 8 Hz, H_2-3 and 5), 7.42 (2H, *br d*, J = 8 Hz, H_2-2 and 6). ^{13}C NMR (CD_3OD): Table 2. HR-FAB-MS (negative centroid) *m/z*: 533.1858 $[M-H]^-$ ($C_{23}H_{33}O_{14}$ requires 533.1871).

Compound **8**. Amorphous powder. $[\alpha]_D^{24}$ −90.0° (MeOH, *c* 0.50). UV λ_{max}^{MeOH} nm (log ε): 214 (3.25), 251 (2.47), 258 (2.49), 263 (2.42). ^{1}H NMR (CD_3OD): δ 3.26 (H, *dd*, J = 8 and 9 Hz, H-2‴), 3.50 (H, *d*, J = 12 Hz, H-5″a), 3.53 (H, *d*, J = 12 Hz, H-5″b), 3.56 (H, *dd*, J = 8 and 9 Hz, H-2′), 3.63 (H, *dd*, J = 2 and 12 Hz, H-6′a or 6‴a), 3.65 (H, *d*, J = 10 Hz, H-4″a), 3.68 (H, *t*, J = 10 Hz, H-3′), 3.70 (H, *dd*, J = 6 and 12 Hz, H-6‴a or 6′a), 3.88 (H, *dd*, J = 2 and 12 Hz, H-6′b or 6‴b), 3.90 (H, *dd*, J = 2 and 12 Hz, H-6‴b or 6′b), 3.97 (H, *d*, J = 2 Hz, H-2″), 3.98 (H, *d*, J = 10 Hz, H-4″b), 4.45 (H, *d*, J = 8 Hz, H-1′), 4.57 (H, *d*, J = 8 Hz, H-1‴), 4.65 (H, *d*, J = 12 Hz, H-7a), 4.92 (H, *d*, J = 12 Hz, H-7b), 5.45 (H, *d*, J = 2 Hz, H-1″), 7.30 (H, *br t*, J = 7 Hz, H-4), 7.32 (2H, *br t*, J = 7 Hz, H_2-3 and 5), 7.43 (2H, *br d*, J = 7 Hz, H_2-2 and 6). ^{13}C NMR (CD_3OD): Table 2. HR-FAB-MS (negative centroid) *m/z*: 563.1974 $[M-H]^-$ ($C_{24}H_{35}O_{15}$ requires 563.1976).

Compound **9**. Amorphous powder. $[\alpha]_D^{29}$ −50.6° (MeOH, *c* 0.83). IR ν_{max}^{KBr} cm^{-1}: 3300, 2850, 1610, 1455, 1360, 1270, 1240, 1160, 1065, 1035, 760. UV λ_{max}^{MeOH} nm (log ε): 215 (3.81), 278 (3.40). ^{1}H NMR (CD_3OD): δ 3.77 (1H, *dd*, J = 6 and 12 Hz, H-6′a), 3.87 (1H, *dd*, J = 5 and 12 Hz, H-5″b), 4.12 (1H, *dd*, J = 2 and 12 Hz, H-6′b), 4.73 (1H, *d*, J = 12 Hz, H-7a), 4.91 (1H, *d*, J = 12 Hz, H-9b), 4.37 (1H, *d*, J = 8 Hz, H-1′), 4.40 (1H, *d*, J = 8 Hz, H-1″), 6.79 (1H, *dd*, J = 1 and 8 Hz, H-6), 6.81 (1H, *dt*, J = 1 and 8 Hz, H-5), 7.13 (1H, *dt*, J = 1 and 8 Hz, H-4), 7.33 (1H, *dd*, J = 1 and 8 Hz, H-3). ^{13}C NMR (CD_3OD): Table 3. HR-FAB-MS (negative centroid) *m/z*: 417.1413 $[M-H]^-$ ($C_{18}H_{25}O_{11}$ requires 417.1397).

