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FIVE TRIMERIC SECOIRIDOID GLUCOSIDES FROM *JASMINUM POLYANTHUM*

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Key Word Index—*Jasminum polyanthum*; Oleaceae; flowers; structure elucidation; secoiridoid glucosides; oleopolyanthosides; jaspolyoleosides; oleoside; 10-hydroxyoleoside.

Abstract—Investigation of the crude drug "Ye su xin", the dried flowers of *Jasminum polyanthum*, has led to the isolation of five new secoiridoid glucosides, oleopolyanthosides A and B, and jaspolyoleosides A, B, and C. The structures of the new compounds were elucidated by spectroscopic and chemical means. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

In the course of our chemical studies on the glycosides of oleaceous plants, we have recently investigated the constituents of the dried flowers of *Jasminum polyanthum* Franch., which have been used as a crude drug ("Ye su xin") in Chinese folk medicine [1], and reported the isolation and structure elucidation of one monomeric and eight dimeric secoiridoid glucosides, as well as three secoiridoid glucosides esterified with a linear monoterpene unit [2–4]. In continuation of this study, we have further examined the methanolic extract of the same plant and isolated five minor trimeric secoiridoid glucosides. This paper deals with the structure determination of these novel secoiridoid glucosides.

RESULTS AND DISCUSSION

The *n*-BuOH-soluble fraction of the methanolic extract of the dried flowers of *J. polyanthum* was fractionated by column chromatography on ODS and then purified by prep. HPLC, affording five secoiridoid glucosides **1**–**5**, named oleopolyanthosides A and B, and jaspolyoleosides A, B, and C.

Oleopolyanthoside A (**1**) was analysed for $C_{52}H_{70}O_{32}$ (HR-SIMS). Its UV spectrum showed typical absorption at 236.5 nm (log ε 4.36) of iridoidic enol ether systems conjugated with a carbonyl group. It showed IR bands at 3401 (OH), 1732 (esters), 1705 and 1632 (α,β-unsaturated esters) cm^{-1}. The ^{1}H NMR (Table 1) spectral features of **1** [H-3a, H-3b, H-3c (δ 7.51, 7.53, 7.54), H-1a, H-1b, H-1c (δ 5.97, 5.92, 5.86), three anomeric protons (δ 4.811, 4.813, 4.818), and four methoxyls (δ 3.67, 3.69, 3.71, 3.72), two ethylidene groups (δ 6.10, 6.12 (each 1H, *qd*) and 1.73 (6H, *br d*)), an olefinic proton at δ 6.05 (*ddd*) and methylene protons at δ 4.71 and 4.78] were very similar to those of jaspolyanthoside (**6**), except for the appearance of additional signals assignable to an oleoside methyl ester unit. These observations suggested that the glucoside **1** was composed of a jaspolyanthoside unit (a and b parts) and an oleoside methyl ester unit (c part). The chemical shifts of carbon signals ascribable to the jaspolyanthoside portion in the ^{13}C NMR spectrum of **1** were superimposable on those of **6**, except for the signals arising from the glucose moiety (Table 2). The downfield shift of C-6′ and upfield shift of C-5′ of **1**, relative to **6**, were ascribed to the acylation of 6′-hydroxyl group in the glucose moiety.

To confirm the six ester linkages, extensive NMR studies including ^{1}H-^{1}H COSY, DEPT, HMQC and HMBC experiments were performed on compound **1**. The HMBC technique revealed cross peaks between the methoxyl signals at δ 3.69, 3.71 and 3.72 and conjugated carbonyl carbons at δ 168.35, 168.65 and 168.70, establishing methoxyl groups at C-11 in each of three secoiridoid moieties. On the other hand, the methoxyl signal at δ 3.67 was correlated with the carbon signal at δ 173.35, which was assigned to C-7a of the 10-hydroxyoleoside (**7**) unit on the basis of correlations between H$_2$-6a (δ 2.54, 2.79) and C-7a and C-5a (δ 32.51), and between H-8a (δ 6.05) and C-5a and C-10a (δ 62.11). Furthermore, an important ^{3}J correlation between H$_2$-10a (δ 4.71, 4.78) and C-7b at δ 172.62 indicated an ester linkage of the C-7 of oleo-

