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TETRACYCLIC TRITERPENES AND NEROLIDOL DERIVATIVES FROM *SANTOLINA OBLONGIFOLIA*

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Key Word Index—*Santolina oblongifolia*; Compositae; triterpenes; dammarane; sesquiterpenes; nerolidol derivatives; oblongifolidiol.

Abstract—Three new dammarane type triterpenes, six polyoxygenated nerolidol derivatives and one tricyclic sesquiterpene, named oblongifolidiol, were isolated from the hexane extract of *Santolina oblongifolia*. The assigned structures were based on their spectral properties and/or chemical correlations.

INTRODUCTION

In previous papers, we reported the composition of the essential oil of *S. oblongifolia* [1, 2]. In this paper, we report the components of the neutral fraction of a previously steam-distilled hexane extract, and also those isolated from the benzene extract of the roots.

From the benzene extract of the roots, we isolated the acetylenes **1–6**, previously reported as components of the roots of *S. rosmarinifolia* [3], and the triterpenes 3-epifriedelinol (**7**), dammaradienone (**8**) [4], dammaradienyl acetate (**9**), and dammaradienol (**10**) [5].

The non volatile neutral part of the hexane extract, gave, beside the compounds **3–6**, **9** and **10**, three tetracyclic triterpenes with the dammarane skeleton (**11–13**), one tricyclic sesquiterpene (**14**), named onlongifolidiol, and six polyoxygenated nerolidol derivatives (**15–20**).

RESULTS AND DISCUSSION

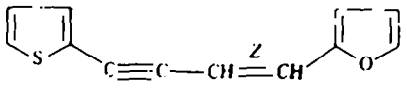
Compound **11** was a solid with a $[M]^+$ at *m/z* 484 ($C_{32}H_{52}O_3$). The mass spectral fragmentations were characteristic of triterpenes with a dammarane skeleton [6] and with a side chain C_8H_{13} (*m/z* 109) with two unsaturations. The IR spectrum showed absorptions due two hydroxyl and acetoxyl groups and $C{=}CH_2$ unsaturations, which were confirmed by the ^1H NMR and ^{13}C NMR spectra [7–10] (Table 1), with signals due to five Me–C and one Me–C= groups, one equatorial secondary acetoxyl group and two $C{=}CH_2$ unsaturations. The presence in the ^{13}C NMR spectrum of **11**, of a signal at 75.42 ppm, due to a quaternary-C atom, was evidence for one C–OH group, and comparison of the ^{13}C NMR spectra of **9** and **11**, and consideration of the induced effects on the chemical shifts of the carbon atoms of a cyclopentane ring by one hydroxyl group [11] (C-13, +7.3; C-16, +8.9; C-17, +30.1) allowed us to locate the hydroxyl group on C-17, identifying **11** as 3β-acetoxydammara-20,25-dien-17α-ol.

The IR spectrum of compound **12** ($C_{30}H_{50}O_2$) suggested the presence of hydroxyl groups and unsaturations. The ^1H NMR and ^{13}C NMR spectra were very similar to those exhibited by compound **10**, suggesting that **12** was a hydroxydammaradienol, with the most significant differences at the side chain, which in **12** was identified as $-C(=CH_2)-CH_2-CH=CH-C(OH)Me_2$ by the ^1H NMR signals at δ4.79 and 4.77 (2H, 2*br s*), 5.65 (1H, *d*, *J* = 17 Hz), 5.62 (1H, *dt*, *J* = 17 and 4 Hz), 2.68 (2H, *d*, *J* = 4 Hz) and 1.32 (6H, *s*), and confirmed by the ^{13}C NMR spectrum (Table 1), identifying **12** as 23(*E*)-dammara-20,23-dien-3β,25-diol. This structure was confirmed by oxidation of dammaradienol (**10**), with $^1O_2$ and Bengal rose as a sensitizer [12]. Photooxidation of compound **10**, followed by reduction *in situ* of the hydroperoxide mixture with $NaBH_4$, gave two diols (1:1), which were isolated by chromatography. The diol with the lower R_f, was identical in all respects with compound **12**, and the other (**12a**) was identified by spectral methods as dammara-20,25-dien-3β,24-diol.

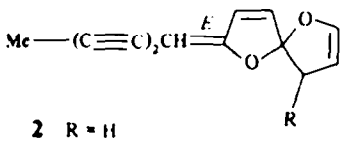
Compound **13** showed IR bands of hydroxyl groups and double bonds. The ^1H NMR spectrum was very similar to that of compound **12**, showing as the only significant differences, the absence of the signal due to the $C{=}CH_2$ group and the presence of one additional doublet at δ0.92 (*J* = 7 Hz), assignable to an Me–CH group. This fact was confirmed in the ^{13}C NMR spectrum by the presence of two additional signals at 36.41 and 18.34 (Me–CH) and the absence of signals at 152.70 and 107.60 ($C{=}CH_2$), identifying the triterpene **13** as dammara-23-en-3β,25-diol.

