Phytochemistry, Vol. 26, No. 2, pp. 497–501, 1987.
Printed in Great Britain.

0031–9422/87 $3.00 + 0.00
Pergamon Journals Ltd.

URSANE AND OLEANANE TRITERPENOIDS FROM *SALVIA ARGENTEA*

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(*Received* 12 *June* 1986)

Key Word Index—*Salvia argentea*; Labiatae; triterpenes; ursane and oleanane derivatives.

Abstract—From the aerial parts of *Salvia argentea* four new ursene and two new oleanene triterpenoids have been isolated, together with the already known ursolic and oleanolic acids. The structures of the new substances were established by chemical and spectroscopic means.

INTRODUCTION

In continuation of our studies on the terpenoid compounds from *Salvia* spp. [1–3], we have now investigated the aerial parts of *S. argentea* L., a species from the root of which several new abietane diterpenoids have been isolated [4]. From the aerial parts of this plant eight triterpenoid compounds have been isolated, two of which are the previously known ursolic and oleanolic acids, and the other six are new substances, whose structures are established as 3β-acetoxy-urs-12-ene-2α, 11α-diol (**1**), 3β-acetoxy-urs-12-ene-1β,2α,11α-triol (**4**), 3β-acetoxy-urs-12-ene-2α,11α,20β-triol (**11**), 3β-acetoxy-urs-12-ene-1β,2α,11α,20β-tetraol (**9**), 3β-acetoxy-olean-12-ene-2α,11α-diol (**3**) and 3β-acetoxy-olean-12-ene-1β,2α,11α-triol (**7**).

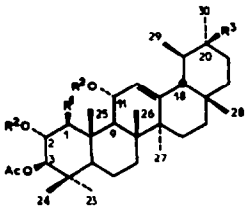
RESULTS AND DISCUSSION

The first of the new triterpenoids (**1**) had a molecular formula $C_{32}H_{52}O_4$ and its ^{1}H NMR spectrum (Table 1) showed signals for two secondary methyl groups, six C-Me singlets, an equatorial acetoxyl group (δ2.08, 3H, *s*; δ4.52, 1H, *d*, $J_{aa'}$ = 10.0 Hz) placed between a tetrasubstituted sp^3 carbon atom and an equatorial hydroxymethine grouping (δ3.81, 1H, *td*, $J_{aa'} = J_{aa''}$ = 10.0 Hz, $J_{ae''}$ = 4.3 Hz), and another hydroxymethine group (δ4.28, 1H, *dd*, J_1 = 9.2 Hz, J_2 = 3.3 Hz) which must also be equatorial and placed between a trisubstituted double bond (olefinic proton at δ5.19, *d*, J = 3.3 Hz) and a methine group.

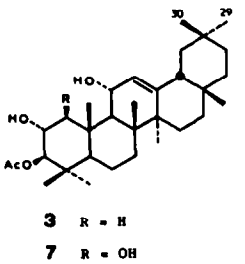
All the above data can be accommodated only on an urs-12-ene triterpenoid structure for compound **1** with an acetoxyl group at the C-3β position and two secondary (and equatorial) hydroxyl groups, one of which must be placed at the C-2α position, while the other may be attached to the C-11α position. In accord with this conclusion, the ^{1}H NMR spectrum of **1** (Table 1) showed a clear one-proton double doublet at δ2.74 (J_{gem} = 12.8 Hz, $J_{ea'}$ = 4.3 Hz) that must be attributed to the equatorial C-1β proton in a C-11α equatorially hydroxylated triterpene structure [1, 5]. Moreover, double resonance experiments confirmed all the above assignments.

Acetic anhydride–pyridine treatment of compound **1** yielded a triacetate (**2**, δ2.05, 3H, *s*, 1.96, 3H, *s* and 1.93, 3H, *s*) the ^{1}H NMR spectrum of which showed a strong paramagnetic shift of the signals of the H-2β ($\Delta\delta$ + 1.25) and H-11β ($\Delta\delta$ + 1.17) protons, whereas the H-3α proton was only slightly shifted ($\Delta\delta$ + 0.21, Table 1). This result confirmed the attachment of the acetoxyl group of **1** at its C-3β position. Thus, the new triterpenoid is 3β-acetoxy-urs-12-ene-2α,11α-diol (**1**). This structure was also supported by additional data obtained for compound **5** (see below).

