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NEW TRITERPENOIDS FROM *SALVIA NICOLSONIANA*

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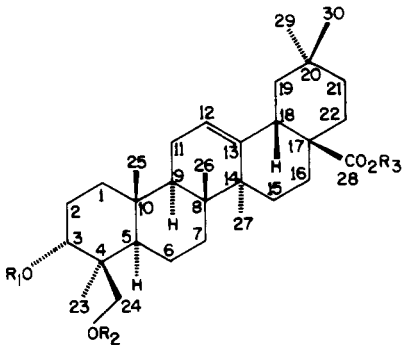
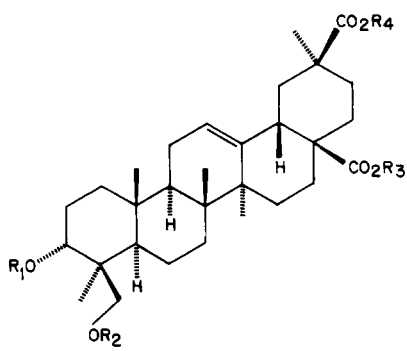
ABSTRACT.—Two new triterpenoids have been isolated from aerial parts of *Salvia nicolsoniana*. These are 3α,24-dihydroxy-olean-12-en-28-oic acid (**1**) and 3α,24-dihydroxy-olean-12-en-28,30-dioic acid (**9**). Betulinic, oleanolic, ursolic, and 3-*epi*-ursolic acids as well as β-sitosterol and its 3β-glucoside were also isolated from this species. The structures were elucidated by spectroscopic methods and chemical transformations.

During the course of our chemical investigations of Mexican Labiatae (1), we have obtained several triterpenoids from *Salvia nicolsoniana* Ramamoorthy, which is endemic to the Sierra Madre del Sur, México. This paper describes the isolation and structure elucidation of two new triterpene acids, 3α-24-dihydroxy-olean-12-en-28-oic acid (**1**) and 3α,24-dihydroxy-olean-12-en-28,30-dioic acid (**9**), which occur as minor constituents in this species.

Exhaustive chromatography of the Me_2CO extract of the air-dried aerial parts yielded—in addition to betulinic, oleanolic, ursolic, and 3-*epi*-ursolic acids—a small amount of the two new triterpenoid acids (**1**,**9**).





1 $R_1=R_2=R_3=H$
2 $R_1=R_3=H$, $R_2=Ac$
3 $R_1=R_2=Ac$, $R_3=H$
4 $R_1=R_2=H$, $R_3=CH_3$
5 $R_1=H$, $R_2=Ac$, $R_3=CH_3$
6 $R_1=R_2=Ac$, $R_3=CH_3$
7 $>C_3=O$, $R_2=Ac$, $R_3=CH_3$
8 $R_1=R_2=TAC$, $R_3=CH_3$
TAC: $CONHCOCCl_3$

9 $R_1=R_2=R_3=R_4=H$
10 $R_1=R_2=H$, $R_3=R_4=CH_3$
11 $R_1=R_2=Ac$, $R_3=R_4=CH_3$

Compound **1** had the molecular composition $C_{30}H_{48}O_4$ (elemental analysis and ms). Its ir spectrum showed absorption for hydroxyl (3427 cm^{-1}), carbonyl (1696 cm^{-1}), olefin (1633 cm^{-1}), and *gem*-dimethyl groups (1379 cm^{-1}). It formed amorphous acetates (monoacetate **2** and diacetate **3**) upon acetylation. It also afforded a methyl

[1]Contribution No. 767.

TABLE 1. ^{1}H-nmr Spectra of Compounds **1-11** (80 MHz, $CDCl_3$, TMS as Internal Standard)[a]

