Dammarane Triterpenes of *Trevoa trinervis*: Structure and Absolute Stereochemistry of Trevoagenins A, B, and C[1]

Carmen Betancor, Raimundo Freire, Rosendo Hernández, and Ernesto Suárez *
Instituto de Productos Naturales Orgánicos, C.S.I.C., and Departamento de Química Orgánica, Universidad de La Laguna, Tenerife, Spain
Manuel Cortés
Facultad de Química, Pontificia Universidad Católica de Chile, Santiago, Chile
Thierry Prangé and Claudine Pascard
Institut de Chimie des Substances Naturelles, C.N.R.S., 91190 Gif-sur-Yvette, France

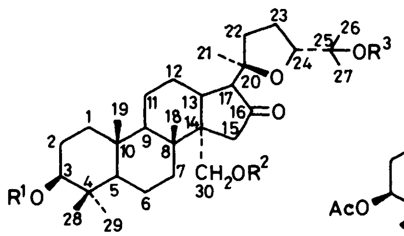
Trevoagenins A, B, and C, extracted from *Trevoa trinervis* Miers, are shown, by chemical and spectral means, to be isomeric dammarane triterpenes possessing the general 3β,25,30-trihydroxy-(20,24)-epoxydammaran-16-one structure with stereoisomeric side-chains of the ocotillol type. Trevoagenin A (20*R*,24*R*)-(1), whose stereochemistry has been established by chemical methods and confirmed by *X*-ray analysis, was transformed into (20*R*,24ξ–ocotillone (26) and the C-24 stereochemistry was assigned as *R*. As a consequence, the C-24 stereochemistry for ocotillol-related compounds of the (20*R*)-series, unestablished so far, has been determined. The stereochemistry of trevoagenin B, (20*S*,24*R*)-(13), was established by chemical correlation with trevoagenin A. Moreover, trevoagenin B was transformed into ocotillol (20*S*,24*R*)-(21) and its recently questioned C-24 stereochemistry has been reaffirmed. Trevoagenin C, (20*S*,24*S*)-(17), is the C-24 isomer of trevoagenin B as shown by degradation of both compounds to the lactone (16).

Trevoa trinervis Miers (Rhamnaceae) is a spiny shrub found in the central zone of Chile and known by the popular names of ' trevu ' or ' tebó '. Infusions of this plant have been used for a long time in folk-medicine[2] for the treatment of many diseases.

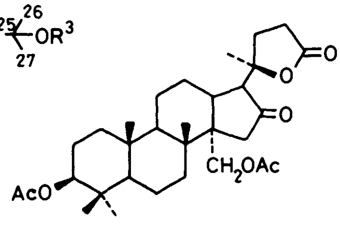
Although a number of dammarane saponins and sapogenins have been isolated from other genera of the rhamnaceae, *e.g. Zizyphus*,[3] *Hovenia*,[3] *Emmenospermum*,[4] and *Colletia*,[5] to date the genus *Trevoa* has received little chemical attention. In fact previous work[6] on *Trevoa trinervis* has only led to the isolation of friedelin.

From an ethanolic extract of the leaves and twigs of *T. trinervis* three compounds, which we have named trevoagenin A (1), B (13), and C (17), were isolated after acid hydrolysis. All three compounds have the molecular formula $C_{30}H_{50}O_5$ (from elemental and mass spectral analysis). Their i.r. spectra disclosed the same functional groups; hydroxy ($\nu_{max.}$ 3 420 cm^{-1}) and saturated carbonyl ($\nu_{max.}$ 1 725—1 730 cm^{-1}) and their mass spectra gave very similar fragmentation patterns (Scheme 1) which suggested that they were stereoisomers. Trevoagenins A, B, and C each gave a diacetate [*e.g.* (2)] when treated with acetic anhydride and pyridine at room temperature but a triacetate [*e.g.* (3)] was formed when they were refluxed with acetic anhydride and sodium acetate, and these compounds did not show any hydroxylic absorption in their i.r. spectra. By careful saponification of the diacetate [*e.g.* (2)] the monoacetate [*e.g.* (4)] was obtained. A spectroscopic study of these acetates suggested the presence of a primary hydroxy-group [AB (*J* 12 Hz) system at δ 3.97 and 4.06 in the ^{1}H n.m.r. spectrum of compound (4) which was shifted to δ 4.33 and 4.60 in that of compound (2)], a secondary hydroxy-group [one-proton doublet of doublets at δ 3.42 in the ^{1}H n.m.r. spectrum of compound (1), shifted to δ 4.48 in that of compound (2)] and a tertiary hydroxy-group in the molecule.

The ^{1}H n.m.r. spectra of the trevoagenins also showed a signal corresponding to one proton on a carbon bearing an oxygen atom [doublet of doublets at δ 3.67 for compound (2)] which was only slightly (if at all) affected by acetylation, and seven tertiary methyl groups. The mass spectra of the trevo-



(1) R¹ = H, R² = H, R³ = H
(2) R¹ = Ac, R² = Ac, R³ = H
(3) R¹ = Ac, R² = Ac, R³ = Ac
(4) R¹ = Ac, R² = H, R³ = H
(5) R¹ = Ac, R² = Ts, R³ = H