The tetracyclic nature of triterpenes **9** and **11–13** (Table 2), was also easily deduced from the analysis of their fragmentation patterns in mass spectroscopy. By cleavage of the C-ring, compounds **9** and **11** gave a fragment at *m/z* 249, and compounds **12** and **13** gave an ion at *m/z* 207. This fact was evidence for a dammarane skeleton and excluded the euphane and lanostane ones [13]. The loss of the side chain between C-17 and C-20 gave fragments at *m/z* 359 (compound **9**), 375 (compound **11**), 317 (compounds **12** and **13**).

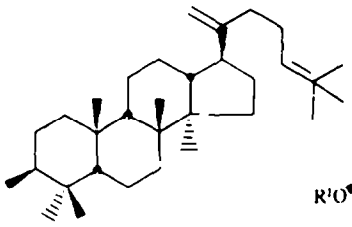
Sesquiterpene **14** was isolated as a colourless oil with $[M]^+$ at *m/z* 236, in agreement with the formula $C_{15}H_{24}O_2$. The IR and ^1H NMR spectra showed the presence of the following groups: Me–C [δ0.88 (3H, *s*)], Me–C=CH [δ1.69 (3H, *dd*, *J* = 1.9 and 2 Hz) and 5.25 (1H, *br s*)], two C–CH_2OH [δ3.55 and 3.66 (4H, 2*dd*, 2AB



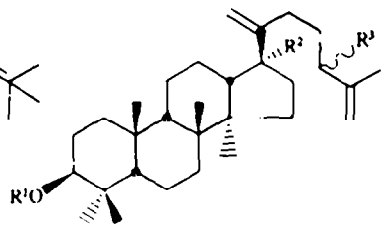
1



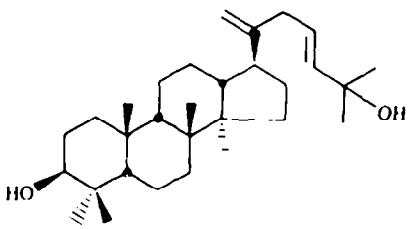
2 R = H
3 R = OAc
4 R = OAc (2,1′Z)
5 R = OH
6 R = OCO—CH=CH(Me)Me



9 R = Ac
10 R = H



11 R^1 = Ac, R^2 = OH, R^3 = H
12a R^1 = H, R^2 = H, R^3 = OH



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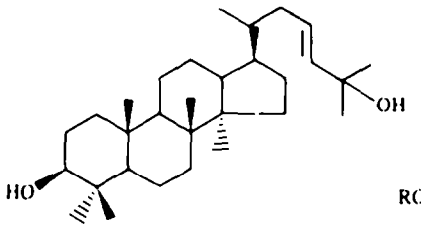

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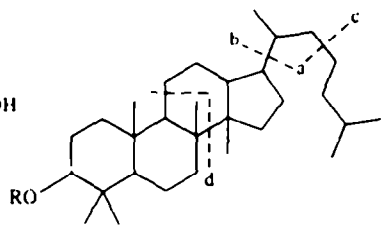

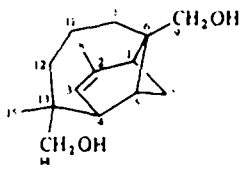

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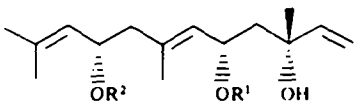
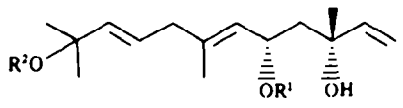


15 R^1 = R^2 = Ac
16 R^1 = H, R^2 = Ac
17 R^1 = R^2 = H



18 R^1 = Ac, R^2 = H
19 R^1 = R^2 = H
20 R^1 = H, R^2 = Ac

systems, J = 10 and 15 Hz)] and three methyne groups, two of them allylic [δ2.29 (1H, *br s*), 2.18 (1H, *dd*, J = 2 and 7 Hz) and 2.03 (1H, *d*, J = 7 Hz)]. The ^{13}C NMR spectrum confirmed all these groups as well as the presence in the molecule of four secondary and two quaternary carbon atoms. By irradiation at 5.25 ppm, the signal at 1.69 (*dd*) became a doublet (J = 2 Hz) and the broad singlet at 2.29 became a doublet (J = 2 Hz). By irradiation at 2.29 ppm, the signal at 1.69 (*dd*) collapsed to a doublet (J = 1.9 Hz) and the signal at 2.18 (*dd*) became