Compounds	C_{12}-H	C_{18}-H	C_3-H	C_4-CH_2-OR	CH_3						CO_2Me	O Ac
					C_{23}	C_{25}	C_{26}	C_{27}	C_{29}	C_{30}		
1[b]	5.25 m (W½=10)	2.80 dd (18)[d]	3.77 m (W½=6)	3.65 d (11.5) 3.37 d (11.5)	0.89 bs	1.05 s	0.76 s	1.14 s	0.89 bs	0.89 bs	—	—
2	5.25 m (W½=7)	2.80 dd (18)[d]	3.63 t[e,f] (3)	4.18 d (11.5) 3.92 d (11.5)	0.91 bs	1.05 s	0.75 s	1.17 s	0.89 s[g]	0.91 bs[h]	—	2.03 s
3	5.25 m (W½=8)	2.80 dd (18)[d]	4.93 t[e,f] (3)	4.18 d (11.5) 3.92 d (11.5)	0.94 bs	0.94 bs	0.74 s	1.19 s	0.91 bs[g]	0.94 bs[h]	—	2.03 s 2.06 s
4	5.25 m (W½=8)	2.85 dd (18)[d]	3.83 t[e,f] (3)	3.72 d (11.5) 3.50 d (11.5)	0.91 bs	1.09 s	0.76 s	1.14 s	0.91 bs[g]	0.93 s[h]	3.60 s	—
5	5.25 m (W½=7)	2.85 dd (18)[d]	3.68 t[e,f] (3)	4.18 d (11.5) 3.92 d (11.5)	0.93 bs	1.05 s	0.71 s	1.14 s	0.90 s[g]	0.93 bs[h]	3.60 s	2.03 s
6	5.25 m (W½=8)	2.85 dd (18)[d]	4.92 t (3)	4.18 d (11.5) 3.92 d (11.5)	0.93 bs	0.93 s	0.71 s	1.17 s	0.90 s[g]	0.93 bs[h]	3.60 s	2.04 s 2.06 s
7	5.25 m (W½=8)	2.85 dd (18)[d]	—	4.60 d (12) 3.92 d (12)	1.14 s	1.10 s	0.76 s	1.14 s	0.88 s[g]	0.91 s[h]	3.60 s	1.98 s
8	5.25 m (W½=7)	2.85 dd (18)[d]	5.08 t (3)	4.47 d (12) 4.16 d (12)	0.96 s	1.11 s	0.74 s	1.19 s	0.89 s[g]	0.91 s[h]	3.60 s	—
9[c]	5.25 m (W½=8)	3.05 dd (18)[d]	4.16 m (W½=6)	3.84 d (11.5) 3.55 d (11.5)	0.76 s	0.81 s	0.69 s	0.97 s	0.90 s	—	—	—
10	5.25 m (W½=8)	2.85 dd (18)[d]	3.84 t[e,f] (3)	3.72 d (11.5) 3.49 d (11.5)	0.90 s	1.03 s	0.73 s	1.14 s	1.16 s	—	3.60 s 3.62 s	—
11	5.25 m (W½=7)	2.85 dd (18)[d]	4.93 t (3)	4.20 d (11.5) 3.90 d (11.5)	0.94 bs	0.94 bs	0.74 s	1.17 s	1.15 s	—	3.59 s 3.61 s	2.04 s 2.06 s

[a]Coupling constants (Hz) in parentheses
[b]Solvent $CDCl_3$-DMSO-d_6
[c]Solvent Pyridine-d_5
[d]Coupling constant $J_{AX}+J_{BX}$
[e]Approximate triplets
[f]Signal resolved into a triplet after D_2O exchange
[g and h]The assignments might have to be reversed

ester **4** upon methylation. The ^{1}H-nmr spectrum (Table 1) of **1** showed resonances for six tertiary methyl groups and, as expected for the olean-12-ene skeleton with a secondary hydroxyl substituent, a one-proton multiplet around δ 3.77 assignable to H-3 was observed. An AB system (δ 3.37, 3.65; J=11.5 Hz), which shifted downfield on acylation in **2** and **3**, indicated the presence of an axial hydroxy methylene group attached to an asymmetric center, and finally, one signal at δ 5.25 gave evidence of the presence of a trisubstituted double bond. The mass spectrum of this triterpene showed diagnostically important peaks at *m/z* 248 (base peak, retro Diels-Alder fragmentation around ring C), 207, 203 [248-COOH]$^+$, 202 [248-HCOOH]$^+$, 189 [207-H_2O]$^+$, and 133, which are consistent with the fragmentation pattern characteristic for Δ^{12} pentacyclic triterpenes (2,3). From the above mass spectral fragments, it is also evident that the two hydroxyl groups are present in the A/B ring portion. The location of the secondary hydroxyl at C-3 is highly probable on a biogenetic basis, and the evidence in favor of its

TABLE 2. ^{13}C-nmr Spectra of Compounds **4-6** and **10** (20.0 MHz, $CDCl_3$, TMS as Internal Standard)