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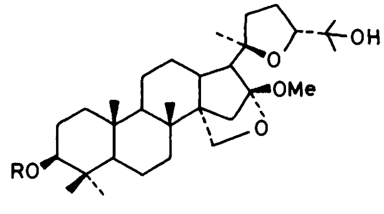
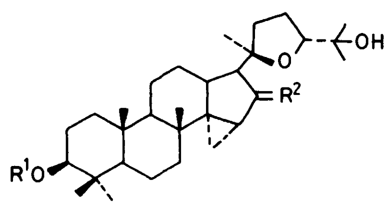
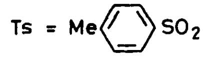
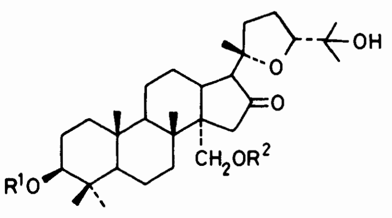


(7) R = H
(8) R = Ac

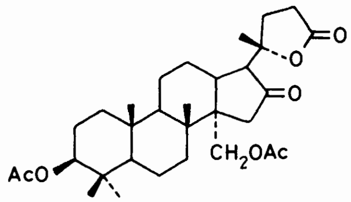


(9) R¹ = Ac, R² = O
(10) R¹ = H, R² = O
(11) R¹ = H, R² = α−H, β−OH
(12) R¹ = H, R² = β−H, α−OH





(13) R[1] = H, R[2] = H
(14) R[1] = Ac, R[2] = Ac
(15) R[1] = Ac, R[2] = H



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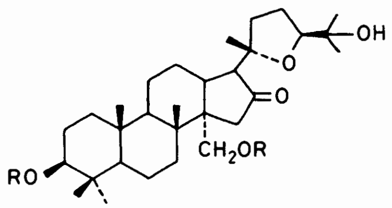
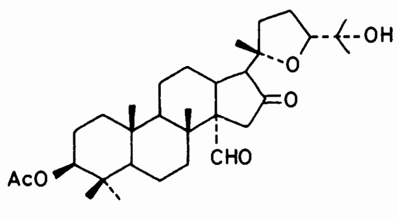
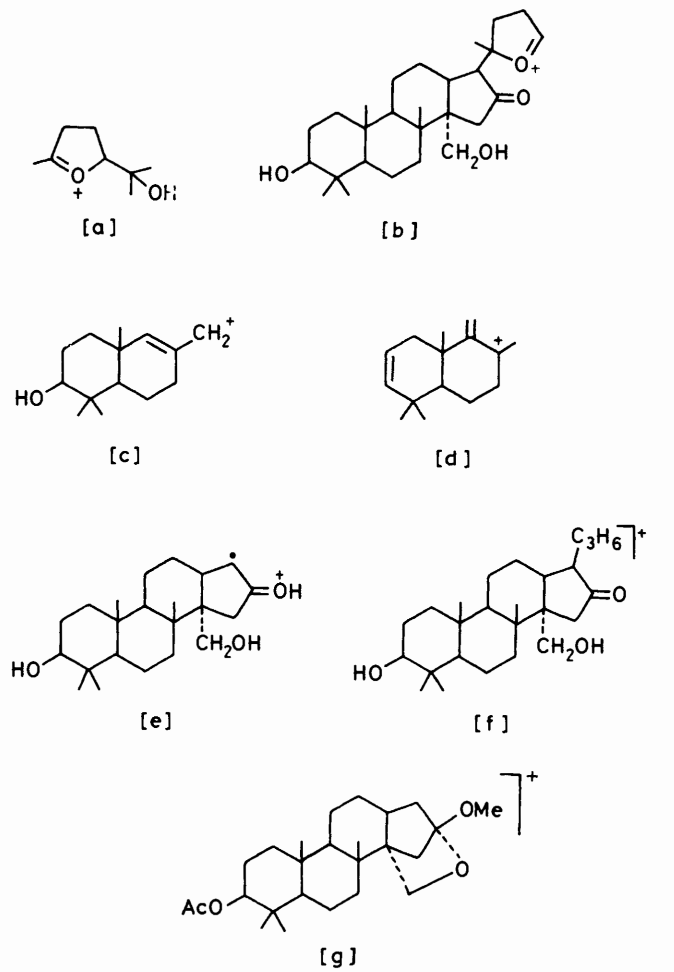


(17) R = H
(18) R = Ac



(19)



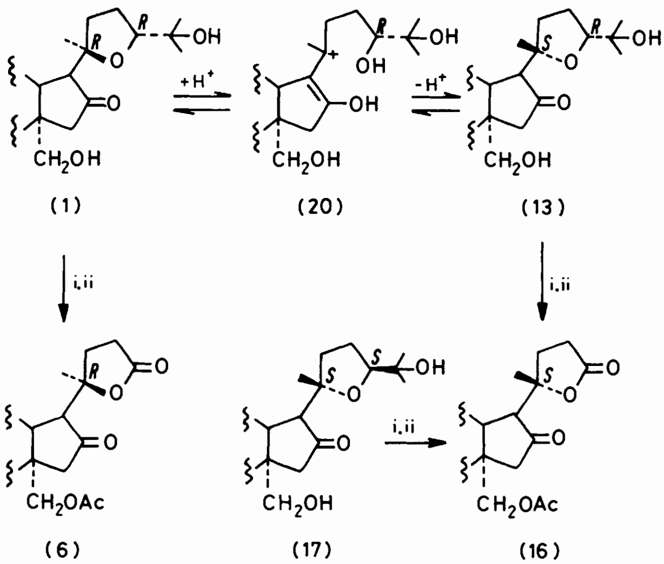
Scheme 1.