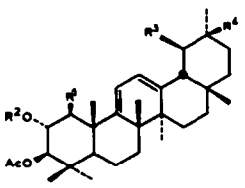
The triterpenoid **3** had the same molecular formula ($C_{32}H_{52}O_4$) as compound **1**, and their ^{1}H NMR spectra (Table 1) were identical, except for the presence in **3** of eight C-Me singlets instead of the two secondary methyl groups and the six C-Me singlets of compound **1**. This substance must therefore have the structure of 3β-acetoxy-olean-12-ene-2α,11α-diol (**3**). This conclusion was also in agreement with the ^{13}C NMR data of the closely related triterpene derivative **8** (see below).



	R^1	R^2	R^3
1	H	H	H
2	H	Ac	H
4	OH	H	H
5	OH	Ac	H
9	OH	H	OH
10	OH	Ac	OH
11	H	H	OH
12	H	Ac	OH



3 R = H
7 R = OH



	R^1	R^2	R^3	R^4
6	OH	Ac	Me	H
8	OH	H	H	Me
13	H	Ac	Me	OH

Table 1. ^{1}H NMR data of compounds 1–13 ($CDCl_3$, TMS as internal standard)

	1*	2*	3*	4*	5†	6*	7*	8†	9*	10*	11*	12*	13†
H-1α	‡	‡	‡	3.34 *d*	3.57 *d*	3.82 *d*	3.34 *d*	3.60 *d*	3.34 *d*	3.55 *d*	‡	‡	‡
H-1β	2.74 *dd*	‡	2.59 *dd*	—	—	—	—	—	—	—	2.74 *dd*	‡	2.40 *dd*
H-2β	3.81 *td*	5.06 *ddd*	3.80 *td*	3.70 *dd*	5.04 *dd*	5.12 *dd*	3.69 *dd*	4.60‡	3.68 *dd*	5.03 *dd*	3.80 *ddd*	5.08 *ddd*	5.20 *ddd*
H-3α	4.52 *d*	4.73 *d*	4.52 *d*	4.67 *d*	4.75 *d*	4.79 *d*	4.67 *d*	4.60 ‡	4.66 *d*	4.74 *d*	4.52 *d*	4.73 *d*	4.76 *d*
H-11β	4.28 *dd*	5.45 *dd*	4.22 *dd*	4.34 *dd*	5.42‡	6.59 *d*§	4.31 *dd*	6.68 *d*§	4.33 *dd*	5.41‡	4.27 *dd*	5.45 *dd*	5.63 *d*§‖
H-12	5.19 *d*	5.16 *d*	5.24 *d*	5.24 *d*	5.42‡	5.47 *d*	5.28 *d*	5.54 *d*	5.26 *d*	5.41 ‡	5.22 *d*	5.20 *d*	5.49 *d*‖
CH(Me)	0.86 *d*	0.78 *d*	—	0.87 *d*	‡	0.80 *d*	—	—	0.92 *d*	0.82 *d*	0.91 *d*	0.83 *d*	0.84 *d*
