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TRITERPENES FROM THE STEM BARK OF *PHYLLANTHUS FLEXUOSUS*

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Key Word Index—*Phyllanthus flexuosus*, Euphorbiaceae, stem bark, oleananes, lupanes

Abstract—Five new triterpenes were isolated together with the known triterpene diol, betulin, from the stem bark of *Phyllanthus flexuosus*. The structures were characterized as olean-12-en-3β,15α-diol, lup-20 (29)-en-3β,24-diol, olean-12-en-3β,24-diol, oleana-11:13(18)-dien-3β,24-diol and olean-12-en-3β,15α,24-triol on the basis of spectroscopic evidence.

INTRODUCTION

Recently, we reported that the bark extract of *Phyllanthus flexuosus* (Sieb. et Zucc) Muell. -Arg. contained *ent*-3β-hydroxykaur-16-ene and six triterpenes including oleana-9(11):12-dien-3β-ol and oleana-11:13(18)-dien-3β-ol besides bergenin and the mixtures of *n*-alkanes, *n*-alkanols and phytosterols [1]. The present paper reports the further isolation and characterization of five new triterpenes along with the known compound, betulin.

RESULTS AND DISCUSSION

Continuous column chromatography of the bark extract afforded, beside the known compound, betulin (**3a**), five new triterpenes. Betulin was identified by direct comparison with authentic material. We now wish to describe the structures of the five new compounds.

Compound **1a**, M^+ at *m/z* 442.3806 ($C_{30}H_{50}O_2$ requires 442.3811), displayed ^1H NMR signals (Table 1) for two axially oriented secondary carbinolic methine protons (δ 3.23 and 4.24) and one ethylenic proton. The presence of eight methyl resonances in the ^{13}C NMR spectrum (Table 2) suggested **1a** to have the olean-12-ene skeleton [2]. On acetylation it gave a diacetate (**1b**), while oxidation afforded a dione (**1c**). In the EIMS of **1a**, a fragment peak appeared at *m/z* 207.1762 $[C_{14}H_{23}O]^+$ and indicated that one of the two hydroxyl groups was at the usual C-3 (β) position, while other prominent peaks at *m/z* 234.1980 $[C_{16}H_{26}O]^+$ and 219.1746 $[C_{15}H_{23}O]^+$ suggested the second to be in either the D or E ring. That **1c** provided a base peak at *m/z* 233.1909 $[C_{16}H_{25}O]^+$ and lacked fragments at *m/z* 232 and 216 clearly indicated the presence of an oxo-function at C-15 [3, 4]. Hence, **1a** was confirmed to be olean-12-en-3β,15α-diol. Although **1a** has been prepared by sodium borohydride reduction of 15α-hydroxyolean-12-en-3-one which had once been isolated from *Castanopsis lamontii* (Fagaceae) [5], it has not formerly been reported as a natural product.

Compound **4a**, M^+ at *m/z* 442.3846 ($C_{30}H_{50}O_2$), showed ^1H NMR signals [Table 1] for five tertiary methyls, one vinylic methyl, one terminal methylene, a C-3α carbinolic methine proton and a hydroxymethyl group, suggesting it to be a lupene-type triterpene diol. On acetylation **4a** gave a diacetate (**4b**). The EIMS of **4a** and **4b** exhibited, besides fragments arising from the D/E rings at *m/z* 229, 218, 203 and 189, two prominent peaks due to A/B rings at *m/z* 223.1649 $[C_{14}H_{23}O_2]^+$ and 205.1593 $[C_{14}H_{21}O]^+$ for **4a** and *m/z* 307.1928 $[C_{18}H_{27}O_4]^+$ and 247.1740 ($C_{16}H_{23}O_2{}^+$) for **4b**, respectively. These data suggested that the hydroxymethyl group could be located at either C-23 or C-24 [3]. In contrast with the ^{13}C NMR spectrum of lup-20 (29)-en-3β,23-diol [6] which had already been found from *Glochidion macrophyllum* (Euphorbiaceae) [7] and some Sri Lankan *Glochidion* ssp of plants [8], compound **4a** exhibited signals for C-23 methyl and C-24 hydroxymethyl at δ 22.42 and 64.49 (Table 2), respectively, accompanied by an *ca* 5.6 ppm upfield shift of the C-23 methyl signal compared to that of lupeol (δ 28.0) [9]. From the foregoing evidence, **4a** was proved to be lup-20 (29)-en-3β,24-diol which has not yet been reported previously in nature.