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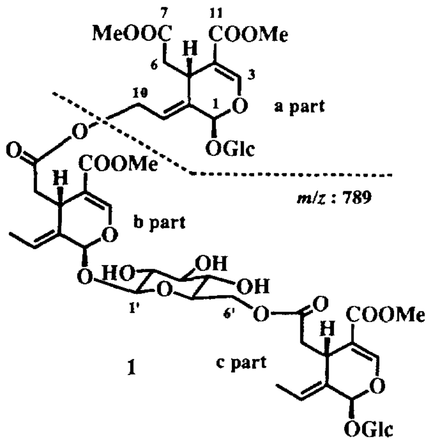

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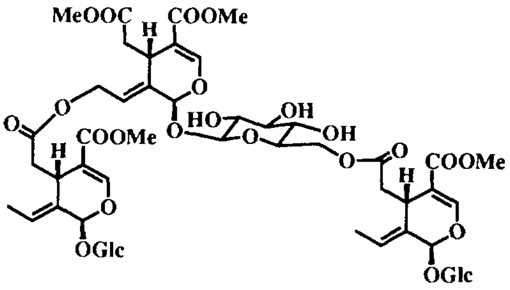
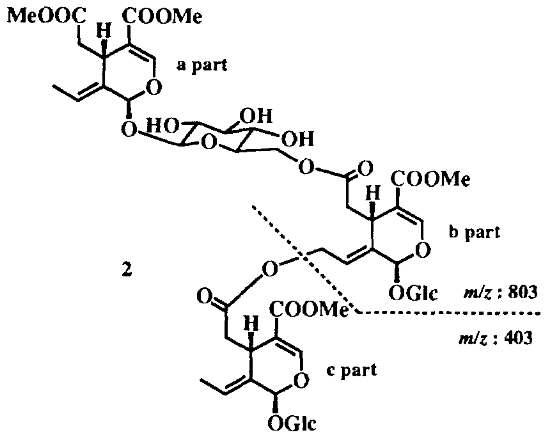


1a



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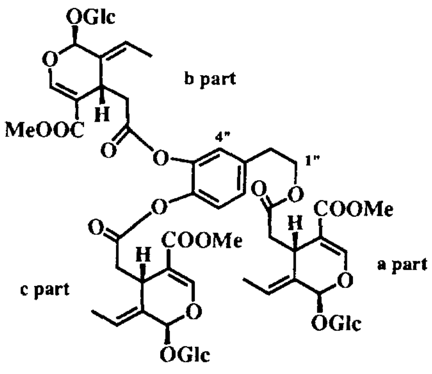

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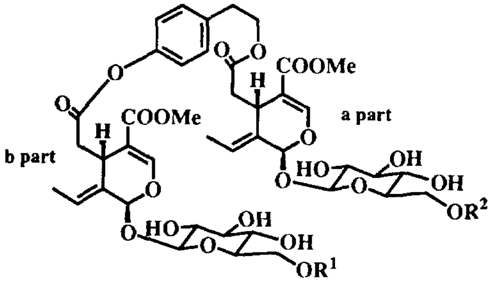

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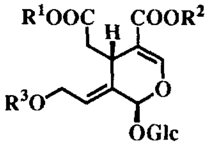
5 : R^1= H, R^2= ole (c part)
14 : R^1= R^2= H



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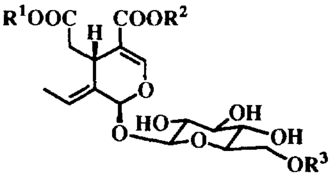
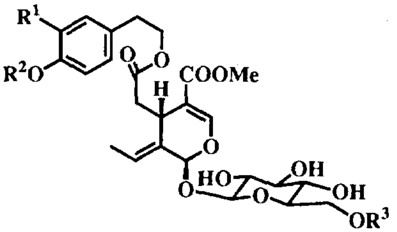
11 : R^1= R^3= H, R^2= Me



8 : R^1= R^3= H, R^2= Me
10 : R^1= R^2= R^3= H
12 : R^1= R^2= Me, R^3= H
15 : R^1= R^2= Me, R^3= ole



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16 : R^1= R^2= R^3= H
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ole =

