Pergamon
0031-9422(95)00945-0
Phytochemistry, Vol. 42, No. 2, pp. 495–499, 1996

0031-9422/96 $15.00 + 0.00

TRITERPENES AND TRITERPENE GLYCOSIDES FROM *PARADRYMONIA MACROPHYLLA*

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(*Received* 16 *October* 1995)

Key Word Index—*Paradrymonia macrophylla*; Gesneriaceae; pentacylic triterpenes; triterpene glycosides; 24-epi-pinfaensic acid; 24-epi-pinfaensin; paradrymonoside.

Abstract—Seven pentacyclic triterpenes and triterpene glycosides have been isolated from the stems and roots of *Paradrymonia macrophylla* and their structures elucidated by means of ^{1}H and ^{13}C NMR spectroscopy. Three of them are described for the first time as natural products, namely: 2α,3β,19α-trihydroxy-24-oxo-urs-12-en-28-oic acid (24-epi-pinfaensic acid), 2α,3β,19α-trihydroxy-24-oxo-urs-12-en-28-oic acid ester glucoside (24-epi-pinfaensin) and 2α,3β,19α-trihydroxy-24-oxo-olean-12-en-28-oic acid ester glucoside (paradrymonoside).

INTRODUCTION

In the course of our investigations of plants from the Panamanian flora, the chemical content of *Paradrymonia macrophylla* Wiehl has been studied. *P. macrophylla* is an endemic plant of Panama [1]. The Gesneriaceae family is quite widespread in Panama, but has only been the subject of few chemical investigations. No phytochemical analysis of the genus *Paradrymonia* has been reported up to now. While different species of the Gesneriaceae are used by the Panamanian traditional healers for various indications [2], *P. macrophylla* is not known to have a specific use in traditional medicine.

Stems and roots of *P. macrophylla* were collected in the Province of Chiriqui (Panama), dried, powdered and extracted successively with dichloromethane and methanol. A series of Δ^{12}-ursene and Δ^{12}-oleanene triterpenes were isolated from the methanolic extract, and this report describes the isolation and structural elucidation of three new pentacyclic triterpenes: 24-epi-pinfaensic acid (**1**), 24-epi-penfaensin (**4**) and paradrymoniside (**6**), and four known triterpenes.

RESULTS AND DISCUSSION

The methanolic extract was separated on a silica gel column (gradient of chloroform and methanol) to give 19 fractions (I–XIX). Separation of triterpene-containing fractions by different chromatographic techniques led to the isolation of seven triterpenes (**1**–**7**). Compound **1** was obtained after further purification of fraction VI. Its EI mass spectrum displayed a molecular peak $[M]^+$ at m/z 502, which was in agreement with the cationized ion peak $[M+NH_4]^+$ at m/z 520 obtained in the CI mass spectrum. These results were consistent with the molecular formula $C_{30}H_{46}O_6$ previously established on the basis of the ^{13}C NMR and DEPT spectra. These spectra, together with the ^{1}H NMR spectrum, demonstrated the presence of six methyl groups, one aldehyde residue, one carboxylic acid unit, two hydroxyl groups attached to tertiary carbons and one hydroxyl on a quaternary carbon. These data allowed the identification of **1** as a pentacyclic triterpene of the urs-12-ene type by comparison of the ^{13}C NMR chemical shifts with those of similar compounds [3]. Distinction between an urs-12-ene moiety and the isomeric olean-12-ene system was easily made by observation of the chemical shifts recorded for carbons of the $\Delta^{12,13}$-double bond; these signals were observed at δ 127.7 (C-12) and 139.9 (C-13), while the chemical shifts of the corresponding pair of signals in an olean-12-ene derivative would be around δ 123 and 145, respectively [3]. The presence of a doublet (δ 1.12, $J = 6.4$ Hz) for the C-30 methyl group in the ^{1}H NMR spectrum was further evidence for the presence of an urs-12-ene system.