Compound **10**. Amorphous powder. $[\alpha]_D^{29}$ −34.0° (MeOH, *c* = 1.03). IR ν_{max}^{KBr} cm^{-1}: 3300, 2875, 1710, 1600, 1490, 1465, 1375, 1285, 1245, 1050, 760. UV λ_{max}^{MeOH} nm (log ε): 212 (4.19), 275 (3.49); ^{1}H NMR (CD_3OD): δ 3.56 (1H, *dd*, J = 8 and 9 Hz, H-2″), 3.66 (2H, *dd*, J = 5 and 12 Hz, H_2-6‴a and 6⁗a), 3.72 (1H, *dd*, J = 5 and 12 Hz, H-6″a), 3.84 (2H, *dd*, J = 2 and 12 Hz, H_2-6‴b and 6⁗b), 3.89 (1H, *dd*, J = 2 and 12 Hz, H-6″b), 4.94 (2H, *d*, J = 7 Hz, H_2-1‴ and 1⁗), 4.94 (1H, *d*, J = 8 Hz, H-1″), 5.45 (1H, *d*, J = 13 Hz, H-7′a), 5.63 (1H, *d*, J = 13 Hz, H-7′b), 6.97 (2H, *d*, J = 8 Hz, H_2-3 and 5), 7.08 (1H, *dt*, J = 1 and 8 Hz, H-5′), 7.23 (1H, *dd*, J = 1 and 8 Hz, H-3′), 7.31 (1H, *dt*, J = 1 and 8 Hz, H-4′), 7.36 (1H, *t*, J = 8 Hz, H-4), 7.52 (1H, *dd*, J = 1 and 8 Hz, H-6′). ^{13}C NMR (CD_3OD): Table 3. HR-FAB-MS (negative centroid) *m/z*: 745.2153 $[M-H]^-$ ($C_{32}H_{41}O_{20}$ requires 745.2192).

Compound **11**. Needles, mp 173–174° (MeOH). $[\alpha]_D^{19}$ −74.3° (MeOH, *c* 0.77). IR ν_{max}^{KBr} cm^{-1}: 3300, 2900, 1590, 1505, 1290, 1210, 1165, 1125, 1065, 1010, 825. UV λ_{max}^{MeOH} nm (log ε): 204 (4.10), 217 (3.82), 277 (3.39). ^{1}H NMR (CD_3OD): δ 2.70 (2H, *t*, J = 7 Hz, H_2-7), 3.37 (1H, *ddd*, J = 2, 5 and 10, H-5′), 3.69 (2H, *t*, J = 7 Hz, H_2-8), 3.72 (1H, *dd*, J = 5 and 12 Hz, H-6′a), 3.79 (1H, *d*, J = 10 Hz, H-4″a), 3.89 (1H, *dd*, J = 2 and 12 Hz, H-6′b), 3.99 (1H, *d*, J = 4 Hz, H-2″), 4.12 (1H, *d*, J = 10 Hz, H-4″b), 4.72 (1H, *dd*, J = 8 Hz, H-1′), 5.33 (1H, *d*, J = 4 Hz, H-1″), 6.63 (1H, *dd*, J = 2 and 8 Hz, H-6), 6.72 (1H, *d*, J = 2 Hz, H-2), 7.17 (1H, *d*, J = 8 Hz, H-5). ^{13}C NMR (CD_3OD): Table 3. HR-FAB-MS (negative centroid) *m/z*: 447.1511 $[M-H]^-$ ($C_{19}H_{27}O_{12}$ requires 447.1503).

Compound **12**. Needles, mp 232–234° (MeOH). $[\alpha]_D^{28}$ −52.5° (H_2O, *c* 1.01). UV λ_{max}^{MeOH} nm (log ε): 214 (3.85), 270 (3.11). ^{1}H NMR (DMSO-d_6 with trace amount of D_2O): δ 3.16 (2H, *t*, J = 7 Hz, H_2-2′ and 2″), 3.46 (2H, *dd*, J = 5 and 12 Hz, H_2-6′a and 6″a), 3.67 (2H, *dd*, J = 2 and 12 Hz, H_2-6′b and 6″b), 4.78 (2H, *d*, J = 7 Hz, H_2-1′ and 1″), 6.97 and 7.16 (each 2H, each *m*, H_2-3 and 6, and H_2-4 and 5). ^{13}C NMR (DMSO-d_6): Table 3. HR-FAB-MS (negative centroid) *m/z*: 433.1330 $[M-H]^-$ ($C_{18}H_{25}O_{12}$ requires 433.1346).