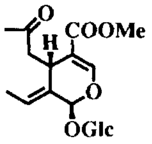

Table 1. ^{1}H-NMR spectral data of compounds **1**–**5** in CD_3OD

	1			**2**			**3**			**4**			**5**		
H	a part	b part	c part	a part	b part	c part	a part	b part	c part	a part	b part	c part	a part	b part	c part
1	5.97 *br s*	5.92[a] *br s*	5.86[a] *br s*	5.91 *br s*	5.88 *br s*	5.93 *br s*	5.912 *br s*	6.036[c] *br s*	6.039[c] *br s*	5.92 *br s*	5.98 *br s*	5.86 *br s*	5.84 *br s*	6.04 *br s*	5.89 *br s*
3	7.51 *s*	7.53[a] *s*	7.54[a] *s*	7.511[b] *s*	7.547 *s*	7.509[b] *s*	7.522 *s*	7.571[c] *s*	7.574[c] *s*	7.51 *s*	7.58 *s*	7.49 *s*	7.52[e] *s*	7.50[e] *s*	7.58[e] *s*
5	4.00 *dd* (9.5, 4.5)	3.99 *dd* (9.5, 4.5)	3.99 *dd* (9.5, 4.5)	3.98[b] *dd* (9.5, 4.5)	4.02 *dd* (9.5, 4.5)	4.04[b] *dd* (9.5, 4.5)	3.950 *dd* (9.0, 4.5)	4.098[c] *dd* (9.5, 4.5)	4.103[c] *dd* (9.5, 4.5)	3.94 *dd* (9.5, 5.0)	4.10 *dd* (9.5, 4.5)	3.96 *dd* (9.0, 5.0)	3.93 *dd* (9.5, 4.5)	4.12 *dd* (9.5, 4.5)	3.98 *dd* (8.5, 4.5)
6	2.54 *dd* (15.0, 9.5) 2.79 *dd* (15.0, 4.5)	2.43 *dd* (14.5, 9.5) 2.73 *dd* (14.5, 4.5)	2.48 *dd* (14.0, 9.5) 2.76 *dd* (14.0, 4.5)	2.46 *dd* (14.0, 9.5) 2.78 *dd* (14.0, 4.5)	2.49 *dd* (14.5, 9.5) 2.80 *dd* (14.5, 4.5)	2.44 *dd* (14.0, 9.5) 2.75 *dd* (14.0, 4.5)	2.44 *dd* (14.0, 9.0) 2.71 *dd* (14.0, 4.5)	2.77[c] *dd* (15.0, 9.5) 2.96[c] *dd* (15.0, 4.5)	2.78[c] *dd* (15.0, 9.5) 2.97[c] *dd* (15.0, 4.5)	2.44 *dd* (14.0, 9.5) 2.71 *dd* (14.0, 5.0)	2.70 *dd* (14.0, 9.5) 2.97 *dd* (14.0, 4.5)	2.32 *dd* (14.0, 9.0) 2.67 *dd* (14.0, 5.0)	2.40 *dd* (14.0, 9.5) 2.697[e] *dd* (14.0, 4.5)	2.74 *dd* (15.0, 9.5) 2.973 *dd* (15.0, 4.5)	2.41 *dd* (14.0, 8.5) 2.702[e] *dd* (14.0, 4.5)
8	6.05 *ddd* (7.0, 5.5, 1.0)	6.10[a] *qd* (7.0, 1.5)	6.12[a] *qd* (7.0, 1.5)	6.09 *qd* (7.0, 1.5)	6.08 *ddd* (7.0, 6.0, 1.0)	6.12 *qd* (7.0, 1.5)	6.06 *qd* (7.0, 1.0)	6.18 *qd* (7.0, 1.0)	6.18 *qd* (7.0, 1.0)	6.06 *qd* (7.0, 1.5)	6.18 *qd* (7.0, 1.0)	6.06 *qd* (7.0, 1.5)	6.03 *qd* (7.0, 1.0)	6.19 *qd* (7.0, 1.0)	6.09 *qd* (7.5, 1.5)
10	4.71 *ddd* (13.5, 5.5, 1.0) 4.78 *dd* (13.5, 7.0)	1.73 *br d* (7.0)	1.73 *br d* (7.0)	1.73 *dd* (7.0, 1.5)	4.74 *ddd* (13.5, 6.0, 1.0) 4.81 *dd* (13.5, 7.0)	1.71 *dd* (7.0, 1.5)	1.61 *dd* (7.0, 1.5)	1.77[c] *dd* (7.0, 1.5)	1.78[c] *dd* (7.0, 1.5)	1.59 *dd* (7.0, 1.5)	1.73 *dd* (7.0, 1.5)	1.69 *dd* (7.0, 1.5)	1.57 *dd* (7.0, 1.5)	1.77 *dd* (7.0, 1.5)	1.71 *dd* (7.5, 1.5)