Compound **2a**, M^+ at *m/z* 442.3816 ($C_{30}H_{50}O_2$), was also a triterpene diol and gave a diacetate (**2b**) on acetylation. The ^1H and ^{13}C NMR spectra of **2a** showed signals characteristic for olean-12-enes [Tables 1 and 2]. Furthermore, signals for one hydroxymethyl group [δ_H 3.34 (*d*) and 4.21 (*d*), δ_C 64.37 (C-24)] and a secondary carbinolic methine group [δ_H 3.44 (H-3α); δ_C 80.73 (C-3)] were in close agreement with those of both **4a** and soyasopogenol C (oleana-12:21-dien-3β,24-diol) [10, 11]. Consequently, **2a** was established as olean-12-en-3β,24-diol. This is the first report of the isolation of **2a** in nature, although it has been prepared by acidic rearrangement of (4β)-D-friedoolean-14-en-3β,24-diol (taraxer-14-en-3β,24-diol) [12].

Compound **5a**, M^+ at *m/z* 440.3663 ($C_{30}H_{48}O_2$ requires 440.3654), was a triterpene diol containing a heteroannular diene system (UV λ_{max} 243, 250, 260 nm) in the molecule. Acetylation gave a diacetate (**5b**). The ^1H and ^{13}C NMR spectra of **5b** (Tables 1 and 2) were closely similar to those for the acetate of oleana-11:13 (18)-dien-3β-ol isolated from this plant [1], except for the presence of signals for one acetoxymethyl group [δ_H 4.16 (*d*) and 4.35 (*d*); δ_C 65.28 (C-24)] instead of the absence of a methyl

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Table 1. ^{1}H NMR chemical shifts for compounds **1–6** in $CDCl_3$ solution (300 MHz)