agenins (Scheme 1) showed a strong ($\sum_{100} 50\%$) base peak [a] at m/z 143 (composition $C_8H_{15}O_2$) that loses one (m/z 125, m^* 109.2) and two (m/z 107, m^* 91.6) molecules of water and a fragment [b] m/z 431. This strongly suggested a tetracyclic triterpene structure with a side-chain of the gratiogenin-[7] or ocotillol-type.[8] Chemical support for this hypothesis was obtained by treatment of the diacetate of trevoagenin A, compound (2), with Jones' reagent; the lactone (6) ($\nu_{max.}$ 1 770 cm^{-1}) formed is usually obtained [8] by oxidation of this type of compound. Fragments [c] and [d], tentatively ascribable [9,10a,10b,11b] to the AB rings of tetracyclic triterpenes, suggest a skeleton with a methyl group at C-8 (dammarane) and with one hydroxy-group as the sole functional group in these two rings; this confines the location of the primary hydroxy-group to C-30. Trevoagenin A (1) has a c.d. spectrum with a strong negative Cotton effect ($\lambda_{max.}$ 302 nm; θ −12 500) which suggests that the carbonyl group is at C-16.[12]

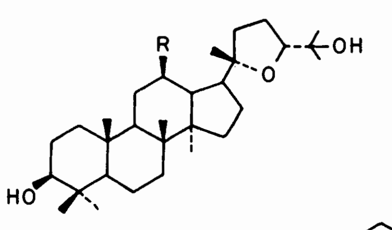
The relative positions of the carbonyl and the primary hydroxy-group were established by chemical methods. Reactions of trevoagenin A (1) with methanolic hydrogen chloride gave the acetal (7) whose ^1H n.m.r. spectrum showed a resonance of a methoxy-group at δ 3.38; its i.r. spectrum showed no absorption due to a carbonyl group. Esterification of the acetal (7) with acetic anhydride in pyridine afforded the 3-monoacetate (8). The 30-tosylate (5), obtained from the monoacetate (4), was solvolysed with anhydrous sodium acetate in acetone to give compound (9). Spectroscopic data showed the absence of the primary alcohol function and the presence of a α–β cyclopropyl ketone system in compound (9). The i.r. spectrum of the derived alcohol (10) showed the absorption of the carbonyl group at 1 700 cm^{-1} and, in the ^1H n.m.r. spectra of the reduced compounds (11) and (12), resonances of the cyclopropyl protons appeared at δ 0.0 and 0.6, respectively.

Side-chain Stereochemistry of Trevoagenins.—The trevoagenins A (1) and B (13) equilibrate (*ca.* 1 : 1), *via* a carbonium ion (20) (Scheme 2) stabilized by the presence of the keto-group at C-16, on treatment with 2M hydrochloric acid in ethanol. This keto-group was essential for the isomerization to take place because compounds lacking it were stable to these acid conditions. Therefore, both trevoagenins must have the same stereochemistry at C-24 and they must therefore differ at C-20. This is also in agreement with the finding that Jones oxidation of the diacetate of trevoagenin A, compound (2), and that of trevoagenin B, compound (14), gave different lactones (6) and (16), respectively. Furthermore, oxidation of the diacetate of trevoagenin C, compound (18), led to the lactone (16), identical with that obtained from compound (14). Hence, trevoagenins B (13) and C (17) only differ from each other in their stereochemistry at C-24. In order to establish the absolute configurations of these substances, the 3-monoacetate of trevoagenin B, compound (15), was oxidized with Collins' reagent to give the keto-aldehyde (19), Huang-Minlon reduction of which afforded ocotillol (21) which was shown to be identical with an authentic sample.[8]

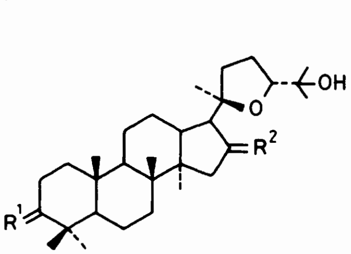
From the lichen *Pyxine endochrysina*, Yosioka *et al.*[10a,b] isolated a dammarane triterpene, pyxinol (22), whose structure and side-chain stereochemistry (20*S*,24*R*) were unambi-



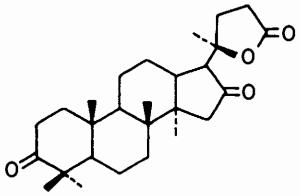
Scheme 2. *Reagents:* i, Ac_2O-pyridine; ii, Jones' reagent



(21) R = H
(22) R = OH



(23) $R^1 = \alpha$-H, β-OH, $R^2 = O$
(24) $R^1 = \alpha$-H, β-OH, $R^2 = \sim$OH,H
(25) $R^1 = \alpha$-H, β-OH, $R^2 = H,H$
(26) $R^1 = O$, $R^2 = H,H$



(27)

guously determined by *X*-ray analysis of its 3,12-di-*O*-*p*-bromobenzoate.[10c] As pyxinol has been shown to be chemically similar to ocotillol,[10b,*] trevoagenin B (13) must have the same configuration (20*S*,24*R*) and hence we can deduce a (20*R*, 24*R*)-configuration for trevoagenin A (1) and 20*S*,24*S* for trevoagenin C (17) (Scheme 2).

Since trevoagenins A (1) and B (13) equilibrate on treatment with 2M hydrochloric acid in ethanol and since the hydrolysis of the glycosides in the isolation process was carried out with a similar treatment, it is possible that one of these triterpenes is an artefact. The (20*R*)-epimer of trevoagenin C has not been isolated, so in this case the corresponding equilibrium, if any, is strongly displaced towards the (20*S*)-isomer.

* Although not specifically stated by Yoskioka *et al.* (ref. 10), we have found that ocotillol and 12-desoxypysinol are identical.