According to the molecular weight, three hydroxyl groups were present in **1**. Two of them were assigned to C-2 and C-3 by analogy with similarly substituted triterpenes [3]. The ^{1}H and ^{13}C chemical shifts at C-2 and C-3 in 2,3-hydroxylated triterpenes confirmed the 2α- and 3β-dihydroxy-configurations [3, 4]. The third hydroxyl was attributed to the 19α-position according

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to the chemical shifts of protons and carbons in 19α-hydroxy-urs-12-ene derivatives [5]. This was confirmed by EI mass spectrometry measurements showing an ion peak at m/z 264 in the spectrum as a result of the *retro*-Diels–Alder fragmentation of ring C; this peak indicated the presence of a hydroxyl group on Ring D or E. In addition, the ^{13}C NMR spectrum displayed a signal at δ 207.2 and the ^1H NMR spectrum showed a peak at δ 10.45. These data were consistent with the presence of an aldehyde group. Its position on ring A was deduced by comparison of ^{13}C NMR data for **1** with those for related triterpenes [3, 5–7]. In addition, differentiation between 23- and 24-oxygenated isomers could be made by observation of the ^{13}C chemical shifts of the β-methyl group (23-oxygenated triterpenes) and the α-methyl group (24-oxygenated triterpenes). The difference in these shifts was indeed large enough (10–15 ppm) to determine the configuration at C-4. The free carboxylic acid was attributed unequivocally to position C-28. Thus, the structure of **1** was established as 2α,3β,19α-trihydroxy-24-oxo-urs-12-en-28-oic acid, which is a new natural compound. By analogy with pinfaensic acid, the 23-oxo-isomer isolated from *Rubus pinfaensis* [7], **1** was named 24-epi-pinfaensic acid.

Compounds **4** and **6** were isolated from fraction XII. The D/CI mass spectrum of the former showed a peak at m/z 682 $[M + NH_4]^+$, corresponding to the cationized molecule, and a peak at m/z 520 $[(M - 162) + NH_4]^+$ (cationized aglycone) resulting in the loss of a hexosyl moiety. The base peak at m/z 180 $[162 + NH_4]^+$ was due to the ionized sugar unit. The ^{13}C NMR spectrum of **4** displayed the same signals as those recorded for triterpene **1**, except the peak at δ 176.8, corresponding to the carbon of the carboxylic acid, which was shifted to higher fields because of its esterification by a sugar. Moreover, the six peaks of the sugar observed in this spectrum corresponded exactly to those of an esterified β-glucosyl moiety [5, 7]. This was also demonstrated by TLC analysis of the sugar moiety after basic hydrolysis of **4** (comparison with an authentic sample of glucose). Consequently, triterpene **4** was identified as 2α,3β,19α-trihydroxy-24-oxo-urs-12-en-28-oic acid ester glucoside, a new natural compound. According to the literature [7], compound **4** was named 24-epi-pinfaensin.

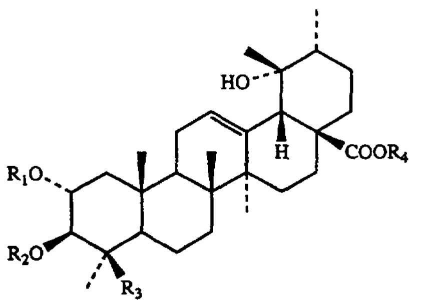
The D/CI mass spectrum of **6** exhibited the same ions as those seen for **4**, implying the presence of isomers. Their similar chromatographic behaviour observed during the isolation procedure also suggested similar structures for **4** and **6**. Analysis of the ^{13}C NMR spectrum of **6** revealed the typical features of an olean-12-ene derivative [3] with the same substituents as those present in the previously described triterpenes **1** and **4**. The differences observed in their ^{13}C NMR spectra were mainly the chemical shifts of C-12 and C-13 (double bond), which appeared at δ 123.4 and 144.4 for the olean-12-ene triterpene **6**. The signal for the C-30 methyl group appeared as a singlet in the ^1H NMR spectrum, meaning it was attached to a quaternary carbon. The presence of a hydroxyl group on a tertiary carbon (C-19 at δ 80.9 in the ^{13}C NMR spectrum) also suggested the presence of an olean-12-ene skeleton. Moreover, the proton of the 19-hydroxyl group was observed as a doublet at δ 6.07 in the ^1H NMR spectrum, confirming the observation made for similar 19-hydroxylated olean-12-ene derivatives [8]. The sugar unit linked to the carboxylic group was demonstrated to be β-glucose. Thus, the structure of **6** was elucidated as 2α,2β,19α-trihydroxy-24-oxo-urs-12-en-28-oic acid ester glucoside. The name of paradrymonoside was given to the newly described compound **6**.

