Six Secoiridoid Glucosides from *Jasminum polyanthum*

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Reinvestigation of the dried flowers of *Jasminum polyanthum* has led to the isolation of six new secoiridoid glucosides, jaspolyanoside, polyanoside, isojaspolyosides A, B and C, and 6″-*O*-*β*-D-glucopyranosyloleuropein, together with the known secoiridoid glucoside, angustifolioside B and flavonoid glycosides, nicotiflorine, kaempferol 3-*O*-(2-*O*-*α*-L-rhamnopyranosyl-*β*-D-galactopyranoside) and mauritianin. The structures of the new compounds were elucidated on the basis of chemical and spectroscopic evidence. Comparison of the spectral data of 6″-*O*-*β*-D-glucopyranosyloleuropein and those reported for angustifolioside A, previously recognized as 6″-*O*-*β*-D-glucopyranosyloleuropein, led to the conclusion that the structure of angustifolioside A should be revised to 5″-*O*-*β*-D-glucopyranosyloleuropein.

Key words *Jasminum polyanthum*; Oleaceae; secoiridoid glucoside; oleoside dimer; angustifolioside A; structure revision

Jasminum polyanthum FRANCH. (Oleaceae) is a medicinal plant whose dried flowers have been used as the crude drug "Ye su xin" in Chinese folk medicine for the treatment of orchitis, menorrhalgia and stomachalgia.[1] In the course of our chemical studies on the secoiridoid glucosides from the family Oleaceae, we have recently investigated the constituents of this crude drug and isolated two new dimeric secoiridoid glucosides, jaspolyoside (**1**) and jaspolyanthoside, as well as oleuropein (**2**), ligstroside (**3**) and Gl 5.[2] In this preliminary study, we found that the crude drug contained a complicated mixture of minor secoiridoid glucosides. This paper deals with the re-examination of the same plant materials and the isolation and structural elucidation of six more novel secoiridoid glucosides.

Fractionation of the MeOH extract from the dried flowers of *J. polyanthum* afforded seven secoiridoid glucosides, **4**—**10**, and three flavonoid glycosides, **11**—**13**. Compounds **10**, **11**, **12** and **13** were identified as angustifolioside B,[3] nicotiflorine,[4] kaempferol 3-*O*-(2-*O*-*α*-L-rhamnopyranosyl-*β*-D-galactopyranoside)[5] and mauritianin,[5,6] respectively, by comparison of their spectral data with those described in the literature.

Compound **4** was isolated as a colorless amorphous powder, $[\alpha]_D$ −161° (MeOH). The HR-SI-MS of **4** exhibited a strong $(M+Na)^+$ at *m/z* 933.3018, indicating a molecular formula of $C_{42}H_{54}O_{22}$ for **4**. Its UV spectrum, besides the typical absorption (237sh nm) of the iridoidic enol ether system conjugated with a carbonyl group, presented additional absorptions at 229, 276.5 and 285sh nm due to a phenolic function. It showed IR bands at 3409 (OH), 1732 (esters), 1707 and 1630 (*α*,*β*-unsaturated esters) and 1518 (aromatic ring) cm^{-1}. Its ^{1}H-NMR spectrum (Table 1) showed duplicate signals due to two oleoside methyl ester moieties [H-3a, H-3b at *δ* 7.49, 7.52, H-8a, H-8b at *δ* 6.06, 6.09 (each qd), H_3-10a, H_3-10b at *δ* 1.62, 1.71 (each dd), two carbomethoxyl groups at *δ* 3.67, 3.71] as well as an ABX_2 system of a $COOCH_2$-CH_2Ar moiety at *δ* 4.08 (1H, dt), 4.19 (1H, dt) and 2.77 (2H, t), indicating that **4** was structurally similar to **1**, although there were remarkable differences in the spectra, with the aromatic protons of **4** appearing as an AA′XX′ spin system at *δ* 6.70 and 7.01 instead of an ABX spin system as in **1**. The ^{13}C-NMR signals of **4** (Table 2) were also superimposable on those of **1**, except for the aromatic carbon signals. These findings indicated the presence in **4** of a *p*-hydroxyphenethyl moiety instead of a 3,4-dihydroxyphenethyl moiety as in **1**. The ester linkage of two oleoside methyl ester units and a *p*-hydroxyphenethyl moiety was determined by heteronuclear multiple-bond correlation (HMBC) experiments, which showed cross-peaks between the methoxyl signals (*δ* 3.67, 3.71) and C-11a/11b (*δ* 168.61, 168.65), between H-1″ (*δ* 4.19) and C-7a (*δ* 172.96) and between H-6′a (*δ* 4.20) and C-7b (*δ* 172.99). Thus, the structure of **4** was established as jaspolyanoside.

Compound **5** showed similar spectral features to **4**. The ^{1}H-NMR spectrum of **5** revealed signals attributable to a *p*-hydroxyphenethyl moiety and two oleoside 11-methyl ester units, with an additional signal due to an anomeric proton at *δ* 4.87. Its ^{13}C-NMR spectrum was also very similar to that of **4**, except for the appearance of signals assignable to an additional *β*-glucose moiety and the chemical shifts of aromatic carbons. Attachment of the new glucose unit at the hydroxyl group of the aromatic ring was verified by downfield shifts observed for the signals of C-6″ ($\Delta\delta$ +0.66 ppm), C-3″ ($\Delta\delta$ +3.34 ppm) and C-5″, 7″ ($\Delta\delta$ +1.64 ppm). The anomeric configuration of the glucosyl linkage was determined to be *β* from the coupling constant of the anomeric proton (J=8.0 Hz). The above arguments were further supported by comparative studies on the NMR spectra of the isolate and angustifolioside B (**10**). Although these findings suggested its structure to be **5a**, there was another plausible structure, **5**, in which the second oleoside unit was esterified with the hydroxyl group at C-6‴ in the glucose attached to the *p*-hydroxyphenethyl moiety instead of with that at C-6′a in the first oleoside moiety. Acylation shifts were observed for C-6′a or C-6‴ and C-5′a or C-5‴, when compared with the ^{13}C-NMR data of **10**, but it was rather difficult to differentiate between C-6′a and C-6‴ by spectroscopic methods. In order to solve this problem, the following reactions were performed. The isolated compound was treated with trityl chloride to yield **14**, in which two