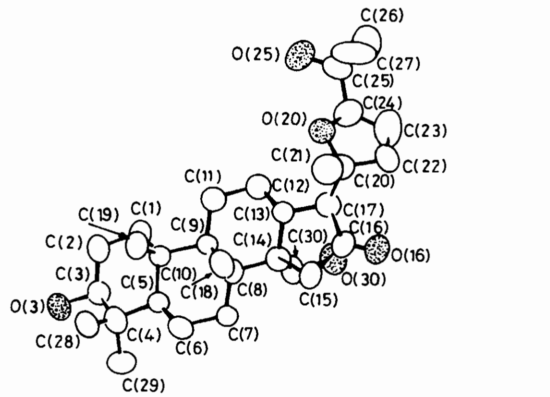


Figure. *X*-Ray crystal structure of trevoagenin A (1). Oxygen atoms are shaded

Configuration at C-24 *of the* 20R-*Ocotillones*.—Only the stereochemistry of the C-24 isomers of the 20*S* series of dammarane triterpenes of the ocotillol type has been well established, the (20*S*,24*S*)-isomers [13] by *X*-ray analysis of 25-bromo-(20*S*,24*S*)-epoxydammarane-3α,12β-diol and the (20*S*,24*R*)-isomers [10c] by *X*-ray analysis of 3,12-di-*O*-*p*-bromobenzoyl pixynol. Compounds with the (*R*)-configuration at C-20 have been isolated, *e.g.* kapurone,[14] ($20\xi_1$)-ocotillone,[15] and (20*R*,$24\xi_2$)-ocotillone [11b] [(24ξ)-(26)] but their stereochemistry at C-24 remains undetermined to this day.†‡

The stereochemistry of trevoagenin A (1) was chemically correlated with that of (20*R*,$24\xi_2$)-ocotillone [(24ξ)-(26)] by the following reactions; the cyclopropyl derivative (10) was reduced with lithium in liquid ammonia to give a mixture of the ketone (23) and the alcohol (24). The i.r. spectrum of compound (23) showed the absorption due to the cyclopentanone at 1 725 cm^{-1}. Huang-Minlon reduction of the ketone (23) afforded the diol (25) which, by oxidation with Collins' reagent, yielded (20R,$24\xi_2$)-ocotillone (26). This compound was shown to be identical with that isolated by Wahlberg and Enzell.[11b] This interrelation led us to establish the stereochemistry at C-24 of the (20*R*,$24\xi_2$)-ocotillone as *R*. Moreover, we may deduce that ($20\xi_1$)-ocotillone [15] and kapurone [14] must both have the (20*R*,24*S*)-configuration since both compounds have been degraded to the same lactone (27) as reported for (20*R*,$24\xi_2$)-ocotillone.[11b]

The relative stereochemistry of trevoagenin A (1) was unambiguously elucidated by a single-crystal *X*-ray analysis. Details of the *X*-ray analysis are given in the Experimental section and the positional parameters, bond distances, bond angles, and torsional angles are given in Tables 1—4. An ORTEP perspective drawing of compound (1) as determined from the *X*-ray crystallographic analysis is shown in the Figure.

The results of the *X*-ray analysis of trevoagenin A (1) and the chemical correlation with trevoagenin B (13) and in turn that of trevoagenin B with ocotillol (21) led us to confirm the *R*-stereochemistry at C-24 for ocotillol, as previously determined by Nagai *et al.*[13b,c] Recently, Lavie *et al.*[16] claimed the stereochemistry of ocotillol to be 20*S*,24*S*, based principally on their correlation of the stereochemistries of cabraleone [17] with that of eichlerianic acid and of this latter compound with that of shoreic acid. The structure of shoreic acid has been

† Kapurone and ($20\xi_1$)-ocotillone have the same physical constants and are assumed to be identical.

‡ The ξ_1 and ξ_2 symbolism has been used by Ourisson and coworkers [11a] and Enzell.[11b]

Table 1. Positional parameters (× 10^4) and averaged isotropic temperature factors U (× 10^3) for compound (1). Mean e.s.d.s are: x (1), y (2), z (1), and U (1)

	x	*y*	*z*	*U*
C(1)	6 200	1 431	6 554	91
C(2)	6 069	175	7 071	62
C(3)	5 681	170	7 572	44
C(4)	5 438	686	5 916	52
C(28)	5 402	−215	4 153	61
C(29)	5 063	870	6 848	71
C(5)	5 591	1 934	5 325	46
C(6)	5 368	2 600	3 744	56
C(7)	5 475	3 949	3 690	55
C(8)	5 864	4 154	3 211	46
C(9)	6 097	3 379	4 662	43
C(10)	5 997	1 997	4 787	46
C(11)	6 496	3 596	4 389	54
C(12)	6 604	4 922	4 554	56
C(13)	6 382	5 656	3 110	48
C(14)	5 974	5 516	3 548	47
C(15)	5 827	6 454	2 058	56
C(16)	6 095	7 453	2 036	52
C(17)	6 448	7 017	2 909	49
C(18)	5 924	3 825	934	60
C(19)	6 090	1 307	2 848	57
C(20)	6 772	7 411	1 620	57
C(21)	6 745	6 989	−576	74
C(22)	6 838	8 761	1 820	73
C(23)	7 091	8 775	3 599	116
C(24)	7 242	7 617	3 931	68
C(25)	7 650	7 351	3 956	78
C(26)	7 762	7 852	1 976	124
C(27)	7 841	8 168	5 496	151
C(30)	5 866	5 942	5 705	58
O(3)	5 558	−1 012	8 130	62
O(16)	6 040	8 440	1 286	59
O(20)	7 090	6 845	2 454	63
O(25)	7 752	6 170	4 327	119
O(30)	5 964	7 167	6 067	65

