

Norditerpenes and Norsesterterpenes from *Salvia yosgadensis*

Gülaçti Topcu*[†] and Ayhan Ulubelen^{†,‡}

TUBITAK, Marmara Research Center, Research Institute for Basic Sciences, Department of Chemistry, P.O. Box 21, 41470 Gebze, Kocaeli, Turkey, and Faculty of Pharmacy, University of Istanbul, 34452 Beyazit, Istanbul, Turkey

Timothy Chit-Ming Tam and Chun-Tao Che

Department of Chemistry, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong

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The aerial parts of *Salvia yosgadensis* afforded five new terpenes with unusual skeletons, together with two known norditerpenes, ambreinolide and norambreinolide. The new compounds were elucidated as 6 α -hydroxyambreinolide, 6 α -hydroxynorambreinolide, 6 α -hydroxy-8 α -acetoxy-13,14,15,16-tetranorlabdan-12-oic acid, and two 19,20-dinorsesterterpenes, named as yosgadensonol and 13-*epi*-yosgadensonol. Their structures were determined by spectroscopic means, particularly by extensive 1D and 2D NMR studies.

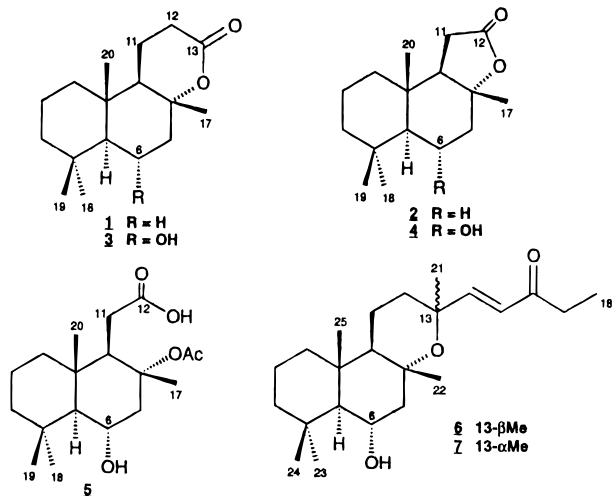
Salvia species are pharmacologically active and used in folk medicine all around the world. Several plants of this genus have been associated with antibacterial, estrogenic, antioxidant, and antitumor activities^{1–4} and are used in the treatment of eczema, psoriasis, and tuberculosis.^{5,6} There are about 90 species of *Salvia* growing in Turkey, 44 of which are endemic. As part of our continuing chemical investigation of Turkish *Salvia* species, we have now studied an endemic species, *S. yosgadensis* Freyn. et Bornm. (Lamiaceae) for its terpenic constituents. A literature survey showed that this species has not hitherto been studied chemically or biologically. In this report, we describe the isolation and characterization of five new terpene structures, as well as two previously known compounds, ambreinolide (1)^{7,8} and norambreinolide (2).⁹ The new compounds were established as 6 α -hydroxyambreinolide (3), 6 α -hydroxynorambreinolide (4), 6 α -hydroxy-8 α -acetoxy-13,14,15,16-tetranorlabdan-12-oic acid (5), and two 19,20-dinorsesterterpenes, yosgadensonol (6) and 13-*epi*-yosgadensonol (7).

been isolated previously from the aerial parts of *Salvia aethiopsis*.¹⁰

Results and Discussion

Ambreinolide (1) and norambreinolide (2) were identified by analysis of the spectral data and by comparison with literature.^{7–10} ¹H- and ¹³C-NMR spectral data unambiguously, assigned by a combination of 1D and 2D techniques, served as reference values for the structure elucidation of new compounds 3–7.