	1a	**1b**	**1c**	**2a**	**2b**	**4a**	**4b**	**5a**	**5b**	**6a***	**6b**
Me	0.79 0.87 0.88 0.88 0.95 1.00 1.04 1.16	0.85 0.87 0.88 0.89 0.94 0.96 1.04 1.25	0.91 0.93 0.94 1.03 1.06 1.06 1.10 1.36	0.82 0.87 0.87 0.89 0.93 1.13 1.24	0.83 0.88 0.88 0.96 0.98 1.02 1.13	0.78 0.78 0.94 1.00 1.22 1.68	0.79 0.87 0.94 0.99 1.02 1.68	0.68 0.75 0.85 0.95 0.96 1.05 1.24	0.71 0.75 0.94 0.95 0.96 1.02 1.05	0.91 0.92 0.99 1.02 1.16 1.53 1.57	0.87 0.89 0.94 0.97 1.025 1.034 1.25
Ac		1.99 2.05			2.04 2.06		2.03 2.06		2.04 2.06		1.99 2.04 2.06
H-2			2.48 *ddd* $J = 15.4$ 7.0 3.9								
H-2			2.55 *ddd* $J = 15.4$ 10.7 7.0								
H-3	3.23 *dd* $J = 11.5$ 5.5	4.50 *dd* $J = 11.5$ 5.5		3.44 *dd* $J = 11.5$ 5.5	4.59 *dd* $J = 11.5$ 5.5	3.45 *dd* $J = 12$ 6	4.56 *dd* $J = 12$ 6	3.46 *dd* $J = 11.5$ 5.5	4.61 *dd* $J = 11.5$ 5.5	3.67 *dd* $J = 11.5$ 5.5	4.58 *dd* $J = 11.5$ 5.5
H-11								5.48 *dd* $J = 10.5$ 1.8	5.49 *dd* $J = 10.5$ 1.8		
H-12	5.29 *t* $J = 3.5$	5.31 *t* $J = 3.5$	5.52 *t* $J = 3.5$	5.18 *t* $J = 3.5$	5.19 *t* $J = 3.5$			6.38 *dd* $J = 10.5$ 3.3	6.40 *dd* $J = 10.5$ 3.3	5.39 *t* $J = 3.5$	5.31 *t* $J = 3.5$
H-15	4.24 *dd* $J = 11.5$ 5.5	5.41 *dd* $J = 11.5$ 5.5								4.52 *dd* $J = 11.5$ 5.5	5.41 *dd* $J = 11.5$ 5.5
H-16			2.48 *d* $J = 15.4$ 2.95 *d* $J = 15.4$								
H-24				3.34 *d* $J = 11.5$ 4.21 *d* $J = 11.5$	4.14 *d* $J = 11.5$ 4.37 *d* $J = 11.5$	3.33 *d* $J = 11.5$ 4.18 *d* $J = 11.5$	4.12 *d* $J = 11.5$ 4.34 *d* $J = 11.5$	3.35 *d* $J = 11.5$ 4.18 *d* $J = 11.5$	4.16 *d* $J = 11.5$ 4.35 *d* $J = 11.5$	3.73 *d* $J = 11.5$ 4.53 *d* $J = 11.5$	4.14 *d* $J = 11.5$ 4.34 *d* $J = 11.5$
H-29						4.65 *d* $J = 2.5$ 4.69 *d* $J = 2.5$	4.566 *d* $J = 2.5$ 4.573 *d* $J = 2.5$				

*Measured in pyridine-d_5.

signal. Therefore, compound **5a** was proved to be oleana-11:13(18)-dien-3β,24-diol. To our knowledge, it has not been described previously in the literature.

Compound **6a** showed a strong hydroxyl band in the IR spectrum (see Experimental). On acetylation, it gave a triacetate (**6b**). In the EIMS, **6a** showed significant ions [m/z 234.1951 (base peak) and 219.1724] identical with those of **1a** [3] except for the region above 400 mass units, in which peaks for m/z 458.3727 (M^+, calc for $C_{30}H_{50}O_3$: 458.3760), 440.3712 ($[M-H_2O]^+$) and 426.3509 ($[M-MeOH]^+$) have been observed. The ^{1}H and ^{13}C NMR spectra of **6b** showed signals due to seven tertiary methyls

Table 2. ^{13}C NMR chemical shifts for compounds **1–6** in $CDCl_3$ solution (75 4 MHz)

