Terpenoids from *Salvia kronenburgii*

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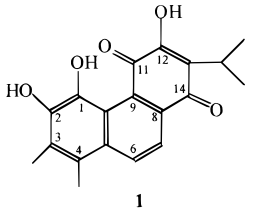
A new norditerpenoid and six new triterpenoids were isolated from the roots of *Salvia kronenburgii*. The new diterpenoid was kronenquinone (**1**). The new triterpenoids were 1*β*,2α,3*β*,11α-tetrahydroxy-olean-12-ene (**2**), 1*β*,2α,3*β*,11α-tetrahydroxy-urs-12-ene (**3**), 2α-acetoxy-urs-5,12-diene-3*β*,11α-diol (**4**), 3α-acetoxy-urs-12-ene-1*β*,11α-diol (**5**), 1*β*,3α,11α-trihydroxy-urs-12-ene (**6**), 2α,3*β*,11α-trihydroxy-urs-12-ene (**7**), and the known triterpenes 3*β*-acetoxy-urs-12-ene-1*β*,2α,11α-triol (**8**) and 3*β*-acetoxyolean-12-ene-1*β*,2α,11α-triol (**9**). Structures were determined by NMR and MS techniques.

There are about 500 *Salvia* species grown naturally in the world. Turkey has 90 species, 44 of them endemic. Until now, we have investigated 35 *Salvia* species[1−5] and isolated more than 50 triterpenoids and about 150 diterpenoids as well as some flavonoids. When we studied the biological aspects of these diterpenoids we found antibacterial[4] and antitubercular[2] activities. In continuation of our studies on Turkish *Salvia* species, we have now studied the roots of an endemic plant *Salvia kronenburgii* Rech. (Lamiaceae) and have isolated nine known diterpenoids: taxodione,[6] ferruginol,[7] salvipisone,[8] 12-hydroxy-sapriparaquinone,[5] royleanone, 7-acetoxyroyleanone,[9] 6-hydroxysalvinolone, 1-oxosalvibretol,[10] and Δ^7-manool[11] and a new norditerpenoid, kronenquinone (**1**). The same extract has also yielded eight triterpenoids, six of which are new compounds (**2**−**7**).



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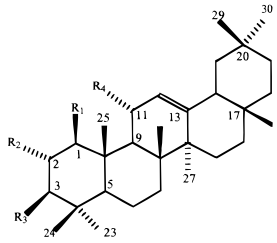
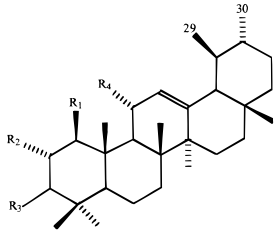


2 $R_1 = R_2 = R_3 = R_4 = OH$
9 $R_1 = R_2 = R_4 = OH$, $R_3 = OAc$
10 $R_1 = R_3 = OH$, $R_2 = R_4 = H$
11 $R_1 = R_2 = R_4 = OH$, $R_3 = OAc$
12 $R_1 = OH$, $R_2 = R_3 = R_4 = OAc$
13 $R_1 = OH$, $R_2 = R_4 = H$, $R_3 = OAc$



3 $R_1 = R_2 = R_4 = OH$, $R_3 = \beta$-OH
4 $R_1 = H$, $R_2 = OAc$, $R_3 = \beta$-OH, $\Delta^{5,6}$
4a $R_1 = H$, $R_2 = R_3 = R_4 = OAc$, $\Delta^{5,6}$
5 $R_1 = R_4 = OH$, $R_2 = H$, $R_3 = \alpha$-OAc
6 $R_1 = R_4 = OH$, $R_2 = H$, $R_3 = \alpha$-OH
7 $R_1 = H$, $R_2 = R_4 = OH$, $R_3 = \beta$-OH
8 $R_1 = R_2 = R_4 = OH$, $R_3 = \beta$-OAc