The ¹³C NMR spectrum (APT and DEPT experiments) of compound 3 (Table 1) displayed four methyl, six methylene, three methine, and four quaternary carbons. The HREIMS gave a molecular ion peak at *m/z* 280.2031. The CIMS gave a [M + 1]⁺ ion peak at *m/z* 281, indicating the molecular formula C₁₇H₂₈O₃, which is consistent with a hydroxyl derivative of ambreinolide. An intense signal appeared at *m/z* 263 for [M + 1 – H₂O]⁺. The IR spectrum of compound 3 showed absorption signals at 1716 cm⁻¹ (six-membered lactone) and 3454 cm⁻¹ (hydroxyl). The ¹H-NMR spectrum exhibited four methyl singlets at δ 0.89, 1.02, 1.19, and 1.45, a methine proton at δ 3.90 (*J* = 4, 11, 12 Hz). The multiplicity and *J* values of the last signal indicate that a secondary hydroxyl group is located between a methine and a methylene group, possibly on either C-6 or C-11 of ambreinolide. The placement of the hydroxyl on C-6 was deduced by the following reasons. First, the chemical shift of C-7 was observed at δ 51.87 with a downfield shift of *ca.* 17 ppm relative to that of 1. Second, a concomitant downfield shift of C-5 at δ 61.14 is also indicative of a hydroxyl group located at C-6. Spin decoupling and phase-sensitive COSY experiments confirmed the relationship between H-6 (δ 3.90) and H-7 β (δ 2.33, dd, *J* = 4, 13 Hz) and H-7 α (δ 1.78, dd, *J* = 11, 13 Hz), as well as between H-6 and H-5 (δ 1.10, d, *J* = 12 Hz). The stereochemistry of the hydroxyl group at C-6 was determined as α on the basis of the coupling constants of H-6 and the NOESY results (Figure 1). Thus, H-6 was found to show NOE with H-17, H-19, and H-20, all oriented at β positions. Due to the α orientation of the hydroxyl group at C-6, H-18 and C-18 were shifted more downfield than expected (δ _H 1.19, δ _C 36.47). All carbons could be assigned by HMQC (Table



Norditerpenes and norsesterterpenes are not common in *Salvia* species; however, two tetranorlabdanes have

[†] TUBITAK.

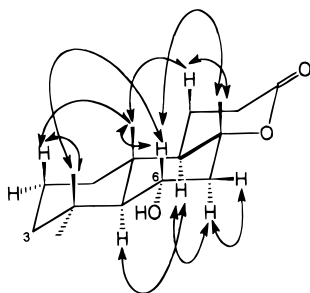
[‡] University of Istanbul.

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Table 1. ^1H - and ^{13}C -NMR Data of Compounds **3**, **4**, and **5**^a (in CDCl_3 , 400 MHz)

position	3		4		5	
	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
1	1.59 br dd, 0.98 m	39.28	1.42 ddd, 1.09 m	39.46	1.5 m, 1.1 m	40.44
2	1.61 m, 1.48 m	18.18	1.68 ddd, 1.47 m	17.89	1.62 m, 1.45 m	19.15
3	1.22 m, 1.39 dt	43.42	1.32 m, 1.43 m	43.65	1.22 m, 1.32 m	44.81
4		33.67		33.82		34.66
5	1.10 d	61.14	1.24 d	62.10	1.17 d	61.38
6	3.90 ddd	68.45	3.99 ddd	69.82	3.80 ddd	69.53
7	2.33 dd, 1.78 dd	51.87	2.42 dd, 1.82 dd	49.90	2.93 dd, 1.94 dd	50.40
8		82.53		84.25		8.65
9	1.53 dd	53.09	2.02 dd	58.81	2.26 dd	55.82
10		37.71		35.51		39.76
11	1.76 ddd, 1.67 dt	15.93	2.25 dd, 2.44 dd	28.80	2.34 dd, 2.42 dd	31.55
12	2.68 ddd, 2.54 dd	28.71		176.39		171.94
13		171.40				
17	1.45 s	24.01	1.37	22.90	1.56 s	21.80
18	1.19 s	36.47	1.18	36.20	1.19 s	37.00
19	1.02 s	21.96	1.02	21.54	0.99 s	22.40
20	0.89 s	16.22	0.95	16.39	0.88 s	17.30
$\text{CH}_3\text{C}=\text{O}$					1.92 s	22.68
$\text{CH}_3\text{C}=\text{O}$						170.00