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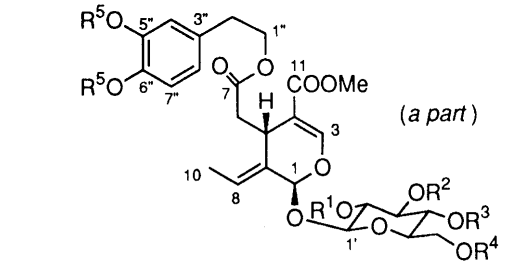

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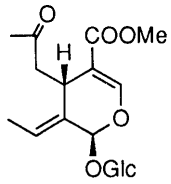

1 : $R^1 = R^2 = R^3 = R^5 = H$, R^4 = ole
19 : $R^1 = R^2 = R^3 = R^5$ = Ac, R^4 =oleAc
2 : $R^1 = R^2 = R^3 = R^4 = R^5 = H$
6 : $R^2 = R^3 = R^4 = R^5 = H$, R^1 = ole
7 : $R^1 = R^3 = R^4 = R^5 = H$, R^2 = ole
8 : $R^1 = R^2 = R^4 = R^5 = H$, R^3 = ole
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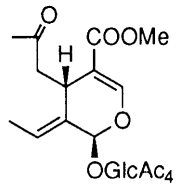
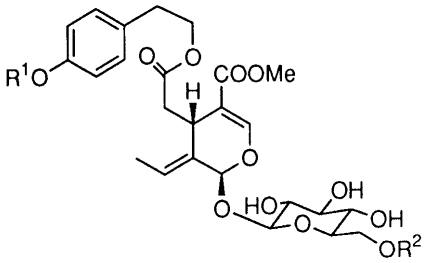
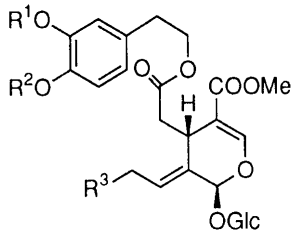
oleAc =

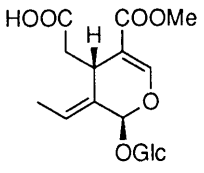




3 : $R^1 = R^2 = H$
4 : $R^1 = H$, R^2 = ole
10 : R^1 = Glc, $R^2 = H$



9 : $R^1 = R^3 = H$, R^2 = Glc
21 : $R^1 = H$, R^2 = Glc, R^3 = OH
22 : R^1 = Glc, $R^2 = R^3 = H$



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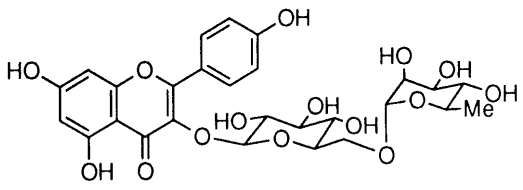

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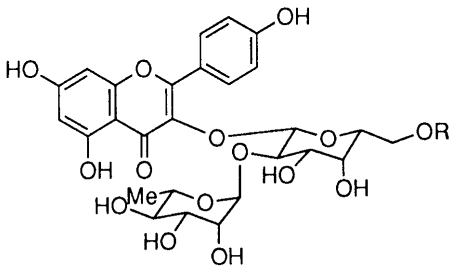

12 : R = H
13 : R = Rha

Chart 1

primary hydroxyl groups were protected with trityl groups. Subsequent hydrolysis of **14** afforded **15** and **16**, the latter of which was characterized as its acetate, **17**. The result suggested that the original glucoside possesses two intact hydroxyl groups at C-6′a and C-6′b and an acylated hydroxyl group at C-6‴. Consequently, the structure of the new compound was represented by **5** and designated polyanoside.

Compounds **6** and **7**, named isojaspolyosides A and B, were recognized as isomers of jaspolyoside (**1**), $C_{42}H_{54}O_{23}$, from their HR-SI-MS. UV and IR spectral features of both compounds were analogous to those of **1**. The ^{1}H- and ^{13}C-NMR (Tables 1, 2) spectra of each glucoside exhibited duplicated signals ascribable to the oleoside 11-methyl ester together with resonances relevant to a 3,4-dihydroxyphenethoxyl group. The only significant differences in the ^{13}C-NMR spectra of **6**, **7** and **1** could be accounted for by the point of ester linkage of two oleoside 11-methyl ester (**18**) units. The downfield shift of C-2′a ($\Delta\delta$ +0.36 ppm) and upfield shifts of C-1′a ($\Delta\delta$ −1.64 ppm) and C-3′a ($\Delta\delta$ −2.15 ppm) in **6**, when compared with the corresponding signals of oleuropein (**2**), suggested that the hydroxy group at C-2′a was esterified in place of the one at C-6′a in **1**. On the other hand, the downfield shift of C-3′a ($\Delta\delta$ +1.11 ppm) and upfield shifts of C-2′a ($\Delta\delta$ −1.89 ppm) and C-4′a ($\Delta\delta$ −1.92 ppm) in **7** were ascribable to acylation of the hydroxyl at C-3′a. Thus, the structures of isojaspolyosides A and B were determined to be **6** and **7**, respectively.

Compound **8** was obtained as a mixture with **1**. The compound was repeatedly separated by preparative HPLC on an octadecyl silica (ODS) column with MeOH–H_2O

Table 1. ^{1}H-NMR Spectral Data of Compounds **4**, **5**, **6**, **7** and **8** in CD_3OD