Results and Discussion

The molecular formula of the new norditerpene kronenquinone (**1**), $C_{19}H_{18}O_5$, indicated 11 double bond equivalents, of which three were accounted for by a tricyclic skeleton, two by quinoid oxo groups, and six by double bonds. The ^{1}H NMR spectrum exhibited four methyl signals; two of them, at δ 2.54 and 2.65, indicated two aromatic methyl groups. Two other methyl groups, observed at δ 1.32 and 1.33 (Me-16 and Me-17), together with the signal at δ 3.38, indicated the presence of an isopropyl group. Two aromatic protons were observed at δ 7.18 and 7.64. The UV spectrum exhibited maxima at 395 and 280 nm, indicating an extended unsaturated structure. The IR spectrum indicated a paraquinoid ring system, supported by ^{13}C NMR signals at δ 182.8 and 184.2. The ^{13}C NMR (APT) spectrum exhibited four CH_3, three CH, and 12 quaternary carbon signals. There were five oxygen functions in the molecule, two accounted for by the paraquinoid group. The remaining three oxygens were hydroxy groups attached to carbons whose signals appeared at δ 135.7, 150.5, and 153.2.

In a previous study with *S. multicaulis*[2] we isolated two fully aromatic and two orthoquinoid diterpenoids with spectra similar to those of compound **1**. The HETCOR experiment showed a direct relation between protons and carbons, and the unambiguous structure of **1** was deduced by a COLOC experiment giving correlations between C-1 and H-18, C-2 with H-18 and H-19, C-5 with H-7 and H-19, C-6 with H-10, C-8 with H-6 and H-7, C-9 with H-7, C-10 with H-6, C-12 with H-15, C-13 with H-16 and H-17, C-14 with H-7, and C-15 with H-16 and H-17. Thus, the structure of kronenquinone (**1**) was established as 1,2,12-trihydroxy-11,14-dioxo-abieta-1,3,5(10),6,8,12-hexaene.

The isolated triterpenoids appeared to have either olean-(**2**, **7**, **9**) or ursane-(**3**, **4**, **5**, **6**, **8**) type skeletons from their

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Table 1. ^{1}H NMR Data (δ) of Compounds **2**−**7** (in $CDCl_3$)[a]

proton	2	3	4	4a	5	6	7
H-1α	3.25 d	3.24 d	1.89 dd		3.75 dd	3.97 dd	1.99 dd
H-1*β*			2.60 dd				2.64 dd
H-2*β*	3.60 dd	3.60 dd	5.00 ddd	5.08 ddd	2.03 dd; 1.14 dd	2.01 dd; 1.16 dd	3.72 ddd
H-3α	3.15 d	3.14 d	3.20 d	4.74 d			3.02 d
H-3*β*					4.77 t	3.62 t	
H-6			5.20 dd	5.20 dd			
H-9	1.68 d	1.66 br d			1.78 d	1.77 d	1.72 br d
H-11*β*	4.31 dd	4.36 dd	4.27 dd	5.45 dd	4.36 dd	4.35 dd	4.30 dd
H-12	5.27 d	5.21 d	5.17 d	5.17 d	5.25 d	5.24 d	5.17 d
CH-Me		0.86 d	0.85 d	0.88 d	0.88 d	0.84 d	0.84 d
		0.88 d	0.90 d	0.91 d	0.92 d	0.93 d	0.88 d
C-Me	0.83 s	0.70 s	0.80 s	0.79 s	0.80 s	0.80 s	0.79 s
	0.86 s	0.92 s	0.89 s	0.90 s	0.86 s	0.86 s	0.86 s
	0.88 s	1.03 s	1.04 s	0.91 s	0.91 s	0.95 s	0.92 s
	0.89 s	1.06 s	1.06 s	1.09 s	1.05 s	1.03 s	1.05 s
	0.98 s	1.15 s	1.15 s	1.19 s	1.10 s	1.08 s	1.06 s
	1.03 s	1.17 s	1.20 s	1.22 s	1.24 s	1.19 s	1.16 s
	1.10 s						
	1.21 s						
OAc			2.06 s	2.06 s; 1.93 s; 1.97 s	2.08 s		