C	**1a**	**1b**	**1c**	**2a**	**2b**	**4a**	**4b**	**5b**	**6a***	**6b**
1	38 67	38 36	39 48	38.33	38 44	38 49	38.63	37.98	39 06	36.53
2	27.15	23 53	23 32	27 60	23 57	27.83	23 74	23 56	28 52	23 60
3	78 78	80 81	217 49	80.73	80.23	80.92	80 31	80 23	80.17	80.14
4	38 67	36 87	47 37	42 68	41 05	42.82	41 19	41.14	43 16	46 19
5	54 80	54 71	55 16	55 81	55 95	55 89	56 05	54 20	56 17	55 36
6	18 57	18 55	19 56	18 42	19.36	18 43	19 34	19 47	19 48	19 78
7	36 76	34 17	34 15	32 88	33 05	34 85	34 67	32 68	37 23	34 54
8	41 11	41 03	40 58	39 79	39 76	40 85	40 86	40 16	41.56	40.97
9	47 66	47 57	47 01	47 71	47 71	50 52	50 56	55.47	48 34	55 36
10	37 01	37 59	37 15	36 65	36 78	38 03	37 04	36 54	37 08	40 83
11	23 63	23 49	23 32	23 77	23 62	21.17	21 81	126 05	24.34	23 60
12	123 04	123 58	124 34	121 56	121 53	25 11	25 14	124 70	123 68	123 44
13	146.06	145.25	142 65	145 22	145 16	36 90	38 10	138 56	146 85	145 22
14	47 42	46 26	57 38	41 67	41 67	42 82	42 82	42 29	48.22	47.55
15	68 16	71 71	216 11	26 88	26 92	27 44	27 45	24.40	66 92	71 68
16	36 03	33 26	33 50	26 13	26 13	35 56	35 57	35 24	37 08	33 30
17	33 02	32 93	34 57	32 48	32 48	43 01	43 02	34 67	33 30	36.84
18	47 55	47 41	48 75	47.20	47 24	47 98	48 02	133 18	48 30	47 55
19	46 31	46 26	45 80	46.84	46 81	48 29	48 30	38.89	46.73	46 25
20	30 99	30 99	31 02	31 08	31 10	150 94	150 93	33 07	31.17	32.91
21	34 57	34 53	34 84	34 73	34 73	29 85	29 87	36 08	34 93	34 65
22	37 40	36 56	35 88	37 12	33 12	40 00	40.01	37 86	38.67	38 53
23	28 07	28 08	26.48	22 39	22 51	22.42	22 45	22 31	23.77	22 59
24	15 57†	16 66	15 36	64 37	65.47	64 49	65 39	65 28	64 66	65 59
25	15.59†	15 54	15.36	16.08	15 46	15.91	15 83	16 32	16 38	15 40
26	17 45	17 39	17 39	16 73	16 61	16 65	16 02	17.65	17 71	17 17
27	20 18	21 89	21 47	25 96	25 85	14.56	14 52	20 12	20.93	21 13
28	28 88	28 52	29 42	28 37	28 38	18.01	18 04	25 34	21 28	28 52
29	33 29	33 26	33 30	33 31	33.33	109 36	109 42	32 42	33 50	33 25
30	23 63	23 60	23 44	23 69	23.68	19 33	19 34	24 08	23 57	23 49
$MeCO_2$		21 24			21 14		21 18	21 14		21.13
		21 35			21 22		21 20	21 22		21 21
										21.89
$MeCO_2$		170 48			170 62		170 65	170 59		170 51
		171 02			171 02		171 04	171 02		170.62
										171 02

*Measured in pyridine-d_5

†Assignment may be interchangeable

and one trisubstituted ethylene bond (Tables 1 and 2). In addition, signals for one acetoxymethyl [δ_H 4.14 (*d*) and 4.34 (*d*), δ_C 65.59 (C-24)] and two acetoxymethine groups [δ_H 4.58 (*dd*) and 5 41 (*dd*), δ_C 80.14 and 71.68] have been confirmed. The former was attributed to a C-24 acetoxymethyl group by comparison with that of **4b**, and the latter two were assigned to C-3 (H_α) and C-15 (H_β), respectively, on the basis of close analogy to those in **1b**. All the above evidence plainly indicated that **6a** was olean-12-en-3β,15α,24-triol, which has not been described in the literature

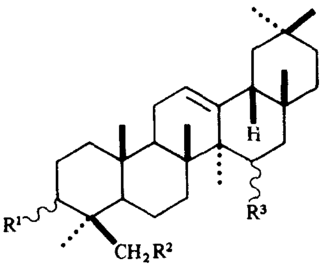
It is noteworthy that compound **6a** was the most abundant constituent among the 12 triterpenes found so far from the stem bark, though it contained considerable amounts of compounds **1a**, **3a**, lupeol and glochidone [1].

