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SESTERTERPENE LACTONES FROM *SALVIA AETHIOPIS*. SALVIAETHIOPISOLIDE AND 13-EPI-SALVIAETHIOPISOLIDE

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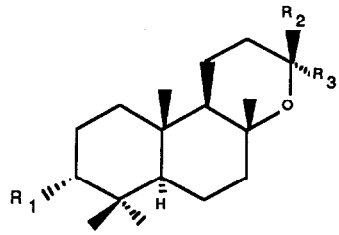
ABSTRACT. Two sesterterpene lactones and two tetranorlabdanes were isolated from the aerial parts of *Salvia aethiopis*. Their structures were elucidated by spectroscopic methods, including 2D-NMR experiments, and by the correct interpretation of several chemical transformations.

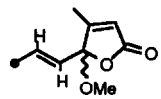
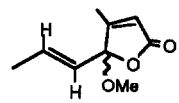
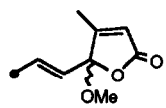
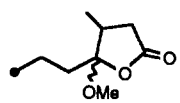
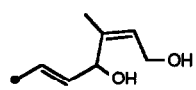
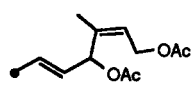
INTRODUCTION

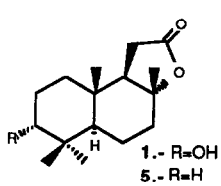
In the last few years many diterpenes with abietane[1,2], pymarane[3] and neoclerodane[4] skeletons were isolated from plants of the genus *Salvia* . Recently two structurally related sesterterpenes have been communicated as components of *S. hypoleuca* [5] and *S. syriaca* [6] . From *S. aethiopis* only the components of the roots were studied [7,8]. We now report the components of aerial parts of *S. aethiopis* where , beside several known sterols and triterpenes, we isolated two tetranorditerpenes: 3α-hydroxy-nor-ambreinolide, **1**, and methyl 3α–hydroxy-8α- acetoxy-13,14,15,16-tetranorlabdan-12-oate, **2**, and two sesterterpene lactones with a partial structure of 13-epi-manoyl oxide and manoyl oxide, **3**, and **4**, both as epimeric pairs at the anomeric carbon atom (C-16) of a γ-methoxybutenolide. These were named 3-epi-salviaethiopisolide and salviaethiopisolide respectively.

RESULTS AND DISCUSSION

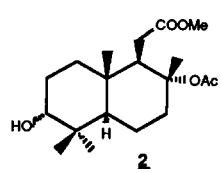
Compound **1** was a solid with a m.p. 190-191º and $[\alpha]_D$= + 22.2º. The molecular ion of its mass spectrum (M^+=266) is in agreement with the molecular formula $C_{16}H_{26}O_3$. The IR spectrum showed bands due to hydroxyl groups and a γ-lactone ring (3580 and 1760 cm^{-1}). The ^{1}H-NMR spectrum (see experimental) showed signals assignable to four methyl groups on quaternary carbon atoms, one axial-OH-geminal proton (3.45 ppm, dd, J=2.7 and 2.9 Hz.) and two protons on an



	R_1	R_2	R_3
3	OH		CH_3
4	OH	CH_3	
6	OAc		CH_3
7	OH		CH_3
8	OH		CH_3
9	OAc		CH_3
10	H	$-CH=CH_2$	CH_3
11	OH	-COOH	CH_3
12	H	CH_3	$-CH=CH_2$