OMe	3.69[a] *s* 3.67 *s*	3.71[a] *s*	3.72[a] *s*	3.69[b] *s* 3.64 *s*	3.71[b] *s*	3.72[b] *s*	3.697 *s*	3.738[c] *s*	3.740[c] *s*	3.71[d] *s*	3.68[d] *s*	3.74[d] *s*	3.71[e] *s*	3.66[e] *s*	3.74[e] *s*
1′	4.811[a] *d* (7.5)	4.813[a] *d* (7.5)	4.818[a] *d* (7.5)	4.80[b] *d* (8.0)	4.84 *d* (8.0)	4.81[b] *d* (8.0)	4.82 *d* (8.0)	4.80 *d* (8.0)	4.80 *d* (8.0)	4.81 *d* (7.5)	4.83 *d* (7.5)	4.78 *d* (8.0)	4.82 *d* (7.5)	4.83 *d* (7.0)	4.80 *d* (7.5)
2′	3.30–3.44 *m*	3.30–3.44 *m*	3.30–3.44 *m*	3.30–3.44 *m*	3.30–3.44 *m*	3.30–3.44 *m*	3.30–3.43 *m*	3.30–3.43 *m*	3.30–3.43 *m*	3.30–3.45 *m*	3.30–3.45 *m*	3.30–3,45 *m*	3.30–3.45 *m*	3.30–3.45 *m*	3.30–3.45 *m*
3′	3.30–3.44 *m*	3.30–3.44 *m*	3.30–3.44 *m*	3.30–3.44 *m*	3.30–3.44 *m*	3.30–3.44 *m*	3.30–3.43 *m*	3.30–3.43 *m*	3.30–3.43 *m*	3.30–3.45 *m*	3.30–3.45 *m*	3.30–3,45 *m*	3.30–3.45 *m*	3.30–3.45 *m*	3.30–3.45 *m*
4′	3.30–3.44 *m*	3.30–3.44 *m*	3.30–3.44 *m*	3.30–3.44 *m*	3.30–3.44 *m*	3.30–3.44 *m*	3.30–3.43 *m*	3.30–3.43 *m*	3.30–3.43 *m*	3.30–3.45 *m*	3.30–3.45 *m*	3.30–3,45 *m*	3.30–3.45 *m*	3.30–3.45 *m*	3.30–3.45 *m*
5′	3.30–3.44 *m*	3.55 *ddd* (9.0, 6.0, 1.5)	3.30–3.44 *m*	3.55 *ddd* (9.0, 5.5, 1.5)	3.30–3.44 *m*	3.30–3.44 *m*	3.30–3.43 *m*	3.30–3.43 *m*	3.30–3.43 *m*	3.30–3.45 *m*	3.53 *ddd* (9.5, 6.0, 2.0)	3.30–3.45 *m*	3.55 *ddd* (9.0, 5.5, 2.0)	3.30–3.45 *m*	3.30–3.45 *m*
6′	3.68[a] *dd* (11.5, 6.0) 3.89[a] *dd* (11.5, 1.5)	4.20 *dd* (11.5, 6.0) 4.34 *dd* (11.5, 1.5)	3.65[a] *dd* (11.5, 6.0) 3.90[a] *dd* (11.5, 1.5)	4.24 *dd* (12.0, 5.5) 4.32 *dd* (12.0, 1.5)	3.66[b] *dd* (11.5, 6.0) 3.89[b] *dd* (11.5, 1.5)	3.68[b] *dd* (11.5, 6.0) 3.88[b] *dd* (11.5, 1.5)	3.68[c] *dd* (12.0, 6.0) 3.88[c] *dd* (12.0, 1.5)	3.64[c] *dd* (12.0, 6.0) 3.85[c] *dd* (12.0, 1.5)	3.64[c] *dd* (12.0, 6.0) 3.86[c] *dd* (12.0, 2.0)	3.66[d] *dd* (12.0, 6.0) 3.88[d] *dd* (12.0, 2.0)	4.13 *dd* (12.0, 6.0) 4.26 *dd* (12.0, 2.0)	3.65[d] *dd* (12.0, 5.5) 3.89[d] *dd* (12.0, 2.0)	4.20 *dd* (12.0, 5.5) 4.35 *dd* (12.0, 2.0)	3.68 *dd* (12.0, 6.0) 3.84[e] *dd* (12.0, 1.5)	3.68 *dd* (12.0, 6.0) 3.88[e] *dd* (12.0, 2.0)
1″	4.18 *dt* (10.5, 6.5) 4.30 *dt* (10.5, 6.5)			4.16 *dt* (11.0, 6.5) 4.29 *dt* (11.0, 6.5)									4.14 *dt* (11.0, 6.5) 4.27 *dt* (11.0, 6.5)		
2″	2.96 *t* (6.5)			2.93 *t* (6.5)									2.89 *t* (6.5)		
4″	7.11 *d* (2.0)			7.26 *d* (8.5)									7.25 *d* (8.5)		
5″											6.98 *d* (8.5)		7.03 *d* (8.5)		
7″	7.12 *d* (8.5)			6.98 *d* (8.5)									7.03 *d* (8.5)		
8″	7.20 *dd* (8.5, 2.0)			7.26 *d* (8.5)									7.25 *d* (8.5)		

