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CYCLOARTANES FROM *LINDHEIMERA TEXANA*

WERNER HERZ, KINZO WATANABE, PALANIAPPAN KULANTHAIVEL and JOHN F. BLOUNT*

Department of Chemistry, The Florida State University, Tallahassee, FL 32306, U.S.A.; * Research Division, Hoffmann-LaRoche, Inc., Nutley, NJ 07110, U.S.A.

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Key Word Index—*Lindheimera texana*; Compositae; Heliantheae; triterpenes; cycloartanes; labdanes; norambreinolide; X-ray analysis.

Abstract—The following new cycloartanes were isolated from the aerial parts of *Lindheimera texana*: (16*S*,23*S*)- and (16*S*,23*R*)-16,23-epoxycycloart-24-en-3-one, (3*S*,16*S*,23*S*)- and (3*S*,16*S*,23*R*)-16,23-epoxycycloart-24-en-3ol, (16*S*,23*R*)-16,23-epoxy-23,25-epidioxycycloartan-3-one, (16*S*)-23,24,25,26,27-pentanorcycloartan-3-one-16,22-olide, (16*S*,23*S*,24*R*)- or (16*S*,23*R*,24*S*)-23,24-epoxycycloartan-3-one-16,25-diol and (16*S*,23ζ,24ζ)-cycloartan-3-one-16,23,24,25-tetrol. Structures were established by chemical transformations and spectroscopic methods and, in the case of (16*S*,23*R*)-16,23-epoxy-23,25-epidioxycycloartan-3-one, by X-ray crystallography. Norambreinolide, several known labdanes and oleanolic acid were also isolated.

INTRODUCTION

The North American genus *Lindheimera* (Compositae) consists of two species of whose chemistry very little is known. The occurrence of a polyacetylene in an unspecified part of *Lindheimera texana* is referred to in a review [1]. In the following we report isolation from the aerial parts of *Lindheimera texana* Gray et Engelm. (Texas star) of eight new cycloartane derivatives **1a**, **1b**, **2**, **3a**, **3b**, **4**, **5a** (or **5b**), and **6a**, the known labdanes and norlabdanes **12** (norambreinolide), **13** and **14a**, **14b**, and oleanolic acid. The major triterpene constituent was **1b**; the remaining compounds were present in smaller amounts.

RESULTS AND DISCUSSION

We begin with the structures of **1a** and **1b**, both $C_{30}H_{46}O_2$ (high resolution MS), which were difficult to separate, **1a** being obtained at best in 95% purity. The IR and ^1H NMR spectra (Table 1) indicated the presence in both compounds of a cycloartane skeleton with a ketone group on C-3, an oxygen function linking C-16 and C-23 and a 24,25-double bond, i.e. gross structure **1**. This was evidenced by the absence of a hydroxyl band and the presence of ketone absorption at 1705 cm^{-1} in the IR spectra and, in the ^1H NMR spectra, by H-2 multiplets at δ2.71 and 2.30, the typical H-19 doublets at 0.85 and 0.58 (J = 4.5 Hz), four methyl singlets in the range expected for H-18, H-28, H-29 and H-30, a methyl doublet (H-21), a *dt* or quartet near δ4 (H-16), two vinyl methyl resonances (H-26 and H-27) allylically coupled to a broadened doublet (H-24) at 5.30 (for **1a**) and 5.39 (for **1b**) which in turn was coupled to a *ddd* (H-23) at 4.26 (for **1a**) and 4.51 (for **1b**). Comparison of the ^{13}C NMR spectra of **1a** and **1b** (Table 2) with the ^{13}C NMR spectra of cycloartan-3-one and related compounds [2–4] corroborated these conclusions. There is disagreement [2, 3] on the chemical shift of C-28 in cycloartan-3-ones which should not be affected significantly by the presence or absence of substitutents in rings C and D. Examination of the data in Table 2 indicates that a signal near δ22.2, absent only from the spectrum of **3b** which exhibits the signals of C-28 and C-29 at the expected frequencies of δ25.47 and δ14.01 [2–4], should be that of C-28. The C-26 and C-27 quartets, absent only from the spectrum of **4**, could be identified without difficulty, but no attempt has been made in Table 2 to discriminate between three other quartets which correspond to the signals of C-18, C-21 and C-30.

The negative Cotton effect of **1b** (and of **4**, **5** and **6a**—*vide infra*) near 295 nm paralleled that of cycloartenone; hence the absolute stereochemistry of the tetracyclic ring system is that shown in the formulae. That the stereochemistry is 17*R*,20*R* was assumed in analogy with all other known cycloartanes and confirmed by subsequent work. Cycloartanes unsubstituted at C-16 are 17*S*, but the presence of a 16-oxygen atom results in inversion of the priorities at C-17.

The relatively small differences in the chemical shifts and coupling constants of H-16 and the significantly larger differences in the shifts and coupling constants of H-23 suggested that **1a** and **1b** were C-23 epimers, the 16-oxygen being assigned the β-orientation in both compounds (16*S*) because of the coupling constants and, on biogenetic grounds, the presence in the plant of the *cis*-fused pentanorlactone **4** (*vide infra*). If this were so and if the tetrahydropyran ring were a boat rather than a chair as seemed to be indicated by the coupling constants involving H-22 and H-23, inspection of Dreiding models revealed that H-16 and H-23 would be in proximity in the 23*S*-epimer and that H-16 and H-24 would be in proximity in the 23*R*-epimer, with H-16 of the latter being deshielded somewhat by the double bond. In **1a**, $J_{22,23}$ = 7.0, 4.5 Hz and in **1b**, $J_{22,23}$ = 10.5, 7.5 Hz. These values are not compatible with a chair conformation of the tetrahydropyran ring (model). As the minor epimer, with H-16 at somewhat higher field, exhibited a strong (15%) NOE between H-16 and H-23 and none between H-16 and H-24, and as the major isomer exhibited a significant NOE (7%) between H-16 and H-24 and none between H-16 and H-23, the former was assigned the 23*S*-

Table 1. ^{1}H NMR spectra of compounds 1–7 ($CDCl_3$, 270 MHz)