H	**4**		**5**		
	a part	b part	a part		b part
1	5.85 br s	5.88 br s	5.895[c,x] br s		5.898[d,x] br s
3	7.52[a,x] s	7.49[b,x] s	7.51[x] s		7.53[x] s
5	3.95 dd (9.0, 4.0)	3.98 dd (9.0, 4.0)	4.01 dd (9.0, 4.5)		3.94 dd (9.0, 4.5)
6	2.40 dd (14.0, 9.0)	2.37 dd (14.0, 9.0)	2.44 dd (14.0, 9.0)		2.42 dd (14.0, 9.0)
	2.70 dd (14.0, 4.0)	2.69 dd (14.0, 4.0)	2.78 dd (14.0, 4.5)		2.68 dd (14.0, 4.5)
8	6.06 qd (7.0, 1.0)	6.09 qd (7.5, 1.0)	6.05[c,x] qd (7.0, 1.0)		6.08[d,x] qd (7.0, 1.0)
10	1.62 dd (7.0, 1.5)	1.71 dd (7.5, 1.5)	1.63[c,x] dd (7.0, 1.5)		1.69[d,x] dd (7.0, 1.5)
OMe	3.67[a,x] s	3.71[b,x] s	3.69[x] s		3.70[x] s
1′, 1‴	4.82 d (8.0)	4.80 d (8.0)	4.80 d (8.0)	4.87 d (8.0)	4.78 d (8.0)
2′, 2‴	3.36 m	3.32 m	3.32—3.48 m	3.32—3.48 m	3.32—3.48 m
3′, 3‴	3.41[x] t (9.0)	3.43[x] t (9.0)			
4′, 4‴	3.39[x] t (9.0)	3.31[x] t (9.0)			
5′, 5‴	3.54 ddd (9.0, 5.0, 2.0)	3.34 m		3.65 m	
6′, 6‴	4.20 dd (12.0, 5.0)	3.67 dd (12.0, 5.0)	3.66[e,x] dd (12.0, 6.0)	4.22 dd (11.5, 6.0)	3.67[f,x] dd (11.0, 5.0)
	4.33 dd (12.0, 2.0)	3.88 dd (12.0, 2.0)	3.89[e,x] dd (12.0, 1.5)	4.36 dd (11.5, 2.0)	3.87[f,x] br d (11.0)
1″	4.08 dt (10.5, 7.0)		4.14 dt (11.0, 7.0)		
	4.19 dt (10.5, 7.0)		4.25 dt (11.0, 7.0)		
2″	2.77 t (7.0)		2.87 t (7.0)		
4″	7.01 d (8.5)		7.18 d (8.5)		
5″	6.70 d (8.5)		7.02 d (8.5)		
7″	6.70 d (8.5)		7.02 d (8.5)		
8″	7.01 d (8.5)		7.18 d (8.5)		

H	**6**		**7**		**8**	
	a part	b part	a part	b part	a part	b part
1	5.82 br s	5.96 br s	5.96 br s	5.90 br s	5.91 br s	5.98 br s
3	7.49 s	7.51 s	7.54 s	7.52 s	7.53[x] s	7.51[x] s
5	3.95 dd (9.0, 4.5)	3.99 dd (9.0, 4.0)	3.96 dd (9.5, 4.5)	4.01 dd (7.0, 5.0)	3.97 dd (9.0, 4.5)	4.03 dd (9.0, 4.0)
6	2.41 dd (14.0, 9.0)	2.60 dd (15.0, 9.0)	2.44 dd (14.0, 9.5)	2.73 m	2.44 dd (14.5, 9.0)	2.59 dd (14.5, 9.0)
	2.69 dd (14.0, 4.5)	2.72 dd (15.0, 4.0)	2.70 dd (14.0, 4.5)		2.70 dd (14.5, 4.5)	2.87 dd (14.5, 4.0)
8	5.98 qd (7.0, 0.5)	6.09 qd (7.0, 0.5)	6.11 qd (7.5, 1.0)	6.08 qd (7.0, 1.0)	6.08 qd (7.0, 1.0)	6.15 qd (7.0, 1.0)
10	1.66 dd (7.0, 1.5)	1.73 dd (7.0, 1.5)	1.78 dd (7.5, 1.5)	1.66 dd (7.0, 1.5)	1.66 dd (7.0, 1.5)	1.76 dd (7.0, 1.5)
OMe	3.69[x] s	3.70[x] s	3.71[x] s	3.73[x] s	3.71[x] s	3.72[x] s
1′	4.94 d (8.0)	4.81 d (8.0)	4.88 d (8.0)	4.80 d (8.0)	4.80 d (7.5)	4.80 d (7.5)
2′	4.78 dd (9.5, 8.0)	3.33 m	3.46 dd (9.5, 8.0)	3.31 dd (9.5, 8.0)	3.40[x] dd (10.0, 7.5)	3.31[x] m
3′	3.60 t (9.5)	3.41 t (9.5)	4.95 t (9.5)	3.41 t (9.5)	3.58 t (10.0)	3.41 t (10.0)
4′	3.39 m	3.28 m	3.49 t (9.5)	3.27 t (9.5)	4.73 t (10.0)	3.32 m
5′	3.38[g,x] m	3.34[h,x] m	3.42 ddd (9.5, 6.0, 2.0)	3.36 ddd (9.5, 6.0, 2.5)	3.52 ddd (10.0, 6.0, 2.5)	3.34 m
6′	3.69[g,x] dd (12.0, 6.0)	3.67[h,x] dd (12.0, 6.5)	3.68 dd (11.5, 6.0)	3.66 dd (12.0, 6.0)	3.69 dd (11.5, 6.0)	3.69 dd (11.5, 6.0)
	3.89[g,x] br d (12.0)	3.91[h,x] dd (12.0, 2.0)	3.87 dd (11.5, 2.0)	3.91 dd (12.0, 2.5)	3.89 br d (11.5)	3.89 br d (11.5)
1″	4.10 dt (11.0, 7.0)		4.10 dt (11.0, 7.0)		4.11 dt (11.0, 7.0)	
	4.20 dt (11.0, 7.0)		4.20 dt (11.0, 7.0)		4.21 dt (11.0, 7.0)	
2″	2.76 t (7.0)		2.76 t (7.0)		2.76 t (7.0)	
4″	6.66 d (2.0)		6.66 d (2.0)		6.66 d (2.0)	
7″	6.69 d (8.5)		6.69 d (8.0)		6.69 d (8.0)	
8″	6.54 dd (8.5, 2.0)		6.55 dd (8.0, 2.0)		6.55 dd (8.0, 2.0)	

Values in parentheses are coupling constants in Hz. *a*—*h*) Signals with the same superscript are ascribable to the same part in the structure. *x*) Assignments may be reversed horizontally between a and b parts.