	0.91 *d*	0.91 *d*	—	0.92 *d*	‡	0.91 *d*	—	—	—	—	—	—	—
C(Me)	1.17 *s*	1.19 *s*	1.22 *s*	1.16 *s*	1.25 *s*	1.38 *s*	1.22 *s*	1.30 *s*	1.23 *s*	1.20 *s*	1.22 *s*	1.21 *s*	1.35 *s*
	1.16 *s*	1.18 *s*	1.14 *s*	1.15 *s*	1.18 *s*	1.17 *s*	1.13 *s*	1.13 *s*	1.16 *s*	1.18 *s*	1.17 *s*	1.19 *s*	1.21 *s*
	1.06 *s*	1.08 *s*	1.00 *s*	1.03 *s*	1.03 *s*	0.96 *s*	0.99 *s*	1.00 *s*	1.15 *s*	1.17 *s*	1.15 *s*	1.18 *s*	1.17 *s*
	0.91 *s*	0.92 *s*	0.91 *s*	0.91 *s*	0.90 *s*	0.90 *s*	0.91 *s*	0.91 *s*	1.03 *s*	1.03 *s*	1.05 *s*	1.08 *s*	0.93 *s*
	0.90 *s*	0.91 *s*	0.90 *s*	0.89 *s*	0.87 *s*	0.90 *s*	0.89 *s*	0.91 *s*	0.91 *s*	0.92 *s*	0.90 *s*	0.93 *s*	0.93 *s*
	0.79 *s*	0.78 *s*	0.89 *s*	0.80 *s*	0.79 *s*	0.85 *s*	0.89 *s*	0.91 *s*	0.89 *s*	0.89 *s*	0.89 *s*	0.91 *s*	0.87 *s*
	—	—	0.88 *s*	—	—	—	0.89 *s*	0.87 *s*	0.84 *s*	0.83 *s*	0.83 *s*	0.82 *s*	0.87 *s*
	—	—	0.83 *s*	—	—	—	0.84 *s*	0.87 *s*	—	—	—	—	—
OAc	2.08 *s*	2.05 *s*	2.11 *s*	2.11 *s*	2.03 *s*	2.07 *s*	2.14 *s*	2.12 *s*	2.12 *s*	2.03 *s*	2.10 *s*	2.03 *s*	2.05 *s*
	—	1.96 *s*	—	—	2.01 *s*	2.06 *s*	—	—	—	2.01 *s*	—	1.95 *s*	2.00 *s*
	—	1.93 *s*	—	—	1.90 *s*	—	—	—	—	1.90 *s*	—	1.91 *s*	—
J (Hz)													
1α,1β	12.8	‡	13.2	—	—	—	—	—	—	—	13.3	‡	13.0
1α,2β	10.0	10.0	10.0	9.2	9.2	9.4	9.1	9.0	9.1	9.5	9.8	9.6	9.8
1β,2β	4.3	4.7	4.4	—	—	—	—	—	—	—	4.5	4.6	4.6
2β,3α	10.0	10.3	10.0	10.3	10.6	10.6	10.4	‡	10.6	10.5	10.2	10.4	10.8
11β,9α	9.2	9.0	8.5	8.1	‡	—	8.0	—	8.2	‡	9.0	8.9	—
11β,12	3.3	3.4	3.6	3.6	‡	6.0§	4.0	6.0§	3.5	‡	3.1	3.3	6.0§
CH(Me)	6.0	6.0		6.0	‡	6.4	—	—	6.4	6.4	6.4	6.4	6.4
	6.6	6.6	—	6.8	‡	6.6	—	—	—	—	—	—	—