1.- R=OH
5.- R=H



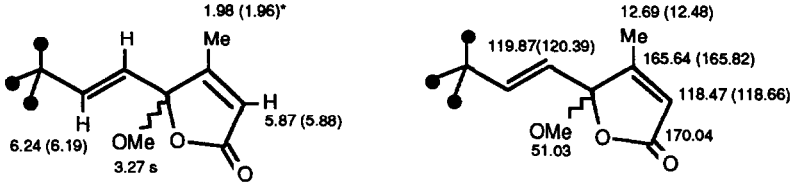
2

allylic carbon atom with respect to a carbonyl group. The ^{13}C-NMR spectrum (Table 2) confirmed the presence of the four Me-C, the γ-lactonic C=O (176.48,s) and the secondary hydroxyl groups, with a doublet due to one carbon atom at 75.86 ppm. The rest of the signals agreed with the presence of five methylenes, two methines and three quaternary carbon atoms, one of them supporting the oxygen atom of the lactone ring at 86.13 ppm. All these data are very similar to those exhibited by the nor-ambreinolide **5** [9]. The most significant differences were one additional signal in the ^{1}H-NMR spectrum, due to the geminal proton of a secondary axial hydroxyl group, and the different chemical shifts in the ^{13}C-NMR spectrum, for the secondary axial hydroxyl group at C-3[10].

The experimental correlation of spectra, ^{1}H-^{1}H (COSY-H4) and ^{1}H-^{13}C (HCCORR), allowed us to assign unequivocally all the signals of the ^{1}H and ^{13}C-NMR spectra and to identify compound **1** as 3α-hydroxy-nor-ambreinolide . The absolute configuration was assigned by comparison of optical rotation with that exhibited by other 13,14,15,16-tetranor-labdanes[11].

Compound **2** , $C_{19}H_{32}O_5$, showed an IR spectrum with bands due to hydroxyl, acetoxyl and methoxy carbonyl groups. The ^{1}H and ^{13}C-NMR spectra (Table 2) were very similar to those of compound **1**, but with additional signals due to the methoxyl and acetoxyl groups. Saponification of **2** (KOH/MeOH) followed by treatment with p-toluenesulfonic acid, afforded a product identical to **1** . This allowed us to identify **2** as methyl 3α-hydroxy-8α-acetoxy-13,14,15,16-tetranorlabdan-12-oate.

Compound **3** , $C_{26}H_{40}O_5$, with $[\alpha]_D$= + 32º , is a very viscous oil which we were unable to crystallize. Elution with different solvents and TLC (Si gel/$AgNO_3$) always afforded one spot, although the ^{1}H and ^{13}C NMR spectra (Table 1 and 2) revealed the duplicity of several signals ^{1}H: 1.98/1.96, 5.34/5.43, 5.88/5.87 and 6.24/6.19; ^{13}C: 12.69/12.48 , 165.64/165.82, 119.87/120.39 and 118.47/118.66 with a relative intensity of 55/45 for all of them. These data suggested the presence of two epimeric compounds, with the epimeric carbon atom between two double bonds. The IR bands at 3620, 1765 and 1655 cm^{-1}, also showed the presence of hydroxyl groups, olefinic protons and a γ-lactone ring.



Acetylation of **3** gave a monoacetate **6** , $C_{28}H_{42}O_6$, whose IR spectrum showed the absence of hydroxyl groups. Compound **3** also showed UV absorptions at 218.5 (ε= 16.460) and 272.5 (ε= 3.800) nm, providing evidence for a γ-substituted-γ-alcoxybutenolide ring[12].Additional signals of the ^{1}H and ^{13}C NMR spectra at 3.27 (3H, s) and 170.04 (γ-lactonic CO), 145.11 (C=CH), 108.82 (O-C-O) and 51.03 (OMe) ppm together with the ^{1}H -^{1}H -COSY and ^{1}H - ^{13}C (HCORR) spectra suggested the partial structure **A**, with an E stereochemistry for the disubstituted double bond (two pairs of doublets, J=16.4 Hz.)

The partial structure **A** was confirmed because the catalytic hydrogenation of **3** gave **7**, whose IR spectrum showed a band assignable to a γ-alcohoxybutanolide at 1775 cm^{-1} and a ^1H NMR spectrum showing the absence of signals due to olefinic protons and signals at 1.05 (3H, d, J=7 Hz) and 2.45 (2H,br.s).