(47 : 53), but on evaporation of the solvent, the fraction of **8** showed a small peak of **1** again by HPLC analysis, implying an artificial formation of **1** from **8**. Therefore, the structural elucidation of **8** was carried out on the mixture. Conventional acetylation of the mixture afforded two isomeric acetates, **19** and **20**, which showed nearly identical spectral features, indicating **8** to be an isomer of **1**. Comparison of the ^{13}C-NMR spectrum of **8** with that of oleuropein (**2**) suggested a linkage of the C-7b carboxyl group of an oleoside 11-methyl ester (**18**) unit to the hydroxyl group at C-4′a of the oleuropein moiety in **8** (Table 2). The fact that **8** was transformed into **1** could be reasonably explained by acyl rearrangement between the hydroxyl groups at C-4′a and C-6′a in the glucose moiety. Accordingly, glucoside **8** was characterized as isojaspolyoside C.

The finding that **8** was not obtained from **1** allowed it to be considered as a natural metabolite. On the other

Table 2. ^{13}C-NMR Spectral Data of Compounds **2** and **4**—**9** in CD_3OD

C	4		5			6		7		8		9		2
	a part	b part	a part		b part	a part	b part	a part	b part	a part	b part			
1	95.27	95.16	95.19		95.40	95.64	95.45	95.67	95.36	95.27	95.51	95.29		95.21
3	155.16[a,x]	155.17[b,x]	155.23[x]		155.17[x]	155.05	155.28	155.14	155.36	155.10[x]	155.41[x]	155.23		155.14
4	109.49	109.43	109.53		109.41	109.51	109.66	109.23	109.37	109.51	109.36	109.35		109.37
5	31.83	31.89	31.80		31.85	31.79	31.43	31.76	31.58	31.85	31.64	31.89		31.79
6	41.27	41.41	41.51		41.27	41.23	40.82	41.22	40.71	41.30	40.76	41.22		41.25
7	172.96	172.99	173.15		172.90	173.15	172.09	173.18	172.88	173.25	172.38	173.23		173.21
8	125.18	124.91	124.93[c,x]		125.07[d,x]	125.17	125.26	125.09	124.99	124.95	125.42	124.91		124.87
9	130.25	130.52	130.48		130.48	130.28	130.24	130.47	130.39	130.50	130.78	130.57		130.46
10	13.60	13.81	13.65[c,x]		13.76[d,x]	13.65	13.93	13.73	13.55	13.60	13.84	13.58		13.53
11	168.65[a,x]	168.61[b,x]	168.63[x]		168.67[x]	168.63	168.77	168.99	168.67	168.68	168.68	168.72		168.69
OMe	52.00[a,x]	51.96[b,x]	52.00[x]		52.05[x]	51.95[x]	51.98[x]	51.94[x]	51.95[x]	51.97	51.97	51.97		51.92
1′, 1‴	100.99	100.90	100.88	102.38	101.07	99.24	100.95	100.95	100.92	100.79	101.23	100.95	104.84	100.88
2′, 2‴	74.70[x]	74.77[x]	74.75[x]	74.86[x]	74.79[x]	75.09	74.77	72.84	74.72	74.80[x]	74.71[x]	74.96	74.80	74.73
3′, 3‴	77.84[x]	77.99[x]	77.87[x]	77.94[x]	77.94[x]	75.76	77.97	79.02	77.95	75.72	77.95	77.66[x]	77.97[x]	77.91
4′, 4‴	71.40[x]	71.49[x]	71.47[x]	71.58[x]	71.54[x]	71.54	71.61	69.52	71.64	72.67	71.30	71.34[x]	71.55[x]	71.44
5′, 5‴	75.48	78.43	78.46[x]	75.23	78.37[x]	78.63[g,x]	78.48[h,x]	78.08	78.34	76.13	78.39	78.34[i,x]	78.44[j,x]	78.38
6′, 6‴	64.87	62.73	62.72[e,x]	64.96	62.83[f,x]	62.81[g,x]	62.57[h,x]	62.28	62.82	62.51[x]	62.54[x]	62.82[i,x]	62.45[j,x]	62.70
1″	66.90		66.69			66.90		66.88		66.93		66.66		66.88
2″	35.25		35.24			35.43		35.37		35.43		35.46		35.37
3″	130.09		133.43			130.76		130.73		130.78		135.36		130.74
4″	131.05		131.09			117.08		117.06		117.09		117.75		117.06
5″	116.39		118.03			146.27		146.21		146.27		148.55		146.20
6″	157.05		157.71			144.96		144.89		144.95		145.56		144.89
7″	116.39		118.03			116.47		116.44		116.48		119.49		116.44
8″	131.05		131.09			121.35		121.31		121.36		121.54		121.31

a—*j*) Signals with the same superscript are ascribable to the same part in the structure and are correlated to the proton signals with the same superscript as in Tables 1 and 2 by means of HMBC or HMQC. *x*) Assignments may be reversed horizontally between a and b parts.