	1a	**1b**	**2**	**3b§**	**3c**	**4**	**5**	**5+TAI**	**7**	**7+TAI**	**6a**	**6a+TAI**	**6b**	**6c**
H-1a	1.86 *m*	1.86 *m*	†	†	†	1.87 *br dt* (4.5, 14)	1.85 *br dt*	1.85	†	†	1.84 *br dt*	1.85	†	†
H-2a	2.71 *dt* (7, 14)	2.71 *dt*	2.71 *dt*	†	†	2.72 *dt*	2.71 *dt*	2.71	2.72 *dt*	2.70	2.71 *dt*	2.70	2.78 *dt*	2.69 *dt*
H-2b	2.30 *ddd* (14, 4.5, 2)	2.30 *ddd*	2.30 *ddd*	3.28 *dd*‡ (11, 5)	3.47 *m*‡ ($W_{1/2}$ = 5 Hz)	2.32 *ddd*	2.30 *ddd*	2.31	2.31 *ddd*	2.33	2.29 *ddd*	2.31	2.30 *ddd*	2.30 *ddd*
H-15a	1.91 *dd* (14, 7.5)	1.88 *dd*	1.91 *dd*	1.85 *dd*	†	2.09 dd (14, 8)	†	†	†	†	2.05 *dd* (14, 8)	2.22	†	†
H-15b	†	1.62 *br dd* (14, 7.5)	†	†	†	†	†	†	†	†	1.39 *br dd* (14, 4.5)	1.52	†	†
H-16	3.99 *dt* (6, 7.5)	4.15 *q* (7.5)	3.99 *dt* (6, 7.5)	4.14 *q* (7.5)	4.14 *q*	5.04 *dt* (5, 8)	4.52 *dt* (4, 5, 7)	5.60	†	†	4.47 *dt* (4.5, 8)	5.48	5.66 *dt* (4.5, 7.5)	5.65 *dt*
H-17	†	1.53 *br d* (7.5)	†	†	†	2.40 *br d* (8)	†	†	†	†	†	†	†	†
H-19a	0.85 *br d* (4.5)	0.85 *br d*	0.85 *br d*	0.62 *br d*	0.59 *br d*	0.87 *br d*	0.82 *br d*	0.81	0.86 *br d*	0.85	0.83 *br d*	0.81	0.75 *br d*	0.77 *br d*
H-19b	0.57 *d* (4.5)	0.58 *d*	0.57 *d*	0.32 *d*	0.34 *d*	0.59 *d*	0.59 *d*	0.61	0.60 *d*	0.59	0.59 *d*	0.62	0.58 *d*	0.60 *d*
H-20	†	†	†	†	†	2.66 *dq* (1, 7.5)	†	†	†	†	†	†	†	†
H-21*	0.98 *d* (7)	0.95 *d*	0.97 *d*	0.94 *d*	0.94 *d*	1.36 *d* (7.5)	1.02 *d*	0.99	0.91 *d*	0.88	1.03 *d*	0.98	0.99 *d*	1.02 *d*
H-23	4.26 *ddd* (8.5, 7, 4.5)	4.51 *ddd* (10.5, 8.5, 7.5)	—	4.50 *ddd*	4.50 *ddd*	—	4.04 *br d* (11)	4.29	4.30 *br d*	4.37	3.73 *ddd* (9, 7.5, 3)	5.60 *ddd* (11, 2, 1.5)	5.90 *ddd* (11.5, 2.5, 1.5)	5.80 *ddd*
H-24	5.30 *br d* (8.5)	5.39 *br d* (8)	2.50 *d* (12) 2.38 *d* (12)	5.39 *br d* (9)	5.39 *br d*		3.01 *br*	4.61	3.37 *br*	3.82	3.21 *d* (7.5)	5.34 *d* (1.5)	5.54 *d* (2.5)	5.29 *d*
H-26*	1.71 *br*	1.71 *br*	1.37	1.71 *d*	1.71 *d*	—	1.31	1.41	1.17‖	1.53	1.29	1.72	1.85	1.41
H-27*	1.67 *br*	1.66 *br*	1.36	1.65 *d* (1)	1.65 *d*	—	1.28	1.21‖	1.14‖	1.48	1.27	1.67	1.66	1.27‖
H-18*	1.18	1.17	1.13	1.14	1.14	1.14	1.20	1.23‖	1.12‖	1.11	1.20	1.20	1.25	1.23‖
H-28*	1.05	1.05	1.05	0.95	0.97	1.07	1.05	1.06	1.07	1.06	1.05	1.05	1.06	1.06
H-29*	1.10	1.10	1.10	0.88	0.81	1.11	1.10	1.10	1.12	1.11	1.10	1.09	1.04	1.03
H-30*	0.89	0.89	0.88	0.88	0.87	0.92	0.90	0.90	1.11	1.11	0.91	0.95	1.03	1.01
Misc								9.55 (NH) 8.72 (NH)		8.22 (NH)		8.93, 8.83 (NH) 8.73, 8.70 (NH)	¶	¶

*Intensity three protons.

†Location of signal not determined.

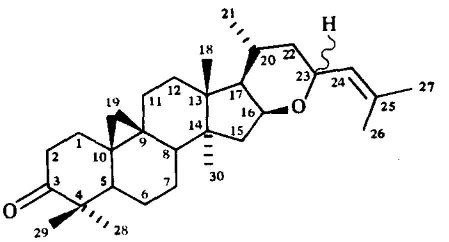
‡H-3.

§In **3a** H-16 3.97 *qt* (6, 7.5); H-23 4.24 *ddd* (8.5, 7, 4.5), H-24 5.29 *br d* (8.5).

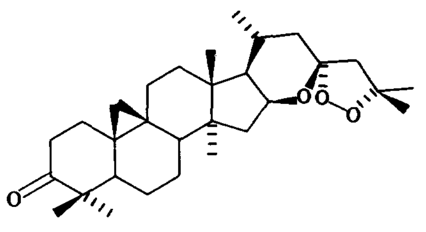
‖Assignments interchangeable.

¶Benzoate signals: in **6b** 8.1c, 7.89 *br d* (8), 7.8–7.3c, 7.16 *br t* (8) 7.04 *br t* (8); in **6c** 7.89 *br d* (8, 2H), 7.59 *br t* (8, 5H) 7.44 *br t* (8, 3H), 7.34 *br t* (8, 1H), 7.15 *br t* (8, 2H), 7.07 *br t* (8, 2H).

Coupling constants (*J*, Hz) are given in parentheses.



1a H−23α (23*S*)
1b H−23β (23*R*)



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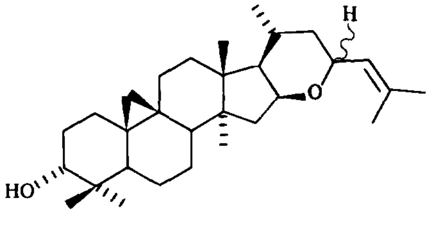
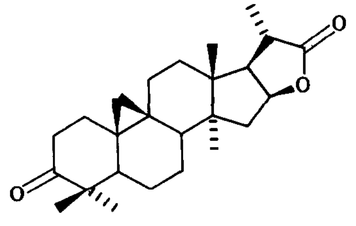


3a 3−OHβ, H−23α
3b 3−OHβ, H−23β
3c 3−OHα, H−23β



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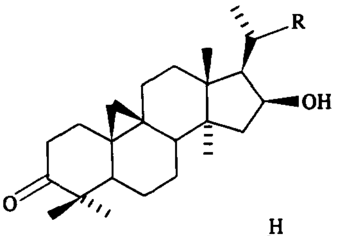
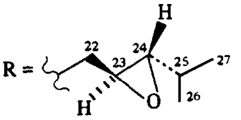
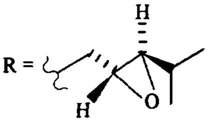
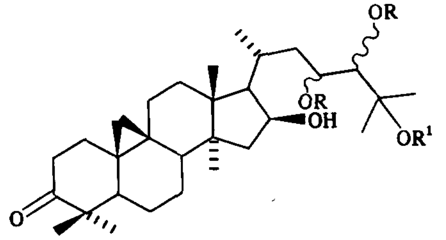


5a R =



5b R =





6a R, R^1 = H
6b R, R^1 = Bz
6c R = Bz, R^1 = H

configuration (**1a**) and the latter the 23*R*-configuration (**1b**). These assignments are also compatible with the observation that C-16 and C-24 of **1b** and the compounds derived from it (**3b**, **9b** and **10b**) are upfield of C-16 and C-24 of **1a**, **9a** and **10a** and that C-17 of **1b**, **9b** and **10b** is downfield of **1a**, **9a** and **10a** (Table 2).

Hydroxylation of **1a** and **1b** using OsO_4 gave in each case a major and a minor diol. In accordance with the models the major and minor diols from **1a** were assigned the 23*S*,24*S* stereochemistry (**10a**) and the 23*S*,24*R* stereochemistry (**9a**), respectively, approach to the double bond of the favored **1a** conformation (where H-24 is essentially *anti* to H-23) being less hindered from the direction opposite to the ether bridge. Analogously the two diols from **1b**, in a conformation with the side chain directed away from the tetrahydropyran ring, were assigned the 23*R*,24*S*-configuration (**10b**) for the major product and the 23*R*,24*R*-configuration (**9b**) for the minor product. Differences in the chemical shifts and coupling constants involving H-16, H-23 and H-24 (Table 3) can be rationalized in terms of preferred conformations adopted by the various epimers.