^a The spectrum of **5** was taken in ($\text{CDCl}_3 + \text{CD}_3\text{OD}$); assignments were confirmed by ^1H - ^{13}C correlations. J (Hz): $J_{1\alpha,2\alpha} = 4.5$; $J_{1\alpha,2\beta} = 11$; $J_{1\beta,2\alpha} = 8$; $J_{1\beta,2\beta} = 4.5$; $J_{1\alpha,1\beta} = 13$; $J_{2\alpha,2\beta} = 13.5$; $J_{5,6} = 12$; $J_{6,7\alpha} = 11$; $J_{6,7\beta} = 4$; $J_{7\alpha,7\beta} = 13$. Only for **3**: $J_{9,11\beta} = 11.5$; $J_{9,11\alpha} = 6$; $J_{11\alpha,11\beta} = 14$; $J_{11\alpha,12\alpha} = 2.5$; $J_{11\beta,12\beta} = 4$; $J_{11\alpha,12\beta} = 8.5$; $J_{12\alpha,12\beta} = 17.5$. For **4** and **5**: $J_{9,11\alpha} = 6.5$; $J_{9,11\beta} = 14$; $J_{11\alpha,11\beta} = 16$.

**Figure 1.**

1) and HMBC (Table 2) experiments. Compound **3** was therefore established as a trinorlabdane, 6α -hydroxyambrinolide.

The HREIMS of compound **4** exhibited a molecular ion peak at m/z 266.1869, indicating $\text{C}_{16}\text{H}_{26}\text{O}_3$, consistent with a hydroxyl derivative of norambrinolide. The ^{13}C NMR (APT and DEPT) displayed four methyl, five methylene, three methine, and four quaternary carbons. The ^1H NMR spectrum (Table 1) of **4** displayed four tertiary methyl singlets at δ 0.95, 1.02, 1.18, and 1.37 and a methine proton at δ 3.99 (ddd, $J = 4, 11, 12$ Hz), indicating a secondary hydroxyl group between methyl and methylene groups as in compound **3**. Spin decoupling and COSY experiments showed the relationships between H-6 (3.99) and H-7 β (δ 2.42, dd, $J = 4, 13$ Hz) and H-7 α (1.82, dd, $J = 11, 13$ Hz) as well as between H-6 and H-5 (δ 1.24, d, $J = 12$ Hz), as in compound **3**. After acetylation, H-6 was shifted to δ 5.19 (ddd, $J = 4.0, 11.5, 13$ Hz) and an acetyl signal appeared at δ 2.07 (3H, s). Compounds **3** and **4** had quite similar ^1H -NMR spectra, whereas differences could be found in the IR spectra with the observation of a five-membered lactone ring (1785 cm^{-1}) in **4** instead of a six-membered ring (1716 cm^{-1}) in **3**. Unambiguous assignment of ^1H - and ^{13}C -NMR data was made possible by a combination of HMQC (Table 1) and HMBC (Table 2) experiments. By comparing the spectral data with those of **3** and similar tetranorlabdanes,¹⁰ compound **4** was established as a tetranorlabdane, 6α -hydroxynorambrinolide.

The molecular ion peak of compound **5** at m/z 326.2088 (HREIMS) was analyzed for a molecular formula of

Table 2. HMBC Data of Compounds **3**, **4**, and **5**

H	long-range correlated carbons		
	3	4	5
1		C-20	
2			C-1, C-10
3			C-19
5		C-19	
7	C-6, C-8, C-17	C-5, C-6, C-8, C-9, C-17	
9	C-8, C-10, C-11, C-17, C-20	C-8, C-10, C-11, C-17, C-20	C-1, C-11
11	C-8, C-9, C-12,	C-8, C-9, C-12	C-8, C-9, C-10
17	C-7, C-8, C-9	C-7, C-8, C-9	C-7, C-8, C-9
18	C-3, C-4, C-5, C-19	C-3, C-4, C-5, C-19	C-3, C-4, C-5, C-19
19	C-3, C-4, C-5, C-18	C-3, C-4, C-5, C-18	C-3, C-4, C-5, C-18
20	C-1, C-5, C-9, C-10	C-1, C-5, C-9, C-10	C-5, C-9, C-10