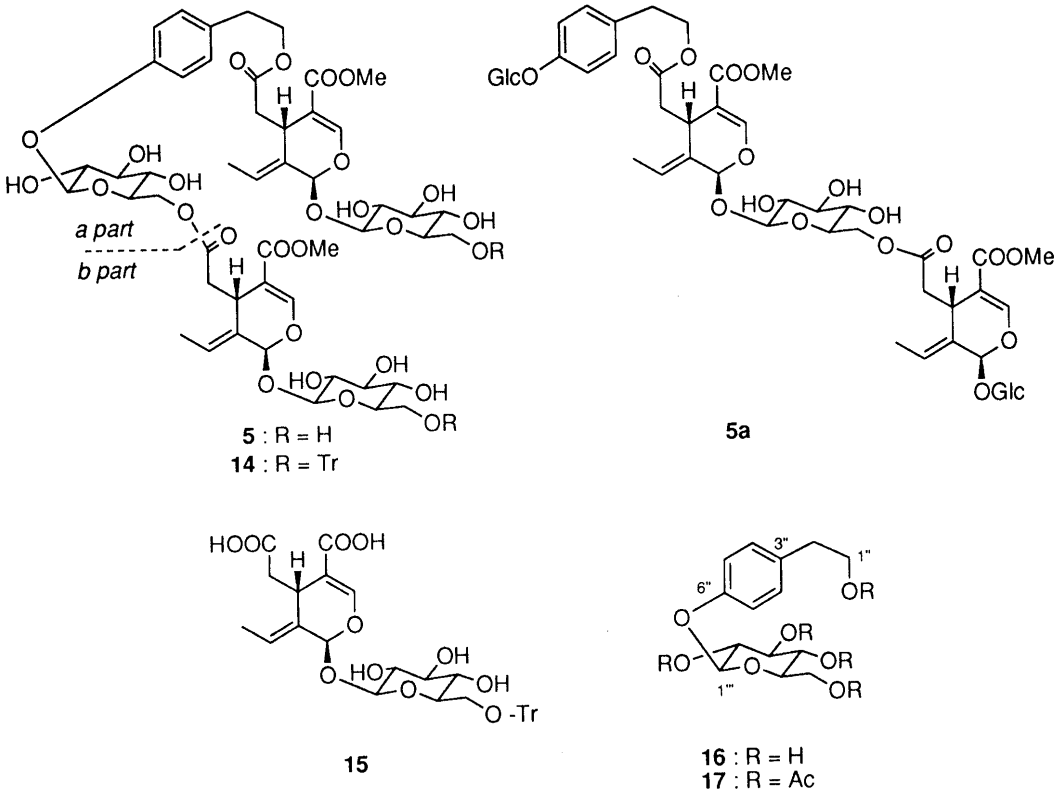

Chart 2

hand, the possibility that **1** was an artifact of **8** could not be completely excluded, but we suppose that jaspolyoside (**1**), one of the major products of this plant material, is also a natural product, judging from the co-occurrence of diverse glucosides such as **4**, **6**, **7** and **8** with different esterification patterns.

The ^{1}H- and ^{13}C-NMR spectra (Tables 1, 2) indicated that **9** has a structure similar to **2**, but with an additional

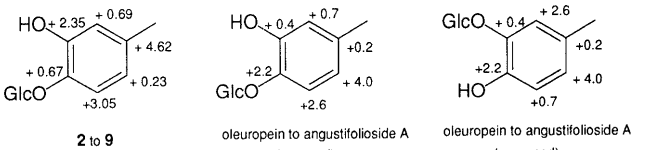

Fig. 1. ^{13}C-NMR Chemical Shift Differences in the Aromatic Ring of Secoiridoid Glucosides

β-glucose unit attached to a phenolic hydroxyl group. Furthermore, its SI-MS showed a quasi-molecular ion peak $(M-H)^-$ at m/z 701, indicating an increase of 162 mass units consistent with $C_6H_{10}O_5$ in comparison with that of **2**. These findings suggested that isolated compound **9** is a 5″- or 6″-*O*-glucosylated derivative of **2**. To determine the position of glucosylation, all aromatic carbon signals were definitely assigned by a combination of heteronuclear multiple quantum coherence (HMQC) and HMBC experiments. The HMQC technique permitted unambiguous assignment of three protonated carbon signals, C-4″, 7″ and 8″. The HMBC experiment with **9** revealed a ^3J interaction between H-8″ (δ 6.67, dd, $J=8.5$, 2.0 Hz) and the carbon signal at δ 145.56, allowing us to assign the aromatic carbon signal to C-6″, and thereby another oxygenated aromatic carbon at δ 148.55 to C-5″, with the remaining aromatic quarternary carbon at δ 135.36 to C-3″. Hence the hydroxyl at C-6″ was concluded to be glucosylated in **9** by appreciable downfield shifts of *ortho*-related (C-5″, 7″) and *para*-related (C-3″) carbons by 2.35, 3.05, and 4.62 ppm, respectively, when compared with those in **2**[7] (Fig. 1). The trend of glucosylation shifts observed was the same as that discussed for flavonoid glucosides and insularoside-6‴-*O*-β-D-glucoside.[8,9] Furthermore, the ^{13}C-NMR signals due to the aromatic ring of **9** were in good agreement with those of multiroside (**21**),[10] although the assignments of C-5″ and C-6″ in the aromatic ring in **21** should be reversed. Accordingly, the glucoside **9** was characterized as 6″-*O*-β-D-glucopyranosyloleuropein.

A comparison of the ^{1}H- and ^{13}C-NMR spectroscopic data obtained for **9** with the data of angustifolioside A,[3] previously reported as 6″-*O*-β-D-glucopyranosyloleuropein, however, revealed significant differences in the chemical shifts of the aromatic protons and carbons. In contrast, there were close similarities between the two in the proton and carbon signals attributable to the glucose and oleoside 11-methyl ester (**18**) moieties. These findings indicated that angustifolioside A was isomeric with **9**, with the position of the phenolic hydroxyl and glucosyloxy groups interchanged, but this was not properly characterized before. Supposing that the assignments of C-4″ and C-7″ were reversed, significant downfield shifts of C-4″, C-6″ and C-8″ could be reasonably explained by the glucosylation of the hydroxyl group at C-5″, but not by the 6″-*O*-glucosylation (Fig. 1). The foregoing data and observations led us to the conclusion that the structure of angustifolioside A is not represented by 6″-*O*-β-D-glucopyranosyloleuropein (**9**), but rather, by 5″-*O*-β-D-glucopyranosyloleuropein (**22**).

Experimental

The UV spectra were recorded on a Shimadzu UV-240 spectrophotometer and the IR spectra on a Shimadzu FT-IR-8200 IR spectrophotometer. The optical rotations were measured on a Jasco DIP-370 digital polarimeter. SI-MS and HR-SI-MS were obtained with a Hitachi M-4100 mass spectrometer, with glycerol or 3-nitrobenzyl alcohol (3-NOBA) as the matrix. The NMR experiments were performed with a Varian VXR-500 spectrometer, with tetramethylsilane as an internal standard. HPLC was performed using a Waters system (600E Multisolvent Delivery System, 486 Tunable Absorbance Detector). Thin-layer chromatography was performed on pre-coated Kieselgel 60F_{254} plates (Merck), and spots were visualized under UV light.