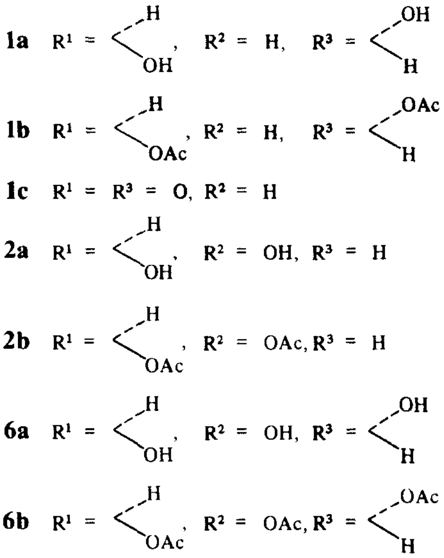
EXPERIMENTAL

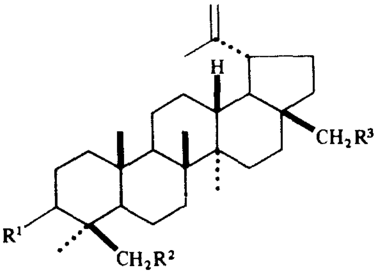
Mps uncorr, optical rotations: $CHCl_3$, unless otherwise noted, UV 95% aldehyde-free EtOH, IR KBr discs, ^1H NMR 300 MHz, $CDCl_3$, TMS as int standard, ^{13}C NMR 75 4 MHz, $CDCl_3$, TMS, probe, 70 eV, CC Kieselgel 60 (70–230 mesh, Merck), TLC silica gel 60 HF_{254} and PF_{254} (Merck)

Extraction and isolation of compounds The collection, extraction and fundamental separation of the stem bark of *P flexuosus* (3 75 kg) by CC has already been described [1] Continuous silica gel CC of the Et_2O extract (28 4 g) with C_6H_6–$CHCl_3$ (1 1), $CHCl_3$ and $CHCl_3$–EtOAc (10 1–5 1) yielded fractions 1 (684 mg), 2 (671 mg) and 3 (932 mg) Repeated CC of fraction 1 over silica gel (70 g) with C_6H_6–$CHCl_3$ (2 1–1 1) afforded **1a** (597 mg) Fraction 2 on repeated silica gel (70 g) CC furnished **2a** (145 mg), betulin (**3a**) (20 mg), **4a** (382 mg) and **5a** (11 mg) from the fractions eluted with C_6H_6–$CHCl_3$ (2 1–1 1) and $CHCl_3$, respectively Rechromatography of fraction 3 on the same adsorbent (95 g) with $CHCl_3$–EtOAc (10 1–5 1) gave **6a** (870 mg)

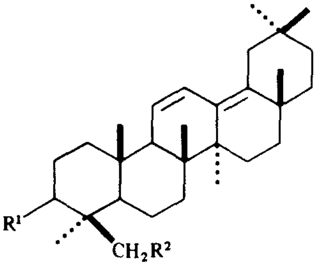
Olean-12-en-3β,15α-diol (**1a**) Colourless needles, mp 245–246 5° (MeOH–$CHCl_3$), $[\alpha]_D^{23}$ + 82 5° (*c* 1 21) (lit. [5] mp 243–246°, $[\alpha]_D$ + 84 0°), IR ν_{max} cm^{-1} 3650–3200, 1640, 1030, 1025, 825, 812, EIMS *m/z* (rel int) 442 $[M]^+$ (12), 424 (4), 409 (2),







3a R^1 = R^3 = OH, R^2 = H
3b R^1 = R^3 = OAc, R^2 = H
4a R^1 = R^2 = OH, R^3 = H
4b R^1 = R^2 = OAc, R^3 = H