Table 1. ^{13}C NMR spectra of several dammarane derivatives

C*	9	10	11	12	12a	13
1	38.80	38.96	38.83	38.98	39.04	38.93
2	23.72	27.46	23.76	27.41	27.50	27.49
3	80.98	78.95	80.98	78.93	79.03	78.95
4	37.90	39.16	37.97	39.14	39.21	39.27
5	55.91	56.00	56.03	55.93	56.00	55.97
6	18.20	18.28	18.22	18.30	18.37	18.36
7	35.40	35.38	35.31	35.45	35.52	35.40
8	40.51	40.53	40.53	40.50	40.56	40.14
9	50.90	50.84	50.71	50.95	51.05	50.54
10	37.16	37.15	37.17	37.12	37.31	31.13
11	21.41	21.37	21.31	21.34	21.44	21.39
12	25.00	25.00	25.00	24.94	25.05	25.53
13	47.80	47.64	55.10	47.63	47.68	47.60
14	49.43	49.50	49.52	49.43	49.53	48.92
15	31.38	31.38	31.26	31.37	31.42	32.05
16	28.95	29.40	37.90	28.86	29.29	29.45
17	45.33	45.38	75.42	45.32	45.58	44.88
18	16.30†	15.93†	16.30†	15.81†	16.03†	15.83†
19	15.66†	15.74†	15.59†	15.66†	15.72†	16.05†
20	152.63	152.64	151.78	151.41	152.70	36.27
21	107.54	107.60	108.63	108.15	107.60	14.04
22	34.20	34.32	34.20	37.24	31.42	31.76
23	27.11	27.15	24.54	125.04	33.74	125.35
24	124.50	124.60	31.72	139.43	75.76	139.43
25	131.33	131.42	145.51	70.00	147.65	70.74
26	25.71	25.71	109.60	29.83	111.02	29.98
27	17.70	17.70	17.63	29.83	17.63	30.09
28	16.52	16.22	16.53	16.20	16.24	16.52
29	28.00	28.06	28.02	28.04	28.09	16.52
30	15.91†	15.40†	15.94†	15.38†	15.42†	15.65†
MeCO	21.29		21.29			
MeCO	171.00		171.00			

*To differenciate the multiplicity of CH_3, CH_2, CH, C, the sequence DEPt was used.

†The signals may be interchanged.

Table 2. Mass spectral fragmentations of compounds 9 and 11–13

Fragment	a	b	c	c−18	d	d−OR
9	359 (2.5)	109 (100)	83 (44)	—	249 (15)	189 (90)
11	375 (2.0)	109 (14)	83 (100)	—	249 (15)	189 (16)
12	317 (1.5)	125 (13)	99 (54)	81 (100)	207 (24)	189 (19)
13	317 (1.0)	127 (27)	99 (45)	81 (100)	207 (14)	189 (19)

Relative intensities are given in parentheses.

a doublet (J = 7 Hz). By irradiation at 2.18 ppm, the signal at 2.29 became a doublet (J = 2 Hz) a the doublet at 2.03 became a singlet.

These decoupling experiments showed that the molecule of oblongifolidiol (14) had a cross-ring [14], and its coupling system was very similar to that exhibited by *cis*-chrysanthenol [15, 16] and α-pinene, with $J_{1,5}$ = 7 Hz, $J_{3,8}$ = 1.9 Hz and $J_{3,4} = J_{4,5}$ = 2 Hz, from which we could deduce for compound 14 the α-pinene partial structure, plus one additional isoprene unit.

One similar structure was supported by comparison of the ^{13}C NMR spectra of compound 14 and α-pinene (Table 3). The C-4 methylene and the C-10 methyl groups, were replaced in 14 by one C-methyne and one C-methylene respectively, revealing that the additional isoprene unit, consisting of two methylene (δ21.00 and 40.98), one quaternary carbon atom (δ40.41), one methyl (δ22.89) and one hydroxymethylene (δ68.11), was connected between C-4 and C-10 in oblongifolidiol.

Comparison of the ^{13}C NMR chemical shifts assigned

Table 3. ^{13}C NMR spectra of compounds **14**, **14a** and related compounds

C	14	14a	Vulgarona-A	α-Pinene
1	45.90	45.91	68.60	47.20
2	147.24	147.10	139.70	144.40
3	117.55	117.60	121.40	116.10
4	49.50	49.86	55.60	31.50
5	39.61	40.67	65.10	41.50
6	40.89	40.36	37.10	38.10
7	28.76	29.45	205.70	31.30
8	23.38	23.24	23.50	20.80
9	68.21	66.00	27.70	26.50
10	34.04	33.90	33.20	22.90
11	21.05	20.71	21.50	
12	40.98	40.67	42.20	
13	40.41	40.36	35.20	
14	68.11	66.00	30.50	
15	22.89	22.66	26.10	
MeCO		170.91		
MeCO		20.71		

to C-6 and C-13 in vulgarone-A (δ 37.1 and 35.2) [17] with those of compound **14** (δ 40.89 and 40.41), and consideration of the shifts induced by hydroxyl groups (+3.4 −4.5) [18], allowed us to locate the primary alcoholic groups at C-9 and C-14. Acetylation of compound **14** gave a diacetate, whose spectral data agreed with the proposed structure.