Carbon atom	Compound			
	4[a]	**5**	**6**	**10**[b]
1	33.91	33.11	33.61	33.19
2	26.39	25.34	22.59	25.28
3	70.01	70.85	73.47	70.64
4	43.85	41.34	40.59	42.71
5	50.10	49.62	50.91	49.58
6	19.09	18.60	18.42	18.71
7	33.64	33.00	33.00	32.99
8	39.94	39.59	39.58	40.01
9	48.06	47.70	47.75	47.10
10	37.49	37.04	36.93	36.89
11	23.97	23.59	23.59	23.72
12	122.95	122.39	122.35	122.36
13	144.10	143.88	143.84	143.85
14	42.02	41.83	41.83	41.18
15	28.07	27.79	27.84	27.80
16	23.47	23.22	23.24	23.24
17	46.98	46.84	46.83	45.94
18	41.86	41.46	41.49	42.73
19	46.16	46.08	46.15	41.31
20	30.78	30.75	30.73	43.98
21	34.02	34.02	34.02	30.56
22	32.83	32.52	32.48	33.58
23	23.37	22.33	22.04	21.68
24	65.82	67.84	66.78	66.52
25	15.94	15.56	15.61	15.63
26	17.14	16.83	16.85	16.71
27	26.07	26.08	26.05	25.42
28	177.91	178.21	178.09	178.86
29	33.10	33.11	33.11	27.93
30	23.69	23.71	23.69	176.53
C_3OAc	—	—	170.32	—
			21.17	
C_{24}OAc	—	171.04	170.98	—
		20.84	20.81	
COOMe	51.74	51.45	51.43	51.54
COOMe	—	—	—	51.73

[a]Solvent Pyridine-d_5
[b]Solvent DMSO-d_6

axial (α) orientation was obtained from nmr data analysis of **6** and **4**: the ^{1}H-nmr spectrum of **6** (Table 1) disclosed the presence of a triplet-like signal centered at δ 4.92 with a splitting pattern typical of a 3α-acetoxyl group (4). In addition, the ^{13}C-nmr spectrum of **4** (Table 2) displayed the signal for C-3 at considerably higher field (δ 70.01) than those observed values for related compounds with the 3β-OR configuration (5-7). It is apparent that the presence of the β-oriented CH_2-OR on C-4 as well as the spatial proximity of the 3α-OR to C-23 gave rise to the large upfield shift of the latter. This result and the upfield shift showed for C-1 represent typical γ-gauche shielding effects (8-11). Further evidence for the C-4 stereochemistry was obtained by comparison of the average chemical shift value of the acetoxy methylene protons of **6** [$\frac{1}{2}(\delta_A+\delta_B)=4.05$] with ^{1}H-nmr data reported for similar compounds (12,13).

The triterpenoid **9** analyzed for $C_{30}H_{46}O_6$ (elemental analysis and ms) and its ir spectrum showed hydroxyl (3422 cm^{-1}), carbonyl (1693 cm^{-1}) and olefin (1637 cm^{-1}) absorptions. Treatment of **9** with ethereal CH_2N_2 afforded the diester **10**, therefore showing that the compound was a triterpene carboxylic acid. Prolonged treatment of **10** with Ac_2O-pyridine gave the diacetyl derivative **11**. The nmr features of this triterpene suggested a structure closely related to compound **1**. The ^{1}H-nmr spectrum of **9** (Table 1) showed five methyl singlets, an AB system centered at δ 3.55 and 3.84 (2H, J=11.5 Hz), corresponding to the β-oriented hydroxy methylene group at C-4, a triplet at δ 4.16 indicating a secondary hydroxyl group and finally, a one-proton multiplet at δ 5.25 suggestive of a Δ^{12} double bond. The ms analysis of the methyl ester **10** indicated that the A, B, and C rings were the same as those in compound **4**. Furthermore, the appropriate mass increment (*m/z* 44) observed in the distinctive peaks at 530 M^+, 306, and 247 suggested the presence of a carbomethoxy group at C-20 (2,14), and consequently, confirming that **9** was an olean-12-en-28,30-dicarboxylic acid derivative. Finally, the observed chemical shifts for the ^{13}C nucleus of the E ring (Table 2) and the values for the methyl singlets in ^{1}H nmr (Table 1) of **10** were in excellent agreement with those values calculated for a 30-carbomethoxy structure (14-19).

It is interesting to point out that the ir spectra of the esters **4** and **10** are consistent with the proposed diaxial configuration for the α-hydroxyl at C-3 and the β-hydroxymethylene group on C-4. Both compounds displayed their hydroxyl absorptions as a sharp band, due to the lack of intramolecular hydrogen bonding, at 3627 and 3624 cm^{-1}, respectively (20).