Table 2. Bond distances (Å) for compound (1). Mean e.s.d.s *ca.* 0.004 Å

C(1)–C(2)	1.519	C(13)–C(14)	1.563
C(1)–C(10)	1.527	C(13)–C(17)	1.539
C(2)–C(3)	1.490	C(14)–C(15)	1.536
C(3)–C(4)	1.534	C(14)–C(30)	1.553
C(3)–O(3)	1.441	C(15)–C(16)	1.498
C(4)–C(28)	1.542	C(16)–C(17)	1.523
C(4)–C(29)	1.547	C(16)–O(16)	1.221
C(4)–C(5)	1.551	C(17)–C(20)	1.545
C(5)–C(6)	1.530	C(20)–C(21)	1.527
C(5)–C(10)	1.563	C(20)–C(22)	1.528
C(6)–C(7)	1.553	C(20)–O(20)	1.457
C(7)–C(8)	1.511	C(22)–C(23)	1.508
C(8)–C(9)	1.556	C(23)–C(24)	1.425
C(8)–C(14)	1.585	C(24)–C(25)	1.557
C(8)–C(18)	1.563	C(24)–O(20)	1.419
C(9)–C(10)	1.583	C(25)–C(26)	1.481
C(9)–C(11)	1.527	C(25)–C(27)	1.540
C(10)–C(19)	1.532	C(25)–O(25)	1.390
C(11)–C(12)	1.532	C(30)–O(30)	1.431
C(12)–C(13)	1.507		

Table 3. Bond angles (°) for compound (1). Mean e.s.d.s *ca.* 0.1°

C(2)–C(1)–C(10)	113.0	C(12)–C(13)–C(17)	119.8
C(1)–C(2)–C(3)	111.6	C(14)–C(13)–C(17)	105.8
C(2)–C(3)–C(4)	114.7	C(8)–C(14)–C(13)	108.9
C(2)–C(3)–O(3)	111.9	C(8)–C(14)–C(15)	117.8
C(4)–C(3)–O(3)	109.5	C(8)–C(14)–C(30)	110.6
C(3)–C(4)–C(28)	110.3	C(13)–C(14)–C(15)	99.5
C(3)–C(4)–C(29)	107.7	C(13)–C(14)–C(30)	113.1
C(3)–C(4)–C(5)	107.2	C(15)–C(14)–C(30)	106.6
C(28)–C(4)–C(29)	107.7	C(14)–C(15)–C(16)	105.6
C(28)–C(4)–C(5)	115.2	C(15)–C(16)–C(17)	110.0
C(29)–C(4)–C(5)	108.5	C(15)–C(16)–O(16)	124.0
C(4)–C(5)–C(6)	113.7	C(17)–C(16)–O(16)	125.8
C(4)–C(5)–C(10)	117.2	C(13)–C(17)–C(16)	101.8
C(6)–C(5)–C(10)	110.8	C(13)–C(17)–C(20)	116.9
C(5)–C(6)–C(7)	110.0	C(16)–C(17)–C(20)	112.6
C(6)–C(7)–C(8)	113.5	C(17)–C(20)–C(21)	112.6
C(7)–C(8)–C(9)	109.2	C(17)–C(20)–C(22)	111.0
C(7)–C(8)–C(14)	111.4	C(17)–C(20)–O(20)	108.3
C(7)–C(8)–C(18)	107.8	C(21)–C(20)–C(22)	113.2
C(9)–C(8)–C(14)	107.3	C(21)–C(20)–O(20)	106.2
C(9)–C(8)–C(18)	112.4	C(22)–C(20)–O(20)	105.0
C(14)–C(8)–C(18)	108.7	C(20)–C(22)–C(23)	100.3
C(8)–C(9)–C(10)	115.9	C(22)–C(23)–C(24)	111.2
C(8)–C(9)–C(11)	112.9	C(23)–C(24)–C(25)	124.4
C(10)–C(9)–C(11)	113.1	C(23)–C(24)–O(20)	106.3
C(1)–C(10)–C(5)	106.9	C(25)–C(24)–O(20)	106.7
C(1)–C(10)–C(9)	108.8	C(24)–C(25)–C(26)	101.4
C(1)–C(10)–C(19)	108.6	C(24)–C(25)–C(27)	110.5
C(5)–C(10)–C(9)	106.6	C(24)–C(25)–O(25)	116.8
C(5)–C(10)–C(19)	112.8	C(26)–C(25)–C(27)	103.3
C(9)–C(10)–C(19)	112.9	C(26)–C(25)–O(25)	115.7
C(9)–C(11)–C(12)	113.8	C(27)–C(25)–O(25)	108.3
C(11)–C(12)–C(13)	109.3	C(14)–C(30)–O(30)	112.1
C(12)–C(13)–C(14)	111.7	C(20)–O(20)–C(24)	109.1