$\text{C}_{18}\text{H}_{30}\text{O}_5$. The ^{13}C -NMR spectrum clearly displayed signals for five methyl, five methylene, three methine, and five quaternary carbons. The IR spectrum showed a large hydroxyl band at $3240\text{--}3400\text{ cm}^{-1}$ and two carbonyl absorptions at 1685 cm^{-1} (carboxylic acid) and at 1725 cm^{-1} (acetyl). These carbonyl functional groups were substantiated by two carbonyl signals present at δ 171.94 and δ 170.0, as well as an acetyl methyl signal at δ 22.68 in its ^{13}C -NMR spectrum. The ^1H -NMR spectrum (Table 1) gave five methyl singlets at δ 0.88, 0.99, 1.19, 1.56, and 1.92, the last assigned to an acetyl methyl. A methine proton was observed at δ 3.80 (ddd, $J = 4, 11, 12$ Hz) consistent with H-6 as in compounds **3** and **4**. Connectivity of H-9 and H-11, as well as H-5, H-6, and H-7, was confirmed by the COSY experiment, and the 6α -hydroxyl group was deduced from the NOESY results. Thus, H-6 showed NOE with all β -oriented methyl groups [δ 1.56 (C-17), 0.99 (C-19), and 0.88 (C-20)] in the molecule. Following above-mentioned NOESY results, the acetoxy group must be located at C-8 with an α orientation, thus retaining the same stereochemistry at this asymmetric center as in compounds **1**–**4**. The HMQC (Table 1) and HMBC (Table 2) experiments allowed the assignments of all carbons and protons, and the structure of **5** was deduced as 6α -hydroxy- 8α -acetoxy-13,14,15,16-tetranorlabdan-12-oic acid.

The HREIMS spectrum of compound **6** gave a molecular ion peak at m/z 362.2815 corresponding to a

Table 3. ¹H- and ¹³C-NMR Data of Compounds **6**, **6a**, and **7** (in CDCl₃, 400 MHz)^a

position	6		6a		7	
	¹ H	¹³ C	¹ H	¹³ C	¹ H	¹³ C
1	1.60 m, 1.34 m	39.91	1.58 m, 1.28 m	38.80	1.60 m, 0.91 m	39.23
2	1.52 m	18.20	1.40 m	18.11	1.47 m	18.33
3	1.42 m, 1.27 m	43.54	1.38 m, 1.21 m	43.30	1.39 m, 1.16 m	43.60
4		33.70		33.28		31.68
5	1.00 d	61.69	1.12 d	58.85	1.02 d	61.69
6	3.87 ddd	69.15	5.12 ddd	70.72	3.84 ddd	69.13
7	2.20 dd, 1.58 dd	54.29	2.12 dd, 1.60 dd	49.69	2.13 dd, 1.48 dd	53.97
8		74.75		74.47		75.64
9	1.19 dd,	54.86	1.14 dd	54.88	1.25 brd	57.65
10		37.70		37.80		32.92
11	1.62 dd, 1.36 dd	15.39	1.62 m, 1.34 m	15.38	1.60 dd, 1.38 dd	16.05
12	2.08 m, 1.56 m	34.86	2.02 m, 1.58 m	34.85	2.20 dd, 1.57 dd	36.44
13		73.03		73.07		72.84
14	6.77 d	154.17	6.97 d	154.17	6.98 d	154.62
15	6.25 d	125.31	6.22 d	125.38	5.99 d	125.18
16		195.31		201.68		201.51
17	2.58 dq	33.96	2.58 dq	33.90	2.61 dq	35.13
18	1.10 t	8.11	1.08 t	8.20	1.11 t	8.08
21	1.29 s	28.81	1.29 s	28.78	1.22 s	25.26
22	1.35 s	26.87	1.40 s	26.68	1.18 s	33.78
23	1.16 s	36.44	1.00 s	36.00	1.15 s	37.55
24	0.99 s	21.84	0.84 s	21.98	0.97 s	21.80
25	0.80 s	16.58	0.86 s	16.50	0.74 s	17.23
CH ₃ C=O			2.04 s	21.89		
CH ₃ C=O				170.13		

^a *J* (Hz): *J*_{5,6} = 12, *J*_{6,7α} = 11, *J*_{6,7β} = 4; *J*_{7α,7β} = 12.5; *J*_{9,11α} = 2.5; *J*_{9,11β} = 11; *J*_{11α,11β} = 13; *J*_{11α,12β} = 3; *J*_{11β,12β} = 4.5; *J*_{12β,12β} = 14; *J*_{14,15} = 16; *J*_{17,18} = 7.5.