From the chemotaxonomic point of view, it is of interest to note that triterpenoids possessing 28,30 dicarboxyl group of the β-amyrin series were found previously only in the genera *Phytolacca, Mollugo,* and *Serjanica* (7,25). The presence of a Δ^{12}-oleanene dicarboxylic acid derivative has no precedent in the *Salvia* genus.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points are uncorrected. The ir spectra were taken on a Perkin-Elmer 283B instrument. ^{1}H-nmr and ^{13}C-nmr spectra were determined on a Varian FT-80 apparatus. Mass spectra were recorded on a Hewlett-Packard 5985-B spectrometer by direct inlet probe at 75 eV.

PLANT MATERIAL.—Aerial parts of *S. nicolsoniana* were collected in February 1984, in Sierra Madre del Sur, Guerrero, México. Voucher specimens are deposited in the National Herbarium, Instituto de Biología, UNAM, voucher No. 6191 M.

EXTRACTION.—Dried and finely powdered plant material (4.5 kg) was extracted with Me_2CO at room temperature for 5 days. After filtration, the solvent was evaporated, yielding a gum (76 g).

ISOLATION OF THE TRITERPENOIDS.—The crude extract (76 g) was chromatographed on a column over Si gel (Merck, No. 70-230 mesh ASTM, 1.8 kg deactivated with 10% H_2O) using n-hexane-EtOAc gradient elution system. Fractions of 1,500 ml were collected.

The low polarity fractions 1-15, containing waxes and fats, were discarded. β-sitosterol (4.7 g), iden-

tified by standard sample comparison (mmp, ir, ^{1}H nmr, tlc), was the main component in fractions 15-24. Treatment of fractions 27-45 (6.43 g) with CH_2N_2-Et_2O and further column chromatography allowed the separation of betulinic (11,21) (264 mg), oleanolic (11,22) (1.5 g), ursolic (23) (380 mg), and 3-*epi*-ursolic (24) (8 mg) acids, as their methyl ester derivatives, which were identified by comparison (mmp, tlc, ir, ^{1}H nmr) with authentic samples.

The polar fractions 76-94 (4.35 g), eluted with *n*-hexane-EtOAc (1:1), were rechromatographed over Si gel (180 g) eluting with *n*-hexane-EtOAc-Me_2CO (2:1:1). The fractions 34-51 afforded a residue that was washed with Et_2O to give compound **1** (250 mg): mp>300°; ir ν max (KBr) cm^{-1} 3427, 2941, 1696, 1633, 1457, 1379, 1019; ^{1}H nmr see Table 1; eims *m/z* (% rel. abundance), 248 (100), 207 (10), 203 (82), 202 (12), 189 (23), 175 (49), 161 (24), 145 (20), 133 (34). (Found: C, 76.38; H, 10.25. $C_{30}H_{48}O_4$ requires C, 76.27; H, 10.23%).

Subsequent fractions 96-102, from the original column, when eluted with the same solvent system, gave 60 mg of **9**: mp>300°; ir ν max (KBr) cm^{-1} 3422, 2938, 1693, 1637, 1463, 1389, 1021, 669, 460; ^{1}H nmr see Table 1; eims *m/z* (% rel. abundance), 502 [M]$^+$ (0.3), 484 (0.1), 456 (1), 278 (78), 233 (83), 232 (15), 219 (14), 173 (13), 187 (100), 133 (10). (Found: C, 71.72; H, 9.23. $C_{30}H_{46}O_6$ requires C, 71.68; H, 9.22%).

The more polar fractions 126-138, eluted with EtOAc-Me_2CO (8:2), afforded 325 mg of sitosteryl 3β-glucoside, identified by standard sample procedures (tlc, ir, ^{1}H nmr) for both the glycoside as well as its hydrolysis and acetylation products.

ACETYLATION OF **1**.—Compound **1** (50 mg) was dissolved in 5 ml Ac_2O and 1 ml pyridine. After 1 h, the reaction mixture was worked up as usual to yield, after cc purification, two products: an amorphous monoacetate **2** (8 mg): ir ν max ($CHCl_3$) cm^{-1} 3624, 2948, 1725, 1604, 1468, 1378, 1254, 1038, 985; ^{1}H nmr see Table 1; eims *m/z* (% rel. abundance), 514 [M$^+$] (1.4), 496 (1.2), 454 (1.5), 248 (95.6), 203 (55.2), 202 (7), 189 (16), 175 (4), 133 (18), 43 (100); and a diacetate **3** (24 mg): mp 262-264°; ir ν max ($CHCl_3$) cm^{-1} 3020, 2949, 1725, 1715, 1602, 1460, 1389, 1376, 1252, 1031, 985, 909; ^{1}H nmr see Table 1; eims *m/z* (% rel. abundance), 556 [M$^+$] (0.5), 512 (0.4), 510 (0.5), 497 (0.8), 496 (2.4), 436 (2.1), 249 (22.9), 248 (94.7), 203 (53.9), 202 (7), 189 (14), 175 (6), 161 (4), 133 (15), 43 (100).