[a–e] Assignments may be reversed horizontally.

Table 2. ^{13}C-NMR spectral data of compounds **1**–**5** in CD_3OD

	1			**2**			**3**			**4**			**5**		
C	a part	b part	c part	a part	b part	c part	a part	b part	c part	a part	b part	c part	a part	b part	c part
1	94.50	95.23^{a}	95.43^{a}	95.24	94.55	95.33	95.14	95.21^{c}	95.24^{c}	95.24	95.71	95.21	95.33	95.26	95.17
3	155.00^{a}	155.19^{a}	155.21^{a}	155.22^{b}	154.98	155.28^{b}	155.19	155.38	155.38	155.20	155.36	155.20	155.17^{e}	155.17^{e}	155.33^{e}
4	109.48	109.18^{a}	109.51^{a}	109.43^{b}	109.18	109.48^{b}	109.44	109.35	109.35	109.41^{d}	109.40^{d}	109.48^{d}	109.43	109.46	109.37
5	32.51	31.87	31.87	31.93	32.49	31.86	31.92	31.68^{c}	31.72^{c}	31.84^{d}	31.93^{d}	31.93^{d}	31.92	31.83	31.83
6	40.89	41.59	41.28	41.51	41.24	41.03	41.36	40.67	40.67	41.16^{d}	41.37^{d}	41.30^{d}	41.39	41.16	41.26
7	173.35	172.62	173.11	173.01	173.15	172.84	173.13	170.73^{c}	170.81^{c}	173.18	171.42	172.92	172.89	171.61	172.98
8	124.48	124.95^{a}	124.28^{a}	124.93	124.69	125.21	125.01	125.47	125.47	125.01	125.39	124.93	125.33	125.19	124.95
9	133.96	130.41	130.55	130.56	133.79	130.39	130.46	130.51	130.51	130.50	130.50	130.50	130.08	130.67	130.53
10	62.11	13.85	13.85	13.87	62.09	13.98	13.62	13.96^{c}	14.04^{c}	13.63	13.82	13.82	13.61	13.91	13.84
11	168.35^{a}	168.65^{a}	168.70^{a}	168.69^{b}	168.69^{b}	168.30^{b}	168.69	168.61	168.61	168.66	168.66	168.66	168.61^{e}	168.64^{e}	168.71^{e}
OMe	52.04^{a}	52.09^{a}	52.09^{a}	52.07	52.07	52.07	52.02	52.11	52.11	52.05	52.05	52.05	51.99^{e}	52.02^{e}	52.05^{e}
1′	101.07^{a}	100.95^{a}	101.10	100.97^{b}	101.18	101.03^{b}	100.89	100.95	100.95	100.95	100.35	100.35	100.93^{e}	101.00^{e}	101.00^{e}
2′	74.62^{a}	74.76^{a}	74.78^{a}	74.64^{b}	74.77^{b}	74.80^{b}	74.76^{c}	74.76^{c}	74.80^{c}	74.67^{d}	74.68^{d}	74.82^{d}	74.70^{e}	74.78^{e}	74.80^{e}
3′	77.90^{a}	77.98^{a}	77.98^{a}	77.81^{b}	78.00^{b}	78.05^{b}	78.01	78.01	78.01	77.84^{d}	77.99^{d}	77.99^{d}	77.83^{e}	77.98^{e}	77.98^{e}
4′	71.53	71.53	71.53	71.25^{b}	71.44^{b}	71.54^{b}	71.49^{c}	71.56^{c}	71.56^{c}	71.44^{d}	71.51^{d}	71.58^{d}	71.42^{e}	71.47^{e}	71.50^{e}
5′	78.42^{a}	75.51	78.56^{a}	75.50	78.45	78.45	78.47	78.47	78.47	78.45^{d}	75.49	78.50^{d}	75.51	78.45^{e}	78.47^{e}
6′	62.76^{a}	65.07	62.84^{a}	64.79	62.77	62.77	62.82^{c}	62.68^{c}	62.75^{c}	62.75^{d}	64.95	62.85^{d}	64.89	62.71	62.71
1″							66.14			66.48			66.44		
2″							35.28			35.38			35.40		
3″							138.66			137.25			137.25		
4″							124.54			131.13			131.12		
5″							143.44			122.83			122.80		
6″							142.19			150.79			150.82		
7″							125.01			122.83			122.80		
8″							128.41			131.13			131.12		