Isolation of Glucosides The source of plant material is described in a previous publication.[1] The crude drugs (124 g) were extracted with hot MeOH. A part (41.3 g) of the MeOH extract (47.1 g) was suspended in H_2O and successively partitioned with $CHCl_3$ and *n*-BuOH, to give three fractions weighing 0.91 g ($CHCl_3$), 33.76 g (*n*-BuOH) and 5.80 g (H_2O). The *n*-BuOH-soluble fraction was chromatographed on a Wakogel LP-40C_{18} (Wako Pure Chemical Industries, Ltd., Osaka, Japan) column. Elution with MeOH–H_2O mixtures of the increasing MeOH content (0—90%) gave 30 fractions. Fraction No. 14 (10% MeOH effluent, 822 mg) was further purified by a combination of preparative HPLC (μBondasphere 5μC18-100 Å, MeOH–H_2O, 4:6) and preparative TLC ($CHCl_3$–MeOH, 7:3 or 6:4), giving **9** (7.6 mg), **13** (54.5 mg), **10** (30.9 mg), **12** (12.4 mg), jaspolyanthoside[2] (17.2 mg) and **11** (3.9 mg). The following fractions were also purified by preparative HPLC (μBondasphere 5μC18-100 Å, MeOH–H_2O, 4:6, 9:11, 47:53, 1:1 or 53:47) and preparative TLC ($CHCl_3$–MeOH, 7:3 or 6:4 or acetone–$CHCl_3$–H_2O, 8:2:1). Fraction No. 16 (12% MeOH effluent, 1.57 g) yielded **9** (9.7 mg), **13** (15.3 mg), **10** (35.2 mg), **12** (21.7 mg), jaspolyanthoside[2] (51.6 mg), **1** (947 mg) and **11** (6.1 mg); fraction No. 20 (30% MeOH effluent, 0.96 g): **3** (25.4 mg from 80 mg of the fraction); fraction No. 21 (40% MeOH effluent, 0.49 g): **5** (37.9 mg), **1** (53.7 mg), I (5.0 mg); fraction No. 23 (40% MeOH effluent, 0.89 g): **1** (229 mg), **7** (22.1 mg), a mixture of **8** and **1** (20.7 mg), II (238 mg), III (7.6 mg); fraction No. 24 (40% MeOH effluent, 0.49 g): II (15.8 mg), **4** (12.0 mg), **6** (6.7 mg); fraction No. 25 (40% MeOH effluent, 0.89 g): **4** (20.6 mg), **6** (24.1 mg), Gl-5 (100 mg), IV (24.4 mg). Compounds I—IV are unidentified glucosides. Studies on the structures of these compounds are in progress.

Jaspolyanoside (4) A white amorphous powder, $[\alpha]_D^{28}$ −161° ($c=0.82$, MeOH). UV λ_{max}^{MeOH} nm (log ε): 229 (4.30), 237sh (4.27), 276.5 (3.27), 285sh (3.17). IR ν_{max}^{KBr} cm^{-1}: 3409, 1732, 1707, 1630, 1518, 1078. ^{1}H- and ^{13}C-NMR: Tables 1 and 2. Significant HMBC correlations: H-3a/H-3b→C-11a/C-11b, OCH_3(a)/OCH_3(b)→C-11a/C-11b, H-6′a (δ 4.20)→C-7b, H-1″ (δ 4.19)→C-7a. HR positive-mode SI-MS m/z: Calcd for $C_{42}H_{54}NaO_{22}$ $(M+Na)^+$: 933.3006. Found: 933.3018.

Polyanoside (5) A white amorphous powder, $[\alpha]_D^{24}$ −181° ($c=1.11$, MeOH). UV λ_{max}^{MeOH} nm (log ε): 227 (4.40), 236 (4.39), 270sh (3.33), 277sh (3.20). IR ν_{max}^{KBr} cm^{-1}: 3393, 1731, 1707, 1632, 1512, 1078. ^{1}H- and ^{13}C-NMR: Tables 1 and 2. Significant HMBC correlations: H-1a/H-1b→C-1′a/C-1′b, H-3a/H-3b→C-11a/C-11b, OCH_3(a)/OCH_3(b)→C-11a/C-11b, H-6′a (δ 4.22)→C-7b, H-1″ (δ 4.25)→C-7a. HR positive-mode SI-MS m/z: Calcd for $C_{48}H_{64}NaO_{27}$ $(M+Na)^+$: 1095.3535. Found: 1095.3540.

Isojaspolyoside A (6) A white amorphous powder, $[\alpha]_D^{25}$ −188° ($c=0.96$, MeOH). UV λ_{max}^{MeOH} nm (log ε): 234 (4.43), 282 (3.52). IR ν_{max}^{KBr} cm^{-1}: 3408, 1726, 1705, 1632, 1529, 1078. ^{1}H- and ^{13}C-NMR: Tables 1 and 2. Significant HMBC correlations: H-3a/H-3b→C-11a/C-11b, OCH_3(a)/OCH_3(b)→C-11a/C-11b, H-2′a→C-7b, H_2-1″→C-7a. HR negative-mode SI-MS m/z: Calcd for $C_{42}H_{53}O_{23}$ $(M-H)^-$: 925.2979. Found: 925.2956.

Isojaspolyoside B (7) A white amorphous powder, $[\alpha]_D^{28}$ −188° ($c=0.89$, MeOH). UV λ_{max}^{MeOH} (log ε): 234 (4.40), 281.5 (3.50). IR ν_{max}^{KBr} cm^{-1}: 3421, 1730, 1701, 1630, 1522, 1078. ^{1}H- and ^{13}C-NMR: Tables 1 and 2. Significant HMBC correlations: H-3a/H-3b→C-11a/C-11b, OCH_3(a)/OCH_3(b)→C-11a/C-11b, H-1″ (δ 4.10)→C-7a. HR positive-mode SI-MS m/z: Calcd for $C_{42}H_{54}NaO_{23}$ $(M+Na)^+$: 949.2955. Found: 949.2951.