Table 1. ^1H NMR spectral data of 3 and 4 (200 MHz, $CDCl_3$, TMS as int. standard).

H	3	4	H	3	4
1a	1.40 ddd	1.38 ddd	12a	2.05 m	2.20 ddd
1b	1.18 m	1.26 m	12b	2.32 ddd	2.42 ddd
2a	1.95 m	1.90 m	14*	6.24(6.19) d	6.10(6.12) d
2b	1.58 m	1.58 m	15*	5.34(5.43) d	5.64(5.62) d
3b*	3.40 dd	3.41 dd	18*	5.88(5.87) q	5.84 q
5a*	1.45 dd	1.42 dd	20*	1.98(1.96) d	2.00(2.03) d
6a,b	1.53 m	1.60 m	21	1.15 s	1.26 s
7a	1.37 m	1.35 m	22	1.13 s	1.24 s
7b*	1.76 ddd	1.81 ddd	23	0.94 s	0.94 s
9a*	1.32 dd	1.12 dd	24	0.81 s	0.81 s
11a	0.85 m	1.30 m	25	0.72 s	0.78 s
11b	1.64 m	1.30	O-Me	3.27 s	3.29 s

J [Hz]: 1α, 1β=13; 1α, 2α=4.5; 1α, 2β=11; 2α, 3β=2.7; 2β, 3β=2.9; 5α,6α=2.5; 5α, 6β=12; 6α, 7β=6β, 7α=2.5; 7α, 7β=2.5; 9α, 11α=2.5; 9α, 11β=11; 11α, 12β=2.5; 11β, 12β=4.5; 12α, 12β=13; 14, 15=16.4; 18, 20=1.5. *These assignments were made with the aid of ^1H - ^1H (COSY) correlation and were confirmed by decoupling.

Reduction of **3** with $LiAlH_4$ gave **8**, mp 159º (C_6H_6) and $[\alpha]_D$= + 23.75º (c, 0.80, MeOH), whose IR spectrum showed bands due to hydroxyl groups and the absence of C=O groups. The ^1H-NMR spectrum showed signals assignable to six methyl groups, one of them Me-C= ; olefinic protons at 5.85 (1H, dd, J=15.5 and 1.8 Hz), 5.60 (1H, dd, J=15.5 and 7 Hz) and 5.36 (1H, br. dd, J=9 and 6 Hz) and OH- geminal protons at 3.40 (1H, dd, J=2.7 and 2.9 Hz, H-3), 4.16 (1H, dd, J=12 and 9 Hz, H-19), 4.20 (1H, dd, J=12 and 6 Hz, H-19') and 5.05 (1H, dd, J=7 and 1.8 Hz).

Acetylation of **8** gave a triacetate **9**, whose mass spectrum showed a molecular ion M^+=532, in agreement with the molecular formula $C_{31}H_{48}O_7$ .The IR and ^1H-NMR spectra (see Experimental) confirmed the presence of three acetoxy groups, two of them secondary and the other primary.

The presence of five ter-methyl groups, six methylenes, three methines - one of them supporting a hydroxyl group - and four quaternary carbon atoms two of them supporting the oxygenated function was - evidenced by ^{13}C-NMR spectrum DEPT experiments.

The ^1H-NMR spectrum confirmed the presence of the five methyl groups, and the secondary axial hydroxyl group (3.40 ppm, dd, J=2.7 and 2.9 Hz). The chemical shifts for the carbon atoms C-1 C-6 and C-23 C-25 were identical to those exhibited by compounds **1** and **2**, whereas the signal