Compound **2** was isolated from fraction IX and displayed a molecular ion at m/z 504 $[M]^+$ in the EI mass spectrum. In addition, its NMR data were similar to those measured for **1**, except that the aldehyde group was replaced by a hydroxyl group fixed on a secondary carbon. All measured data were in good agreement with those for 24-hydroxytormentic acid, which has already been isolated from *Desfontainia spinosa* (Loganiaceae) [6]. The more polar compound **5**, isolated from fraction XIII, was rapidly identified as the ester glucoside of **2**; this triterpene glycoside is also known from *D. spinosa* [6].

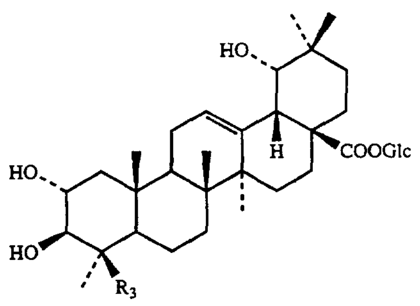
Fraction VII contained **1**, together with another constituent, but a good separation of these products was not possible. Fraction VII was then acetylated under standard conditions before separation on a silica gel open column (petrol–ethyl acetate, 1 : 1). Thus, **1a**, the diacetate of **1**, was then isolated. The second triterpene (**3**) was obtained as a diacetate (**3a**) after the acetylation, which was identified by NMR and mass spectroscopy as the diacetate of tormentic acid (**3**). Compound **3** was previously described as a constituent of *Potentilla tormentosa* [9]. The ^1H and ^{13}C NMR measurements of fraction VII before acetylation did not exhibit signals corresponding to acetyl groups. Thus, lack of acetyl groups before acetylation proved the presence of tormentic acid (**3**) in the extract of *Paradrymonia macrophylla*. It has to be noted that position C-19 in 19-hydroxy-urs-12-ene derivatives was not acetylated under standard conditions, due to steric considerations.

The seventh product isolated was obtained from the same fraction as **5** and appeared to have a similar structure. Analysis of the NMR spectra and comparison with the compounds described above allowed identification of **7** as 2α,3β,19α,24-tetrahydroxy-olean-12-en-28-oic acid ester glucoside, known as sericoside, previously isolated from *Terminaria sericea* [10].

Paradrymonia macrophylla has proved to be a species rich in triterpenes and triterpene glycosides, indicating that the Gesneriaceae family could be a potential source of saponins. This class of natural products is highly interesting with regard to its wide range of biological activities [11]. Among them, molluscicidal activity is one of the most important activities of saponins, because of its potential use for the local control of schistosomiasis, a tropical parasitic disease.



	R$_1$	R$_2$	R$_3$	R$_4$
1	H	H	CHO	H
1a	Ac	Ac	CHO	H
2	H	H	CH_2OH	H
3	H	H	CH_3	H
3a	Ac	Ac	CH_3	H
4	H	H	CHO	Glc
5	H	H	CH_2OH	Glc



	R$_3$
6	CHO
7	CH_2OH

The methanolic extract of the plant, as well as the different isolated compounds were tested for molluscicidal activity against *Biomphalaria glabrata* snails, one of the intermediate hosts of schistosomiasis [12]. None of the compounds showed toxicity to the snails, confirming the observation that monodesmosidic saponins with a sugar chain at the C-28 position are generally devoid of activity [11].