5a R^1 = R^2 = OH
5b R^1 = R^2 = OAc

369 (2), 234 (100), 219 (25), 207 (22), 205 (8), 191 (17), 189 (6), 133 (10) Physical, ^{1}H NMR and EIMS data of **1a** were in good agreement with those already published

Diacetate (**1b**) Acetylation of compound **1a** (20 mg) with Ac$_2$O–pyridine (1 1 4 ml) as usual gave a solid, which was purified by prep TLC (*n*-hexane–EtOAc, 10 1) to give olean-12-en-3β,15α-yl diacetate (**1b**) (18 mg), mp 208–210° (MeOH–CHCl$_3$), $[\alpha]_D^{23}$ + 49 0° (*c* 0 64), IR ν_{max} cm^{-1} 1723, 1650, 1240, 827, 818, EIMS *m/z* (rel int) 526 [M]$^+$ (19), 481 (1), 466 (90), 451 (11), 424 (6), 406 (9), 391 (16), 369 (4), 285 (10), 276 (26), 234 (60), 219 (15), 216 (100), 204 (49), 201 (40), 189 (65)

CrO$_3$ oxidation of **1a** To a soln of **1a** (25 mg) in pyridine (3 ml) was added a soln of CrO$_3$ (20 mg) in pyridine (3 ml) containing one drop of H$_2$O at 10° under stirring and the reaction mixture was left at room temp overnight Usual work-up gave a residue, which was purified by prep TLC (*n*-hexane–EtOAc, 5:1) to give olean-12-en-3,15-dione (**1c**) (19 mg), mp 218–219° (MeOH–CHCl$_3$), IR ν_{max} cm^{-1} 1700, 1665, 1410, 822, 810, EIMS *m/z* (rel int) 438 [M]$^+$ (8), 423 (3), 299 (2), 273 (17), 271 (15), 259 (8), 245 (7), 233 (100), 217 (8), 205 (18), 191 (4), 189 (2)

Olean-12-*en*-3β,24-*diol* (**2a**) Colourless needles, mp 251–253° (MeOH–CHCl$_3$), $[\alpha]_D^{23}$ + 84 7° (*c* 0 46) (lit [12] mp 248°, $[\alpha]_D^{30}$ + 77 6°), IR ν_{max} cm^{-1}. 3600–3100, 1630, 1038, 1020, 810, EIMS *m/z* (rel int) 442 [M]$^+$ (3), 424 (2), 218 (100), 203 (56), 189 (8)

Diacetate (**2b**) Compound **2a** (25 mg) was acetylated (Ac$_2$O–pyridine, 1 1, 8 ml) as usual to give a crude product, which was purified by prep TLC (*n*-hexane–EtOAc, 10 1) to give olean-12-en-3β,24-yl diacetate (**2b**), mp 185–186 5° (MeOH–CHCl$_3$), $[\alpha]_D^{23}$ + 72 5° (*c* 0 48) (lit [12] mp 183–184°, $[\alpha]_D^{30}$ + 73.6°), IR ν_{max} cm^{-1}, 1732, 1655, 1257, 1238, 860, 810, EIMS *m/z* (rel int) 526 [M]$^+$ (16), 511 (2), 466 (19), 307 (2), 218 (100), 203 (77), 189 (17)

Betulin (**3a**) Colourless needles, mp 255–256° (MeOH–CHCl$_3$), $[\alpha]_D^{23}$ + 20 1° (pyridine, *c* 0 58) (lit [13] mp 261°, $[\alpha]_D$ + 20 (pyridine)), Diacetate (**3b**), mp 224–225° (lit [13] mp 223–224°, $[\alpha]_D$ + 22), EIMS *m/z* 526 [M]$^+$ Betulin was identified by direct comparison (mmp, IR, ^{1}H NMR, EIMS) with authentic sample