Two other closely related cycloartanes which could not be separated satisfactorily from each other possessed structures **3a** and **3b** on the basis of their IR, ^{1}H NMR and ^{13}C NMR spectra. The C-3 hydroxyl group of these compounds was equatorial as shown by the coupling constants involving H-2 and H-3. That the major component of this mixture had the 23*R*-configuration (**3b**) was inferred from the similarity of the chemical shifts of H-16, H-23, C-20 and C-24 to those of **1b** and was verified by $NaBH_4$ reduction of **1b** which gave a pure sample of **3b** as the major product. A minor product of the $NaBH_4$ reduction was the C-3 epimer **3c**.

The structure of the pentanorcycloartane lactone **4** was apparent from its formula $C_{25}H_{36}O_3$ (high resolution

Table 2. ^{13}C NMR spectra of compounds obtained from *L. texana* ($CDCl_3$, 67.89 MHz)

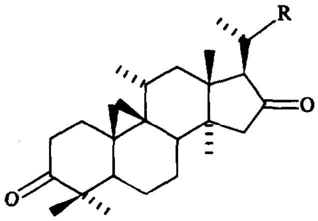
	1a	**1b**	**2**	**3b**	**4**	**5**	**6a**	**9a**	**9b**	**10a**	**10b**	**14b**
C-1	33.42 *t*	33.37 *t*	33.33 *t*	31.97 *t*	33.30 *t*	33.33 *t*	33.33 *t*	33.42 *t*	33.36 *t*	33.47 *t*	33.36 *t*	40.25 *t*
C-2	37.45 *t*	37.40 *t*	37.40 *t*	30.39 *t*	37.30 *t*	37.39 *t*	37.39 *t*	37.45 *t*	37.42 *t*	37.45 *t*	37.41 *t*	18.50 *t*
C-3	216.40	216.20	216.36	78.77 *d*	215.94	216.32	216.26	216.41	216.37	216.41	216.50	42.51 *t*
C-4	50.21	50.16	50.17	40.51	50.12	50.18	50.20	50.23	50.20	50.23	50.19	33.21
C-5	47.54 *d*	47.46 *d*	47.44 *d*	47.11 *d*	47.10 *d*	47.88 *d*	47.91 *d*	47.46 *d*	47.53 *d*	47.45 *d*	47.44 *d*	57.19 *d*
C-6	21.35 *t*	21.33 *t*	21.27 *t*	20.94 *t*	21.09 *t*	21.41 *t*	21.41 *t*	21.29 *t*	21.27 *t*	21.28 *t*	21.26 *t*	21.22 *t*
C-7	26.55 *t*	26.48 *t*	26.40 *t*	26.24 *t*	26.13 *t*	26.33 *t*	26.36 *t*	26.43 *t*	26.42 *t*	26.45 *t*	26.41 *t*	40.66 *t*
C-8	48.47 *d*	48.40 *d*	48.30 *d*	47.57 *d*	48.20 *d*	48.43 *d*	48.44 *d*	48.46 *d*	48.35 *d*	48.44 *d*	48.37 *d*	81.75
C-9	20.99	20.89	20.77	19.83	20.62	20.91	20.91	20.89	20.89	20.89	20.43	60.93 *d*
C-10	26.41	26.29	26.44	26.44	26.51	26.11	26.14	§	26.42	26.45	26.31	36.54
C-11	26.09 *t*	26.02 *t*	25.97 *t*	26.24 *t*	25.96 *t*	25.93 *t*	25.96 *t*	26.12 *t*	26.03 *t*	26.09 *t*	26.02 *t*	28.86 *t*
C-12	32.42 *t*	33.10 *t*	32.88 *t*	33.23 *t*	30.71 *t*	32.42 *t*	32.45 *t*	32.49 *t*	32.84 *t*	32.53 *t*	32.93 *t*	75.99 *d*
C-13	44.99	44.65	44.51	44.65	44.84	45.33	45.22	45.07	44.72	44.95	44.68	137.56
C-14	45.88	45.82	46.21	45.92	49.24	46.75	46.81	45.94	45.98	45.97	46.02	129.77 *d*
C-15	44.44 *t*	44.43 *t*	43.68 *t*	44.46 *t*	43.65 *t*	47.54 *t*	47.80 *t*	44.28 *t*	44.29 *t*	44.20 *t*	43.82 *t*	58.43 *t*
C-16	76.58 *d**	71.89 *d**	73.17 *d*	72.00 *d**	83.21 *d*	72.62 *d**	72.68 *d*†	79.05 *d*	74.49 *d*	77.30 *d**	73.05 *d**	64.92 *t*
C-17	54.55 *d*	57.51 *d*	55.86 *d*	57.56 *d*	55.97 *d*	56.58 *d*	56.53 *d*	54.33 *d*	56.64 *d*	55.02 *d*	56.97 *d*	24.49 *q*
C-19	30.17 *t*	30.02 *t*	30.01 *t*	30.39 *t*	29.96 *t*	29.82 *t*	29.84 *t*	30.19 *t*	30.06 *t*	30.17 *t*	30.06 *t*	21.08 *q*
C-20	24.03 *d*	26.56 *d*	26.44 *d*	26.60 *d*	36.69 *d*	26.68 *d*	24.54 *d*	24.67 *d*	26.66 *d*	23.91 *d*	25.96 *d*	16.06 *q*
C-22	37.76 *t*	38.00 *t*	38.62 *t*	38.07 *t*	181.11	41.91	41.21 *t*	34.21 *t*	33.95 *t*	33.73 *t*	35.59 *t*	‖
C-23	70.09 *d*	70.69 *d*	109.38	70.71 *d*	—	70.01 *d**	72.33 *d*†	73.64 *d*	74.61 *d*	75.42 *d**	74.78 *d**	
C-24	127.42 *d*	125.61 *d*	59.11 *t*	125.70 *d*	—	78.13 *d**	78.85 *d*	77.51 *d*	77.88 *d*	77.89 *d**	77.04 *d**	
C-25	133.91	133.70	83.74	133.68	—	74.13	73.58	73.31	72.65	72.87	73.30	
C-26	25.80 *q*	25.96 *q*	26.94 *q*†	25.97 *q*	—	27.15 *q*†	27.18 *q*‡	26.95 *q*‡	26.79 *q*†	26.45 *q*†	26.12 *q*†	
C-27	18.27 *q*	17.95 *q*	24.44 *q*†	17.97 *q*	—	26.83 *q*†	26.71 *q*‡	26.63 *q*‡	26.42 *q*†	24.48 *q*†	24.59 *q*†	
C-28	22.20 *q*	22.18 *q*	22.16 *q*	25.47 *q*	22.16 *q*	22.18 *q*	22.19 *q*	22.20 *q*	22.18 *q*	22.20 *q*	22.18 *q*	
C-29	20.90 *q*	20.76 *q*	20.77 *q*	14.01 *q*	20.74 *q*	20.76 *q*	20.77 *q*	20.81 *q*	20.79 *q*‡	20.81 *q*	20.79 *q*‡	
C-18	19.87 *q*	19.64 *q*	19.51 *q*	19.66 *q*	19.67 *q*	19.93 *q*	19.96 *q*	19.79 *q*	19.64 *q*	19.76 *q*	19.61 *q*	
C-21	20.41 *q*	20.45 *q*	20.44 *q*	20.43 *q*	18.54 *q*	18.88 *q*	18.91 *q*	20.43 *q*	20.89 *q*‡	20.47 *q*	20.87 *q*‡	
C-30	21.53 *q*	20.76 *q*	20.77 *q*	20.80 *q*	19.29 *q*	20.18 *q*	19.96 *q*	21.29 *q*	21.18 *q*	21.13 *q*	20.91 *q*‡	

*Assignment by single frequency spin decoupling.

