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Fitoterapia 73 (2001) 406–410

FITOTERAPIA

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Short report

**Oleanane glycosides from the leaves of
*Diploclisia glaucescens***

U.L.B. Jayasinghe^{a,*}, C.P. Jayasooriya^a, Y. Fujimoto^b

^a*Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka*

^b*Department of Chemistry and Materials Science, Tokyo Institute of Technology, Meguro,
Tokyo 152-8551, Japan*

Received 24 August 2001; accepted 17 May 2002

Abstract

Complete ¹H and ¹³C NMR assignments are described for two known oleanane glycosides, 3-*O*-β-D-glucopyranosyl(1 → 3)-β-D-glucopyranosyl-28-*O*-β-D-glucopyranosyloleanolic acid and 3-*O*-β-D-xylopyranosyl(1 → 2)-β-D-glucopyranosyl-28-*O*-β-D-glucopyranosyloleanolic acid isolated from the methanol extract of the leaves of *Diploclisia glaucescens*. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: *Diploclisia glaucescens*; Oleanane glycosides; Saponins, NMR

Plant. *Diploclisia glaucescens* (Bl.) Diels (*Cocculus macrocarpus* W. and A.) (Menispermaceae) leaves were collected from the Central Province of Sri Lanka in April 2000 and identified by Mr S.P. Ekanayake, Environmental and Forestry Division, Mahaweli Authority, Polgolla, Sri Lanka. A voucher specimen is deposited at the Institute of Fundamental Studies.

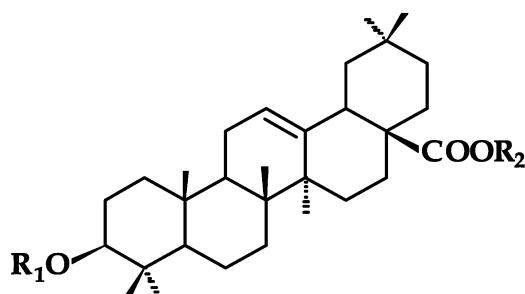
Used in traditional medicine. Leaves for biliousness and venereal diseases [1].

Previously isolated constituents. Alkaloids [2], ecdysones [3–5], triterpenes [6] and triterpenoidal glycosides [6–9].

* Corresponding author. Tel.: +94-8-232002; fax: +94-8-232131.

E-mail address: lalith@ifs.ac.lk (U.L.B. Jayasinghe).

New isolated constituents. 3-*O*- β -D-glucopyranosyl(1 $\rightarrow$ 3)- β -D-glucopyranosyl-28-*O*- β -D-glucopyranosyloleanolic acid (0.16%) and 3-*O*- β -D-xylopyranosyl(1 $\rightarrow$ 2)- β -D-glucopyranosyl-28-*O*- β -D-glucopyranosyloleanolic acid (0.032%) (separation-reversed phase HPLC: STR Prep-ODS 20 $\times$ 250 mm column; 25% H₂O-MeOH, 5 ml/min; UV detection 220 nm). Although the isolation of **1** from *Anchusa officinalis* [10] and **2** from *Panax japonicus* [11] was described previously, the present study fully established their structures on the basis of high-resolution NMR data including H-H COSY, HMQC and HMBC spectra.



	<u>R₁</u>	<u>R₂</u>
1	glc-3glc-	-glc
2	xyl-2glc-	-glc

glc = - β -D-glucopyranosyl

xyl = - β -D-xylopyranosyl

3-*O*- β -D-glucopyranosyl(1 $\rightarrow$ 3)- β -D-glucopyranosyl-28-*O*- β -D-glucopyranosyloleanolic acid (**1**): mp 243–244 °C; IR $\nu_{\max}$, KBr, cm⁻¹: 3376, 2912, 1721, 1635; ¹HNMR and ¹³CNMR (see Table 1); FABMS(+) *m/z*: 965[M + Na]⁺, 803[M + Na-C₆H₁₀O₅]⁺, 439[aglycone-OH]⁺.

3-*O*- β -D-xylopyranosyl(1 $\rightarrow$ 2)- β -D-glucopyranosyl-28-*O*- β -D-glucopyranosyloleanolic acid (**2**): mp 234–235 °C; IR $\nu_{\max}$, KBr cm⁻¹: 3400, 2928, 1731, 1635, 1452, 1158, 1072; ¹HNMR and ¹³C NMR (see Table 1); FABMS(+) *m/z*: 935 [M + Na]⁺, 773[M + Na-C₆H₁₀O₅]⁺, 439[aglycone-OH]⁺.