[a-e] Assignments may be reversed horizontally.

side 11-methyl ester (**8**) unit with the 10-hydroxyl group of 10-hydroxyoleoside 7,11-dimethyl ester (**9**) moiety, thus confirming the same ester linkages as in jaspolyanthoside (**6**). All these findings allowed us to propose two plausible structures, **1** and **1a**, for the new glucoside. An HMBC interaction between the proton signal (δ 4.20) and C-7c (δ 173.11) pointed to the acylation of the 6′-hydroxyl of glucose moiety with the C-7 of an extra oleoside 11-methyl ester unit, but it was impossible to assign the proton signal to H-6′a or H-6′b by the NMR studies. Finally, two plausible structures were discriminated by SIMS which exhibited a peak at m/z 789 ($[M-C_{18}H_{25}O_{11}]^-$) generated from the b and c parts by fission of the allylic C—O bond in **1**. Thus, the structure of **1** was established as oleopolyanthoside A.

Oleopolyanthoside B (**2**) was isomeric with **1**, $C_{52}H_{70}O_{32}$, and exhibited UV and IR spectra analogous to those of **1**. The ^1H and ^{13}C NMR spectra of **2** revealed four methoxyl groups and signals attributable to a 10-hydroxyoleoside (**7**) unit and two oleoside (**10**) units as seen in **1**. However, there were remarkable differences in the results of the HMBC experiments. In the HMBC spectrum of **2**, a methoxyl signal at δ 3.64 was coupled with the C-7a (δ 173.01) of an oleoside 11-methyl ester moiety, but not with the carbon signal at δ 173.15, which was assigned to C-7b of the 10-hydroxyoleoside 11-methyl ester moiety by a series of HMBC and HMQC correlations starting from the methylene protons at C-10b. The H-6′a (δ 4.24) was associated with C-7b. These findings led us to conclude that in the structure of oleopolyanthoside B, the C-7b carboxyl group of the 10-hydroxyoleoside 11-methyl ester (**11**) unit was linked to the C-6′a hydroxyl group of the oleoside dimethyl ester (**12**) portion. Furthermore, another ^3J correlation observed between H_2-10b (δ 4.74, 4.81) and C-7c (δ 172.84) established an ester linkage of C-7c to the hydroxyl group at C-10b. Accordingly, the compound **2** was formulated as shown.