*At 300 MHz.
†At 90 MHz.
‡Overlapped signal.
§Olefinic C-11 proton.
‖These assignments may be reversed.

A C-1β hydroxy derivative of the triterpene **1** was also present in *S. argentea*. The ^{1}H NMR spectrum of this compound (**4**, Table 1) was almost identical to the spectrum of **1**, except for the absence of the H-1β proton signal, the presence of a one-proton doublet at δ3.34 (J = 9.2 Hz, H-1α) and the multiplicity of the H-2β proton, which appeared as a double doublet in **4** instead of the triplet of doublets as in **1** (Table 1).

Treatment of compound **4** with acetic anhydride–pyridine at room temperature gave a triacetate (**5**, $C_{36}H_{56}O_7$, δ2.03, 3H, *s*, 2.01, 3H, *s* and 1.90, 3H, *s*), in which the 1β-hydroxyl group was not esterified ($\delta_{H\text{-}1\alpha}$ 3.57, see Table 1) probably owing to the C-1–C-11 substituent interactions. The ^{13}C NMR spectrum of this derivative (**5**, Table 2) showed carbon atom resonances in complete agreement with a 2α,3β,11α-triacetoxy-urs-12-en-1β-ol structure (**5**) [6, 7].

Furthermore, when a solution of compound **5** in spectroscopic deuteriochloroform was allowed to stand at room temperature for 48 hr, a quantitative transformation of **5** into the 9(11),12-diene derivative **6** [$C_{34}H_{52}O_5$, λ_{max} 281 nm (log ε 3.98); $\delta_{H\text{-}11}$ 6.59 *d*, J = 6.0 Hz, $\delta_{H\text{-}12}$ 5.47 *d*, J = 6.0 Hz] occurred. The elimination of the allylic C-11α acetoxyl group of compound **5** must be caused by the presence of acid impurities in the solvent.

Table 2. ^{13}C NMR chemical shifts of compounds **5**, **8**, **10** and **12** ($CDCl_3$, TMS as internal standard)

C	5	8	10	12
1	77.4 *d**	80.9 *d*†	77.5 *d*	45.0 *t*
2	74.3 *d*	72.6 *d*	74.3 *d*	69.7 *d*
3	80.1 *d*	80.8 *d*†	80.1 *d*	80.3 *d*
4	38.7 *s*	38.7 *s*	38.7 *s*	38.7 *s*†
5	54.0 *d*	45.5 *d*	54.0 *d*	54.6 *d*
6	18.0 *t*	18.1 *t*	18.0 *t*	18.1 *t*
7	32.0 *t*	31.4 *t*	32.6 *t*	33.0 *t*
8	41.6 *s*	40.8 *s*	41.6 *s*	42.0 *s*
9	51.7 *d*	151.2 *s*	51.9 *d*†	52.4 *d*‡
10	43.7 *s*	42.8 *s*‡	43.7 *s*	39.2 *s*†
11	71.0 *d*	118.9 *d*	70.9 *d*	71.0 *d*
12	123.3 *d*	121.2 *d*	123.7 *d*	123.8 *d*
13	145.1 *s*	147.4 *s*	144.6 *s*	144.7 *s*
14	43.4 *s*	44.6 *s*‡	43.4 *s*	43.1 *s*
15	27.8 *t*	27.2 *t*§	27.2 *t*	27.1 *t*
16	27.1 *t*	25.7 *t*§	26.9 *t*	26.6 *t*
17	33.1 *s*	32.1 *s*	31.9 *s*	32.9 *s*
18	57.3 *d*	48.8 *d*	51.7 *d*†	51.6 *d*‡
19	39.3 *d*†	46.7 *t*	40.5 *d*	40.1 *d*
20	39.7 *d*†	31.1 *s*	71.3 *s*	71.2 *s*
21	31.1 *t*	34.6 *t*	35.8 *t*‡	35.8 *t*‖
22	41.2 *t*	37.0 *t*	35.4 *t*‡	35.5 *t*‖
23	28.0 *q*	28.3 *q*	28.0 *q*	28.3 *q*
24	16.8 *q*	17.2 *q*	16.8 *q*	17.5 *q*
25	15.4 *q*	20.0 *q*‖	15.4 *q*	18.0 *q*§
26	18.3 *q*	20.3 *q*‖	18.3 *q*	18.1 *q*§
27	22.2 *q*	21.7 *q*‖	22.1 *q*	22.3 *q*
28	28.7 *q*	28.7 *q*	28.3 *q*	28.4 *q*
29	16.8 *q*	33.2 *q*	12.1 *q*	12.2 *q*
30	21.4 *q*‡	23.7 *q*	30.1 *q*	30.1 *q*
OAc	172.0 *s*	172.5 *s*	172.0 *s*	170.9 *s*
	171.6 *s*	—	171.5 *s*	170.7 *s*
	170.6 *s*	—	170.6 *s*	170.2 *s*
	21.3 *q*‡	21.1 *q*‖	21.3 *q*	21.4 *q*
	20.9 *q*	—	20.9 *q*	21.0 *q*
	20.8 *q*	—	20.8 *q*	20.9 *q*

*SFORD multiplicity.

†,‡,‖,§Assignments bearing the same sign may be interchanged.

An olean-12-ene derivative with the same oxidation pattern as that of the urs-12-ene **4** was also found in the acetone extract of *S. argentea*. This compound (**7**, $C_{32}H_{52}O_5$) showed eight C-Me singlets in its ^{1}H NMR spectrum (Table 1) instead of the two secondary methyl groups and the six C-Me singlets of compound **4**, the rest of the ^{1}H NMR spectra of both triterpenoids (**4** and **7**) being identical.