[a] *J* (Hz) = Compound **2**: 1α,2*β* = 9; 2*β*,3α = 10, 9,11 = 8.5; 11,12 = 3. Compound **3**: 1α,2*β* = 9; 2*β*,3α = 9.8, 9,11 = 9; 11,12 = 3; 19, 29 = 6.5, 20,30 = 6. Compound **4:** 1α,1*β* = 13; 1α,2*β* = 11; 1*β*,2*β* = 5; 3α,2*β* = 10; 6,7α = 4; 6,7*β* = 8; 9, 11 = 9; 11,12 = 3; 19, 29 = 6.5; 20,30 = 6. Compound **4a**: 1α,1*β* = 13; 1α,2*β* = 11; 1*β*,2*β* = 5; 3α,2*β* = 10; 6,7α = 4; 6,7*β* = 8; 9, 11 = 9; 11,12 = 3; 19, 29 = 6.5; 20,30 = 6. Compound **5:** 1α,2*β* = 11; 1α,2 α = 5; 2α,3*β* = 2*β*,3*β* = 3;9,11 = 9; 11,12 = 3.5; 19, 29 = 6.5; 20,30 = 6. Compound **6**: 1α,2*β* = 11.5; 1α,2 α = 5; 2α,3*β* = 2*β*,3*β* = 3;9,11 = 9; 11,12 = 3.5; 19, 29 = 6.5; 20,30 = 6. Compound **7**: 1α,1*β* = 13; 1α,2*β* = 11; 1*β*,2*β* = 4.5; 2*β*,3α = 9.7.

NMR spectra. The HRMS of compound **2** indicated the molecular formula $C_{30}H_{50}O_4$ with six degrees of unsaturation, five of which were accounted for by a pentacyclic skeleton and one by a double bond. In the ^{1}H NMR spectrum, the presence of Δ,[12]11-OH group, followed from signals at δ 5.27 (H-12) and 4.31 (H-11*β*). Similar compounds have been obtained from *Salvia argentea*.[12] The ^{13}C NMR (APT) spectrum of **2** contained eight CH_3, seven CH_2, eight CH, and seven quaternary carbon signals (Table 2). Methyl signals at δ 0.83, 0.86, 0.88, 0.98, 1.04, 1.10, and 1.21 (each 3H, s) indicated an olean-type structure. Three successive secondary hydroxy groups followed from the signals at δ 3.25, 3.60 (H-2*β*), and 3.15 (H-3α). Spin decoupling experiments showed the C_1−C_3 and the C_9−C_{12} sequences. Irradiation of H-2 (δ 3.60) collapsed the signals at δ 3.25 (H-1) and 3.15 (H-3) into singlets, while irradiation of H-11 (δ 4.31) collapsed the doublet signal of H-12 (δ 5.27) and a signal at δ 1.68 (J = 8.5 Hz) into singlets, the latter signal being assigned to H-9. Acetylation of **2** at room temperature yielded a known compound (**11**), first isolated from *Salvia argentea*,[12] while drastic acetylation of **2** yielded the 2α,3*β*,11α-triacetyl derivative (**12**).[12] Thus, compound **2** was deduced to be 1*β*,2α,3*β*,11α-tetrahydroxyolean-12-ene.

Compound **3** was the ursane analogue of compound **2**. The main difference **i**n the ^{1}H NMR spectrum of **3** was observation of two methyl doublets at δ 0.86 and 0.88 assigned to an ursan skeleton and small chemical shift differences for H-11 and H-12. ^{1}H−^{1}H COSY experiments allowed assignment of ring A protons and ring C protons giving correlations among H-1α, H-2*β*, and H-3α, as well as H-9 and H-11 and H-11 and H-12. Therefore, the structure of compound **3** was established as 1*β*,2α,3*β*,11α-tetrahydroxy-urs-12-ene.