Table 4. Selected torsion angles (°) for compound (1). Mean e.s.d.s *ca.* 0.3°

C(1)–C(2)–C(3)–C(4)	56.4
C(2)–C(3)–C(4)–C(5)	−51.2
C(3)–C(4)–C(5)–C(10)	51.2
C(4)–C(5)–C(10)–C(1)	−53.2
C(10)–C(5)–C(6)–C(7)	−61.3
C(5)–C(6)–C(7)–C(8)	58.5
C(6)–C(7)–C(8)–C(9)	−51.7
C(7)–C(8)–C(9)–C(10)	51.4
C(8)–C(9)–C(10)–C(5)	−54.1
C(9)–C(10)–C(5)–C(6)	57.8
C(5)–C(10)–C(1)–C(2)	53.8
C(10)–C(1)–C(2)–C(3)	−57.7
C(8)–C(9)–C(11)–C(12)	53.8
C(9)–C(11)–C(12)–C(13)	−53.4
C(11)–C(12)–C(13)–C(14)	58.1
C(12)–C(13)–C(14)–C(8)	−62.6
C(13)–C(14)–C(8)–C(9)	58.3
C(14)–C(8)–C(9)–C(11)	−54.9
C(13)–C(14)–C(15)–C(16)	−35.2
C(14)–C(15)–C(16)–C(17)	17.4
C(15)–C(16)–C(17)–C(13)	8.7
C(16)–C(17)–C(13)–C(14)	−31.5
C(17)–C(13)–C(14)–C(15)	41.6
O(20)–C(20)–C(22)–C(23)	−26.6
C(20)–C(22)–C(23)–C(24)	17.5
C(22)–C(23)–C(24)–O(20)	−1.3
C(23)–C(24)–O(20)–C(20)	−17.0
C(24)–O(20)–C(20)–C(22)	28.2

established by *X*-ray analysis but no details of this study can be found in the literature.[18] Our findings are in complete agreement with those of Nagai *et al.* and the C-24 stereochemistry [16] of eichlerianic acid and shoreic acid must be reversed. Hence, we believe that compounds whose structures have been based on the stereochemistry of eichlerianic acid must also have their assigned stereochemistry at C-24 changed, *e.g.* a number of triterpenes isolated from *Cistus bourgeanus*.[19]

Experimental

M.p.s were determined with a Kofler hot-stage apparatus and are uncorrected. Optical rotations were measured for solutions in $CHCl_3$ except where shown otherwise. ^1H N.m.r. spectra were recorded with a Perkin-Elmer R-12B (60 MHz) or a R-32 (90 MHz) instrument for solutions in $CDCl_3$ (unless otherwise stated) with Me_4Si as internal reference. I.r. spectra were measured on a Perkin-Elmer 257 spectrophotometer, and u.v. spectra on a Perkin-Elmer 402 spectrophotometer. Mass spectra were recorded with Hewlett-Packard 5930A and VG Micromass ZAB-2F spectrometers. Thin-layer chromatography (t.l.c.) was performed on Merck silica gel 60 and column chromatography on Merck silica gel (0.063—0.2 mm). The spray reagent for t.l.c. was H_2SO_4–AcOH–H_2O (1 : 20 : 4).

Isolation of Trevoagenins.—Air-dried milled leaves and twigs of *Trevoa trinervis* Miers (3.5 kg) collected in Pirque, near Santiago, Chile, were extracted with ethanol in a Soxhlet apparatus. The cold extract was filtered and the filtrate was concentrated under reduced pressure, diluted with aqueous ethanol (2.5 l; 50%), and defatted with benzene in a liquid–liquid extractor. Concentrated hydrochloric acid was added to the solution until the acid strength was 2M, and the mixture was then refluxed for 4 h, poured into water, neutralized with $NaHCO_3$, and filtered. The precipitate was extracted with chloroform. Evaporation of the extract afforded a crude mixture of sapogenins (107 g) which, on chromatography with benzene followed by benzene–ethyl acetate mixtures as eluant, gave sitosterol (0.23 g), *trevoagenin A* (1) (3.5 g), and a mixture of *trevoagenins B* (13) and *C* (17) (3 g). This mixture was acetylated and the products were separated by preparative layer chromatography (p.l.c.) [benzene–ethyl acetate (87 : 13), four developments] to yield *trevoagenin B* (13) (1.62 g) and *trevoagenins C* (17) (0.7 g). Also, a small amount (0.2 g) of trevoagenin D [20] was isolated from the mother liquor from the crystallization of trevoagenin A (1).

Trevoagenin A (1).—This had m.p. 297—300 °C (EtOAc); $[\alpha]_D$ −49° (*c*, 0.23 in dioxan); *m/z* 490 (0.1%, M^+), 431.3171 (20%, $C_{27}H_{43}O_4$ = 431.3161, [b]), 389.3049 (2%, $C_{25}H_{41}O_3$ = 389.3057, [f]), 371.2948 (2.5%, $C_{25}H_{39}O_2$ = 371.2950, [f] − H_2O), 348.2651 (1.3%, $C_{22}H_{36}O_3$ = 348.2664, [e]), 207.1730 (2.4%, $C_{14}H_{23}O$ = 207.1749, [c]), 203.1775 (2.4%, $C_{15}H_{23}$ = 203.1800, [d]), 189.1606 (3%, $C_{14}H_{21}$ = 189.1643, [c] − H_2O), 143.1088 (100%, $C_8H_{15}O_2$ = 143.1072, [a]), 125.0931 (12%, $C_8H_{13}O$ = 125.0966, [a] − H_2O), and 107.0880 (11%, C_8H_{11} = 107.0861, [a] − $2H_2O$); two metastable ions at *m/z* 109.2 (143 ⟶ 125) and 91.6 (125 ⟶ 107) were also observed; $\nu_{max.}$ (KBr) 3 420 and 1 725 cm^{-1}; δ([$^2H_5$]pyridine) 0.92, 1.03, 1.13, 1.18, 1.33, 1.33, and 1.39 (total 21 H, s, 7 × Me), 3.42 (1 H, dd, $w_{\frac{1}{2}}$ 18 Hz, 3α-H), 3.88 (1 H, dd, $w_{\frac{1}{2}}$ 15 Hz, 24-H), and 4.35 (2 H, s, $w_{\frac{1}{2}}$ 2 Hz, 30-H_2); c.d. (*c*, 1.14 in dioxan) $[\theta]_{233}$ O, $[\theta]_{302}$ −12 500, $[\theta]_{312}$ −10 400, $[\theta]_{324}$ −4 300, and $[\theta]_{344}$ O (Found: C, 73.5; H, 10.3. $C_{30}H_{50}O_5$ requires C, 73.4; H, 10.3%).