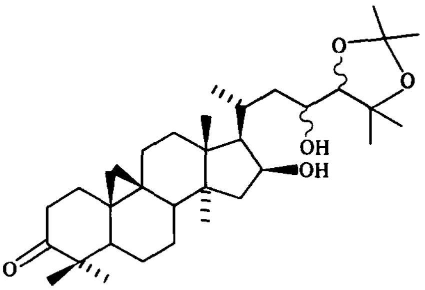
†‡Assignments with the same sign in each column may be interchanged.

§Signal not detected.

‖Acetate, 170.46, 21.08 *q*.



7 *R* as in **5a** or **6**



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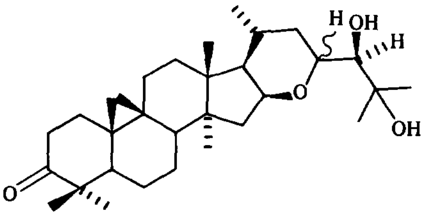
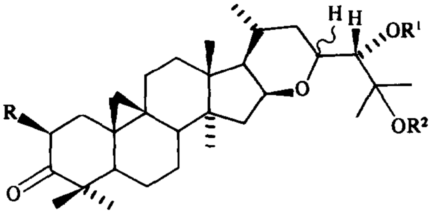
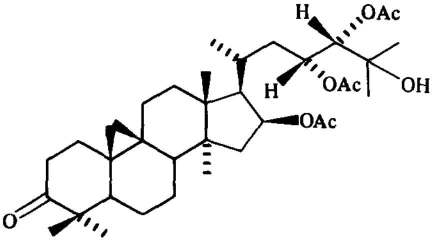


9a H−23α
9b H−23β



10a R, R¹, R² = H, H−23α
10b R, R¹, R² = H, H−23β
10c R, R² = H, R¹ = Ac, H−23β
10d R = H, R¹, R² = Ac, H−23β
10e R = OAc, R¹, R² = Ac, H−23β



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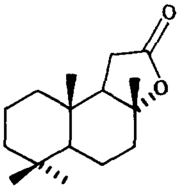

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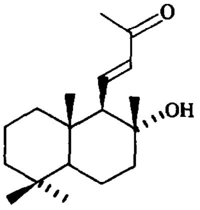

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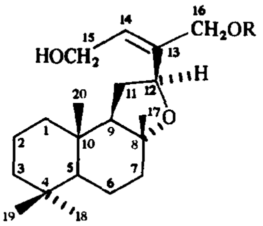


14a R = H
14b R = Ac

MS), the IR bands at 1765 (γ-lactone) and 1705 cm^{-1} (3-ketone), the ^{1}H NMR spectrum which exhibited the H-16, H-17, H-20 and H-21 signals at considerably lower field (Table 1), a circumstance which permitted sequential decoupling of all protons in the lactone ring, and the ^{13}C NMR spectrum (Table 2) which lacked the resonances of C-23 through C-27 and exhibited the expected chemical shift changes for carbons C-14 through C-17 and C-20 through C-22. The γ-lactone function attached to ring D was necessarily *cis*, and if H-17 were α, as in other cycloartanes, H-16 had to be α as well, i.e. compound 4 possessed 16*S*,17*R* stereochemistry. This was also in accord with the coupling constants $J_{15a,16} = 5$ Hz, $J_{15b,16} = J_{16,17} = 8$ Hz.

The gross structure and partial stereochemistry of the unusual peroxyacetal 2, $C_{30}H_{46}O_4$ (high resolution MS),

Table 3. ^{1}H NMR spectra of compounds **8**, **9a**, **9b** and **10a**–**10e** ($CDCl_3$, 270 MHz)

	8	**8+TAI**	**9a**	**9b**	**10a**	**10b**	**10c**	**10d**	**10e**
H-2a	2.71 *dt* (11, 5)	2.71	2.70 *dt*	2.71 *dt*	2.72 *dt*	2.70 *dt*	2.71 *dt*	2.70 *dt*	5.27 *dd* (6, 3)
H-2b	2.31 *ddd* (14, 7.5)	†	2.30 *ddd*	2.30 *ddd*	2.30 *ddd*	2.29 *ddd*	2.31 *ddd*	2.29 *ddd*	—
H-15a	†	†	1.93 *dd* (14, 7.5)	†	1.93 *dd*	†	†	†	†
H-15b	†	†	†	†		†	†	†	†
H-16	4.50 *dt* (5, 7.5)	5.38	3.97 *dt* (6.5, 7)	4.30 *q* (7)	3.97 *dt* (6.5, 7)	4.13 *q* (7)	4.22 *q*	4.06 *q*	4.22 *q*
H-19a	0.82 *br d* (4.5)	0.80	0.85 *br d*	0.84 *br d*	0.84 *br d*	0.83 *br d*	0.84 *br d*	0.82 *br d*	0.71 *br d*
H-19b	0.60 *d* (4.5)	0.61	0.59 *d*	0.58 *d*	0.58 *d*	0.57 *d*	0.58 *d*	0.57 *br d*	0.44 *d*
H-21*	1.04 *d* (7.5)	1.02	0.97 *d*	1.00 *d*	0.98 *d*	0.98 *d*	0.95 *d*	0.93 *d*	0.93 *d*
H-23	3.71 *dt* (2.5, 8)	5.27	3.88 *ddd* (8, 4, 2)	3.97 *ddd* (10, 6.5, 4)	3.63 *dt* (3, 8)	3.86 *ddd* (10, 9, 7)	4.08 *dt* (7, 10)	4.03 *dt*	4.03 *dt*
H-24	3.45 *d* (8)	3.64	3.13 *d* (2)	3.16 *d* (4)	3.32 *d* (8)	3.42 *d* (9)	4.95 *d* (10)	5.38 *d* (9)	5.38 *d* (9)
H-26*	1.40	1.41	1.27	1.26	1.23	1.24	1.26	1.50	1.50
H-27*	1.37	1.31	1.24	1.24	1.22	1.22	1.12‡	1.50	1.50
H-18*	1.20‡	1.18‡	1.15	1.15	1.15	1.16	1.15‡	1.13	1.13
H-28*	1.05	1.05	1.05	1.05	1.03	1.03	1.05	1.04	1.00‡
H-29*	1.10	1.09	1.10	1.10	1.10	1.09	1.10	1.09	0.98‡
H-30*	0.90	0.96	0.89	0.86	0.89	0.86	0.87	0.86	0.87
Misc.	1.33* 1.26*‡	1.24*‡ 1.23*‡					2.08 (Ac)*	2.08* 1.93*	2.15*, 2.08* 1.94*

*Intensity three protons.
†Location of signal not determined.
‡Assignments interchangeable.

was deduced from the ^{1}H NMR and ^{13}C NMR spectra. One of the four oxygens was a C-3 carbonyl oxygen, the second the usual ether oxygen at C-16 (*dt* at δ3.99, carbon doublet at δ73.17). The ^{13}C NMR spectrum exhibited only two other C–O frequencies, both quarternary, at δ109.38 and δ83.74, the former being appropriate for a carbon carrying two oxygen atoms, i.e. C-23, the latter being assigned to C-25 because the chemical shifts of H-26 and H-27 were considerably upfield from the H-26 and H-27 resonances in **1a**, **1b** and **3a**, **3b**. Consequently the presence of an epidioxide linking C-23 and C-25 was suspected. The C-24 resonance was a triplet and in the ^{1}H NMR spectrum the H-24 protons flanked by the peroxide bridge appeared as an AB system (J_{AB} = 12 Hz) centred at 2.44. Confirmation for the presence of a peroxy group was the facile loss of molecular oxygen from the molecular ion and a positive peroxide colour test [5].