Compound **3** was obtained as an amorphous powder. The HR-SIMS measurement revealed the molecular formula $C_{59}H_{76}O_{33}$. The ^1H NMR spectral (Table 1) features suggested that the glucoside **3** was composed of three oleoside 11-methyl ester units [H-3a, H-3b and H-3c (δ 7.522, 7.571, 7.574), three anomeric protons (δ 4.80 × 2, 4.82) and three methoxyls (δ 3.697, 3.738, 3.740)] and a 3,4-dihydroxyphenethyl moiety [an ABX_2 system of a OCH_2CH_2Ar moiety at δ 4.18 (1H, *dt*), 4.30 (1H, *dt*) and 2.96 (2H, *t*) and an aromatic ABX spin system at δ 7.12 (*d*, $J = 8.5$ Hz), 7.11 (*d*, $J = 2.0$ Hz) and 7.20 (*dd*, $J = 8.5$, 2.0 Hz)]. HMBC experiments with **3** showed a ^3J interaction between H_2-1″ and C-7a (δ 173.13), indicating the same ester linkage as in oleuropein (**13**). Comparison of the ^{13}C NMR data of **3** with those of **13** [3] revealed significant differences in the signals arising from the aromatic moiety. The downfield shifts of C-3″, C-4″, C-7″ and C-8″ ($\Delta\delta$ +7.92, +7.48, +8.57 and +7.10 ppm) as well as the upfield shifts of C-5″ and C-6″ ($\Delta\delta$ −2.76 and −2.70 ppm), when compared with the corresponding signals of **13**, suggested the attachment of two oleoside 11-methyl ester units to the hydroxyl groups on the aromatic ring in **3**. This received support from the chemical shifts of H_2-6b and H_2-6c as well as the C-7b and C-7c carbon signals [5]. Consequently, the structure of the new compound was represented by **3** and designated jaspolyoleoside A.

Jaspolyoleosides B (**4**) and C (**5**) were recognized as isomers, $C_{59}H_{76}O_{32}$, from their HR-SIMS. The ^1H and ^{13}C NMR spectra (Tables 1 and 2) of each glucoside exhibited triplicated signals ascribable to three oleoside 11-methyl ester moieties as well as signals due to a *p*-hydroxyphenethyl alcohol moiety. Comparative studies of the ^1H and ^{13}C NMR spectra of **4** and **5** with those of Gl 5 (**14**), a constituent of the plant material [2], together with HMBC experiments, showed both compounds to be esters of Gl 5 with oleoside 11-methyl ester (**8**). The structural difference between **4** and **5** could be accounted for only by the point of ester linkage of the third oleoside 11-methyl ester unit. In the respective ^{13}C NMR spectra, the carbon signals of C-5′ and C-6′ of the glucose moiety underwent typical acylation shifts, implying an attachment of the third oleoside unit to the hydroxy group at C-6′a or C-6′b of **14**. The position of attachment was confirmed by selective methanolysis of the phenolic ester linkage [5]. On standing in MeOH at 80°, compound **4** yielded **15** and ligstroside (**16**), while compound **5** produced **12** and jaspolyanoside (**17**) [3]. Thus, the degradation products established the structures of jaspolyoleosides B and C as **4** and **5**, respectively.

Trimeric secoiridoid glucosides of the oleoside- and 10-hydroxyoleoside types have so far been found only in *J. sambac* [6, 7], *J. amplexicaule* [8] and *J. urophyllum* [9]. The present work gives additional examples of trimeric secoiridoid glucosides.

EXPERIMENTAL

Mp: uncorr.; ^1H (300 or 500 MHz) and ^{13}C (125 MHz) NMR: TMS as int. standard; SIMS: glycerol or 3-nitrobenzyl alcohol as matrix; TLC: silica gel.

Plant material and isolation of glucosides

The source of plant material and fractionation of the MeOH extract are described in previous publications [2, 3]. Fr. 21 (40% MeOH effluent, 492 mg) was further purified by repeated preparative HPLC (μBondasphere 5μC18-100 Å, H_2O–MeOH, 11:9 or H_2O–MeCN, 31:19), giving **1** (9.9 mg) and **2** (15.7 mg). The following frs were also purified by a combination of prep HPLC (μBondasphere 5μC18-100 Å, H_2O–MeOH, 9:11 or 47:53 or H_2O–MeCN, 7:3 or 13:7). Fr. 26 (50% MeOH effluent, 305.8 mg) yielded Gl 5 (**14**) (6.1 mg) and **3** (3.3 mg); fr. 27 (50–55% MeOH effluent, 204.0 mg) gave **4** (6.2 mg) and **5** (4.4 mg).

Oleopolyanthoside A (**1**). Colourless amorphous powder, $[\alpha]_D^{27}$ −151° (c 0.48, MeOH). UV λ_{max}^{MeOH} nm (log ε): 236.5 (4.36); IR ν_{max}^{KBr} cm^{-1}: 3401, 1732, 1705, 1632, 1077, 818; ^{1}H and ^{13}C NMR (CD_3OD): Tables 1 and 2; SIMS m/z: 1205 $[M-H]^-$, 789 $[M-C_{18}H_{25}O_{11}]^-$; HR-SIMS Found: 1205.3779 $[M-H]^-$; $C_{52}H_{69}O_{32}$ requires 1205.3774.