Compound **4**, 2α-acetoxy-urs-5,12-diene-3*β*,11α-diol, had the molecular formula $C_{32}H_{50}O_4$ (HRMS). A signal at δ 5.00 in the ^{1}H NMR spectrum of **4** indicated a hydrogen geminal to an acetyl group, with the acetyl signal at δ 2.06. This was also evident from ^{13}C NMR signals at δ 167.8 and 21.2 (Table 2) and IR absorption bands at 1725 and 1270 cm^{-1}. The multiplicity (ddd) of the methine at δ 5.00 indicated

Table 2. ^{13}C NMR Data (δ) of Compounds **2**−**7** (in $CDCl_3$)

C	2	3	4	5	6	7
1	76.5 d	76.8 d	44.2 t	76.1 d	75.8 d	38.6 t
2	75.1 d	75.0 d	73.2 d	27.2 t	28.3 t	69.2 d
3	79.7 d	79.9 d	71.3 d	70.4 d	72.1 d	82.4 d
4	38.2 s	38.2 s	40.4 s	38.2 s	38.2 s	38.1 s
5	54.6 d	54.6 d	144.9 s	55.1 d	55.2 d	55.2 d
6	18.1 t	18.0 t	121.7 d	18.0 t	18.1 t	18.3 t
7	31.3 t	31.3 t	37.3 t	32.6 t	32.7 t	33.1 t
8	41.4 s	41.3 s	40.6 s	40.2 s	40.2 s	40.4 s
9	55.0 d	54.6 d	54.3 d	54.3 d	54.2 d	54.5 d
10	43.6 s	43.8 s	38.6 s	38.2 s	38.3 s	37.8 s
11	69.5 d	69.2 d	70.1 d	70.2 d	70.3 d	70.1 d
12	123.5 d	123.4 d	124.6 d	124.5 d	124.6 d	124.2 d
13	145.1 s	144.2 s	145.3 s	145.2 s	145.3 s	144.9 s
14	44.6 s	44.5 s	44.7 s	44.6 s	44.5 s	43.8 s
15	27.7 t	27.8 t	27.6 t	27.5 t	27.6 t	28.0 t
16	27.8 t	27.9 t	27.5 t	27.4 t	27.5 t	27.2 t
17	32.2 s	32.8 s	32.6 s	32.7 s	32.7 s	33.0 s
18	40.3 d	60.1 d	59.8 d	59.9 d	60.0 d	59.7 d
19	46.2 t	41.8 d	41.6 d	40.3 d	40.2 d	39.8 d
20	31.1 s	41.8 d	41.6 d	41.6 d	41.5 d	40.9 d
21	33.7 t	30.9 t	31.0 t	31.0 t	31.1 t	30.8 t
22	32.4 t	41.5 t	41.4 t	41.6 t	41.7 t	41.5 t
Me's	28.2 q	28.1 q	28.3 q	28.2 q	28.2 q	28.1 q
	15.8 q	16.0 q	16.1 q	16.9 q	16.9 q	16.8 q
	15.7 q	16.1 q	20.7 q	15.9 q	16.0 q	16.1 q
	16.8 q	16.9 q	16.9 s	16.7 q	16.6 q	16.5 q
	27.4 q	23.3 q	24.4 q	23.5 q	23.6 q	23.6 q
	32.5 q	28.4 q	28.5 q	28.2 q	28.2 q	28.3 q
	24.6 q	17.5 q	17.8 q	17.1 q	17.2 q	17.3 q
	21.4 q	21.4 q	21.5 q	21.2 q	21.5 q	21.6 q
OAc			21.2 q	21.0 q		
			167.8 s	170.7 s		