From the chemical shift and coupling constants involving H-16, the C-16 stereochemistry of **2** was deduced to be the same as that of **1a**, **1b** and **3a**, **3b**, i.e. 16*S*, and that at C-17 and C-20 was assumed to be *R* by analogy with the other compounds. However, the configuration at C-23 remained questionable. To ascertain this point and to verify the stereochemistry at the other centers an X-ray analysis of **2** was undertaken.

Crystal data are listed in the Experimental section. Figure 1 is a stereoscopic view of the molecule which also represents the absolute configuration because of the negative Cotton effects exhibited by the congeners **1b**, **4**, **5** and **6a**. The configurations at C-16, C-17 and C-20 are as deduced earlier and that of the spiro carbon atom is 23*R*. Selected torsion angles are listed in Table 4. Compared with other cycloartanes for which such data have been reported [6, 7] the presence of the C-3 carbonyl group has produced the expected flattening of ring A which is a slightly deformed chair. Ring B is a distorted half-chair, somewhat more distorted than those of cyclograndisolide *bis-p*-bromobenzoate [6] and methyl passiflorate [7], whereas ring C closely approximates the 1,3-diplanar conformation of the cyclograndisolide derivative [6]. The five-membered ring D is a slightly distorted envelope, with C-15, C-16, C-17 and C-18 almost in a plane and C-14 as the flap, whereas the tetrahydropyran ring E is a boat.

The seventh new cycloartane was an epoxyketodiol of formula $C_{30}H_{48}O_4$ (high resolution MS) (**5a** or **5b**). Comparison of the ^{1}H NMR and ^{13}C NMR spectra with those of **1a**, **1b**, **2**, **3a**, **3b** and **4** showed that the carbonyl group was at C-3. The presence of one secondary and one tertiary hydroxyl group was indicated spectroscopically and by reaction with trichloroacetylisocyanate (TAI) [8] which resulted in a paramagnetic shift of the H-16 resonance and appearance of two NH signals and by oxidation with Jones reagent which furnished a monohydroxydiketone **7**. Comparison of the ^{1}H NMR and ^{13}C NMR spectra of **5** and the ^{1}H NMR spectrum of **7** with those of the other cycloartanes also showed that the secondary hydroxyl was at C-16 and β-orientated and that the tertiary hydroxyl was located at C-25. The fourth

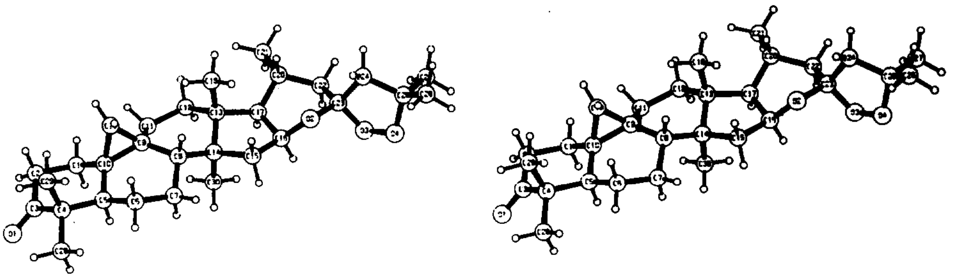


Fig. 1. Stereoscopic view of compound **2**.

Table 4. Torsion angles (°) in **2** with standard deviations in parentheses

C(5)-C(10)-C(1)-C(2)	55.6 (6)
C(10)-C(1)-C(2)-C(3)	−51.9 (7)
C(1)-C(2)-C(3)-C(4)	52.4 (7)
C(2)-C(3)-C(4)-C(5)	−50.5 (7)
C(3)-C(4)-C(5)-C(10)	51.8 (6)
C(4)-C(5)-C(10)-C(1)	−56.8 (6)
C(10)-C(5)-C(6)-C(7)	−55.8 (6)
C(5)-C(6)-C(7)-C(8)	66.3 (6)
C(6)-C(7)-C(8)-C(9)	−45.3 (7)
C(7)-C(8)-C(9)-C(10)	16.3 (6)
C(8)-C(9)-C(10)-C(5)	−8.8 (7)
C(9)-C(10)-C(5)-C(6)	28.7 (7)
C(14)-C(8)-C(9)-C(11)	−5.1 (6)
C(8)-C(9)-C(11)-C(12)	−26.7 (7)
C(9)-C(11)-C(12)-C(13)	10.0 (7)
C(11)-C(12)-C(13)-C(14)	36.4 (6)
C(12)-C(13)-C(14)-C(8)	−70.6 (6)
C(13)-C(14)-C(8)-C(9)	52.5 (6)
C(17)-C(13)-C(14)-C(15)	45.3 (5)
C(13)-C(14)-C(15)-C(16)	−42.6 (5)
C(14)-C(15)-C(16)-C(17)	22.8 (5)
C(15)-C(16)-C(17)-C(13)	5.0 (6)
C(16)-C(17)-C(13)-C(14)	−31.0 (5)
O(2)-C(16)-C(17)-C(20)	15.9 (7)
C(16)-C(17)-C(20)-C(22)	42.2 (7)
C(17)-C(20)-C(22)-C(23)	−64.7 (7)
C(20)-C(22)-C(23)-O(2)	23.0 (7)
C(22)-C(23)-O(2)-C(16)	40.7 (6)
C(23)-O(2)-C(16)-C(17)	−62.6 (6)
O(3)-C(23)-C(24)-C(25)	−2.1 (7)
C(23)-C(24)-C(25)-O(4)	−24.1 (7)
C(24)-C(25)-O(4)-O(3)	40.8 (6)
C(25)-O(4)-O(3)-C(23)	−44.7 (5)
O(4)-O(3)-C(23)-C(24)	27.5 (6)

oxygen atom of the empirical formula was that of an epoxide linking C-23 and C-24 as evidenced by two mutually coupled signals at δ4.04 (*br d*, $J = 11$ Hz) and 3.01 (*br*) and by carbon doublets at δ70.01 (C-23) and 78.13 (C-24). The small coupling constant between H-23 and H-24 indicated *trans*-stereochemistry for the epoxide ring (23*S*,24*R* or 23*R*,24*S*), but the absolute stereochemistry at C-23 and C-24 remains unknown.