It has to be noted that the methanolic extract of *Drymonia turrialvae*, another Gesneriaceae species from Panama, showed interesting molluscicidal activity (200 mg l^{-1}) against *B. glabrata*. Work is actually underway to isolate the active principles of this plant.

EXPERIMENTAL

General. Mps: uncorr., measured on a Mettler FP 80/82 hot-stage apparatus. EI-MS and D/CI-MS (NH_3, positive ion mode) detection were performed on a quadrupole triple-stage MS instrument, TSQ 700 Finnigan MAT. ^{1}H and ^{13}C NMR spectra were measured at 200.06 and 50.03 MHz, respectively, in pyridine-d_5 with TMS as int. standard. $[\alpha]_D$ values were determined on a Perkin-Elmer 241 polarimeter.

Plant material. P. macrophylla Wiehl was collected in January 1994 at Quebrada Arena, Fortuna, Province of Chiriqui, Panama. The plant material was identified by C. Galdames and Prof. M. Correia from the Herbarium of the University of Panama, where a voucher sample of the plant is deposited.

Extraction and isolation. The powder of the dried stems and roots (1100 g) was extracted successively with CH_2Cl_2 and MeOH (3 × 2 l of each). The MeOH extract (60 g) was fractionated on two parallel silica gel Si 60 open columns (60 × 5 cm) using a step-gradient of $CHCl_3$–MeOH (49:1–3:7) and finally MeOH to give 19 frs (I–XIX). Triterpenes **1** (80 mg) and **2** (90 mg) were obtained as pure compounds from fr. VI and IX (200 mg each), respectively, by separating the frs on silica gel with $CHCl_3$–MeOH (9:1) and purifying the products on Sephadex LH 20 ($CHCl_3$–MeOH 1:1). Fr. VII (300 mg) was acetylated in 20 ml pyridine–Ac_2O (1:1) for 24 hr at room temp. and sepd on silica gel with petrol–EtOAc (1:1) to yield the diacetates **1a** (20 mg) and **3a** (18 mg). Fr. XII (1 g) was eluted on Sephadex LH 20 ($CHCl_3$–MeOH, 1:1), and fractionation of fr. XII.I (200 mg) on RP-18 with MeOH–H_2O (9:11) yielded glycosides **4** (55 mg) and **6** (25 mg). Compounds **5** (45 mg) and **7** (14 mg) were obtained from fr. XIII (500 mg) with the same chromatographic conditions as **4** and **6**, except for the MeOH–H_2O ratio which was 21:29.

2α,3β,19α-Trihydroxy-24-oxo-urs-12-en-28-oic acid (24-epi-pinfaensic acid) (**1**). Amorphous powder, mp 215–219°. $[\alpha]_D$ +24 (MeOH; c 0.2). EIMS (probe) 70 eV, m/z (rel. int.): 502 $[M]^+$ (4), 456 $[M - HCO_2H]^+$ (100), 384 (84), 264 (50), 246 (61), 201 (42), 146 (33). ^{1}H NMR: δ 10.45 (1H, *s*, H-24), 5.57 (1H, *coarse t*, H-12), 4.59 (1H, *split t*, $J = 9$ Hz, H-2β), 3.62 (1H, *d*, $J = 8.5$ Hz, H-3α), 3.03 (1H, *s*, H-18), 1.70, 1.55, 1.44, 1.03, 0.92 (3H each, *s*, Me-23, Me-25–Me-27, Me-29), 1.12 (3H, *d*, $J = 6.4$ Hz, Me-30). ^{13}C NMR: see Table 1.