METHYL ESTER (**4**) OF **1**.—Compound **1** (200 mg) dissolved in EtOH was alkylated with an excess of CH_2N_2 in Et_2O at 5° to give **4** (197 mg): mp 199-210°; $[\alpha]^{25}D$ +58.8° (0.35, $CHCl_3$); ir ν max ($CHCl_3$) cm^{-1} 3627, 2987, 2947, 1718, 1462, 1381, 1016; ^{1}H nmr see Table 1; ^{13}C nmr see Table 2; eims *m/z* (% rel. abundance), 486 [M$^+$] (1.3), 468 (0.7), 453 (0.5), 247 (1.3), 426 (1.2), 262 (89.9), 224 (10), 203 (100), 189 (20.7), 187 (18.5), 175 (26.7), 133 (35.3).

ACETYLATION OF **4**.—Derivative **4** (180 mg) was dissolved in 5 ml Ac_2O and 1.5 ml pyridine. The reaction mixture was worked up as described for compound **1** affording two products: the monoacetate **5** (50 mg), mp 219-220°; $[\alpha]^{25}D$ +62.8 (0.24, $CHCl_3$); ir ν max ($CHCl_3$) cm^{-1} 3621, 3019, 2950, 1724, 1460, 1389, 1254, 1196, 1167, 1031, 981; ^{1}H nmr see Table 1; ^{13}C nmr see Table 2; eims *m/z* (% rel. abundance), 528 [M$^+$] (1.9), 510 (1.4), 468 (1.2), 451 (1.3), 265 (5), 262 (65.5), 203 (100), 189 (22.9), 187 (18.2), 175 (9), 133 (18), 43 (37.7); and the diacetate **6** (80 mg); mp 196-197°; ir ν max ($CHCl_3$) cm^{-1} 3019, 2950, 1724, 1460, 1434, 1376, 1259, 1176, 1032, 984; ^{1}H nmr see Table 1; ^{13}C nmr see Table 2; eims *m/z* (% rel. abundance), 570 [M$^+$] (0.8), 510 (2.5), 451 (1.8), 450 (1.4), 262 (61.4), 247 (7), 203 (53.9), 189 (18), 187 (15.3), 175 (6), 133 (14), 43 (100).

OXIDATION OF **5**.—The monoacetate derivative **5** (10 mg) was dissolved in 1 ml Me_2CO, and 0.2 ml of Jones reagent (CrO_3-HOAc) were added at room temperature. After shaking 5 min, the solution was diluted with H_2O and extracted with $CHCl_3$. Removal of the excess of solvent left a residue which was purified by cc over Si gel with $CHCl_3$-Me_2CO (9:1). Eluates yielded the 3-oxo derivative **7** (3 mg). Ir ν max ($CHCl_3$) cm^{-1} 3019, 2952, 1723, 1656, 1460, 1388, 1373, 1235, 1170, 1035, 981, 802; ^{1}H nmr see Table 1.

DIMETHYL ESTER (**10**) OF **9**.—The acid **9** (60 mg) dissolved in MeOH was esterified with excess of CH_2N_2 in Et_2O at 5° yielding compound **10**, which was crystallized from $CHCl_3$-MeOH (1:1): mp 205°; ir ν max ($CHCl_3$) cm^{-1} 3624, 2989, 2945, 1718, 1461, 1379, 1014; ^{1}H nmr see Table 1; ^{13}C nmr see Table 2; eims *m/z* (% rel. abundance), 530 [M$^+$] 1.8, 512 (0.6), 470 (1), 306 (72), 247 (83), 246 (15), 233 (8), 224 (1), 187 (100), 43 (32).

ACETYLATION OF **10**.—The dimethyl ester **10** (50 mg) was acetylated with Ac_2O-pyridine. The reaction mixture was kept at room temperature for 3 days and worked in the usual way to give **11**, which was crystallized from EtOAc as white small crystals, mp 272°: $[\alpha]^{25}D$ +89.8 (0.17, $CHCl_3$); ir ν max (KBr) cm^{-1} 3020, 2948, 1735, 1460, 1438, 1374, 1250, 1175, 1030, 983; ^{1}H nmr see Table 1; eims *m/z* (% rel. abundance), 614 [M$^+$], 554 (3), 308 (10), 306 (75), 247 (82), 246 (18), 187 (100), 43 (38).

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