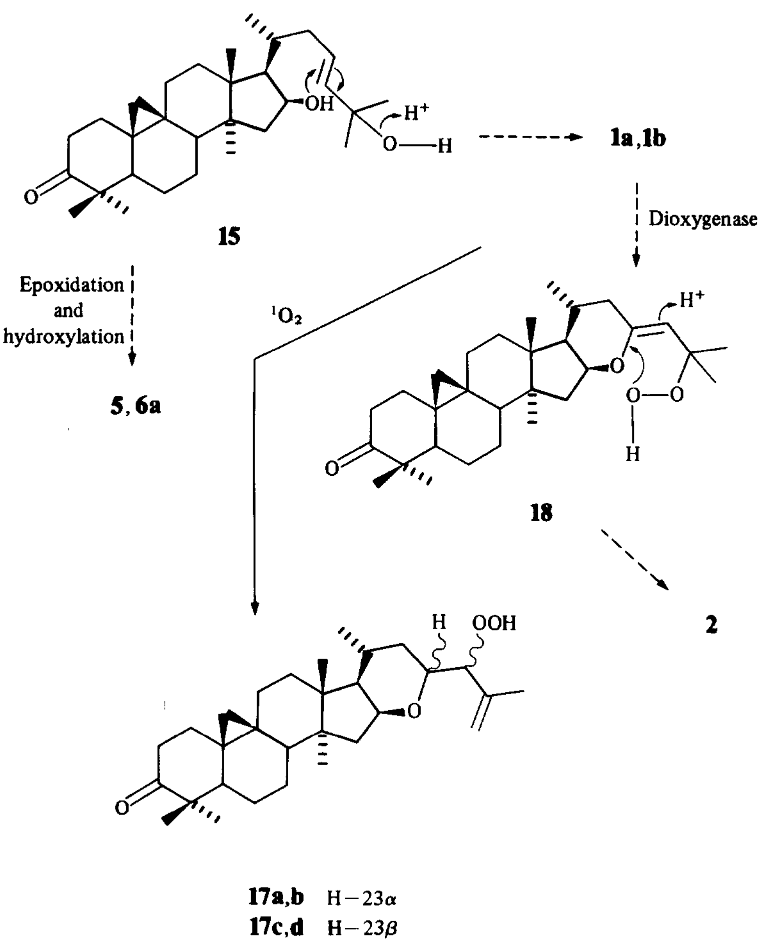
The remaining new compound **6a** was a 3-ketotetrol as demonstrated by reaction with TAI, by the ^{13}C NMR spectrum (Table 2) which exhibited three doublets at δ72.68, 72.33 and 78.85 and a singlet at 73.58 and by conversion to a tetrabenzoate **6b** and a tribenzoate **6c**. Comparison of the ^{1}H NMR and ^{13}C NMR spectra of **5** and **6a** showed that the oxygenation patterns were identical. An initial effort to establish the relative stereochemistry of **6a** at C-23 and C-24 through an acetonide involving the hydroxyl groups at these two centers failed; the only product which was formed was the other possible acetonide **8** (Table 3). An attempt was made to use the exciton chirality method for establishing the absolute configuration of **6a**; however, use of $Ni(acac)_2$ [9] did not significantly alter the CD curve of **6a**. In another attempt to establish the stereochemistry at C-23 and C-24 through correlation with one of the diols from osmylation of **1a** or **1b**, diol **10b** from **1b** was converted to monoacetate **10c** and the latter exposed to the action of $BF_3 \cdot Et_2O–Ac_2O$ in the hope of cleaving the tetrahydropyran ring, probably with inversion at C-23, to form triacetate **11**. Instead the products obtained were the diacetate **10d** and the triacetate **10e**.

The various cycloartanes of *Lindheimera texana* are obviously related biogenetically. Possible routes to them from a hypothetical precursor **15** are shown in Scheme 1. In an attempt to mimic the suggested biogenetic route from **1a**, **1b** to **2**, a mixture of **1a** and **1b** was photooxygenated. However, instead of producing some of the hoped for compound **18**, exclusive attack of singlet oxygen on C-24 produced four isomers of formula **17** which were separated and identified by ^{1}H NMR spectrometry. Spectra of the four isomers are listed in the Experimental section.

Lindheimera belongs to a group of six genera of the Heliantheae for which Stuessy [10] established a subtribe Engelmanniinae and which have more recently been included in Robinson's concept of Ecliptinae [11]. Representatives of five of these have now been studied chemically [12–18]. The information available so far indicates that these genera are not very homogeneous from the chemical point of view although it is interesting that compounds **14a** and **14b** have also been reported from several *Silphium* species [17]. The 12*R* stereochemistry originally assigned to **14a** [17] was subsequently revised to 12*S* by Wahlberg *et al.* [19] because of the chemical shift of the C-17 signal (δ24.5). As the C-17 resonance of **14b** occurs at δ24.49 (Table 2) its stereochemistry is also 12*S*.

EXPERIMENTAL

Isolation of L. texana *constituents.* Above ground parts of *Lindheimera texana* Gray & Engelm. (22 kg), collected in the flowering stage by D. Gage and J. Gershenzon on October 26,



Scheme 1.

1980 near Austin, Texas on the Pleasant Valley Road, 0.5 km S of the Longhorn Dam (voucher on deposit in the University of Texas herbarium) were extracted with $CHCl_3$ and worked up in the usual manner [20]. The crude gum (109 g) was adsorbed on 150 g of silicic acid (Mallinckrodt 100 mesh) and chromatographed over 1 kg of the same adsorbent set in hexane. Fractions were collected as follows: Fr. 1–3 (hexane–EtOAc, 97:3, 3 l.), 4–9 (hexane–EtOAc, 19:1, 3 l.), 10–19 (hexane–EtOAc, 9:1, 5 l.), 20–27 (hexane–EtOAc, 4:1, 4 l.), 28–31 (hexane–EtOAc, 7:3, 2 l.), 32–35 (hexane–EtOAc, 1:1, 2 l.), 36–41 (hexane–EtOAc, 3:7, 3 l.), 42–47 (EtOAc, 3 l.), 48–49 (EtOAc–MeOH, 9:1, 2 l.), 50–51 (EtOAc–MeOH, 4:1, 2 l.).

Fr. 10 (1.6 g) which exhibited one main spot on TLC (C_6H_6–EtOAc, 19:1) was rechromatographed over silica gel (hexane–EtOAc, 19:1). Fr. 19–20 of the rechromatogram eluted 0.16 g of (16*S*,23*S*) 16,23-epoxycycloart-24-en-3-one (**1a**) (*ca* 95% pure by ^{1}H NMR criteria) contaminated with **1b**. Fr. 21 contained 0.12 g of *ca* 90% pure **1a**. ^{1}H NMR and ^{13}C NMR spectra are listed in Tables 1 and 2. [Calc. for $C_{30}H_{46}O_2$: M_r, 438.3498. Found: M_r (MS) 438.3516]. Other significant peaks in the HRMS were at *m/z* (composition, rel. int.): 423 ($C_{29}H_{43}O_2$, 8.6), 311 ($C_{22}H_{31}O$, 3.1), 300 ($C_{21}H_{32}O$, 3.2), and 285 ($C_{20}H_{29}O$, 1.5).

Fr. 11 and 12 were combined (10 g) and rechromatographed over silica gel (hexane–EtOAc, 93:7). Fr. 2 and 3 afforded 1.3 g of a 3:1 mixrure of **1a** and **1b**; fr. 4–6 contained pure (16*S*,23*R*)-16,23-epoxycycloart-24-en-3-one (**1b**, 3.12 g), mp 160–162.5° (hexane); IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1705; ^{1}H NMR and ^{13}C NMR spectra listed in Tables 1 and 2; CD curve (MeOH) θ_{297} −3000, $[\theta]_{245}$ −300, $[\theta]_{210}$ (last reading) −10 000. [Calc. for $C_{30}H_{46}O_2$: M_r, 438.3498. Found: M_r (MS) 438.3486.] Other significant peaks in the LRMS were at *m/z* (rel. int.): 423 (57.8), 311 (13.6), 300 (27), 285 (20) and 109 (100). Continuation of the rechromatogram yielded 35 mg of (16*S*,23*R*)-16,23-epoxy-23,25-epidioxycycloartan-3-one (**2**), mp 214–217° (hexane–EtOAc), after purification by TLC (C_6H_6–EtOAc, 19:1); IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1705; ^{1}H NMR and ^{13}C NMR spectra in Tables 1 and 2. [Calc. for $C_{30}H_{46}O_4$: M_r, 470.3396. Found: M_r (MS), 470.3394.] Other significant peaks in the HRMS were at *m/z* (composition, rel. int.) 455 ($C_{29}H_{43}O_4$, 2.2), 438 ($C_{30}H_{46}O_2$, 16.5), 437 ($C_{30}H_{45}O_2$, 39), 423 ($C_{29}H_{43}O_2$, 5.5), 332 ($C_{21}H_{32}O_3$, 11.1) and 311 ($C_{22}H_{31}O$, 6.7).