2α,3β,19α-Trihydroxy-24-oxo-urs-12-en-28-oic acid diacetate (24-epi-pinfaensic acid diacetate) (**1a**). Amorphous powder, mp 177–181°. $[\alpha]_D$ +16 ($CHCl_3$, c 0.1). EIMS (probe) 70 eV, m/z (rel. int.): 586 $[M]^+$ (4), 540 $[M - HCO_2H]^+$ (100), 384 (84), 264 (50), 246 (61), 201 (42), 146 (33). ^{1}H NMR: δ 10.20 (1H, *s*, H-24), 5.57 (1H, *coarse t*, H-12), 5.88 (1H, *split t*, $J = 10.7$, 4.4 Hz, H-2β), 5.29 (1H, *d*, $J = 10.5$ Hz, H-3α), 3.05 (1H, *s*, H-18), 2.13, 2.09 (3H each, *s*, Ac-2, Ac-3), 1.74, 1.46, 1.23, 0.99, 0.91 (3H each, *s*, Me-23, Me-25–Me-27, Me-29), 1.15 (3H, *d*, $J =$ 6.3 Hz, Me-30). ^{13}C NMR: see Table 1.

2α,3β,19α,24-Tetrahydroxyurs-12-en-28-oic acid (24-hydroxytormentic acid) (**2**). Amorphous powder, mp 241–244°. $[\alpha]_D$ +18° (MeOH; c 0.22). EIMS

Table 1. ^{13}C NMR data for compounds **1**, **1a**, **3a**, **4**, **6** and **7**

C	1	1a	3a	4	6	7
1	47.1	43.5	44.2	47.2	46.8	47.5
2	68.3	69.6	70.1	68.3	68.3	68.6
3	82.1	78.6	80.8	82.2	82.1	85.7
4	54.9	54.3	39.5	55.0	55.1	43.9
5	57.2	56.7	55.0	57.3	57.3	56.6
6	19.5	19.1	18.5	19.6	19.7	19.5
7	33.2	33.1	33.1	33.2	33.0	33.5
8	40.1	40.1	40.2	40.3	40.0	40.2
9	46.4	46.2	47.4	46.5	47.1	48.5
10	38.4	38.4	38.2	38.4	38.6	38.4
11	26.2	26.7	26.3	26.0	24.7	24.5
12	127.6	127.3	127.4	128.1	123.4	123.8
13	139.9	140.0	140.0	139.3	144.4	144.3
14	42.2	42.2	42.1	42.1	42.1	42.0
15	29.1	29.1	29.1	29.0	28.8	28.9
16	26.7	26.9	26.9	26.6	27.8	27.9
17	48.1	48.2	48.2	48.5	46.4	46.4
18	54.4	54.5	54.5	54.3	44.6	44.6
19	72.5	72.6	72.6	72.5	80.9	80.9
20	42.1	42.3	42.3	42.1	35.5	35.5
21	24.7	24.4	23.9	24.4	28.7	29.0
22	38.4	38.4	38.4	37.6	33.0	33.0
23	24.5	24.6	28.5	24.4	24.6	24.6
24	207.2	203.6	16.4	207.1	207.2	65.6
25	16.7	16.7	16.7	16.6	17.3	17.2
26	17.4	16.9	17.8	17.5	17.5	17.5
27	21.5	20.9	24.6	21.9	21.9	24.1
28	180.5	180.5	180.6	176.8	177.1	177.2
29	27.0	26.9	26.9	26.3	28.7	28.7
30	17.0	16.9	17.0	17.3	24.8	24.8
OAc-2		170.3*	170.4*			
		20.5†	20.7†			
OAc-3		170.4*	170.6*			
		20.6†	20.9†			
Glc 1				95.7	95.8	95.8
2				73.9	74.1	74.1
3				79.2	79.3	79.3
4				71.1	71.0	71.0
5				78.8	78.9	78.9
6				62.2	62.1	62.1

*,†Interchangeable values in the same column.