As in the case of the derivative **5**, compound **7** was transformed into the diene **8** ($C_{32}H_{50}O_4$), when its solution in spectroscopic deuteriochloroform was allowed to stand for 48 hr at room temperature. Moreover, the ^{13}C NMR spectrum of **8** (Table 2) was in complete agreement with the proposed structure [6, 7]. Thus, it is clear that this triterpenoid is the olean-12-ene derivative depicted in formula **7**.

Another of the new triterpenoids isolated from *S. argentea* (**9**) had a molecular formula $C_{32}H_{52}O_6$ and its ^{1}H NMR spectrum (Table 1) showed signals for a 3β-acetoxyl group, three equatorial secondary hydroxyl functions at the 1β, 2α and 11α positions, and a C-12 olefinic proton, all identical with those found in compounds **4** and **7**. In addition, triterpenoid **9** possessed a secondary methyl group (δ0.92, 3H, *d*, J = 6.4 Hz) and seven methyl groups attached to fully substituted sp^3 carbon atoms (see Table 1). These data suggested that **9** was a 3β-acetoxy-urs-12-ene-1β,2α11α-triol with an additional tertiary alcohol at the C-19 or C-20 position.

Treatment of compound **9** with acetic anhydride–pyridine at room temperature yielded a triacetate (**10**, $C_{36}H_{56}O_8$), in which the 1β-hydroxyl group and the tertiary one were not esterified (see Tables 1 and 2). A comparison of the ^{13}C NMR spectra of compounds **5** and **10** (Table 2) established that the tertiary hydroxyl group of the latter must be placed at the C-20 position. This was in agreement with the paramagnetic shifts observed on the C-19, C-21 and C-30 carbon atoms and with the shielding effects on the C-18, C-22 and C-29 carbons (see Table 2) [7, 8].

The 20β configuration of the hydroxyl group was supported by the fact that, in this configuration, the calculated values [9] for the chemical shifts of the C-18, C-22 and C-29 carbon atoms (δ49.3, 33.7 and 13.0, respectively) were close to the experimental ones (Table 2) and very different from those calculated [9] for the 20α-hydroxy epimer (δ45.8, 31.2 and 10.5, respectively).

The last triterpenoid (**11**) isolated from *S. argentea* had a molecular formula $C_{32}H_{52}O_5$. It was transformed into a triacetate (**12**, $C_{36}H_{56}O_7$) by acetic anhydride–pyridine treatment under mild conditions, which gave a 9(11),12-diene derivative (**13**, $C_{34}H_{52}O_5$) in acidic chloroform solution. A comparison of the ^{1}H NMR data of compounds **11** and **12** with those of **9** and **10**, respectively (Table 1), and of the ^{13}C NMR data of **12** and **10** (Table 2), clearly established that this new substance (**11**) differed from the triterpenoid **9** only in the absence of the 1β-hydroxyl group.

From a biogenetic point of view, it is important to note that, apart from the C-3β hydroxyl (or acetoxyl) group, oxidation at the C-1 and/or C-2 and/or C-11 positions is a

common feature in the ursane, oleanane and lupane triterpenoids isolated from plants belonging to the *Salvia* genus [1, 10–12].

EXPERIMENTAL

Mps are uncorr. For general details on methods, see refs [1–4]. Plant materials were collected in June 1984, in the Botanic Garden of Palermo (Italy) and voucher specimens were deposited in the Herbarium of this centre.

Extraction and isolation of the triterpenoids. Dried and finely powdered *S. argentea* aerial parts (250 g) were extracted with Me_2CO (2 l.) at room temp. for a week. The extract was evaporated to dryness yielding a residue (17 g) which was carefully chromatographed on a silica gel (Merck, No. 7734, deactivated with 15% H_2O, 200 g) column. Elution with *n*-hexane–EtOAc mixtures and EtOAc gave the following compounds in order of elution: oleanolic acid (7 mg), ursolic acid (40 mg), 3β-acetoxy-olean-12-ene-1β,2α,11α-triol (7, 40 mg), 3β-acetoxy-urs-12-ene-1β,2α,11α-triol (**4**, 130 mg), 3β-acetoxy-olean-12-ene-2α,11α-diol (**3**, 30 mg), 3β-acetoxy-urs-12-ene-2α,11α-diol (**1**, 20 mg), 3β-acetoxy-urs-12-ene-1β,2α,11α,20β-tetraol (**9**, 150 mg) and 3β-acetoxy-2α,11α,20β-triol (**11**, 80 mg). The previously known compounds (ursolic and oleanolic acids) were identified by the physical (mp, $[\alpha]_D$) and spectroscopic (^{1}H NMR, MS) data of their methyl ester derivatives and by comparison (mmp, TLC) with authentic samples.