Compounds **15**–**17** were isolated as viscous oils. The molecular ions in their mass spectra agreed with the formulas $C_{19}H_{30}O_5$, $C_{17}H_{28}O_4$ and $C_{15}H_{26}O_3$ respectively. They were identified as the diacetate (**15**) and monoacetate (**16**) of the same sesquiterpene diol (**17**), because treatment of **15** and **16** with $LiAlH_4$ gave a diol identical in all respects with compound **17**, and acetylation of **16** and **17** gave a diacetate identical with compound **15**.

The ^1H NMR spectrum of compound **16** (Table 4) was characteristic of a nerolidol derivative [1], with two additional signals at 4.60 (1H, *ddd*, J = 2.7, 9 and 11.5 Hz) and 5.65 (1H, *ddd*, J = 9, 9 and 5.5 Hz) assignable to a H–C–OH and H–C–OAc protons respectively. These high chemical shift values and the multiplicity of the signals due to the olefinic protons at 5.11 (1H, *dd*, J = 8 and 1.5 Hz) and 5.25 (1H, *br d*, J = 8 Hz) were evidence for the allylic nature of the oxygenated functions, which located them at C-5 and C-6 respectively on the nerolidol skeleton.

The presence of the hydroxyl group at C-5 was confirmed by oxidation of compound **16** with active MnO_2 [19] to give the hydroxyacetoxyketone **16a** with UV absorption at 239 nm, whose ^1H NMR spectrum compared with that of compound **16**, showed the absence of the signal at δ 4.60 and the upfield shift of the signals due to H-5 and Me-14, which were now shown at 6.02 (1H, *br s*) and 2.15 (3H, *d*, J = 0.8 Hz). The signal due to the

Table 4. ^1H NMR spectral data for compounds **15**–**19** and **16a**

Proton	15	16	16a	17	18	19
1c	5.07 *dd*	5.16 *dd*	5.03 *dd*	5.16 *dd*	5.06 *dd*	5.17 *dd*
	10.8, 1.4	10.8, 1.5	10.8, 1.2	10.8, 1.5	10.8, 1.4	10.8, 1.5
1t	5.24 *dd*	5.36 *dd*	5.22 *dd*	5.36 *dd*	5.25 *dd*	5.17 *dd*
	17, 1.5	17, 1.5	17, 1.2	17, 1.5	17, 1.5	17, 1.5
2	5.88 *dd*	5.93 *dd*	5.92 *dd*	5.36 *dd*	5.89 *dd*	5.93 *dd*
	17, 10.8	17, 10.8	17, 10.8	17, 10.8	17, 10.8	17, 10.8
4	2.01 *dd*	1.78 *dd*		1.72 *dd*	2.04 *dd*	1.82 *dd*
	15, 8.5	15, 11.5	2.69 AB syst.	15, 11.5	15, 11.5	15, 11.5
4'	1.67 *dd*	1.45 *dd*	20, 16	1.54 *dd*	1.75 *dd*	1.52 *dd*
	15, 4.2	15, 2.7		15, 4.0	15, 4.2	15, 4.2
5	5.58 *ddd*	6.60 *ddd*		4.63 *ddd*	4.62 *m*	4.63 *ddd*
	9, 8.5, 4.2	11.5, 9, 2.7		11.5, 9, 2.7		11.5, 9, 2.7
6	5.05 *dc*	5.11 *dc*	6.02 *c*	5.14 *dc*	5.13 *dc*	5.22 *dc*
	9, 1.5	9, 1.5	0.8	15, 4	9, 1.3	9, 1.5
8	2.30 *dd*	2.32 *dd*	2.44 *dd*	2.14 *dd*	2.67 *d*	2.67 *d*
	13.5, 1.2	13.5, 9	13.5, 7.4	13.5, 9	5.3	5.3
8'	2.11 *dd*	2.10 *dd*	2.31 *dd*	1.82 *dd*	2.08 *d*	2.03 *d*
	13.5, 5.5	13.5, 5.5	13.5, 6.4	13.5, 5.5	5.3	5.3
9	5.65 *ddd*	5.65 *ddd*	5.68 *ddd*	4.47 *ddd*	5.61 *m*	5.55 *dt*
	9, 8.2, 5.5	9, 9, 5.5	9, 7.4, 6.4	11.5, 9, 4		17, 5.3
10	5.13 *dc*	5.25 *dc*	5.09 *dc*	5.27 *dc*	5.61 *m*	5.66 *d*
	9, 1.2	9, 1.2	9, 1.2	9, 1.2		17
Me-12	1.70 *d*	1.71 *d*	1.72 *d*	1.69 *d*	1.25 *s*	1.25 *s*
Me-13	1.2	1.2	1.2	1.2	1.31 *s*	1.31 *s*
Me-14	1.75 *d*	1.65 *d*	2.15 *d*	1.73 *d*	1.69 *d*	1.61 *d*
	1.5	1.5	0.8	1.5	1.3	1.5
Me-15	1.27 *s*	1.27 *s*	1.29 *s*	1.27 *s*	1.28 *s*	1.28 *s*
MeCOO	1.99 *s*	1.99 *s*	2.00 *s*	—	2.01 *s*	
	2.00 *s*					