Purification of 0.4 g of fr. 15 (total wt 2.0 g) of the original chromatogram by TLC (C_6H_6–EtOAc, 19:1) furnished 0.12 g of a 1:2 mixture of (3*S*,16*S*,23*S*)- and (3*S*,16*S*,23*R*)-**16**, 23-epoxycycloart-24-en-3-ol (**3a** and **3b**) and 0.14 g of norambreinolide (**12**). Repeated TLC of the mixture improved the **3a**/**3b** ratio to 1:3. ^{1}H NMR spectra of **3a** and **3b** and the ^{13}C NMR spectrum of **3b** are listed in Tables 1 and 2. Compound **12** was identified by its spectral properties and comparison with an authentic sample from oxidation of sclareol.

Fr. 26 and 27 were combined and rechromatographed (silica gel, $CHCl_3$). The initial fractions gave 0.45 g of crude oleanolic acid whose identity was established by conversion to methyl oleanolate, mp 194–195°, and acetyl methyl oleanolate, mp 217–218° [21]. Continuation of the rechromatogram gave 35 mg of (16*S*-23,24,25,26,27-pentanorcycloartan-3-one-16,22-olide (**4**), mp 228–231° (EtOAc) after repurification by TLC (C_6H_6–EtOAc, 4:1), IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1765; 1705; ^{1}H NMR and ^{13}C NMR spectra in Tables 1 and 2; CD curve (MeOH) $[\theta]_{295}$ −2700, $[\theta]_{250}$ −200; $[\theta]_{210}$ −3800 (last reading). [Calc. for $C_{25}H_{36}O_3$: M_r, 384.2654. Found: M_r (MS), 384.2648.] Other significant peaks in the HRMS were at m/z (composition, rel. int.) 385 ($C_{25}H_{37}O_3$, 1.0), 369 ($C_{24}H_{33}O_3$, 4.2), 299 ($C_{20}H_{27}O_2$, 1.9), 246 ($C_{19}H_{22}O_2$, 9.6) and 231 ($C_{15}H_{19}O_2$, 3.8).

Purification of fr. 33 by TLC ($CHCl_3$–MeOH–EtOAc, 38:1:1, two developments) gave 46 mg of 16-acetoxycarterochaetol (**14b**) [17] from the upper band. The lower band (14 mg) was a 3:2 mixture of 14,15-bisnor-8-hydroxy-11*E*-labden-13-one (**13**) [22] and **14a** [17, 19].

Fr. 41 and 42 (2.2 g) were rechromatographed (silica gel, $CHCl_3$–MeOH, 49:1). The initial fractions after repurification by TLC ($CHCl_3$–MeOH–EtOAc, 8:1:1) gave 0.26 g of (16*S*,23*S*,24*R*)- or (16*S*,23*R*,24*S*)-23,24-epoxycycloartan-3-one-16,25-diol (**5a** or **5b**), mp 185–187° (EtOAc). Later fractions furnished 40 mg of (16*S*,23ζ,24ζ)-cycloartan-3-one-16,23,24,25-tetrol (**6a**), dec. 225–228° ($CHCl_3$–MeOH). Substance **5** had IR bands (KBr) at 3400 br and 1700 cm^{-1}; CD curve (MeOH) $[\theta]_{295}$ −2200; $[\theta]_{245}$ 0; $[\theta]_{208}$ (last reading) −2500. [Calc. for $C_{30}H_{48}O_4$: M_r, 472.3550. Found: M_r (MS) 472.3524.] Other significant peaks in the low resolution MS were at m/z (rel. int.): 439 (0.5), 413 (0.6), 383 (5.4), 340 (8.2) and 311 (5.2). Compound **6a** had IR bands (KBr) at 3380 br and 1700 cm^{-1}; CD curve (MeOH) $[\theta]_{295}$ −3000; $[\theta]_{245}$ 0, $[\theta]_{210}$ (last reading) −3000. [Calc. for $C_{30}H_{50}O_5$: M_r, 490.3658. Found: M_r (MS) 490.3662.] Other significant peaks in the low resolution MS were at m/z (rel. int.): 472 (4.6), 457 (1.4), 454 (2.5), 439 (4.3), 400 (6.1), 399 (6.8), 384 (7.4), 383 (26.2), 365 (19.7), 310 (43.4) and 311 (19.2). ^{1}H NMR and ^{13}C NMR spectra of both compounds are listed in Tables 1 and 2. Benzoylation of 10 mg of **6a** (benzoyl chloride–pyridine) and TLC of the crude product gave two gummy fractions **6b** (minor) and **6c** (major) whose ^{1}H NMR spectra are listed in Table 1. Reaction of 10 mg of **6a** with 1 ml of 2,2-dimethoxypropane and 1 mg of *p*-toluenesulphonic acid at room temp. for 4 hr, work-up in the usual way and TLC of the crude product (C_6H_6–EtOAc, 9:1) gave 7 mg of gummy acetonide **8** whose ^{1}H NMR spectrum is listed in Table 3. Rechromatography of fr. 43 and 11 gave 0.24 g of 16-hydroxycarterochaetol (**14a**) [17, 19], mp 180° (lit. mp 175° [17]).

Hydroxylation of compound **1a**. A soln of 0.15 g of **1a** (90–95% pure) in 5 ml pyridine was stirred with 0.10 g OsO_4 at room temp. for 24 hr. A soln of 0.15 g $NaHSO_3$ in 3 ml H_2O and 2 ml pyridine was added and stirring continued for 1 hr. The mixture was extracted with $CHCl_3$ and the organic layer was evaporated at red. pres. TLC of the crude product ($CHCl_3$–MeOH–EtOAc, 18:1:1) furnished 25 mg of **9a** and 80 mg of **10a**. Compound **9a**, mp 215–218° (hexane–EtOAc), had IR bands (KBr) at 3380 and 1700 cm^{-1}; MS m/z (rel. int.): 472 $[M]^+$ (1.3), 457 (0.7), 454 (0.4), 414 (4.9), 396 (4.9), 383 (29.5), 365 (17.2), and 59 (86). ^{1}H NMR and ^{13}C NMR spectra are listed in Tables 2 and 3. Compound **10a**, mp 179–180° (hexane–EtOAc) had IR bands (KBr) at 3410, 3330 and 1700 cm^{-1}; MS m/z (rel. int.): 472 $[M]^+$ (2.3) 457 (1.7), 454 (1.2), 439 (3.3), 414 (5.3), 396 (6), 384 (16.7), 383 (52.4), 365 (29.8), 339 (7.3) and 59 (100). ^{1}H NMR and ^{13}C NMR spectra are listed in Tables 2 and 3.

Reactions of compound **1b**. (a) Reduction of 0.10 g of **1b** with 0.10 g $NaBH_4$ in 5 ml MeOH by stirring for 5 hr at room temp. and purification of the crude product by TLC (C_6H_6–EtOAc, 9:1) gave 14 mg of **3c** and 70 mg of **3b** as gums. ^{1}H NMR and ^{13}C NMR spectra of **3b** are listed in Tables 1 and 3; MS m/z (rel. int.): 441 $[M+1]^+$ (13.7), 440 $[M]^+$ (38.4), 425 (27.4), 422 (8.8), 407 (10.6), 300 (50.1), 285 (41.8) and 109 (100). Calc. for $C_{30}H_{48}O_2$: M_r, 440.3654. Found: M_r (MS), 400.3632. The ^{1}H NMR spectrum of **3c** is listed in Table 1, MS m/z (rel. int.): 441 $[M+1]^+$ (20.2), 440 $[M]^+$ (58.2), 425 (43.1), 422 (5.4), 407 (8.4), 300 (40.9), 285 (46.4) and 109 (100). [Calc. for $C_{30}H_{48}O_2$: M_r, 440.3654. Found: M_r (MS), 440.3633.]