Table 2 ^{13}C NMR spectral data of compounds 1, 2, 3, 4, 5 and 10

n°C	1	2	3	4	5*	10**	12**
1	32.76	32.20	32.48	32.23	39.5	39.4	39.0
2	25.02	25.19	25.34	25.35	18.2	18.7	18.6
3	75.86	75.62	76.02	76.14	42.3	42.2	42.1
4	35.95	37.49	36.69	36.76	33.0	33.4	33.2
5	48.99	48.11	49.01	49.04	56.8	56.5	56.4
6	20.23	19.58	19.58	19.61	20.0	19.9	19.9
7	38.77	38.94	42.89	43.27	29.8	43.1	43.2
8	86.13	86.21	76.14	75.33	86.4	76.1	74.8
9	58.77	55.03	57.80	55.16	59.3	58.5	55.7
				(55.35)			
10	37.45	38.57	37.59	37.59	36.2	36.9	36.9
11	28.80	30.44	15.81	15.25	38.4	15.9	15.4
12	176.48	174.57	35.48	35.92	176.8	34.9	35.8
			(35.67)				
13			72.40	72.78		73.3	73.0
14			145.11	145.86		147.8	147.8
				(145.67)			
15			119.87	120.11		109.5	110.1
			(120.39)				
16			108.82	108.97			
17			165.64	165.74			
			(165.82)	(166.40)			
18			118.47	118.01			
			(118.66)	(118.72)			
19			170.04	170.51			
20			12.69	12.75			
			(12.48)	(12.61)			
21			32.46	29.10		32.7	28.5
22	21.39	22.66	24.06	24.18	21.0	24.0	25.5
23	28.08	28.28	28.20	28.24	33.2	33.3	33.4
24	21.54	21.98	21.82	21.65	21.6	21.3	21.3
25	14.92	15.59	15.70	15.79	15.1	15.9	15.3
O-CH_3		51.52	51.03	51.10			
$\underline{C}H_3$-CO-		19.95					
$\underline{C}H_3$-CO-		169.84					

^{13}C NMR chemical shifts are given in δ-values (ppm) relative to TMS.

Assignments were made with the aid of DEPT experiments.

* See ref. (8).** See ref. (13).

due to the carbon atoms C-8, C-9, C-11, C-13, C-21 and C-22 of compound **3** were shown at a similar field to that of manoyl oxide, **10** , and related compounds[13].

These data were only in agreement with a structure such as **3** (and the epimeric compound at C-16, **3'**). Each of the ^{1}H and ^{13}C NMR signals were assigned by ^{1}H -^{1}H (COSY) and ^{1}H - ^{13}C NMR (HCCORR) spectroscopic correlations and double resonance experiments (spin decoupling experiments).

The relative stereochemistry of **3** (or its epimer at C-16, **3'**) was assigned by decoupling constants of each proton and the results of the NOE experiments. Clear effects were observed for H-25 with H-24, H-2 and H-1 , for H-24 with H-23, for H-3 with H-2 , H-24 and H-23 and for H-5 with H-9 and H-1 , suggesting an axial disposition for the methyl groups C-22 , C-24 and C-25, as well as the 1,3-diaxial arrangement for protons H-5 , H-9 and H-1

Configuration at C-13 was assigned by the chemical shifts due to the methyl groups C-21 and C-22 (1.15 and 1.13 ppm and 32.46 and 24.06 ppm), as well as for the C-9 (57.80 ppm), which are in agreement with those communicated for the 13-epi-manoyl oxides[13].

The positive rotations for **3** and for the triol **8** allowed us to assign the same absolute configuration as for the manoyl oxide of normal series[14].

Lengthy treatment of **3** with KOH/MeOH-H_2O gave a major acid product, **11** , which was identified by spectral data. The appearance of this compound can be explained through the aldehyde formed by retroaldolization, which was oxidised in the alkaline medium of the reaction. All these data suggest the presence of two epimer substances at C-16, with a partial common structure of 3α-hydroxy-13-epi-manoyl oxide.