(probe) 70 eV, *m/z* (rel. int.): 504 $[M]^+$ (4), 458 $[M-HCO_2H]^+$ (61), 386 (30), 264 (63), 246 (78), 201 (100), 146 (69). ^{1}H NMR: δ 5.57 (1H, *coarse t*, H-12), 4.46 (1H, *d*, $J=10.8$ Hz, H-24), 3.72 (1H, *d*, $J=10.7$ Hz, H-24), 4.30 (1H, *split t*, H-2β), 3.55 (1H, *d*, $J=9.2$ Hz, H-3α), 3.04 (1H, *s*, H-18), 1.71, 1.58, 1.44, 1.06, 0.99 (3H each, *s*, Me-23, Me-25–Me-27, Me-29), 1.13 (3H, *d*, $J=4.9$ Hz, Me-30). ^{13}C NMR: see ref. [6].

2α,3β,19α-Trihydroxyurs-12-en-28-oic acid diacetate (*tormentic acid diacetate*) (**3a**). Amorphous powder, mp 137–140°. $[\alpha]_D$ +6 ($CHCl_3$, *c* 0.1). EIMS (probe) 70 eV, *m/z* (rel. int.): 572 $[M]^+$ (15), 526 $[M-HCO_2H]^+$ (78), 454 (21), 264 (20), 248 (100), 201 (43), 146 (47). ^{1}H NMR: δ 5.57 (1H, *coarse t*, H-12), 5.40 (1H, *split t*, $J=10.4$, 4.2 Hz, H-2β), 5.05 (1H, *d*, $J=10.5$ Hz, H-3α), 3.05 (1H, *s*, H-18), 2.14, 2.11 (3H each, *s*, Ac-2 and Ac-3), 1.73, 1.46, 1.05, 0.98, 0.93, 0.91 (3H each, *s*, Me-23–Me-27, Me-29), 1.14 (3H, *d*, $J=6.8$ Hz, Me-30). ^{13}C NMR: see Table 1.

Glucosyl-2α,3β,19α-trihydroxy-24-oxo-urs-12-en-28-oate (*24-epi-pinfaensin*) (**4**). Amorphous powder, mp 198–202°. $[\alpha]_D$ +14 (MeOH; *c* 0.2). EIMS (probe) 70 eV, *m/z* (rel. int.): 502 $[M-Glc]^+$ (4), 456 $[M-Glc-HCO_2H]^+$ (64), 384 (66), 264 (5), 246 (61), 173 (30), 146 (100), D/CIMS (positive ion mode, NH_3), *m/z*: 682 $[M+NH_4]^+$, 520 $[M-Glc+NH_4]^+$, 180 $[Glc+NH_4]^+$. ^{1}H NMR: δ 10.47 (1H, *s*, H-24), 6.29 (1H, *d*, $J=7.8$ Hz, H-1′), 5.53 (1H, *coarse t*, H-12), 4.0–4.7 (6H, *m*, H-2β, H2′-6′), 3.63 (1H, *d*, $J=8.3$ Hz, H-3α), 2.93 (1H, *s*, H-18), 1.67, 1.55, 1.40, 1.15, 0.96 (3H each, *s*, Me-23, Me-25–Me-27, Me-29), 1.08 (3H, *d*, $J=6.4$ Hz, Me-30). ^{13}C NMR: see Table 1.

Glucosyl-2α,3β,19α,24-tetrahydroxyurs-12-en-28-oate (*24-hydroxytormentic acid ester glucoside*) (**5**).