(b) Hydroxylation of 0.40 g of **1b** in 5 ml pyridine with 0.25 g OsO_4 at room temp. for 24 hr, work-up as described for **1a** and TLC ($CHCl_3$–MeOH–EtOAc, 18:1:1) of the crude product furnished 65 mg of **9b** and 310 mg of **10b** whose ^{1}H NMR and ^{13}C NMR spectra are listed in Tables 2 and 3. Compound **9b**, mp 128–130° (hexane–EtOAc) had IR bands (KBr) at 3460, 3400 and 1700 cm^{-1}; MS m/z (rel. int.): 472 $[M]^+$ (1), 457 (0.5), 454 (0.3), 439 (0.9), 414 (5.7), 396 (3.9), 384 (14.4), 383 (48.6), 365 (31.7), 339 (5.3) and 59 (66.6). Compound **10b** was an amorphous powder, IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3420 (br) and 1700; MS m/z (rel. int.): 472 $[M]^+$ (2.1), 457 (1.6), 454 (0.8), 439 (2.7), 384 (17.4), 383 (51.2), 365 (27.4) and 59 (100). Acetylation of 0.20 g of **10b** (Ac_2O–pyridine) followed by the usual work-up gave 192 mg of **10c**, mp 210–213° dec (hexane–EtOAc); IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3440, 1740 and 1705; ^{1}H NMR spectrum in Table 3; MS (CI, isobutane) m/z (rel. int.): 515 $[M+1]^+$ (73.2), 497 (68.0), 455 (21.6), 437 (16.1), 383 (100), 365 (19.9). Further reaction of 0.15 g of **10c** with 3 ml Ac_2O and 0.1 ml $BF_3 \cdot (OEt)_2$ by stirring for 1 hr, decomposition of the reaction mixture with ice, extraction with $CHCl_3$, washing of the extract with $NaHSO_3$ and H_2O, evaporation of the extract and TLC (C_6H_6–EtOAc, 9:1) afforded 30 mg of **10d**, 14 mg of **10e** and 95 mg of starting material. Compounds **10d** and **10e** were gums whose ^{1}H NMR spectra are listed in Table 3; MS (CI) of **10d** m/z (rel. int.): 557 $[M+1]^+$ (7.2), 497 (80.7), 437 (16.7), 383 (100), 365 (18.2).

Photooxygenation of **1a, b** *mixture*. A soln of 1 g of a 1:3 mixture of **1a** and **1b** in 150 ml of CH_2Cl_2 containing 5% MeOH and 15 mg of rose bengal was irradiated in a cylindrical Pyrex Hanovia reactor using two Sylvania DVY-tungsten halogen projection lamps as an internal light source. A stream of O_2 was bubbled through the mixture which was cooled by immersing the mixture in a water–alcohol bath thermostated at < 10°. Irradiation was stopped after 2 hr; evaporation of the mixture *in vacuo* and column chromatography of the residue (silica gel, eluent 10–15% EtOAc in hexane), all fractions being monitored by TLC and ^{1}H NMR spectrometry, gave in fractions 2–7 0.63 g of starting material. The material in fractions 25, 28 and 35 was pure by NMR criteria and represented three different hydroperoxides of formula **17**. Fraction 31 contained a fourth isomer contaminated by the isomer of fr. 28. Comparison of the chemical shifts of H-16 with those of **1a**, **1b**, **9a**, **9b**, **10a** and **10b** (Tables 1 and 3) indicated that fr. 25 and 31 represented the two 23*S* isomers **17a**, **17b** and fr. 28 and 35 the two 23*R* isomers **17c**, **17d**; ^{1}H NMR spectrum of fr. 25: δ 5.01 *br* and 4.92 *br* (H-27), 4.13 *br q* (J = 7 Hz, H-16), 3.99 *d* (J = 9 Hz, H-24), 3.69 *m* (H-23), 2.73 *dt* (J = 7, 14 Hz) and 2.32 *ddd* (J = 14, 4.5, 2 Hz, H-2a, b), 1.74 *br* (H-26), 1.18, 1.11, 1.06, 0.90 (H-18, H-28, H-29, H-30), 0.97 *d* (J = 7 Hz, H-21), 0.87 *d* and 0.59 *d* (J = 4.5 Hz, H-19a, b); NMR of fr. 28 δ 5.07 *br* and 5.07 *br* (H-27), 4.45 *d* (J = 6.5 Hz, H-24), 4.17 *br q* (J = 7 Hz, H-16), 3.80 *dt* (J = 10.5, 6.5 Hz, H-23), 2.70 *dt* and 2.28 *dt* (H-2a, b), 1.79 *br* (H-26), 1.12, 1.08, 1.03 and 0.86 (methyl singlets), 0.94 *d* (J = 7 Hz, H-21), 0.82 *d* and 0.56 *d* (H-19a, b); ^{1}H NMR spectrum of fr. 31: δ 5.05 *br* and 5.01 *br* (H-27), 4.31 *d* (J = 9 Hz, H-24), 4.01 *br q* (J = 7 Hz, H-16), 3.89 *ddd* (J = 9, 7.5, 4.5 Hz, H-23), 2.70 *dt* and 2.28 *ddd* (H-2a, b), 1.75 *br* (H-26), 1.16, 1.09, 1.04 and 0.88 (Me singlets), 0.95 *d* (J = 7 Hz, H-21), 0.86 *d* and 0.53 *d* (H-19a, b); ^{1}H NMR spectrum of fr. 35: δ 4.99 *br* (2p, H-27), 4.37 *d* (J = 9 Hz, H-24), 4.18 *br q* (J = 7 Hz, H-16), 3.99 *ddd* (J = 11, 9, 7 Hz, H-23), 2.69 *dt* and 2.28 *dt* (H-2a, b), 1.72 *br* (H-26), 1.14, 1.08, 1.02 and 0.87 (Me singlets), 0.93 *d* (J = 7 Hz, H-21), 0.83 *d* and 0.56 *d* (H-19a, b).

Oxidation of compound **5**. A soln of 50 mg of **5** in 10 ml of Me_2CO was stirred with 0.5 ml of Jones' reagent for 45 min at 0°. The usual work-up afforded 34 mg of **7** as a gum; IR ν_{max}^{KBr} cm^{-1}: 3500 (br) and 1700 (br); ^1H NMR spectrum in Table 1; MS m/z (rel. int.): 470 $[M]^+$, 455 (3.7), 411 (100), 397 (6.0), 355 (8.3). [Calc. for $C_{30}H_{46}O_4$: M_r, 470.3393. Found: M_r (MS) 470.3370.]

X-ray analysis of compound **2**. Crystals of **2**, prepared by slow crystallization from EtOAc, were orthorhombic, space group $P2_12_12_1$, with $a = 7.027$ (4), $b = 14.802$ (4), $c = 26.021$ (10) A, and $d_{calc} = 1.155$ g cm^{-3} for $Z = 4$ ($C_{30}H_{46}O_4$, $M_r = 470.69$). The intensity data were measured on a Nonius CAD4 diffractometer (graphite-monochromated Cu Kα radiation, $w - 2\theta$ scans). The size of the crystal used for data collection was approximately 0.3 × 0.5 × 0.6 mm. A total of 2320 independent reflections were measured for $\theta < 60°$, of which 1756 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple solution procedure [23] and was refined by full-matrix least squares. In the final refinement, anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic thermal parameters were used for the hydrogen atoms. The hydrogen atoms were used in the structure factor calculations but their parameters were not refined. The final discrepancy indices are $R = 0.059$ and $wR = 0.063$ for the 1756 observed reflections. The final difference map has no peaks greater than ± 0.2 e A^{-3}. Lists of final atomic and final anisotropic thermal parameters, bond lengths and bond angles have been deposited with the Cambridge Crystallographic Data Centre.

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