Compound **4** (and **4'**) exhibits spectroscopic properties very similar to those of **3** (and **3'**) (EM, IR, ^{1}H and ^{13}C NMR spectra), suggesting that both are stereoisomers. The substance gave only one spot in TLC with different solvents, but the ^{1}H and ^{13}C NMR spectra showed the duplicity of several signals with a ratio of 55/45, showing that it was a mixture of epimers, like that of **3** and **3'** at C-16, because the duplicate signals were due to equivalent carbon atoms from the A fragment of compound **3** and that due to C-9 (55.16/55.35 ppm). The most significant differences were the ^{1}H NMR signals due to the methyl groups C-21 and C-22 (1.26 and 1.23) and for the olefinic protons and the ^{13}C NMR signals for the manoyl oxide, **12** , and related compounds[13], specially the signals due to C-9 (55.16/55.35 ppm) and the methyl groups C-21 and C-22 (29.10 and 24.18 ppm). This allowed us to identify **4** (**4'**) as a mixture of epimers at C-16, both of them epimeric at C-13 with respect to the epimeric mixture **3** (**3'**) .

EXPERIMENTAL

M. ps. were determined on a Kofler aparatus and are uncorrected. UV. spectra were recorded in $CHCl_3$ on a Beckman DK-2 spectrometer and IR spectra on a Perkin-Elmer mod. 330 spectrometer. ^{1}H NMR spectra were recorded on a Hitachi Perkin-Elmer R-24(60 MHz) spectrometer and a Bruker WP-200-SY (200MHz). spectrometer using TMS as an internal standard ^{13}C NMR spectrum were run at 50.3 MHz on a Bruker WP-200-SY instrument. Optical rotations were determined with a Perkin-Elmer 241 polarimeter and were measured in $CHCl_3$. MS were obtained on a Hewlett-Packard 5930 A.

Plant material was collected in July 1986 near Los Villares (Salamanca, Spain) and a voucher specimen is deposited at the Herbarium of the Department of Botany, Faculty of Pharmacy (University of Salamanca).

Extraction and isolation. Dried and finely powdered *Salvia aethiopis* aerial parts (1.8 Kg.) were extracted with hot MeOH in a Soxhlet apparatus. After evaporations the residue was treated with MeOH-Hexane-H_2O (1, 1.5, 0.5) and the soluble part was evaporated by reduced pressure. The residue was extracted with Et_2O, which was extracted with aq. 10% $NaCO_3$, to yield the neutral fraction (15.5 g.)

The neutral fraction was chromatographed on a dry column of silica gel (eluent n-Hexane-EtOAc, 1:1) to give four fractions. Fraction 3 (7.2 g.) was chromatographed on a silica gel column and eluted with n-Hexane-EtOAc mixtures of increasing polarity. The homogeneous fractions were repeatedly chromatographed, to give the different components, which were finally purified by prep. TLC or recrystallization.

3 α-Hydroxy-norambreinolide 1. This was eluted with n-Hexane-EtOAc, (7:3) (80 mg.); mp=190-191º. (Hexane-Et_2O); $[\alpha]_D$= + 22º (c, 1.08) ; IR ν_{max} ($CHCl_3$), cm^{-1}; 3580, 1760, 1450, 1380, 1380, 1255, 1190, 1115, 1080, 1010, 920, 860; ^1H NMR (200 MHz, $CDCl_3$) : δ 0.86 (3H, s), 0.92 (3H, s), 0.96 (3H, s), 1.33 (3H, s), 2.07 (1H, dd, J=6.4 and14.5 Hz, H-9), 2.24 (1H, dd, J=6.4 and 16 Hz, H-11α), 2.42 (1H, dd, J=14.5 and 16 Hz, H-11β) and 3.45 (1H, dd, J=2.7 and 2.9 Hz, H-3β); ^{13}C-NMR (Table 2); EIMS m/z (rel. int.): 266[M^+] (12), 248 (7),233 (18), 205 (10), 204 (7), 189 (12), 148 (60), 146 (100), 131 (14).