that it was between a methine and a methylene group. The signal at δ 3.20 and spin decoupling experiments showed the relationship between H-3α and H-2*β*. Irradiation of the signal at δ 3.20 (H-3) collapsed the signal at δ 5.00 (H-2) to a double doublet, while irradiation of H-2 collapsed H-3 to a singlet and collapsed H-1*β* and H-1α to doublets. Therefore, the acetyl group was clearly at C-2. Signals at δ 4.27 and 5.17 indicated an α-hydroxyl at C-11 and a double bond at C-12, as also observed in compounds **2** and **3**. A second double bond in the molecule was deduced from

the signal at δ 5.20. Considering the molecular formula and studying a Dreiding model, this double bond could be situated only between C-5 and C-6. Acetylation of **4** under reflux for 2 h yielded **4a**; in the ^{1}H NMR spectrum, three acetyl groups were observed at δ 1.93, 1.97, and 2.06 (each 3H, s), the latter being originally present at C-2. The signal at δ 3.20 was shifted to 4.74 (H-3α), the signal at δ 4.27 to 5.45 (H-11β), and the signal at δ 5.00 was slightly shifted to 5.08 (H-2β), although the olefinic proton signals at δ 5.17 (H-12) and 5.20 (H-6) were not affected. In 1D NOE experiments, irradiation of 5.08 (H-2β) caused signal enhancements for C-10 Me and C-4 Me protons, indicating the stereochemistry of C-2 acetyl group to be α. HETCOR and the COLOC experiments were carried out with compound **4**, and the methyl groups were assigned as follows: δ 1.20 (Me-24) and 0.89 (Me-25); other Me groups are at δ 0.80 (Me-26), 1.04 (Me-27), 1.06 (Me-28); 0.85 and 0.90 are assigned for Me-29 and Me-30. The HRMS and ^{13}C NMR (APT) spectra of **4** (Table 2) were in agreement with the indicated structure.

Compound **5** ($C_{32}H_{52}O_4$) had seven degrees of unsaturation, five of accounted for by a pentacyclic skeleton, a one by an acetyl carbonyl and one by a double bond. The ^{1}H NMR spectrum of **5** indicated an ursane-type structure (Table 1). COSY experiments clearly showed the relationships between nieghboring protons H-11 and H-12, as well as between H-11 and H-9. The signal at δ 3.75 (H-1α) coupled with H-2β (δ 2.03), the latter showing a cross-peak to the signal at δ 1.14 (H-2α); H-3β also showed cross-peaks to H-2α and H-2β. An acetyl methyl (δ 2.08) and the chemical shift of H-3 (δ 4.77) clearly indicated the presence of an acetyl group at C-3; its α position was deduced from its splitting pattern and comparison with similar compounds having a β-hydroxy or -acetoxy group at C-3. 1β,3β,-11α-Trihydroxy-olean-12-ene (**10**) was isolated from *Maytenus horrida*,[13] and its 3-acetoxy derivative has been prepared (**13**), the differences between compounds **5** and **13** were in the chemical shift and splitting pattern of H-3, as well as in the presence of two methyl doublets (Me-29 and Me-30). The ^{13}C NMR (APT) spectrum of **5** revealed nine CH_3, seven CH_2, nine CH, and seven quaternary signals for 32 carbon atoms of the molecule. Thus, the structure of **5** was established as 3α-acetoxy-urs-12-ene-1β,11α-diol.

The ^{1}H NMR spectrum of **6** indicated an ursane triterpene. A triplet signal at δ 3.62 (J = 3.5 Hz) was very characteristic for a C-3β proton, indicating that it bears an α-hydroxy group. In fact, ^{1}H NMR signals were very similar to those of compound **5**, the only meaningful difference was observed for H-3β (δ 3.62). The chemical shift difference in H-3α compared to that of **5** was attributed to the presence of a hydroxy group at C-3 instead of an acetyl group in compound **6**. This was proven by the lack of an acetyl methyl signal. The HRMS spectrum showed a molecular ion peak at m/z 458.3660, in the EIMS; the loss of the first hydroxy group at m/z 440 and the second at m/z 422 was clearly observed. Deacetylation of **5** yielded compound **6**, verifying its structure. Thus, the structure of compound **6** was established as 1β,3α,11α-trihydroxy-urs-12-ene.