Acetylation of compound (1) with acetic anhydride and pyridine at ambient temperature gave a *diacetate* (2) which was crystallized from methanol, m.p. 134—135 °C; $[\alpha]_D$ −31° (*c*, 0.19); $\nu_{max.}$ (KBr) 3 550 and 1 740 cm^{-1}; δ 0.86 (6 H, s, 4α- and 4β-Me), 0.93 (3 H, s, 10-Me), 1.12 (total 9 H, s, 8-Me and 25-Me_2), 1.18 (3 H, s, 20-Me), 1.98 (3 H, s, 30-OAc), 2.04 (3 H, s, 3-OAc), 3.67 (1 H, dd, $w_{\frac{1}{2}}$ 15 Hz, 24-H), 4.33 and 4.60 (total 2 H, AB system, *J* 12 Hz, together 30-H_2), and 4.48 (1 H, 3α-H) (Found: C, 70.8; H, 9.3. $C_{34}H_{54}O_7$ requires C, 71.1; H, 9.5%).

Trevoagenin A Triacetate (3).—A mixture of trevoagenin A (1) (0.11 g), fused sodium acetate (0.2 g), and acetic anhydride (5 ml) was refluxed for 5 h. After the addition of water, the solution was neutralized with aqueous $NaHCO_3$ and was extracted with chloroform. The residue was purified by column chromatography with benzene–ethyl acetate (97 : 3) as eluant to give the non-crystalline triacetate (3) (0.06 g), $[\alpha]_D$ −21° (*c*, 0.16); $\nu_{max.}$ ($CHCl_3$) 1 730 cm^{-1}; δ 0.87 (6 H, s, 4α- and 4β-Me), 0.93 (3 H, s, 10-Me), 1.13 (total 6 H, s, 8- and 20-Me), 1.44 (6 H, s, 25-Me_2), 1.96 (3 H, s, 25-OAc), 1.98 (3 H, s, 30-OAc), 2.04 (3 H, s, 3-OAc), 3.95 (1 H, dd, $w_{\frac{1}{2}}$ 15 Hz, 24-H), 4.33 and 4.60 (total 2 H, AB system, *J* 12 Hz, together 30-H_2), and 4.49 (1 H, 3α-H).

Trevoagenin A 3-Acetate (4).—To a saturated solution of sodium carbonate in methanol (130 ml) was added compound (2) (0.3 g) and the mixture was stirred at room temperature for 8 h. Water was then added and the mixture was extracted with ethyl acetate. The extract was washed with water, dried (Na_2SO_4), concentrated under reduced pressure, and submitted to column chromatography [benzene–ethyl acetate (3 : 2) as eluant] to give the *monoacetate* (4) (0.22 g) which was crystallized from benzene–ethyl acetate, m.p. 249—251 °C; $[\alpha]_D$ −25° (*c*, 0.16); $\nu_{max.}$ (KBr) 3 520, 3 420, 1 730, and 1 720 cm^{-1}; δ 0.86 (6 H, s, 4α- and 4β-Me), 0.90 (3 H, s, 10-Me), 1.10 (6 H, s, 25-Me_2), 1.14 (3 H, s, 8-Me), 1.18 (3 H, s, 20-Me), 2.04 (3 H, s, 3-OAc), 3.67 (1 H, dd, $w_{\frac{1}{2}}$ 15 Hz, 24-H), 3.97 and 4.06 (total 2 H, AB system, *J* 12 Hz, 30-H_2), and 4.49 (1 H, dd, $w_{\frac{1}{2}}$ 16 Hz, 3α-H) (Found: C, 72.3; H, 9.9. $C_{32}H_{52}O_6$ requires C, 72.1; H, 9.8%).

Trevoagenin A 16,30-Methyl Acetal (7).—To a solution of trevoagenin A (1) (1 g) in dry methanol (60 ml) was added a saturated solution of hydrogen chloride in methanol (0.5 ml) and the mixture was kept at room temperature for 2 d. The usual work-up and column chromatography [benzene–ethyl acetate (7 : 3) as eluant] gave the *acetal* (7) (0.92 g), m.p. 197—200 °C (acetone–n-hexane); $[\alpha]_D$ −33° (*c*, 0.19); $\nu_{max.}$ (KBr) 3 520 and 3 420 cm^{-1}; δ 0.78 (3 H, s, 4α-Me), 0.85 (3 H, s, 4β-Me), 0.98 (3 H, s, 10-Me), 1.10 (6 H, s, 25-Me_2), 1.14 (3 H, s, 8-Me), 1.19 (3 H, s, 20-Me), 3.38 (3 H, s, 16-OMe), 3.65 (1 H, m, $w_{\frac{1}{2}}$ 15 Hz, 24-H), and 3.97 (2 H, s, $w_{\frac{1}{2}}$ 4 Hz, 30-H_2) (Found: C, 73.7; H, 10.4. $C_{31}H_{52}O_5$ requires C, 73.8; H, 10.4%).