molecular formula C₂₃H₃₈O₃. Although the molecular ion peak was at low intensity, [M – Me]⁺ and [M – Me – H₂O]⁺ fragment signals at *m/z* 347 and 329 were significant with high intensities. Its ¹³C-NMR spectrum indicated the presence of six methyl, seven methylene, five methine, and five quaternary carbons. The presence of a secondary hydroxyl group was shown by a methine signal in the ¹H NMR (δ_H 3.87, ddd, *J* = 4, 11, 12 Hz), which was also supported by an IR band at 3460 cm⁻¹. The location of the hydroxyl at C-6 and the connectivity between H-5, H-6, and H-7 were deduced from the COSY spectrum as in compounds **3–5**. Acetylation of compound **6** afforded a monoacetate (**6a**) (Table 3), in which the H-6, was shifted downfield to δ 5.12. The presence of an ether ring in **6** was suggested by two quaternary carbon signals at δ 73.03 and 74.75. Two methyl groups which appeared in the ¹H-NMR spectrum as two singlets at δ 1.29 and 1.35 must be attached to carbon atoms bearing the oxygen atom of the ether bridge. When the ¹³C-NMR spectrum of **6** was compared with those of manoyloxide and its derivatives,^{10,11} it was deduced that compound **6** possesses the same A, B, and C rings as in manoyloxide. The rest of the molecule forms a side chain containing five carbons, in which a conjugated ketone could be assigned in accordance with the following considerations: An IR band at 1625 cm⁻¹ (C=C) and *trans*-coupled two vinylic protons at δ 6.25 and 6.77 (*J* = 16 Hz) indicated a (CH=CH) group. This was confirmed by two olefinic CH carbons at 125.31 and 154.17 ppm. The downfield shift of one of the olefinic carbons further suggested a conjugated system with a ketone carbonyl group (δ_C 195.31; IR_{max} 1695 cm⁻¹). The HMQC (Table 3) and HMBC (Table 4) experiments allowed assignments of all protons and carbons in **6**. The HMBC technique was particularly useful in determining the partial structure of the side chain. Thus, H-14 showed long-range couplings with C-16 carbonyl and C-21 methyl carbons; on the other hand, H-15 could be related via long-range

Table 4. HMBC Data of Compounds **6** and **7**

H	long-range correlated carbons	
	6	7
5	C-4, C-7	
6		C-5
7	C-5, C-6, C-8, C-9, C-22	C-6, C-8
14	C-16, C-21	C-16, C-21
15	C-13, C-17	C-16, C-17
17	C-18	C-16, C-18
18	C-16, C-17	
21	C-12, C-13	
22	C-7, C-8, C-9	C-7, C-8
23	C-3, C-4, C-5, C-24	C-24
24	C-3, C-4, C-5, C-23	C-6, C-23
25	C-1, C-9, C-10	C-1, C-5, C-10

correlation to C-13 and C-17. Compound **6** was therefore deduced as 19,20-dinorsesterterpene consisting of a partial structure of manoyl oxide, and it was named yosgadensonol.

A compound (**7**) exhibiting similar spectral data to that of **6** was also obtained. The ¹H- and ¹³C-NMR data of both compounds (Table 3 and 4) were quite similar, including the 1D NOE difference spectra obtained by irradiation of H-6β, the signals for H-22, H-24, H-25, and H-7*eq* were clearly enhanced, suggesting β orientation of these groups in both compounds. However, a difference has been detected by NOE irradiation of H-22, which is the most downfield methyl signal in both compounds, observing enhancements on H-21 and H-25 in compound **6** indicating the β orientation of these methyl groups. When H-22 of compound **7** was irradiated in the same manner, only H-25 was enhanced. The lack of NOE between H-22 and H-21 in the latter suggested α position of H-21 at C-13. As a result, 1D NOE experiments of both compounds indicated that the only difference is the stereochemistry at C-13. Compound **7** is therefore an 13-epimer of **6** and was named 13-*epi*-yosgadensonol.

Experimental Section

General Procedures. IR: Perkin-Elmer 983 in CHCl_3 ; ^1H - and ^{13}C -NMR spectra were recorded on 200 MHz Bruker AC 200L at TUBITAK, (Gebze-Turkey), and 400 MHz JEOL JNM EX-400 at Hong Kong University of Science & Technology, Hong Kong, with TMS as internal standard. LRMS and HRMS data were obtained on a VG Zab Spec at TUBITAK.