The ^{1}H NMR spectrum of **7** also indicated an ursane skeleton. Two methine proton signals were observed at δ 3.02 and 3.72, assigned to H-3α and H-2β, respectively. Based on spin-decoupling experiments H-1β and H-1α signals were assigned to signals δ 2.64 and 1.99, respectively. The Δ^{12},11-OH moiety was observed in δ 4.30 (dd, J = 3.2, 10.0 Hz, H-11β) and 5.17 (d, J = 3.2 Hz, H-12) as followed in all the above triterpenoids. A similar compound, 2α,3β-dihydroxy-urs-12-ene[14] without the C-11 hydroxy group, had a similar spectrum. The HRMS of **7** gave a molecular ion peak at m/z 458.3554, and the ^{13}C NMR spectrum of **7** was consistent with the assigned structure. Thus, **7** was established as 2α,3β,11α-trihydroxy-urs-12-ene.

Experimental Section

General Experimental Procedures. EIMS and HRMS were recorded on a ZabSpec mass (micromass) spectrometer. ^{1}H and ^{13}C NMR were run on a Bruker Ac 200 L NMR spectrometer at 200 and 50.32 MHz, respectively, in $CDCl_3$. UV spectra were taken on a Varian Techtrone 535, and IR, on a Perkin−Elmer 983 instrument. Si gel 60 (70−230 mesh, E. Merck) was used for column chromatography, preparative TLC was performed on Si gel (UV_{254} precoated) plates.

Plant Material. The roots of *Salvia kronenburgii* were collected from eastern Turkey (Van) in June 1997, at 2250 m altitude and identified by Prof. Dr. M. Koyuncu and Dr. Nasip Demirkus. A voucher specimen is deposited in the Herbarium of 100. Yil University, Van (Demirkuş 5515 VANF).

Extraction and Isolation. The powdered plant material (2.4 kg) was macerated with Me_2CO at room temperature, yielding 30 g of a residue. The residue was roughly separated on a Si gel column (5 × 110 cm) eluting with hexane and gradients of $CHCl_3$ and MeOH. The similar fractions were combined to give five main fractions (A−E). Fraction A (1−20), having only the fatty materials, was discarded. Fraction B (21−29) (220 mg) was subjected to a smaller Si gel column (2 × 70 cm) eluting with $CHCl_3$ to give known diterpenoids taxodione (95 mg), ferruginol (55 mg), salvipisone (22 mg), and 12-hydroxysapriparaquinone (15 mg) and the new diterpenoid kronenquinone (**1**). From fraction C (30−48) (800 mg) on a Si gel column (4 × 100 cm), eluting with $CHCl_3$−Me_2CO (95:5), acetoxyroyleanone (45 mg), royleanone (25 mg), 1-oxosalvibretol (17 mg), and Δ^7-manool (14 mg) were obtained. Fraction D (49−74) (440 mg) was also subjected to a Si gel column (3 × 80 cm) and eluted by $CHCl_3$ and increasing amounts of MeOH to afford 6-hydroxysalvinolone (13 mg) and the new triterpenoids **2** (15 mg), **3** (13 mg), **4** (15 mg), **5** (18 mg), **6** (20 mg), and **7**(14 mg). The known compounds were identified by comparison with literature data.