Oleopolyanthoside B (**2**). Colourless amorphous powder, $[\alpha]_D^{27}$ −185° (c 0.86, MeOH). UV λ_{max}^{MeOH} nm (log ε): 236 (4.43); IR ν_{max}^{KBr} cm^{-1}: 3349, 1734, 1705, 1634, 1076, 818; ^{1}H and ^{13}C NMR (CD_3OD): Tables 1 and 2; SIMS m/z: 1205 $[M-H]^-$, 403; HR-SIMS Found: 1205.3780 $[M-H]^-$; $C_{52}H_{69}O_{32}$ requires 1205.3774.

Jaspolyoleoside A (**3**). Colourless amorphous powder, $[\alpha]_D^{26}$ −175° (c 0.12, MeOH). UV λ_{max}^{MeOH} nm (log ε): 236.5 (4.49); IR ν_{max}^{KBr} cm^{-1}: 3419, 1733, 1705, 1636, 1506, 1076, 818; ^{1}H and ^{13}C NMR (CD_3OD): Tables 1 and 2; SIMS m/z: 1311 $[M-H]^-$, 925 $[M-C_{17}H_{23}O_{10}]^-$, 539 $[M-C_{34}H_{45}O_{20}]^-$; HR-SIMS Found: 1311.4204 $[M-H]^-$; $C_{59}H_{75}O_{33}$ requires 1311.4193.

Jaspolyoleoside B (**4**). Colourless amorphous powder, $[\alpha]_D^{25}$ −180° (c 0.35, MeOH). UV λ_{max}^{MeOH} nm (log ε): 235.5 (4.48); IR ν_{max}^{KBr} cm^{-1}: 3429, 1733, 1705, 1636, 1508, 1076, 816; ^{1}H and ^{13}C NMR (CD_3OD): Tables 1 and 2; SIMS m/z: 1295 $[M-H]^-$, 771 $[M-C_{25}H_{33}O_{12}]^-$, 523 $[M-C_{34}H_{45}O_{20}]^-$; HR-SIMS Found: 1295.4249 $[M-H]^-$; $C_{59}H_{75}O_{32}$ requires 1295.4244.

Jaspolyoleoside C (**5**). Colourless amorphous powder, $[\alpha]_D^{24}$ −167° (c 0.43, MeOH). UV λ_{max}^{MeOH} nm (log ε): 236 (4.49); IR ν_{max}^{KBr} cm^{-1}: 3411, 1734, 1707, 1632, 1508, 1078, 816; ^{1}H and ^{13}C NMR (CD_3OD): Tables 1 and 2; SIMS m/z: 1295 $[M-H]^-$, 910 $[M-C_{25}H_{33}O_{12}]^-$, 523; HR-SIMS Found: 1295.4263 $[M-H]^-$; $C_{59}H_{75}O_{32}$ requires 1295.4244.

Methanolysis of **4**. A soln of **4** (0.1 mg) in MeOH (1 ml) was heated at 80° (bath temp.) for 36 h. Identification of the products was performed by HPLC connected to a photodiode array detector and by LC-MS. For the former, the reaction mixture was subjected to HPLC on a Nova Pak C_{18} column (300 × 3.9 mm) using a solvent of H_2O-MeCN (7:3) at 0.6 ml min^{-1} flow rate and detected by a photodiode array detector. Under these conditions, two major products, **15** and **16**, were eluted at R_t = 6.6 min (λ_{max} 240 nm) and R_t = 8.0 min (λ_{max} 227, 244 sh, 279 nm), respectively. Mass spectral analysis was performed by using atmos. pres. chemical ionization (APCI) methods. The products **15** and **16** showed their respective pseudomolecular ion $[M-H]^{-1}$ peaks at m/z 803 and 523. Product **16** was identical with an authentic sample of ligstroside.

Methanolysis of **5**. A soln of **5** (0.1 mg) in MeOH (1 ml) was heated at 80° for 36 h. Identification of the reaction products was performed by HPLC equipped with a photodiode array detector under the same condition as described above. Two major products, **12** and **17**, were eluted at R_t = 6.0 min (λ_{max} 240 nm) and R_t = 14.1 min (λ_{max} 230, 240 sh, 280 nm) and identified with authentic samples of oleoside 7,11-dimethyl ester and jaspolyanoside, respectively.

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