6″-*O*-β-D-Glucopyranosyloleuropein (9) A white amorphous powder, $[\alpha]_D^{27}$ −149° ($c=0.73$, MeOH). UV λ_{max}^{MeOH} nm (log ε): 226 (4.06), 240sh (4.00), 275.5 (3.35). IR ν_{max}^{KBr} cm^{-1}: 3397, 1707, 1630, 1508, 1076. ^{1}H-NMR (CD_3OD): δ 1.65 (3H, dd, $J=7.5$, 1.5 Hz, H_3-10), 2.46 (1H, dd, $J=14.0$, 8.5 Hz, H-6), 2.68 (1H, dd, $J=14.0$, 4.5 Hz, H-6), 2.82 (2H, t, $J=6.5$ Hz, H_2-2″), 3.30—3.50 (8H, m, H-2′, 3′, 4′, 5′, H-2‴, 3‴, 4‴, 5‴), 3.67 (1H, dd, $J=12.0$, 6.0 Hz, H-6′ or H-6‴), 3.72 (1H, dd, $J=12.0$, 5.0 Hz, H-6‴ or H-6′), 3.71 (3H, s, OMe), 3.88 (2H, dd, $J=12.0$, 2.0 Hz, H-6′, H-6‴), 3.95 (1H, dd, $J=8.5$, 4.5 Hz, H-5), 4.13, 4.25 (each 1H,

dt, $J=10.5$, 6.5 Hz, H_2-1″), 4.72 (1H, d, $J=8.0$ Hz, H-1‴), 4.78 (1H, d, $J=8.0$ Hz, H-1′), 5.86 (1H, br s, H-1), 6.07 (1H, qd, $J=7.5$, 1.0 Hz, H-8), 6.67 (1H, dd, $J=8.5$, 2.0 Hz, H-8″), 6.75 (1H, d, $J=2.0$ Hz, H-4″), 7.12 (1H, d, $J=8.5$ Hz, H-7″), 7.50 (1H, s, H-3). ^{13}C-NMR: Table 2. Significant HMBC correlations: H-3→C-11, OCH_3→C-11, H_2-1″→C-7, H-4″→C-5″, C-6″, C-8″, H-7″→C-3″, C-5″, C-6″, H-8″→C-4″, C-6″, C-7″. HR negative-mode SI-MS *m/z*: Calcd for $C_{31}H_{41}O_{18}$ $(M-H)^-$: 701.2294. Found: 701.2316.

Tritylation of Polyanoside (5) Followed by Hydrolysis To a solution of **5** (9.7 mg) in pyridine (0.2 ml) was added trityl chloride (40 mg), and the mixture was stirred at room temperature for 24 h. After concentration, the residue was purified by prep. TLC ($CHCl_3$–MeOH, 17 : 3), giving rise to **14** (6.4 mg). **14**: ^{1}H-NMR (CD_3OD): δ 1.72, 1.74 (each 3H, br d, $J=6.5$ Hz, H_3-10a, H_3-10b), 2.29, 2.31 (each 1H, dd, $J=15.0$, 9.0 Hz, H-6a, H-6b), 2.46 (2H, m, H_2-2″), 2.59, 2.64 (each 1H, dd, $J=$ 15.0, 5.0 Hz, H-6a, H-6b), 3.64, 3.68 (each 3H, s, 2 × OMe), 3.98, 4.00 (each 1H, dd, $J=9.0$, 5.0 Hz, H-5a, H-5b), 4.27 (1H, br d, $J=12.0$ Hz, H-6‴), 5.97, 6.05 (each 1H, br s, H-1a, H-1b), 6.18 (2H, br q, $J=6.5$ Hz, H-8a, H-8b), 7.15—7.43 (34H, m, H-4″, H-5″, H-7″, H-8″, 6 × C_6H_5), 7.58 (2H, s, H-3a, H-3b). Negative-mode SI-MS *m/z* 1555 $(M-H)^-$.

A solution of **14** (6.4 mg) in dioxane (0.6 ml) and 1 N NaOH (0.6 ml) was stirred at room temperature for 17 h. After neutralization of Amberlite IR-120 (H^+-form), the reaction mixture was concentrated *in vacuo* and submitted to prep. HPLC (μBondasphere 5μC18-100 Å, MeOH–H_2O, 8 : 2) to give a contaminated fraction containing **16** (16.5 mg) and **15** (2.8 mg). The first fraction was acetylated with Ac_2O–pyridine and the crude product was purified by prep. HPLC (μBondasphere 5μC18-100 Å, MeOH–H_2O, 7 : 3) to yield **17** (1.0 mg). **15**: ^{1}H-NMR (CD_3OD): δ 1.81 (3H, dd, $J=7.0$, 1.0 Hz, H_3-10), 2.20 (1H, dd, $J=14.0$, 9.0 Hz, H-6), 2.66 (1H, dd, $J=14.0$, 4.0 Hz, H-6), 4.02 (1H, dd, $J=9.0$, 4.0 Hz, H-5), 6.03 (1H, br s, H-1), 6.22 (1H, qd, $J=7.0$, 0.5 Hz, H-8), 7.20—7.50 (15H, m, 3 × C_6H_5), 7.58 (1H, s, H-1). Negative-mode SI-MS *m/z* 631 $(M-H)^-$. **17**: ^{1}H-NMR ($CDCl_3$): δ 2.04 (× 2), 2.05, 2.06, 2.08 (15H, each s, 5 × Ac), 2.89 (2H, t, $J=7.0$ Hz, H_2-2″), 3.85 (1H, ddd, $J=9.5$, 5.0, 2.0 Hz, H-5‴), 4.17 (1H, dd, $J=12.0$, 2.0 Hz, H-6‴), 4.24 (2H, t, $J=7.0$ Hz, H_2-1″), 4.29 (1H, dd, $J=12.0$, 5.0 Hz, H-6‴), 5.06 (1H, d, $J=7.5$ Hz, H-1‴), 5.17 (1H, t, $J=9.5$ Hz, H-4‴), 5.23—5.30 (2H, m, H-2‴, H-3‴), 6.93, 7.14 (4H, AA′BB′ pattern, $J=8.5$ Hz, H-5″, H-7″ and H-4″, H-8″). EI-MS *m/z* (rel. int. %): 510 (M^+, 0.04), 451 (0.2), 433 (1.1), 389 (0.4), 368 (0.4), 331 (47), 169 (100), 109 (58), 43 (94). Positive-mode SI-MS (+NaCl) *m/z*: 533 $(M+Na)^+$.