methylene group C-4 was now shown as one AB system at 2.59 and 2.77 (2H, 2*d*, J = 16 Hz), confirming the presence in compound **16** of the hydroxyl group at C-5 and the acetoxyl group at C-9. The assigned stereochemistry for the C-6 double bond was *E* because ^{13}C NMR chemical shift (Table 5) due to the methyl group at C-7.

The relative configuration at C-3 and C-5 was deduced by comparison of the ^{1}H NMR and ^{13}C NMR chemical shifts due to the methylene group C-3, with those exhibited by known similar compounds [20]. The signals at δ1.27 and 30.04, allowed us to assign a *threo* relative configuration. The presence of intramolecular H-bonds was evident by the non-equivalence of the H-4 protons in the ^{1}H NMR spectra.

The structures assigned to compounds **15**–**17** agreed with the observed ^{13}C NMR spectra and their assignations were based in those reported for 9-hydroxynerolidol [21] and related compounds. The molecular ions of compounds **18** and **19**, agreed with the formulae $C_{17}H_{28}O_4$ and $C_{15}H_{26}O_3$, respectively, and their fragmentation patterns revealed that they were a sesquiterpene triol and its monoacetate. This was confirmed by treatment of compound **18** with $LiAlH_4$ to give **19**; acetylation of **19** gave a monoacetate identical with compound **18**. Both ^{1}H NMR and ^{13}C NMR spectra, allowed us to identify them as (6*E*,9*E*)5-acetoxy-11-hydroxy-9-en-10-11-dihydronerolidol (**18**) and (6*E*,9*E*)5,11-dihydroxy-9-en-10,11-dihydronerolidol (**19**) with a C-3,C-5 *threo* relative configuration.

Compound **20** was isolated as a viscous oil of formula $C_{16}H_{28}O_3$. Its IR and ^{1}H NMR spectra were both very similar to those of compound **19**, with an additional signal at δ3.00 (3H, *s*), assignable to one methoxyl group, which revealed that compound **20** was the C-11-*O*-methyl derivative of **19**. Acetylation of **20** gave **20a**, whose spectral properties agreed with the proposed structure.

Table 5. NMR spectra of compounds **15**–**19**

C	15	16	17	18	19
1	112.07	112.60	112.59	111.94	112.67
2	144.47	144.08	144.13	144.39	144.06
3	72.42	73.94	73.98	72.43	72.96
4	46.72	46.94	47.52	46.95	47.13
5	69.61	67.09	66.81	69.42	67.19
6	127.46	131.23	131.05	124.05	128.37
7	135.46	133.02	134.42	138.75	136.52
8	45.17	45.22	47.13	42.01	42.06
9	69.37	69.68	67.05	124.73	124.34
10	123.56	123.62	127.13	140.26	140.16
11	137.19	137.06	135.02	70.62	70.69
12	25.61	25.58	25.68	29.79	29.86
13	18.43	18.39	18.19	29.62	29.70
14	17.22	16.84	17.15	16.84	16.59
15	28.42	30.04	29.87	28.43	30.09
MeCO	21.29	21.15		21.30	
	21.21				
MeCO	170.19	170.19		170.15	
	169.93				

EXPERIMENTAL

UV spectra were recorded in EtOH. Optical rotations were measured in $CHCl_3$. Mps are uncorrected. ^{13}C NMR and ^{1}H NMR were recorded in $CDCl_3$ on a 50.3 and 200 MHz respectively. Chemical shifts are reported in δ-values downfield from internal TMS and the coupling constants are quoted in Hz.

Collection and extraction. *S. oblongifolia* was collected in the Sierra de Béjar (Salamanca, W. Spain) at the beginning of June, 1981. The plant was identified by Prof. B. Casaseca Mena, from the Botany Department of Salamanca University, where a specimen is held (Herbarium No. 20.412).