Acetate of **1** (**1a**): mp 143 °C; IR $\nu_{\max}$, KBr cm⁻¹: 3450, 1638, 1216, 1050, 755; ¹HNMR (500 MHz, CDCl₃): δ 0.72, 0.72, 0.88, 0.89, 0.89, 0.90, 1.11 (each 3H, *s*, seven Me), 1.98, 2.007, 2.007, 2.014, 2.015, 2.025, 2.025, 2.064, 2.064, 2.078, 2.123 (each 3H, *s*, eleven OAc), 2.82 (1H, *dd*, *J* 13.4, 4.4 Hz, H-18), 3.03 (1H, *dd*, *J* 11.6, 4.8 Hz, H-3), 5.32 (1H, *m*, H-12), 4.39 (1H, *d*, *J* 8 Hz, H-1'), 5.03 (1H, *dd*, *J* 8.3, 9.8 Hz, H-2'), 3.88 (1H, *t*, *J* 9.6 Hz, H-3'), 4.88 (1H, *m*, H-4'), 3.66 (1H, *m*, H-5'), 4.17 (2H, *m*, H_{a,b}-6'), 4.56 (1H, *d*, *J* 8.0 Hz, H-1''), 4.89 (1H, *t*, *J* 9.1 Hz, H-2''), 5.13 (1H, *t*, *J* 9.4 Hz, H-3''), 5.05 (1H, *t*, *J* 9.8 Hz, H-4''), 3.66 (1H, *m*, H-5''), 4.05 (1H,

d, *J* 12.5, H_a-6''), 4.36 (1H, *dd*, *IJ* 12.5, 4.4 Hz, H_b-6''), 5.58 (1H, *d*, *J* 8.0 Hz, H-1'''), 5.20 (1H, *t*, *J* 8.2 Hz, H-2'''), 5.25 (1H, *t*, *J* 9.3 Hz, H-3'''), 5.13 (1H, *t*, *J* 9.5 Hz, H-4'''), 3.78 (1H, *m*, H-5'''), 4.04 (1H, *d*, *J* 12.4 Hz, H_a-6'''), 4.28 (1H, *d*, *J* 12.5, 4.5 Hz, H_b-6'''). [*'*- inner glucose moiety; *''*- terminal glucose moiety; *'''*- glucose moiety at C-28].

Acetate of **2** (**2a**): mp 129 °C; IR $\nu_{\max}$ KBr cm⁻¹: 3450, 1740, 1641, 1216, 1070,

Table 1
NMR data for **1** and **2** (Py-d₅, 500/125 MHz)

C	1		2	
	δ_{C}	δ_{H}	δ_{C}	δ_{H}
1	38.66	1.20, 1.70	38.79	1.25, 1.70
2	26.48	2.15, 1.75	26.63	2.15, 1.75
3	88.93	3.34 (<i>dd</i> , <i>J</i> 11.7, 4.3 Hz)	89.08	3.27 (<i>dd</i> , <i>J</i> 11.7, 4.2 Hz)
4	39.47	—	39.58	—
5	55.73	0.76 (<i>d</i> , <i>J</i> 16 Hz)	55.87	0.72 (<i>d</i> , <i>J</i> 11.4 Hz)
6	18.48	1.49	18.51	1.49
7	32.53	1.73, 1.83	32.54	1.73, 1.85
8	39.89	—	39.91	—
9	47.98	1.60 (<i>t</i> , <i>J</i> 8 Hz)	48.03	1.59 (<i>t</i> , <i>J</i> 7.8 Hz)
10	36.94	—	36.95	—
11	23.78	1.85	23.42	1.85
12	122.84	5.42 (<i>m</i>)	122.87	5.42 (<i>m</i>)
13	144.16	—	144.18	—
14	42.13	—	42.15	—
15	28.24	2.35 (<i>td</i> , <i>J</i> 16, 4 Hz)	28.25	2.34 (<i>td</i> , <i>J</i> 16, 4 Hz)
16	23.39	2.15, 1.95	23.78	2.10, 1.95
17	46.99	—	47.00	—
18	41.74	3.18 (<i>dd</i> , <i>J</i> 13.7, 3.8 Hz)	41.76	3.19 (<i>dd</i> , <i>J</i> 13.7, 3.9 Hz)
19	46.19	1.24, 1.78	46.21	1.25, 1.75
20	30.76	—	30.77	—
21	33.09	1.45	33.13	1.35
22	33.98	1.30	34.00	1.30, 1.10
23	28.12	1.28	27.91	1.29
24	16.99	0.98	16.44	1.10
25	15.52	0.81	15.52	0.84
26	17.46	1.09	17.46	1.09
27	26.11	1.26	26.11	1.25
28	176.43	—	176.43	—
29	33.11	0.90	33.13	0.89
30	23.63	0.87	23.63	0.87
Glucopyranosyl at C-3			Glucopyranosyl at C-3	
1'	106.36	4.88 (<i>d</i> , <i>J</i> 7.8 Hz)	104.99	4.91 (<i>d</i> , <i>J</i> 7.7 Hz)
2'	74.40	4.03	84.02	4.17
3'	89.01	4.22	78.50	4.30
4'	69.85	4.08	71.59	4.19
5'	77.95	3.93	78.09	3.92
6'	62.49 [#]	4.30	62.81	4.36
		4.50		4.56