Acetylation of compound **7**. Compound **7** (19 mg)

was acetylated with a mixt. of OAc and pyridine (250 μl each) at 50° for 12 hr. The reagents were evapd off under an N_2 stream and the residue purified by prep. TLC on silica gel developed with $CHCl_3$–MeOH (30:1) and then eluted with $CHCl_3$–MeOH (4:1)] to give 21 mg (68%) of an octa-acetate (**7a**). Needles (MeOH), mp 196–199°. $[\alpha]_D^{21}$ −45.9° ($CHCl_3$, *c* 1.35). UV λ_{max}^{MeOH} nm (log ε): 208 (3.85), 252 (2.26), 257 (2.35), 264 (2.24), 267 (2.11). ^{1}H NMR (CD_3OD): δ 1.20 (3H), 2.00 (3H), 2.01 (3H), 2.01 (3H), 2.04 (3H), 2.05 (3H), 2.06 (6H) (each *s*, CH_3CO- × 8), 3.32 (1H, *dd*, *J* = 5 and 12 Hz, H-5″a), 3.59 (1H, *dd*, *J* = 6 and 11 Hz, H-6′a), 3.64 (1H, *ddd*, *J* = 2, 6 and 9 Hz, H-5′), 3.71 (1H, *dd*, *J* = 8 and 10 Hz, H-2′), 3.84 (1H, *dd*, *J* = 2 and 11 Hz, H-6′b), 4.01 (1H, *d*, *J* = 10 Hz, H-4‴a), 4.12 (1H, *dd*, *J* = 9 and 12 Hz, H-5″b), 4.20 (1H, *d*, *J* = 10 Hz, H-4‴b), 4.46 (1H, *d*, *J* = 8 Hz, H-1′), 4.52 (1H, *d*, *J* = 11 Hz, H-5‴a), 4.54 (1H, *d*, *J* = 7 Hz, H-1″), 4.55 (1H, *d*, *J* = 11 Hz, H-5‴b), 4.64 (1H, *d*, *J* = 12 Hz, H-7a), 4.86 (1H, *t*, *J* = 9 Hz, H-4′), 4.91 (1H, *d*, *J* = 12 Hz, H-7b), 5.10 and 5.13 (each 1H, each *s*, H-1‴ and H-2‴), 5.13 (1H, *t*, *J* = 8 Hz, H-3″), 5.16 (1H, *br t*, *J* = 9 Hz, H-3′), 7.3–7.4 (5H, *m*, H_5-1, 2, 3, 4 and 5). ^{13}C NMR ($CDCl_3$): δ 20.6, 20.7, 20.7 (× 2), 20.7 (× 2), 20.8 and 21.1 (CH_3CO- × 8), 61.9 (C-6″), 63.2 (C-5‴), 67.7 (C-6′), 68.8 (C-4′), 69.3 (C-4″), 70.5 (C-2), 70.9 (C-7), 71.2 (C-3″), 72.9 (C-4‴), 73.1 (C-5′), 74.3, 76.1, 76.4, 83.6 (C-3″), 100.1, 100.5, 106.1, 128.0 (C-4), 128.0 (× 2, C-2 and 6, or C-3 and 5), 128.5 (× 2, C-3 and 5, or C-2 and 6), 136.7 (C-1), 169.2, 169.4, 169.7, 169.8, 169.8, 170.0, 170.1 and 170.4 (CH_3CO- × 8). EI-MS (mass range 100–900) *m/z* (rel. int.): 763 (0.5) [$Glu(OAc)_2Xyl(OAc)_3Api(OAc)_3$ oxonium ion]$^+$, 683 (5.1), 533 (5.7), 428 (8.8), 259 (100) [$Xyl(OAc)_3$ and $Api(OAc)_3$ oxonium ion]$^+$, 217 (8.5), 199 (17.6), 187 (5.3), 170 (21.8), 157 (46.4), 139 (99). FAB-MS (negative centroid) *m/z*: 869.2681 $[M-H]^-$ ($C_{39}H_{49}O_{22}$ requires 869.2715).