Roots (500 g) were air-dried, ground and extracted with hot C_6H_6. The extract was concd *in vacuo* and the residual syrup was chromatographed on silica gel (open column) using solvents of increasing polarity from C_6H_6 to Et_2O. The aerial parts of the plant (7.0 kg) were extracted with refluxing hexane in a Soxhlet apparatus giving after evaporation of the solvent, 84.0 g of extract, which after concn, was steam-distilled to yield 28.0 g of essential oil [1, 2]. Dewaxing with MeOH gave the waxes (29.3 g) and the remaining product in Et_2O, was extracted with aq. 10% NaOH, to yield the neutral fraction (22.2 g).

The neutral fraction was chromatographed on a dry column of silica gel (eluent: C_6H_6–EtOAc, 9:1) to give five fractions. Each of them was rechromatographed on silica gel or neutral alumina, to give the different components, which were finally purified by prep. TLC or recrystalization: *Fraction* 1 (6.4 g): **3** (346 mg), **4** (432 mg), **5** (125 mg), **9** (3.456 g), **11** (57 mg). *Fraction* 2 (3.0 g): **6** (74 mg), **10** (1.3 g). *Fraction* 3 (5.1 g): **12** (155 mg), **13** (45 mg), **14** (180 mg), **15** (270 mg). *Fraction* 4 (3.5 g): **16** (780 mg), **18** (463 mg), **20** (87 mg). *Fraction* 5 (3.8 g): **17** (135 mg), **19** (390 mg).

Dammara-20,25-dien-3β-acetoxy-17α-ol (**11**). This was eluted with petrol–Et_2O (8:2); mp 136–137° (hexane); $[\alpha]_D$ = +48.8° (*c* 1.43); IR ν_{max}^{KBr} cm^{-1}: 3400, 3080, 1730, 1645, 1470, 1390, 1250, 1150, 1020, 910, 890; ^{1}H NMR: δ0.87 (12H, *s*), 1.00 (3H, *s*), 1.73 (3H, *s*), 2.03 (3H, *s*), 4.40 (1H, *dd*, J = 7 and 9 Hz), 4.72 (2H, *br s*), 5.00 (2H, *br s*); EIMS *m/z* (rel. int.): 484 (2), 466 (3), 375 (1.5), 297 (1), 249 (1.5), 234 (5), 189 (5), 125 (9), 109 (12), 83 (100). ^{13}C NMR (Table 1).

Dammara-20,23-dien-3β,25-diol (**12**). This was eluted with C_6H_6–Et_2O (1:1); mp 161 162° (hexane); $[\alpha]_D$ = +58.6° (*c* 0.82); IR ν_{max}^{KBr} cm^{-1}: 3360, 3080, 1650, 1140, 1100, 1050, 1040, 990, 890, 730; ^{1}H NMR: δ0.77 (3H, *s*), 0.85 (3H, *s*), 0.86 (3H, *s*), 0.97 (6H, *s*), 1.32 (6H, *s*), 2.68 (2H, *d*, J = 4 Hz), 3.20 (1H, *dd*, J = 6 and 10 Hz), 4.69 and 4.77 (2H, 2 *br s*), 5.26 (1H, *dt*, J = 17 and 4 Hz), 5.65 (1H, *d*, J = 17 Hz); ^{13}C NMR (Table 1); EI *m/z* (rel. int.): 442 (6), 424 (24), 355 (3), 317 (1.5), 234 (2), 216 (4), 207 (24), 189 (19), 125 (4), 107 (58), 81 (100).

Photo-oxidation of compound **10**. A soln of diol **10** (180 mg) in isopropanol (15 ml) was photo-oxidised in the presence of Bengal rose (5 mg). After 3 hr of exposure to sunlight, the soln was evaporated, diluted with MeOH and NBH (180 mg) was added to the mixture, continuing stirring for 1 hr. Afterwards, an aq. 10% soln of KIO_3 (10 ml) and H_2O (10 ml) were added. The reaction mixture was kept for 15 min and then extracted with Et_2O. The ethereal extract was washed with 2 N HCl and H_2O dried with Na_2SO_4 and evaporated, to give a residue (196 mg) which was chromatographed on silica gel to afford compounds **12** (80 mg) and **12a** (78 mg): mp 153–154° (hexane); IR ν_{max}^{KBr} cm^{-1}: 3360, 3080, 1650, 1100, 1055, 1040, 900, 890; ^{1}H NMR: 0.75 (3H, *s*), 0.85 (3H, *s*), 0.97 (6H, *s*), 1.73 (3H, *s*), 3.20 (1H, *dd*, J = 6 and 10 Hz), 4.08 (1H, *t*, J = 6.5 Hz), 4.72 and 4.75 (2H, 2 *br s*), 4.84 and 4.95 (2H, 2 *br s*); ^{13}C NMR (Table 1).