Table 1 (Continued)

C	1		2	
	δ_C	δ_H	δ_C	δ_H
	3- <i>O'</i> -glucopyranosyl		2- <i>O'</i> -xylopyranosyl	
1''	105.97	5.31 (<i>d</i> , <i>J</i> = 7.9 Hz)	106.98	5.28 (<i>d</i> , <i>J</i> 7.6 Hz)
2''	75.53	4.09	76.59	4.12
3''	78.27	4.03	78.24	4.11
4''	71.59	4.22	71.12	4.22
5''	78.73	4.02	67.55	3.69
				4.37
6''	62.58 [#]	4.36		
		4.55		
	Glucopyranosyl at C-28		Glucopyranosyl at C-28	
1'''	95.75	6.33 (<i>d</i> , <i>J</i> 8.1 Hz)	95.77	6.33 (<i>d</i> , <i>J</i> 8.0 Hz)
2'''	74.14	4.21	74.16	4.21
3'''	78.92	4.27	78.92	4.27
4'''	71.08	4.36	71.12	4.36
5'''	79.35	4.03	79.35	4.03
6'''	62.18	4.38	62.20	4.38
		4.46		4.46

[#] The assignments may be interchangeable.

755; ¹HNMR (500 MHz, CDCl₃): δ 0.74, 0.83, 0.89, 0.90, 0.91, 1.01, 1.12 (each 3H, *s*, seven Me), 1.99, 2.00, 2.01, 2.01, 2.02, 2.02, 2.03, 2.04, 2.07, 2.09 (each 3H, *s*, ten OAc), 2.82 (1H, *dd*, *J* 13.5, 4.2 Hz, H-18), 3.08 (1H, *dd*, *J* 11.6, 4.6 Hz, H-3), 5.32 (*t*, *J* 3.5 Hz, H-12), 4.40 (1H, *d*, *J* 7.7 Hz, H-1'), 3.76 (1H, *dd*, *J* 9.4, 7.7 Hz, H-2'), 5.13 (1H, *t*, *J* 9.6 Hz, H-3'), 4.91 (1H, *t*, *J* 9.7 Hz, H-4'), 3.64 (1H, *ddd*, *J* 9.9, 5.3, 2.6 Hz, H-5'), 4.06 (1H, *d*, *J* 12.4 Hz, H_a-6'), 4.21 (1H, *dd*, *J* 12.1, 5.3 Hz, H_b-6'), 4.61 (1H, *d*, *J* 7.6 Hz, H-1''), 4.85 (1H, *t*, *J* 8.5 Hz, H-2''), 5.09 (1H, *t*, *J* 9.2 Hz, H-3''), 4.94 (1H, *td*, *J* 9.5, 5.5 Hz, H-4''), 4.08 (2H, *m*, H-5''), 5.58 (1H, *d*, *J* 8.0 Hz, H-1'''), 5.19 (1H, *t*, *J* 8.7 Hz, H-2'''), 5.25 (1H, *t*, *J* 9.3 Hz, H-3'''), 5.15 (1H, *t*, *J* 9.7 Hz, H-4'''), 3.79 (1H, *ddd*, *J* 9.8, 4.8, 2.3 Hz, H-5'''), 4.10 (1H, *d*, *J* 11.7 Hz, H_a-6'''), 4.40 (1H, *dd*, *J* 12.4, 4.4 Hz, H_b-6'''). [*'*- inner glucose moiety; *''*- terminal xylose moiety; *'''*- glucose moiety at C-28].

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