Kronenquinone (**1**): UV ($CHCl_3$) λ_{max} (log ϵ) 430 (3.0), 395 (3.2), 282 (4.1) nm; IR ($CHCl_3$) ν_{max} 3480, 3050, 2960, 2870, 1675, 1640, 1620, 1595, 1505, 1460, 1380, 950, 880 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.64 (1H, d, J = 9 Hz, H-7), 7.18 (1H, d, J = 9 Hz, H-6), 3.38 (1H, sept, J = 7 Hz, H-15), 2.65 (3H, s, Me-18), 2.54 (3H, s, Me-19), 1.33 (3H, d, J = 7 Hz) and 1.32 (3H, d, J = 7 Hz) (Me-16 and Me-17); ^{13}C NMR ($CDCl_3$) δ C-1 153.2 s, C-2 135.7 s, C-3 141.7 s, C-4 133.4 s, C-5 127.6 s, C-6 122.8 d, C-7 133.5 d, C-8 126.0 s, C-9 127.3 s, C-10 150.1 s, C-11 182.8 s, C-12 150.5 s, C-13 134.9 s, C-14 184.2 s, C-15 26.2 d, C-16 22.8 q, C-17 22.7 q, C-18 21.1 q, C-19 17.7 q; EIMS m/z (rel int) 326 [M]$^+$ (7), 312 (100), 300 (12), 281 (32), 256 (60), 243 (88), 227 (77), 219 (20), 213 (21), 211 (21), 203 (11), 197 (13), 185 (19), 165 (17), 155 (12), 149 (20), 141 (16), 128 (17), 123 (11), 109 (12), 95 (11), 83 (20), 71 (62), 57 (21); HREIMS m/z 326.1136 (calcd for $C_{19}H_{18}O_5$, 326.1144).

1β,2α,3β,11α-Tetrahydroxy-olean-12-ene (**2**): $[\alpha]^{25}_D$ 0.0° (c 0.1, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3450, 3380, 2960, 2850, 1645, 1380, 1260, 1100, 1080, 1050, 980 cm^{-1}; ^{1}H and ^{13}C NMR, Tables 1 and 2; EIMS m/z (rel int) 474 [M]$^+$ (15), 456 [M − H_2O]$^+$ (100), 440 [M − 2×H_2O]$^+$ (17), 423 [M − 2×H_2O − OH]$^+$ (14), 405 [M − 2×H_2O − 2×OH]$^+$ (16), 324 (5), 303 (16), 285 (7), 267 (5), 255 (23), 189 (6), 171 (8), 119 (7), 107 (6), 95 (5); HREIMS m/z 474.3698 (calcd for $C_{30}H_{50}O_4$, 474.3710).

1β,2α,3β,11α-Tetrahydroxy-urs- 12-ene (3): IR($CHCl_3$) ν_{max} 3455, 3380, 2960, 2850, 1645, 1380, 1255, 1100, 1080, 1050, 975 cm^{-1}; ^{1}H and ^{13}C NMR, Tables 1 and 2; EIMS m/z (rel int) 474 [M]$^+$ (12), 456 [M − H_2O]$^+$ (100), 440 [M − 2×H_2O]$^+$ (15), 423 [M − 2×H_2O − OH]$^+$ (10), 405 [M − 2×H_2O − 2×OH]$^+$ (15), 324 (5), 302 (18), 284 (6), 266 (4), 255

(20), 189 (8), 171 (9), 107 (9), 95 (7); HREIMS *m/z* 474.3696 (calcd for $C_{30}H_{50}O_4$, 474.3710).

2α-Acetoxy-urs-5,12-diene-3β,11α-diol (4): $[\alpha]^{25}_D$ − 50.0° (*c* 0.1, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3460, 3050, 2980, 2862, 1725, 1640, 1605, 1360, 1270, 880 cm^{-1}; ^1H and ^{13}C NMR, Tables 1 and 2; EIMS *m/z* (rel int) 498 $[M]^+$ (27), 482 $[M - 16]^+$ (100), 467 $[M - 16 - CH_3]^+$ (18), 441.2 $[M - OCOCH_3]^+$ (72), 423 (20), 407 (19), 389 (17), 329 (20), 269 (21), 255 (45), 234 (34), 218 (15), 204 (20), 191 (22), 171 (14), 145 (18), 133 (25), 123 (25), 109 (28), 95 (35), 69 (32), 57 (22), 43 (24); HREIMS *m/z* 498.3664 (calcd for $C_{32}H_{50}O_4$, 498.3710).