3β-Acetoxy-urs-12-ene-2α,11α-diol (**1**). Mp 205–208° (EtOAc–*n*-hexane); $[\alpha]_D^{18}$ +20.3° ($CHCl_3$; *c* 0.118); ^{1}H NMR (300 MHz, $CDCl_3$): see Table 1; EIMS (70 eV, direct inlet) *m/z* (rel. int.): 500 $[M]^+$ (4), 482 (31), 440 (28), 422 (9), 389 (3), 356 (2), 329 (3), 255 (11), 235 (13), 234 (58), 191 (22), 123 (32), 107 (29), 95 (52), 81 (31), 69 (47), 55 (48), 43 (100). (Found: C, 76.49; H, 10.56. $C_{32}H_{52}O_4$ requires: C, 76.75; H, 10.47%.)

2α,3β,11α-Triacetoxy-urs-12-ene (**2**). Treatment of compound **1** (2 mg) with Ac_2O–C_5H_5N in the usual manner gave the derivative **2** (2 mg): ^{1}H NMR (300 MHz, $CDCl_3$): see Table 1.

3β-Acetoxy-olean-12-ene-2α,11α-diol (**3**). Mp 243–246° (EtOAc–*n*-hexane); $[\alpha]_D^{20}$ +40.0° ($CHCl_3$; *c* 0.162); IR ν_{max}^{KBr} cm^{-1}: 3500, 3430, 3010, 2950, 2860, 1720, 1470, 1380, 1270, 1060, 1050, 915; ^{1}H NMR (300 MHz, $CDCl_3$): see Table 1; EIMS (70 eV, direct inlet) *m/z* (rel. int.): 500 $[M]^+$ (3), 482 (30), 440 (30), 422 (11), 389 (2), 329 (3), 255 (14), 235 (16), 234 (62), 191 (25), 123 (36), 107 (32), 95 (27), 81 (42), 69 (40), 55 (38), 43 (100). (Found: C, 76.84; H, 10.38. $C_{32}H_{52}O_4$ requires: C, 76.75; H, 10.47%.)

3β-Acetoxy-urs-12-ene-1β,2α,11α-triol (**4**). An amorphous powder; $[\alpha]_D^{20}$ +33.9° ($CHCl_3$; *c* 0.106); ^{1}H NMR (300 MHz, $CDCl_3$): see Table 1; EIMS (70 eV, direct inlet) *m/z* (rel. int.): 516 $[M]^+$ (8), 498 (28), 456 (4), 441 (7), 423 (6), 255 (10), 234 (12), 191 (18), 147 (11), 135 (18), 123 (21), 121 (22), 119 (21), 109 (25), 107 (23), 95 (41), 81 (25), 69 (37), 55 (41), 43 (100). (Found: C, 74.26; H, 10.21. $C_{32}H_{52}O_5$ requires: C, 74.37; H, 10.14%.)

2α,3β,11α-Triacetoxy-urs-12-en-1β-ol (**5**). Treatment of **4** (30 mg) with Ac_2O–C_5H_5N for 24 hr at room temp. yielded **5** (32 mg), a thick oil; ^{1}H NMR (90 MHz, $CDCl_3$): see Table 1; ^{13}C NMR (75.4 MHz, $CDCl_3$): see Table 2; EIMS (70 eV, direct inlet) *m/z* (rel. int.): 600 $[M]^+$ (0.3), 540 (48), 480 (1), 405 (7), 387 (9), 324 (3), 309 (3), 255 (12), 171 (10), 133 (10), 119 (13), 109 (13), 95 (20), 85 (11), 81 (13), 69 (22), 55 (20), 43 (100). $C_{36}H_{56}O_7$: *M*, 600.