Plant Material. The aerial parts of *Salvia yosgadensis* Freyn. et Bornm. were collected from Central Turkey (near Sultanhanı, Konya) and identified by Dr. E. Tuzlaci. Voucher specimen is deposited in the Herbarium of Faculty of Pharmacy, University of Istanbul (ISTE 50876).

Extraction and Isolation of the Compounds. Powdered plant (680 g) was extracted with Me_2CO in a Soxhlet, and the extract was evaporated *in vacuo* to give 40 g of a residue. The latter was fractionated on a Si gel column (5.5×70 cm) and eluted with petroleum, first 1 L of petroleum, then followed by a gradient of CHCl_3 up to 100%, and then EtOH. After TLC application, similar fractions were combined and further separated on smaller Si gel or Sephadex LH-20 columns. In the latter case, elution was carried out using petrol- CHCl_3 -MeOH (7:4:1) continuously as solvent. Compounds **4**, **6**, and **7** were obtained during elution of 100% CHCl_3 , while compounds **3** and **5** were obtained with 2–3% EtOH as gradient to CHCl_3 . More purification of some compounds was carried out by prep. TLC plates using different solvent systems, petrol- CHCl_3 (6:4) for compounds **1** and **2**, C_6D_6 - Me_2CO (9:1) for **4**, CHCl_3 - Me_2CO (9:1) for **5**, and CHCl_3 - Me_2CO (85:15) for **3**. The following compounds were obtained successively: norambreinolide (**2**) (9 mg), ambreinolide (**1**) (7 mg), yosgadensonol (**6**) (18 mg), 13-*epi*-yosgadensonol (**7**) (15 mg), 6 α -hydroxynorambreinolide (**4**) (35 mg), 6 α -hydroxyambreinolide (**3**) (18 mg), 6 α -hydroxy-8 α -acetoxy-13,14,15,16-tetranorlabdan-12-oic acid (**5**) (9 mg).

6 α -Hydroxyambreinolide (3): $[\alpha]_{\text{D}} +40.8^\circ$ (*c* 0.1, CHCl_3); IR ν_{max} (CHCl_3) 3454, 2927, 2875, 1716, 1466, 1394, 1275, 1065, 973 cm^{-1} ; ^1H and ^{13}C NMR (400 MHz, in CDCl_3 , see Table 1); HREIMS m/z 280.2031 (calcd for $\text{C}_{17}\text{H}_{28}\text{O}_3$, 280.2038); CIMS m/z (rel int) 281 $[\text{M} + 1]^+$ (0.5), 263 $[\text{M} + 1 - \text{H}_2\text{O}]^+$ (8.3), 247 (10.2), 219 (3.9), 190 (11.4), 156 (100), 124 (55.2), 109 (77.9), 95 (16.6), 69 (22.2), 43 (32.2).

6 α -Hydroxynorambreinolide (4): $[\alpha]_{\text{D}} +61.0^\circ$ (*c* 0.35, CHCl_3); IR ν_{max} (CHCl_3) 3533, 3289, 2921, 2848, 2368, 1789, 1644, 1457, 1400, 1223, 1190, 1052, 940 cm^{-1} ; ^1H and ^{13}C NMR (400 MHz, in CDCl_3 , see Table 1); HREIMS m/z 266.1869 (calcd for $\text{C}_{16}\text{H}_{26}\text{O}_3$, 266.1881); CIMS m/z (rel int) 267 $[\text{M} + 1]^+$ (3.2), 249 $[\text{M} + 1 - \text{CH}_3]^+$ (100), 193 (11.6), 189 (37.3), 165 (24.3), 109 (6.9), 41 (65.6).

Acetylation of 4. Compound **4** (8 mg) in pyridine (1 mL) was treated with Ac_2O (1 mL) and left at room temperature for 24 h to afford a monoacetate (**4a**): $[\alpha]_{\text{D}} +79.1^\circ$ (*c* 0.7, CHCl_3); ^1H NMR (CDCl_3 , in 200 MHz) δ 0.90 (3H, s, Me-20), 1.00 (6H, s, Me-18 and Me-19), 1.42

(3H, s, Me-17), 2.07 (3H, s, OAc), 5.19 (1H, ddd, $J = 4, 11.5, 13$ Hz H-6).