Acetylation of compound **8**. Compound **8** (7.0 mg) was acetylated and purified in a similar manner to compound **7** give 7.5 mg (68%) of a nona-acetate (**8b**). Amorphous powder. $[\alpha]_D^{21}$ −56.5° ($CHCl_3$, *c* 0.51). UV λ_{max}^{MeOH} nm (log ε): 208 (3.90), 252 (2.23), 257 (2.31), 263 (2.21), 267 (2.05). ^{1}H NMR (CD_3OD): δ 1.93, 1.95, 1.99, 2.02, 2.03, 2.04, 2.06, 2.08 and 2.17 (each 3H, each *s*, CH_3CO- × 9), 3.59 (H, *td*, *J* = 4 and 10 Hz, H-5′), 3.77 (H, *dd*, *J* = 8 and 9 Hz, H-2′), 3.79 (H, *ddd*, *J* = 2, 4 and 10 Hz, H-5‴), 3.96 (H, *t*, *J* = 9 Hz, H-3′), 4.02 (H, *dd*, *J* = 2 and 12 Hz, H-6‴a), 4.03 (H, *d*, *J* = 10 Hz, H-4″a), 4.17 (2H, *d*, *J* = 4 Hz, H_2-6′a and 6′b), 4.21 (H, *d*, *J* = 10 Hz, H-4″b), 4.36 (H, *d*, *J* = 8 Hz, H-1′), 4.38 (H, *d*, *J* = 12 Hz, H-5″a), 4.45 (H, *dd*, *J* = 4 and 12 Hz, H-6‴b), 4.57 (H, *d*, *J* = 12 Hz, H-7a), 4.70 (H, *d*, *J* = 12 Hz, H-5″b), 4.84 (H, *dd*, *J* = 7 and 9 Hz, H-2‴), 4.86 (H, *t*, *J* = 9 Hz, H-4′), 4.89 (H, *d*, *J* = 7 Hz, H-1‴), 4.91 (H, *d*, *J* = 12 Hz, H-7b), 5.10 (H, *t*, *J* = 9 Hz, H-4‴), 5.23 (H, *s*, H-2″), 5.31 (H, *t*, *J* = 9 Hz, H-3‴) 5.45 (H, *s*, H-1″), 7.3–7.4 (5H, *m*, H_5-1, 2, 3, 4 and 5). ^{13}C NMR ($CDCl_3$): δ 20.4, 20.5, 20.6 (× 3), 20.6, 20.7, 20.8 and 21.1 (CH_3CO- × 9), 61.6 (C-6′), 62.4 (C-6‴), 64.0 (C-5″), 68.1 (C-4‴), 68.4 (C-4′), 70.5 (C-7), 71.56 (C-5′ or 5‴), 71.6 (C-5‴ or 5′), 72.4 (C-2‴), 72.9 (C-3‴), 73.9 (C-4″), 76.0 (C-2′), 76.5 (C-2″), 80.3 (C-3′), 83.8 (C-3), 99.2 (C-1‴), 99.6 (C-1′), 105.5 (C-1″), 127.9 (C-4), 128.0 (C-2 and 6 or C-3 and 5), 128.4 (C-3 and 5 or C-2 and 6), 136.7 (C-1), 168.6, 169.3, 169.4, 169.7, 170.2, 170.2, 170.4, 170.5 and 170.7 (CH_3CO- × 9). EI-MS (mass range, 100–900) *m/z* (rel. int.): 835 (1.1) [$Glu(OAc)_2Glu(OAc)_4Api(OAc)_3$ oxonium ion]$^+$, 331 (18.9) [$Glu(OAc)_4$ oxonium ion]$^+$, 259 (100) [$Api(OAc)_3$ oxonium ion]$^+$, 236 (12.6), 217 (13.5), 169 (21.0), 157 (20.5), 139 (60.5). FAB-MS (negative centroid) *m/z*: 941.2910 $[M-H]^-$ ($C_{42}H_{53}O_{24}$ requires 941.2927).