2α,3β-Diacetoxy-ursa-9(11),12-dien-1β-ol (**6**). A soln of **5** (30 mg) in spectroscopic $CDCl_3$ was allowed to stand at room temp. for 48 hr yielding quantitatively the diene **6**: an amorphous solid; $[\alpha]_D^{20}$ +164.8° ($CHCl_3$; *c* 0.071); IR ν_{max}^{KBr} cm^{-1}: 3480, 3040, 2980, 2920, 2870, 1750, 1730, 1680, 1460, 1380, 1365, 1250, 1225, 1030, 990, 960, 840; UV λ_{max}^{EtOH} nm (log ε): 281 (3.98); ^{1}H NMR (300 MHz, $CDCl_3$): see Table 1. (Found: C, 75.69; H, 9.81. $C_{34}H_{52}O_5$ requires: C, 75.51; H, 9.69%.)

3β-Acetoxy-olean-12-ene-1β,2α,11α-triol (**7**). Mp 236–238° (EtOAc–*n*-hexane); $[\alpha]_D^{20}$ +39.3° ($CHCl_3$; *c* 0.178); IR ν_{max}^{KBr} cm^{-1}: 3605, 3300 (*br*), 2950, 2860, 1740, 1460, 1400, 1365, 1240, 1120, 1040, 1020, 1010, 970, 900; ^{1}H NMR (300 MHz, $CDCl_3$): see Table 1; EIMS (70 eV, direct inlet) *m/z* (rel. int.): 516 $[M]^+$ (22), 498 (41), 423 (12), 345 (8), 255 (13), 234 (7), 233 (11), 191 (32), 173 (11), 137 (14), 135 (21), 119 (23), 109 (33), 95 (52), 83 (24), 81 (30), 69 (55), 55 (47), 43 (100). (Found: C, 74.46; H, 10.23. $C_{32}H_{52}O_5$ requires: C, 74.37; H, 10.14%.)

3β-Acetoxy-oleana-9(11),12-diene-1β,2α-diol (**8**). A soln of **7** in spectroscopic $CDCl_3$ was allowed to stand at room temp. for 48 hr to give the diene **8** in quantitative yield: mp 117–119° (MeOH); $[\alpha]_D^{20}$ +244.9° ($CHCl_3$; *c* 0.109); IR ν_{max}^{KBr} cm^{-1}: 3450 (*br*), 2950, 2880, 1740, 1640, 1460, 1380, 1250, 1030, 1010, 990, 840; UV λ_{max}^{EtOH} nm (log ε): 280 (3.95); ^{1}H NMR (90 MHz, $CDCl_3$): see Table 1; ^{13}C NMR (75.4 MHz, $CDCl_3$): see Table 2; EIMS (70 eV, direct inlet) *m/z* (rel. int.): 498 $[M]^+$ (100), 483 (4), 480 (0.2), 438 (2), 423 (4), 345 (20), 255 (27), 233 (6), 171 (16), 159 (10), 145 (12), 133 (14), 119 (19), 109 (22), 95 (33), 85 (26), 69 (44), 55 (36), 43 (80). (Found: C, 76.89; H, 10.21. $C_{32}H_{50}O_4$ requires: C, 77.06; H, 10.11%.)

3β-Acetoxy-urs-12-ene-1β,2α,11α,20β-tetraol (**9**). Mp 112–114° (EtOAc–*n*-hexane); $[\alpha]_D^{20}$ +33.1° ($CHCl_3$; *c* 0.136); ^{1}H NMR (300 MHz, $CDCl_3$): see Table 1; EIMS (70 eV, direct inlet) *m/z* (rel. int.): 532 $[M]^+$ (1.5), 514 (31), 496 (17), 421 (6), 404 (4), 345 (6), 271 (15), 201 (6), 171 (12), 145 (12), 133 (12), 119 (14), 95 (17), 85 (19), 71 (19), 69 (14), 55 (24), 43 (100). (Found: C, 71.99; H, 9.69. $C_{32}H_{52}O_6$ requires: C, 72.14; H, 9.84%.)