Acetylation of Isojaspolyoside C (8) A mixture of glucosides **8** and **1** (20.7 mg) was acetylated with Ac_2O–pyridine, and the crude acetate (30.2 mg) was purified by prep. HPLC (μBondasphere 5μC18-100 Å, MeOH–H_2O, 77 : 23) to yield **19** (5.2 mg) and **20** (13.8 mg). **19**: ^{13}C-NMR ($CDCl_3$): δ 13.46, 13.53 (C-10a, C-10b), 20.54, 20.59, 20.63, 20.66, 20.71 (9 × $COCH_3$), 29.85, 30.21 (C-5a, C-5b), 34.30 (C-2″), 39.86, 40.07 (C-6a, C-6b), 51.42, 51.45 (2 × OCH_3), 61.64, 62.05 (C-6′a, C-6′b), 64.57 (C-1″), 68.19, 68.22 (C-4′a, C-4′b), 70.74 (× 2) (C-2′a, C-2′b), 72.20 (× 2) (C-3′a, C-3′b), 72.56 (× 2) (C-5′a, C-5′b), 93.78, 93.94 (C-1a, C-1b), 97.15, 97.21 (C-1′a, C-1′b), 108.62, 108.73 (C-4a, C-4b), 123.38 (C-4″), 123.83 (C-7″), 124.84 (× 2) (C-8a, C-8b), 127.02 (C-8″), 128.15, 128.28 (C-9a, C-9b), 136.64 (C-3″), 140.73 (C-6″), 141.95 (C-5″), 153.01 (× 2) (C-3a, C-3b), 166.69, 166.74 (C-11a, C-11b), 168.19, 168.30, 169.32, 169.39, 170.17, 170.57, 170.69, 170.99 (C-7a, C-7b, 9 × $\underline{C}OCH_3$). **20**: A white amorphous powder, $[\alpha]_D^{27}$ −138° ($c=0.83$, $CHCl_3$); UV λ_{max}^{EtOH} nm: 235 (4.31), 269sh (3.06). IR ν_{max}^{KBr} cm^{-1}: 1759, 1707, 1634, 1508, 1080. ^{1}H-NMR ($CDCl_3$): δ 1.67, 1.74 (each 3H, dd, $J=7.0$, 1.5 Hz, H_3-10b, H_3-10a), 2.019 (× 2), 2.024, 2.027, 2.036, 2.040, 2.115, 2.284, 2.288 (each 3H, s, 9 × Ac), 2.39 (1H, dd, $J=14.0$, 8.5 Hz, H-6a or H-6b), 2.49 (1H, dd, $J=15.5$, 8.5 Hz, H-6b or H-6a), 2.69 (1H, dd, $J=15.5$, 4.5 Hz, H-6b or H-6a), 2.72 (1H, dd, $J=14.0$, 4.5 Hz, H-6a or H-6b), 2.91 (2H, t, $J=7.0$ Hz, H_2-2″), 3.720, 3.721 (each 3H, s, 2 × OMe), 3.71, 3.79 (each 1H, ddd, $J=9.0$, 5.0, 2.0 Hz, H-5′a, H-5′b), 3.93, 3.96 (each 1H, dd, $J=8.5$, 4.5 Hz, H-5a, H-5b), 4.14 (2H, dd, $J=12.5$, 2.0 Hz, H-6′a, H-6′b), 4.18, 4.26 (each 1H, dt, $J=11.0$, 7.0 Hz, H_2-1″), 4.31 (2H, dd, $J=12.5$, 5.0 Hz, H-6′a, H-6′b), 5.02, 5.03 (each 1H, d, $J=8.0$ Hz, H-1′a, H-1′b), 5.09, 5.10 (each 1H, dd, $J=9.0$, 8.0 Hz, H-2′a, H-2′b), 5.10, 5.12 (each 1H, t, $J=9.0$ Hz, H-4′a, H-4′b), 5.24, 5.28 (each 1H, t, $J=9.0$ Hz, H-3′a, H-3′b), 5.68, 5.69 (each 1H, br s, H-1a, H-1b), 5.96, 6.00 (each 1H, qd, $J=7.0$, 1.0 Hz, H-8a, H-8b), 7.05 (1H, d, $J=2.0$ Hz, H-4″), 7.09 (1H, dd, $J=8.0$, 2.0 Hz, H-8″), 7.12 (1H, d, $J=8.0$ Hz, H-7″), 7.44, 7.45 (each 1H, s, H-3a, H-3b). ^{13}C-NMR ($CDCl_3$): δ 13.49, 13.55 (C-10a, C-10b), 20.60, 20.62, 20.63, 20.74 (9 × $COCH_3$), 29.74, 30.25 (C-5a, C-5b), 34.33 (C-2″), 39.34, 40.02 (C-6a, C-6b), 51.44, 51.48 (2 × OCH_3), 61.76, 61.78 (C-6′a, C-6′b), 64.56 (C-1″), 68.25, 68.46 (C-4′a, C-4′b), 70.69 (× 2) (C-2′a, C-2′b), 72.02, 72.22 (C-3′a, C-3′b), 72.51, 72.56 (C-5′a, C-5′b), 93.73, 93.75 (C-1a, C-1b), 97.00, 97.12 (C-1′a, C-1′b), 108.34, 108.71 (C-4a, C-4b), 123.38 (C-4″), 123.82 (C-7″), 124.82, 125.29 (C-8a, C-8b), 127.04 (C-8″), 128.05, 128.31 (C-9a, C-9b), 136.61 (C-3″), 140.73 (C-6″), 141.96 (C-5″), 153.08, 153.15 (C-3a, C-3b), 166.63, 166.76 (C-11a, C-11b), 168.20, 168.30, 169.28, 169.30, 169.42, 169.91, 170.18, 170.24, 170.31, 170.62, 170.99 (C-7a, C-7b, 9 × $\underline{C}OCH_3$). HR positive-mode SI-MS *m/z*: Calcd for $C_{60}H_{72}NaO_{32}$ $(M+Na)^+$: 1327.3907. Found: 1327.3946.

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