Amorphous powder, mp 204–210°. $[\alpha]_D$ −4.5 (MeOH; *c* 0.1). EIMS (probe) 70 eV, *m/z* (rel. int.): 504 $[M]^+$ (10), 458 $[M - HCO_2H]^+$ (59), 386 (35), 264 (20), 246 (35), 201 (55), 146 (100). D/CIMS (positive ion mode, NH_3), *m/z*: 684 $[M + NH_4]^+$, 522 $[M - Glc + NH_4]^+$, 180 $[Glc + NH_4]^+$. ^1H NMR: δ 6.28 (1H, *d*, $J = 7.6$, H-1′), 5.53 (1H, *coarse t*, H-12), 3.7–4.5 (8H, *m*, H-2β, H-24, H-2′–6′), 3.55 (1H, *d*, $J = 8.8$ Hz, H-3α), 2.92 (1H, *s*, H-18), 1.66, 1.57, 1.40, 1.17, 1.04 (3H each, *s*, Me-23, Me-25–Me-27, Me-29), 1.07 (3H, *d*, $J = 6.6$ Hz, Me-30). ^{13}C NMR: see ref. [6].

Glucosyl-2α,3β,19α-trihydroxy-24-oxo-olean-12-en-28-oate (*paradrymonin*) (**6**). Amorphous powder, mp 197–200°. $[\alpha]_D$ +24 (MeOH; *c* 0.11). EIMS (probe) 70 eV, *m/z* (rel. int.): 456 $[M - Glc - HCO_2H]^+$ (22), 384 (15), 264 (64), 246 (47), 201 (100), 124 (46). D/CIMS (positive ion mode, NH_3), *m/z*: 682 $[M + NH_4]^+$, 520 $[M - Glc + NH_4]^+$, 180 $[Glc + NH_4]^+$. ^1H NMR: δ 10.48 (1H, *s*, H-24), 6.39 (1H, *d*, $J = 7.6$ Hz, H-1′), 6.07 (1H, *d*, $J = 5.7$ Hz, OH-19), 5.50 (1H, *coarse t*, H-12), 4.0–4.7 (7H, *m*, H-2β, H-3α, H2′–6′), 3.61 (1H, *d*, $J = 4.6$ Hz, H-19β), 3.55 (1H, *br d*, $J = 4.1$ Hz, H-18), 1.67, 1.55, 1.40, 1.15, 0.96 (3H each, *s*, Me-23, Me-25–Me-27, Me-29), 1.08 (3H, *d*, $J = 6.4$ Hz, Me-30). ^{13}C NMR: see Table 1.

Glucosyl-2α,3β,19α,24-tetrahydroxyolean-12-en-28-oate (*sericoside*) (**7**). Amorphous powder, mp 198–203°. $[\alpha]_D$ −4° (MeOH; *c* 0.07). EIMS (probe) 70 eV, *m/z* (rel. int.): 458 $[M - Glc - HCO_2H]^+$ (5), 386 (5), 264 (78), 246 (63), 201 (100). D/CIMS (positive ion mode, NH_3), *m/z*: 684 $[M + NH_4]^+$, 522 $[M - Glc + NH_4]^+$, 180 $[Glc + NH_4]^+$. ^1H NMR: δ 6.40 (1H, *d*, $J = 7.8$ Hz, H-1′), 6.04 (1H, *d*, $J = 6.1$ Hz, OH-19), 5.50 (1H, *coarse t*, H-12), 4.0–4.7 (8H, *m*, H-2β, H-3α, H-24, H2′–6′), 3.72 (1H, *d*, $J = 8$ Hz, H-24), 3.62 (1H, *d*, $J = 3.7$ Hz, H-19β), 3.55 (1H, *br s*, H-18), 1.67, 1.55, 1.40, 1.15, 0.96 (3H each, *s*, Me-23, Me-25–Me-27, Me-29), 1.08 (3H, *d*, $J = 6.4$ Hz, Me-30). ^{13}C NMR: see Table 1.

Acknowledgements—Financial support has been provided by the Swiss National Science Foundation. The Herbette Foundation of the University of Lausanne is gratefully acknowledged for a travel grant. Thanks are also due to the Organization of American States for the support of the project FLORPAN in Panama through its Regional Scientific and Technological Development Program.

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