Dammara-23-en-3β,25-diol (**13**). Compound **13** was eluted with C_6H_6 EtOAc (9:1); mp 181 182° (hexane); $[\alpha]_D$ = +48.4° (*c*

1.09); IR ν_{max}^{KBr} cm^{-1}: 3350, 3060, 1640, 1160, 1110, 1040, 970, 910; ^1H NMR: 0.80 (3H, *s*), 0.85 (3H, *d*, *J* = 7 Hz), 0.88 (6H, *s*), 0.98 (6H, *s*), 1.31 (6H, *s*), 3.20 (1H, *dd*, *J* = 6 and 10 Hz), 5.60 (2H, *br s*); ^{13}C NMR (Table 1); EIMS *m/z* (rel. int.): 444 (5), 426 (5), 408 (2), 317 (1), 207 (5), 189 (5), 127 (6), 109 (48), 107 (45), 95 (53), 81 (100).

Oblongifolidiol (**14**). Compound **14** was eluted with C_6H_6–EtOAc (1:1); $[\alpha]_D$ = +14.9° (*c* 1.18); IR ν_{max} cm^{-1}: 3340, 3010, 1640, 1450, 1380, 1100, 1070, 1030, 840; ^1H NMR: 0.88 (3H, *s*), 1.30–1.65 (6H, *m*), 1.26 (1H, *s*), 1.69 (3H, *dd*, *J* = 1.9 and 2 Hz), 1.77 (1H, *s*), 2.03 (1H, *d*, *J* = 7 Hz), 2.18 (1H, *dd*, *J* = 7 and 2 Hz), 2.29 (1H, *dd*, *J* = 2 and 1.9 Hz), 3.55 (2H, *dd*, AB system, *J* = 15 and 10 Hz), 3.66 (2H, *dd*, AB system, *J* = 15 and 10 Hz), 5.25 (1H, *br s*); ^{13}C NMR (Table 3); EI *m/z* (rel. int.): 236 (3), 218 (5), 137 (6), 119 (93), 92 (30), 91 (100), 79 (73), 43 (51).

Acetylation of compound **14**. A soln of **14** (50 mg) in Ac_2O–pyridine at room temp. for 10 hr, gave **14a** (56 mg); IR ν_{max} cm^{-1}: 3020, 1740, 1640, 1430, 1370, 1240, 1040, 850; ^1H NMR: 0.85 (3H, *s*), 1.30–1.50 (6H, *m*), 1.66 (3H, *dd*, *J* = 2 and 1.9 Hz), 2.03 (3H, *s*), 2.04 3H, *s*), 2.06 (1H, *d*, *J* = 7 Hz), 2.18 (1H, *dd*, *J* = 7 and 2 Hz), 2.20 (1H, *d*, *J* = 2 Hz), 2.32 (1H, *dd*, *J* = 1.9 and 2 Hz), 3.92 (2H, *dd*, AB system, *J* = 15 and 10 Hz), 4.00 (2H, *dd*, AB system, *J* = 15 and 10 Hz), 5.20 (1H, *br s*); ^{13}C NMR (Table 3); EI *m/z* (rel. int.): 320 (0.5), 200 (3), 136 (45), 129 (7), 119 (15), 91 (24), 79 (15), 43 (100).

(6E)-5,9-*Diacetoxynerolidol* (**15**). Compound **15** was eluted with C_6H_6–EtOAc (95:5); $[\alpha]_D$ = +11.3° (*c* 1.20); IR ν_{max} cm^{-1}: 3440, 3090, 1730, 1640, 1240, 1130, 1090, 985, 900, 890, 830; ^1H NMR and ^{13}C NMR (Tables 4 and 5); EIMS *m/z* (rel. int.): 338 (3), 279 (5), 218 (6), 123 (10), 93 (15), 91 (17), 85 (100), 71 (29), 43 (54).

(6E)-9-*Acetoxy*-5-*hydroxynerolidol* (**16**). Compound **16** was eluted with C_6H_6–EtOAc (8:2); $[\alpha]_D$ = +18.9° (*c* 1.0); IR ν_{max} cm^{-1}: 3400, 3090, 1640, 1240, 1180, 1090, 1020, 985, 890, 830. ^1H NMR and ^{13}C NMR (Tables 4 and 5); EIMS *m/z* (rel. int.): 296 (5), 236 (4), 218 (9), 149 (33), 123 (23), 93 (16), 85 (100). Acetylation of **16** (40 mg) gave **15** (39 mg).