6 α -Hydroxy-8 α -acetoxy-13,14,15,16-tetranorlabdan-12-oic acid (5): IR ν_{max} (CHCl_3) 3240–3400, 2920, 2550, 1725, 1685, 1460, 1380, 1360, 1260, 1170, 1138, 1067, 1052, 755 cm^{-1} ; ^1H and ^{13}C NMR (400 MHz, in $\text{CDCl}_3 + \text{CD}_3\text{OD}$, see Table 1); HREIMS m/z 326.2088 (calcd for $\text{C}_{18}\text{H}_{30}\text{O}_5$, 326.2093); EIMS m/z (rel int) 326 $[\text{M}]^+$ (3.4), 267 $[\text{M} - \text{OAc}]^+$ (22.5), 248 $[\text{M} - \text{HOAc} - \text{H}_2\text{O}]^+$ (100), 239 (20.1), 223 (19.7), 203 (76.2), 189 (34.6), 175 (26.6), 163 (29.3), 145 (35.0), 133 (56.9), 125 (59.8), 109 (53.7).

Yosgadensonol (6): IR ν_{max} (CHCl_3) 3460, 2920, 2860, 1695, 1625, 1459, 1380, 1362, 1257, 1200, 1155, 1120, 1060, 975, 860, 760 cm^{-1} ; ^1H and ^{13}C NMR (400 MHz, in CDCl_3 , see Table 3); HREIMS m/z 362.2815 (calcd for $\text{C}_{23}\text{H}_{38}\text{O}_3$, 362.2093); EIMS m/z (rel int) 362 $[\text{M}]^+$ (3.3), 347 $[\text{M} - \text{Me}]^+$ (63.2), 329 $[\text{M} - \text{H}_2\text{O}]^+$ (50.2), 311 (57.3), 277 (37.6), 261 (32.2), 237 (34.1), 219 (21.3), 201 (47.0), 190 (83.4), 163 (32.0), 138 (32.7), 127 (43.2), 109 (100), 95 (58.6), 81 (52.3), 69 (61.8).

Acetylation of 6. Compound **6** (5 mg) in pyridine (1 mL) was treated with Ac_2O (1 mL) and left at room temperature overnight to yield a monoacetate (**6a**): $[\alpha]_{\text{D}} +75^\circ$ (*c* 0.3, CHCl_3); IR ν_{max} (CHCl_3) 2934, 2875, 1743, 1677, 1466, 1387, 1250, 1078, 1025, 959 cm^{-1} ; ^1H and ^{13}C NMR (400 MHz, in CDCl_3 , see Table 3); CIMS 405.4 $[\text{M} + 1]^+$ (0.5), 390 $[\text{M} + 1 - \text{Me}]^+$ (6.2), 344 $[\text{M} - \text{HOAc}]^+$ (12.8), 329 $[\text{M} - \text{Me}]^+$ (78.1), 311 $[\text{M} - \text{H}_2\text{O}]^+$ (32.9), 259 (30.3), 201 (46.9), 190 (93.8), 149 (75.4), 119 (55.2), 95 (39.3), 69 (45.9), 57 (47.0), 43 (100).

13-*epi*-Yosgadensonol (7): $[\alpha]_{\text{D}} +57^\circ$ (*c* 0.2, CHCl_3); IR ν_{max} (CHCl_3) 3447, 2927, 2875, 1710, 1677, 1624, 1460, 1387, 1269, 1203, 1078, 979, 762 cm^{-1} ; ^1H and ^{13}C NMR (400 MHz, in CDCl_3 , see Table 3); EIMS m/z 362 $[\text{M}]^+$ (0.3), 347 $[\text{M} - \text{Me}]^+$ (39.7), 329 $[\text{M} - \text{H}_2\text{O}]^+$ (34.7), 311 (33.1), 261 (12.0), 245 (19.3), 203 (23.2), 201 (37.6), 190 (100), 176 (31.5), 149 (36.0), 137 (42.1), 119 (51.3), 109 (57.4), 95 (46.7), 69 (58.9), 42 (78.8).

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