Methyl 3α-Hydroxy-8α-acetoxy-tetranor-labdan-12-oate 2. Compound **2** was eluted with Hexane-EtOAc (8:2), (48mg), as a gum of $[\alpha]_D$=-0.79º(c,1.05); IR ν_{max} ($CHCl_3$), cm^{-1}; 3610, 3500,1735,1730,1460,1390,1370,1300,1250,1160,1130,1070, 950,860; ^1H-NMR (200 MHz, $CDCl_3$): δ 0.82 (3H,s), 0.84 (3H,s), 0.96 (3H, s), 1.50 (3H, s), 1.88 (3H, s), 2.35 (2H, m), 3.43 (1H, dd, J=2.7 and 2.9 Hz, H-3β) and 3.67 (3H, s); ^{13}C-NMR (Table 2); EIMS m/z (rel. int.): 340 [M^+] (8), 280 (10), 262 (18), 189 (100), 122 (54), 107 (33). **Saponification of 2.** 3 ml of a methanolic 5% NaOH soln were added to a solution of 25 mg of **2** in 2 ml of MeOH. The resulting mixture was kept a room temp overnight. Evaporation of the solvent and extraction with AcOEt, after 2N ClH acidification, gave 16 mg of an acid, which by treatment with 15 mg of TsOH in dry C_6H_6, stirring for 30 min. at 50º , followed by prep. CC on silica gel, gave 10 mg of **1.**

3-epi-Salviaethiopisolide 3 (and the epimeric compound at C_{16} 3'). Compounds **3** and **3'** were eluted with Hexane EtOAc (7:3), (800 mg) as a very viscous oil of a mixture of epimers, of $[\alpha]_D$= + 32 º (c, 1.53); IR ν_{max} ($CDCl_3$) cm^{-1}; 3620, 32500, 1765, 1655, 1630, 1470, 1390, 1380, 1280, 1230, 1200, 1170, 1090, 1080, 1060, 990, 960, 910, 850. ^1H-NMR and ^{13}C-NMR (Tables 1 and 2); EIMS m/z (rel. int.): 432 [M^+] (6), 414 (12), 383 (5), 287 (40), 279 (22), 261 (60), 202 (31), 187 (37), 127(100), 83(80). UV: λ_{max} (EtOH) at 218.5 (ε= 16.460) and 272 (ε= 3.800) nm.

Acetylation of 3 (3'): A soln of **3** (**3'**) (40 mol) in Ac_2O-pyridine at room temp.for 10hr. gave 6 (38 mg):IR ν_{max} cm^{-1}: 3080, 1765, 1720, 1648, 1460, 1370, 1240, 1200, 1160, 1105, 1080, 1060, 1050, 1010, 985, 915, 840. ^1H-NMR (60 MHz, $CDCl_3$): δ 0.74 (3H,s), 0.82 (3H, s), 0.85 (3H, s), 1.12 (3H, s), 1.15 (3H, s), 1.93 (3H, brs), 2.00 (3H, s), 3.48 (3H, s), 4.57 (1H, brs), 5.30 (5.40) (1H, d, J=17 Hz), 5.76 (1H, brs), 6.15 (6.20) (1H, d, J=17 Hz). EIMS m/z (rel. int): 474 [M^+] (5), 414 (12), 261 (38), 127 (60), 83 (100), 60 (70), 43 (35).

Hydrogenation of 3 (3'): To a suspension of Adam's catalyst (30 mg) in EtOH (15 ml) a soln of **3** (**3'**) (200 mg in 10 ml of EtOH) was added under stirring and atmosphere of H_2, stirring for 48 h. at room temp. After filtering the catalyst followed by prep. CC on silica gel, gave 120 mg of **7**: IR ν_{max} cm^{-1}: 3410, 1775, 1470, 1380, 1250, 1110, 1075, 1050, 1000. ^1H-NMR (60 MHz, $CDCl_3$): δ 0.76 (3H, s), 0.83 (3H, s), 0.92 (3H, s), 1.05 (3H, d, J=7 Hz), 1.12 (3H, s), 1.15 (3H, s), 2.45 (2H, brs), 3.36 (3H, s), 3.45 (1H, brs). EIMS m/z (rel. int.) = 428 [M^+] (10), ($C_{26}H_{36}O_5$).