2α,3β,11α-Triacetoxy-urs-12-ene-1β,20β-diol (**10**). Treatment of **9** (50 mg) with Ac_2O–C_5H_5N for 24 hr at room temp. yielded **10** (55 mg): mp 135–136° (EtOAc–*n*-hexane); $[\alpha]_D^{20}$ −42.0° ($CHCl_3$; *c* 0.252); IR ν_{max}^{KBr} cm^{-1}: 3515, 3490, 2940, 2860, 1740 (*br*), 1460, 1370, 1250 (*br*), 1025, 960, 910; ^{1}H NMR (300 MHz, $CDCl_3$): see Table 1; ^{13}C NMR (75.4 MHz, $CDCl_3$): see Table 2; EIMS (70 eV, direct inlet) *m/z* (rel. int.): 616 $[M]^+$ (0.2), 556 (12), 403 (3), 271 (6), 201 (3), 171 (5), 159 (6), 119 (7), 95 (8), 71 (8), 69 (9), 55 (12), 43 (100). $C_{36}H_{56}O_8$: *M*, 616.

3β-Acetoxy-urs-12-ene-2α,11α,20β-triol (**11**). Mp 116–120° (EtOAc–*n*-hexane); $[\alpha]_D^{20}$ +49.4° ($CHCl_3$; *c* 0.155); IR ν_{max}^{KBr} cm^{-1}: 3440 (*br*), 2940, 2860, 1730, 1460, 1370, 1260, 1040, 1030, 980, 910; ^{1}H NMR (300 MHz, $CDCl_3$): see Table 1; EIMS (70 eV, direct inlet) *m/z* (rel. int.): 516 $[M]^+$ (0.6), 498 (84), 456 (3), 423 (2), 405 (7), 271 (26), 171 (12), 159 (11), 133 (17), 119 (18), 95 (21), 69 (24), 43 (100). (Found: C, 74.49; H, 10.08. $C_{32}H_{52}O_5$ requires: C, 74.37; H, 10.14%)

2α,3β,11α-Triacetoxy-urs-12-en-20β-ol (**12**). Treatment of **11** (52 mg) with Ac_2O–C_5H_5N for 24 hr at room temp. gave **12** (53 mg): mp 216–218° (EtOAc–*n*-hexane); $[\alpha]_D^{20}$ −54.4° (*CHCl*$_3$; *c* 0.204); ^{1}H NMR (300 MHz, $CDCl_3$): see Table 1; ^{13}C NMR (75.4 MHz, $CDCl_3$): see Table 2; EIMS (70 eV, direct inlet) *m/z* (rel. int.): 600 $[M]^+$ (0.3), 540 (22), 480 (3), 439 (22), 289 (3), 271 (6), 171 (6), 133 (10), 119 (11), 95 (11), 69 (12), 55 (13), 43 (100). $C_{36}H_{56}O_7$: *M*, 600.

2α,3β-Diacetoxy-ursa-9(11),12-dien-20β-ol (**13**). A soln of **12** in spectroscopic $CDCl_3$ allowed to stand for 24 hr at room temp. was quantitatively transformed into compound **13**: mp 116–118° (MeOH); $[\alpha]_D^{20}$ +190.9° ($CHCl_3$; *c* 0.132); IR ν_{max}^{KBr} cm^{-1}: 3540, 3030, 2980, 2870, 1740 (*br*), 1460, 1370, 1250, 1230, 1040, 990, 905, 825; UV λ_{max}^{EtOH} nm (log ε): 280 (3.97); ^{1}H NMR (90 MHz, $CDCl_3$): see Table 1; EIMS (70 eV, direct inlet) *m/z* (rel. int.): 540 $[M]^+$ (0.8), 131 (9), 129 (54), 127 (84), 109 (41), 43 (100). $C_{34}H_{52}O_5$: *M*, 540.

Acknowledgements—We thank the Palermo Botanical Garden Office for the facilities given for the collection of plant materials. This work was supported in part by the 'Ministero di Pubblica Istruzione', Italy, and in part by the Spanish 'Comisión Asesora de Investigación Científica y Técnica'.

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