Lup-20 (29)-*en*-3β,24-*diol* (**4a**) Colourless needles, mp 249–250° (MeOH–CHCl$_3$), $[\alpha]_D^{23}$ + 40 5° (*c* 0 58), IR ν_{max} cm^{-1} 3650–3100, 3060, 1635, 1040, 1010, 873, EIMS *m/z* (rel int) 442 [M]$^+$ (44), 427 (7), 424 (12), 229 (13), 218 (45), 205 (38), 203 (47), 189 (35), 81 (100)

Diacetate (**4b**) Compound **4a** (22 mg) was acetylated as usual and the resulting residue was purified by prep TLC (*n*-hexane–EtOAc, 10 1) to give lup-20 (29)-en-3β,24-yl diacetate (**4b**) (20 mg) as colourless needles, mp 200–201° (MeOH–CHCl$_3$), $[\alpha]_D^{23}$ + 29 7 , IR ν_{max} cm^{-1} 3070, 1738, 1728, 1642, 1270, 1242, 880, EIMS *m/z* (rel int) 526 [M]$^+$ (42), 511 (10), 466 (4), 416 (8), 307 (11), 247 (18), 229 (12), 218 (53) 205 (42), 203 (47), 189 (74), 109 (100)

Oleana-11 13 (18)-*dien*-3β,24-*diol* (**5a**) Colourless needles, mp 302–305° (MeOH–CHCl$_3$), UV λ_{max} nm (ε) 243, 250 5, 259 5 (26600, 29900, 19000) [heteroannular diene], IR ν_{max} cm^{-1}

3600–3100, 3030, 1608, 1052, 1038, 989, EIMS. *m/z* (rel. int) 440 $[M]^+$ (100), 425 (12), 422 (7), 255 (12), 229 (19), 215 (23), 203 (19), 189 (18)

Diacetate (**5b**). Compound **5a** (10 mg) was dissolved in Ac_2O–pyridine (1 1, 4 ml) and the mixture was allowed to stand at room temp. for 12 hr Work-up as usual afforded a product, which was purified by prep TLC (*n*-hexane–EtOAc, 10 · 1) to give oleana-11 · 13(18)-dien-3β,24-yl diacetate (**5b**), mp 238–239°, $[\alpha]_D^{23}$ −42 3° (*c* 0 38); IR ν_{max} cm^{-1} 3020, 1720, 1640, 1630, 1255, 1230, 980, 898, EIMS *m/z* (rel int) 524 $[M]^+$ (100), 509 (34), 464 (5), 449 (3), 255 (28), 229 (57), 215 (59), 203 (70), 189 (35), 187 (33)

Olean-12-en-3β,15α,24-triol (**6a**) Colourless needles, mp 251–253°, $[\alpha]_D^{23}$ + 59.9° (pyridine, *c* 0 58), IR ν_{max} cm^{-1} 3600–3100, 1660, 1040, 1020–985, 830, 816, EIMS. *m/z* (rel int) 458 $[M]^+$ (14), 440 (7), 426 (12), 422 (2), 270 (9), 255 (6), 234 (100), 223 (37), 219 (46), 207 (56), 189 (16), 187 (15), 175 (58)

Triacetate (**6b**) Compound **6a** (25 mg) was acetylated (Ac_2O–pyridine, 1 · 1, 8 ml) as usual and the resulting crude material was purified by prep. TLC (*n*-hexane–EtOAc, 5 1) to give olean-12-en-3β,15α,24-yl triacetate (**6b**) as colourless needles, mp 169 5–171° (MeOH–$CHCl_3$), $[\alpha]_D^{23}$ + 52 7° (*c* 0 62), IR ν_{max} cm^{-1} 3050, 1743, 1730, 1715, 1640, 1255–1210, 840, 810, EIMS· *m/z* (rel int) 584 $[M]^+$ (3), 524 (94), 509 (2), 482 (2), 464 (18), 449 (2), 422 (4), 405 (3), 307 (5), 276 (25), 270 (6), 247 (22), 234 (40), 216 (100), 204 (43), 201 (23), 187 (38)

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