Acetylation of 2, 4, and 10. Of each compound (**2**, **4**, and **10**) 5 mg was dissolved in 1 mL of pyridine, and 1 mL Ac_2O was added. The reaction mixtures were left at room temperature for 36 h, evaporated to dryness, and the residues subjected to preparative TLC using $CHCl_2$ to give **11**, **4a**, and **13**.

Drastic Acetylation of Compound 2. Of compound **2** 5 mg dissolved in 1 mL of pyridine, and 1 mL Ac_2O was added. The mixture was refluxed in a water bath for 2 h, left at room temperature for 24 h, and evaporated to dryness to afford compound **12**.

Urs-5,12-diene-2α,3β,11α-triacetate (4a): IR ($CHCl_3$) ν_{max} 2862, 1730, 1722, 1640, 1600, 1360, 1280, 880 cm^{-1}; ^1H NMR, Table 1; HREIMS *m/z* 582.3930 (calcd for $C_{36}H_{54}O_6$, 582.3920).

3α-Acetoxy-urs-12-ene-1β,2α-diol (5): IR ($CHCl_3$) ν_{max} 3440, 3055, 2960, 1727, 1640, 1380, 1265, 890 cm^{-1}; ^1H and ^{13}C NMR, Tables 1 and 2; EIMS (70 eV) *m/z* (rel int) 500 $[M]^+$ (71), 482 $[M - H_2O]^+$ (100), 464 $[M - 2\times H_2O]^+$ (8), 455 (10), 422 $[482 - AcOH]^+$ (65), 406 (35), 389 (33), 329 (11), 288 (12), 273 (14), 255 (30), 217 (82), 189 (72), 175 (62), 135 (45), 109 (36), 95 (51), 81 (20), 69 (26); HREIMS *m/z* 500.3800 (calcd for $C_{32}H_{52}O_4$, 500.3865).

1β,3α,11α-Trihydroxy-urs-12-ene (6): $[\alpha]^{25}_D$ 0.0° (*c* 0.1, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3450, 3380, 2960, 2850, 1645, 1380, 1255, 1100, 1080, 1050, 975 cm^{-1}; ^1H and ^{13}C NMR, Tables 1 and 2; EIMS (70 eV) *m/z* (rel int) 458.3 $[M]^+$ (70), 440.3 $[M - H_2O]^+$ (90), 425.3 $[M - H_2O - CH_3]^+$ (21), 422.3 $[M - 2\times H_2O]^+$ (21) 407.2 $[M - 2\times H_2O - CH_3]^+$ (22), 389.3 (23), 355.2 (7), 288.2 (12), 273.2 (17), 255.2 (40), 247.2 (63), 235.1 (33), 217.1 (45), 203.1 (38), 193.1 (100), 189.1 (72), 175.1 (64), 135.1 (47), 121.1 (56), 108.9 (45), 95.1 (53), 81.0 (23), 69.0 (19); HREIMS *m/z* 458.3660 (calcd for $C_{30}H_{50}O_3$, 458.3759).

2α,3β,11α-Trihydroxy-urs-12-ene (7): IR ($CHCl_3$) ν_{max} 3460, 3380, 2960, 2855, 1640, 1380, 1260, 1100, 1075, 1050, 975 cm^{-1}; ^1H and ^{13}C NMR, Tables 1 and 2; EIMS (70 eV) *m/z* (rel int) 458 $[M]^+$ (15), 442 $[M - 16]^+$ (100), 424 $[442 - H_2O]^+$ (83), 409 $[424 - Me]^+$ (17), 355 (18), 322 (10), 271 (22), 255 (25), 203 (17), 135 (15), 108 (20), 95 (23), 78 (62), 69 (45); HREIMS *m/z* 458.3554 (calcd for $C_{30}H_{50}O_3$, 458.3759).

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