Acetylation of compound **11**. Compound **11** (10.0 mg) was acetylated and purified as described for **7** to give 8.7 mg of an octa-acetate (**11a**). Amorphous powder. $[\alpha]_D^{28}$ −34.5° ($CHCl_3$, *c* 0.58) UV λ_{max}^{MeOH} nm (log ε): 214 (4.00), 272 (3.14). ^{1}H NMR ($CDCl_3$): δ 1.98 (3H), 2.02 (3H), 2.02 (6H), 2.04 (3H), 2.09 (3H) and 2.11 (3H) (CH_3CO- × 7 on alcoholic hydroxyls), 2.31 (3H) (CH_3CO- on a phenolic hydroxyl), 2.89 (2H, *t*, *J* = 7 Hz, H_2-7), 3.77 (1H, *dddd*, *J* = 2, 5 and 9 Hz, H-5′), 3.95 (1H, *dd*, *J* = 7 and 9 Hz, H-2′), 4.06 (1H, *dd*, *J* = 2 and 12 Hz, H-6′a), 4.10 (1H, *d*, *J* = 10 Hz, H-4″a), 4.25 (2H, *t*, *J* = 7 Hz, H_2-8), 4.25 (1H, *dd*, *J* = 5 and 12 Hz, H-6′b), 4.33 (1H, *d*, *J* = 10 Hz, H-4″b), 4.51 (1H, *d*, *J* = 12 Hz, H-5″a), 4.62 (1H, *d*, *J* = 12 Hz, H-5″b), 5.01 (1H, *d*, *J* = 7 Hz, H-1′), 5.08 (1H, *t*, *J* = 9 Hz, H-4′), 5.20 and 5.21 (each 1H, each *s*, H-1″ and 2″), 5.24 (1H, *t*, *J* = 9 Hz, H-3′), 6.95 (1H, *d*, *J* = 1 Hz, H-2), 7.02 (1H, *d*, *J* = 8 Hz, H-5), 7.05 (1H, *dd*, *J* = 1 and 8 Hz, H-6). ^{13}C NMR ($CDCl_3$): δ 20.5, 20.6, 20.6, 20.6, 20.7, 20.7, 20.9, 21.1 (*C*H_3CO- × 8), 34.2 (C-7), 61.8, 63.1, 64.5, 68.4, 71.8, 72.9, 74.1, 76.5, 76.5, 83.6 (C-3″), 99.5 (C-1′), 106.5 (C-1″), 117.4 (C-5), 124.1 (C-2), 127.0 (C-6), 133.4 (C-1), 140.7 (C-4), 146.5 (C-3), 168.9, 169.2, 169.6, 169.7, 170.1, 170.3, 170.5, 171.0 (CH_3CO- × 8). EI-MS (mass range, 100–900) (rel. int.) *m/z*: 664 (0.3) $[M-AcOH\times 2]^+$, 604 (0.7) $[M-AcOH\times 3]^+$, 547 (41) [$Api(OAc)_3$-$Glu(OAc)_3$ oxonium ion]$^+$, 368 (47), 259 (100) [$Api(OAc)_3$ oxonium ion]$^+$. HR-FAB-MS (negative centroid) *m/z*: 783.2375 $[M-H]^-$ ($C_{35}H_{43}O_{20}$ requires 783.2348).

GC analyses of sugars. About 2 mg of each sample (**7**, **8** and **11**) was hydrolysed in 5% HCl in dry MeOH at 95° for 3 hr. The reaction mixt. was neutralized by the addition of Ag_2CO_3 and then filtered. The filtrate was evapd to dryness and then treated with several drops of trimethylsilylimidazole at 60° for 15 min. After partitioning between *n*-hexane and H_2O, the concd organic layer was subjected to GC analysis. Standard sugars were: apiose, 2.71, 2.84, 2.96 and 3.15 min; xylose, 5.28 and 5.86 min; and glucose, 8.18 and 8.87 min. Compound **7**: 2.71, 2.83, 2.96 and 3.14 min (apiose), 5.26 and 5.84 min (xylose), and 8.21 and 8.89 min (glucose). Compound **8**: 2.72, 2.84, 2.97 and 3.16 min (apiose) and 8.17 and 8.87 min (glucose). Com-

pound **11**: 2.71, 2.83, 2.96 and 3.14 min (apiose) and 8.20 and 8.89 min (glucose).

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