(6E)5,9-*Dihydroxynerolidol* (**17**). Compound **17** was eluted with C_6H_6–EtOAc (11); $[\alpha]_D$ = +17.5° (*c* 1.03); IR ν_{max} cm^{-1}: 3400, 3090, 1640, 1189, 1060, 1010, 890, 830; ^1H NMR and ^{13}C NMR (Tables 4 and 5); EIMS *m/z* (rel. int.): 254 (3), 218 (7), 165 (5), 149 (33), 123 (23), 93 (16), 85 (100), 71 (12). Acetylation of **17** (50 mg) gave **15** (53 mg).

Reduction of compound **16**. To a suspension of $LiAlH_4$ (120 mg) in dry Et_2O (25 ml) an ethereal soln of **16** (54 mg/15 ml) was added under stirring, and the mixture was further stirred at room temp. for 3 hr. The excess of reagent was destroyed by slowly adding H_2O (2 ml) and the organic layer was washed successively with 2% H_2SO_4, satd aq. $NaHCO_3$ and H_2O, dried and concd *in vacuo*, to yield an alcohol identical with the natural compound **17**.

Oxidation of compound **16**. Oxidation of **16** (100 mg) with active MnO_2–C_6H_6 [19] yielded **16a** (90 mg); $[\alpha]_D$ = +124.7° (*c* 0.42); UV λ_{max}^{EtOH}: 239 nm (ε = 9.020); IR ν_{max} cm^{-1}: 3450, 3090, 1730, 1680, 1640, 1610, 1240, 1020, 990, 890, 830; ^1H NMR and ^{13}C NMR (Tables 4 and 5); EI *m/z* (rel. int.): 294 (8), 216 (3), 164 (16), 149 (35), 123 (14), 85 (100), 83 (36), 43 (27).

(6E,9E)5-*Acetoxy*-11-*hydroxy*-9-*en*-10,11-*dihydronerolidol* (**18**). Compound **18** was eluted with C_6H_6–EtOAc (1:1); IR ν_{max} cm^{-1}: 3400, 3080, 1720, 1640, 1240, 1150, 1020, 970, 890, 840; ^1H NMR and ^{13}C NMR (Tables 4 and 5); EIMS *m/z* (rel. int.): 296 (2), 218 (10), 149 (13), 123 (14), 93 (34), 85 (36), 71 (57), 43 (100).

(6E,9E)5,11-*Dihydroxy*-9-*en*-10,11-*dihydronerolidol* (**19**). Compound **19** was eluted with C_6H_6–EtOAc (1:1); $[\alpha]_D$ = +17.6° (*c* 1.30); IR ν_{max} cm^{-1}: 3400, 3080, 1640, 1090, 1050, 970, 920, 850; ^1H NMR and ^{13}C NMR (Tables 4 and 5); EIMS *m/z* (rel. int.): 254 (4), 236 (2), 149 (43), 123 (100), 93 (18), 85 (21), 71 (30).

(6E,9E)5-*Hydroxy*-11-*methoxy*-9-*en*-10,11-*dihydronerolidol* (**20**). Compound **20** was eluted with C_6H_6–EtOAc (1:1); $[\alpha]_D$ = +17.8° (*c* 0.90); IR ν_{max} cm^{-1}: 3400, 3080, 1640, 1170, 1080, 890, 920, 850; ^1H NMR: 1.17 (9H, *s*), 1.56 (3H, *s*), 1.50–2.00 (3H, *m*), 2.65 (1H, *d*, *J* = 5.3 Hz), 3.00 (3H, *s*), 4.50 (1H, *dd*, *J* = 10 and 4 Hz), 5.10 (1H, *m*), 5.22 (1H, *dd*, *J* = 17 and 1.4 Hz), 5.40 (2H, *m*), 5.85 (1H, *dd*, *J* = 17 and 10.8 Hz).

Acetylation of **20** (80 mg) gave **20a** (83 mg); $[\alpha]_D$ = +13.4° (*c* 0.96); IR ν_{max} cm^{-1}: 3400, 3080, 1640, 1170, 1080, 890, 850; ^1H NMR: 1.20 (6H, *s*), 1.22 (3H, *s*), 1.67 (3H, *s*), 1.93 (3H, *s*), 1.50–2.00 (3H, *m*), 2.65 (1H, *d*, *J* = 5.3), 3.03 (3H, *s*), 4.95 (1H, *dd*, *J* = 10.8 and 1.4 Hz), 5.10 (1H, *m*), 5.30 (1H, *dd*, *J* = 17 and 1.4 Hz), 5.40 (3H, *m*), 5.82 (1H, *dd*, *J* = 17 and 10.8 Hz); EIMS *m/z* (rel. int.): 310 (3), 235 (2), 149 (8), 123 (17), 93 (27), 85 (31), 71 (43), 43 (100).

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