Reduction of 3 (3') with LAH. Treatment of 165 mg of **3** (**3'**) with 200 mg of LAH in dry ether, followed by prep CC on 10 gr. silica gel, gave , by elution with EtOAc, 110 mg. of **8**: mp =159º (Benzene); $[\alpha]_D$= + 23.75º (c, 0.8, MeOH); IR ν_{max}(KBr) cm^{-1}: 3380, 3080, 3050, 1640, 1460, 1380, 1165, 1090, 1060, 1020, 980, 830, ^{1}H-NMR (200 MHz, $CDCl_3$): d 0.73 (3H, s), 0.83 (3H, s), 0.94 (3H, s), 1.12 (3H, s), 1.20 (3H, s), 1.76 (3H, d, J=1.3 Hz), 3.40 (1H, dd, J=2.7 and 2.9 Hz), 4.16 (1H, dd, J=9 and 12 Hz, H-19), 420 (1H, dd, J=6 and 12 Hz, H-9'), 5.05 (1H, dd, J=1.8 and 7 Hz), 5.36 (1H, br. dd, J=6 and 9 Hz), 5.60 (1H, dd, J=7 and 15.5 Hz) and 5.85 (1H, dd, J=1.8 and 15.5 Hz).

Acetylation of 8 (50 mg) gave **9** (54 mg) : IR ν_{max}($CHCl_3$) cm^{-1} : 1740, 1460, 1380, 1240, 1100, 1080, 1060, 1020, 960, 900, 830. ^{1}H-NMR (60 MHz, $CDCl_3$): δ 0.75 (3H, s), 0.86 (3H, s), 1.13 (3H, s), 1.17 (3H, s), 1.73 (3H, br s), 2.05 (9H, s), 4.60 (1H, br s), 4.72 (1H, d, J=7Hz), 5.28 (1H, br t, J=7Hz), 5.65 (1H, dd, J=6.5 and 16Hz), 5.95 (1H, br d, J=16Hz) and 6.10 (1H, br d, J=6.5Hz). EIMS m/z (rel. int.): 532 [M^+] (5) ($C_{31}H_{48}O_7$), 472 (10), 370 (16), 261 (12), 187 (19), 109 (70), 95 (87), 81 (100), 60 (25), 43 (32).

3α-Hydroxy-15-normanoyl-oxide-14-carboxylic acid. 11. Five ml of a MeOH-H_2O (2:1) 5% KOH soln were added to a solution of 85 mg of **3** (**3'**) in 2 ml of MeOH, and this was kept at 60º for 6 hr. Evaporation of the solvent and extraction with AcOEt, after 2N HCl acidification, gave 25 mg of the acid **11.** IR ν_{max}($CHCl_3$) cm^{-1}: 3560, 3400-2800, 1705, 1460, 1380, 1200, 1100, 1050, 1000. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.72 (3H, s), 0.81 (3H, s), 0.94 (3H, s), 1.16 (3H, s), 1.28 (3H, s), and 3.42 (1H, dd, J=2.7 and 2.9 Hz).

Salviaethiopisolide 4 (4'). Compounds **4** and **4'** were eluted with Hexane-EtOAc (7:3) (174 mg) as a very viscous oil, of a mixture of epimers $[\alpha]_D$= + 16.25º (c, 0.8). IR ν_{max}($CHCl_3$) cm^{-1} (very similar to those of **3** and **3'**). ^{1}H-NMR and ^{13}C-NMR (Tables 1 and 2). EIMS m/z (rel int.): 432 [M^+] (12), 414 (7), 287 (35), 261 (25), 187 (32), 127 (100), 83 (65).

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