Acetylation of compound (7) with acetic anhydride and pyridine at room temperature gave a *monoacetate* (8) which was crystallized from n-hexane, m.p. 165—167 °C; $[\alpha]_D$ −11° (*c*, 0.2); *m/z* 546 (0.3%, M^+), 487 [0.3%, $(M - C_3H_7O)^+$], 403 (30%, [g]), 189 (10%, [c] − H_2O), 143 (100%, [a]), 125 (30%, [a] − H_2O), and 107 (12%, [a] − $2H_2O$); $\nu_{max.}$ ($CHCl_3$) 3 550 and 1 720 cm^{-1}; δ 0.86 (total 9 H, s, 4α-, 4β-, and 10-Me), 1.10 (6 H, s, 25-Me_2), 1.15 (3 H, s, 8-Me), 1.19 (3 H, s, 20-Me), 2.05 (3 H, s, 3-OAc), 3.38 (3 H, s, 16-OMe), 3.66 (1 H, dd, $w_{\frac{1}{2}}$ 15 Hz, 24-H), 3.98 (2 H, m, $w_{\frac{1}{2}}$ 4 Hz, 30-H_2), and 4.5 (1 H, dd, $w_{\frac{1}{2}}$ 17 Hz, 3α-H) (Found: C, 72.6; H, 10.0. $C_{33}H_{54}O_6$ requires C, 72.5; H, 9.95%).

(20R)-3β,30-*Diacetoxy*-16-*oxo*-24,25,26,27-*tetranordammarane*-23, 20-*carbolactone* (6).—To a stirred solution of compound (2) (0.05 g) in acetone (10 ml) was added dropwise an excess of Jones' reagent at room temperature. The excess of reagent was destroyed with methanol and the mixture was then poured into water and extracted with ethyl acetate. The extract was washed in turn with aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and evaporated to dryness under reduced pressure. The residue (0.03 g) was crystallized from methanol to give the *lactone* (6), m.p. 208—211 °C; $[\alpha]_D$ +28° (*c*, 0.18); $\nu_{max.}$ (KBr) 1 770, 1 740, and 1 730 cm^{-1}; δ 0.86 (6 H, s, 4α- and 4β-Me), 0.93 (3 H, s, 10-Me), 1.12 (3 H, s, 8-Me)

1.31 (3 H, s, 20-Me), 1.98 (3 H, s, 30-OAc), 2.04 (3 H, s, 3-OAc), 4.33 and 4.60 (total 2 H, AB system, *J* 12 Hz, $30-H_2$), and 4.47 (1 H, 3α-H) (Found: C, 70.05; H, 9.0. $C_{31}H_{48}O_7$ requires C, 69.9; H, 9.1%).

(20R,24R)-3β-*Acetoxy*-25-*hydroxy*-15α,30-*cyclo*-20,24-*epoxydammaran*-16-*one* (9).—To an ice-cold solution of trevoagenin A 3-acetate (4) (0.15 g) in pyridine (3 ml) was added toluene-*p*-sulphonyl chloride (0.35 g). The reaction mixture, after being stirred for 48 h at 0 °C, was poured into ice–water and extracted with diethyl ether. The extract was washed in turn with dilute hydrochloric acid, aqueous $NaHCO_3$, and water, dried (Na_2SO_4), and concentrated under reduced pressure; the residue, the impure tosylate (5) (0.14 g), was used without purification in the next reaction.

A solution of the crude compound (5) (0.14 g) in acetone (50 ml) containing anhydrous sodium acetate (0.9 g) was refluxed for 20 h. The mixture was then concentrated under reduced pressure to *ca.* half its original volume and poured into water and thoroughly extracted with ethyl acetate. The combined extracts were washed with water, dried (Na_2SO_4), concentrated under reduced pressure, and submitted to column chromatography [benzene–ethyl acetate (4 : 1) as eluant] to give the desired *product* (9) (0.075 g) which was crystallized from chloroform–methanol, m.p. 243—246 °C; $[\alpha]_D$ +62° (*c*, 0.18); *m/z* 514 (0.1%, M^+), 455 (54%), 437 (0.1%), 413 (9%), 395 (4%), 372 (4%), 189 (2%, [c] − H_2O), 143 (100%, [a]), 125 (11%, [a] − H_2O), 109.2 (m^*; 143 ⟶ 125), and 107 (9%, [a] − ($2H_2O$); $\nu_{max.}$ (KBr) 3 520, 3 080, 3 050, and 1 720 cm^{-1}; δ 0.87 (6 H, s, 4α- and 4β-Me), 0.90 (3 H, s, 10-Me), 1.11 (3 H, s, 20-Me), 1.13 (3 H, s, 8-Me), 1.18 (6 H, s, $25-Me_2$), 2.07 (3 H, s, 3-OAc), 3.64 (1 H, dd, $w_{\frac{1}{2}}$ 17 Hz, 24-H), and 4.53 (1 H, dd, $w_{\frac{1}{2}}$ 17 Hz, 3α-H) (Found: C, 74.9; H, 9.9. $C_{32}H_{50}O_5$ requires C, 74.7; H, 9.8%).

Saponification with potassium hydroxide (5%) in methanol gave the *diol* (10) which was crystallized from acetone–n-hexane, m.p. 267—269 °C; $[\alpha]_D$ +37° (*c*, 0.2); *m/z* 472 (0.2%, M^+), 413 (58%), 395 (2.2%), 371 (10%), 353 (0.5%), 330 (5%), 207 (1%, [c]), 203 (1%, [d]), 143 (100%, [a]), 125 (10%, [a] − H_2O), 109.2 (m^*; 143 ⟶ 125), and 107 (7%, [a] − $2H_2O$); $\nu_{max.}$ (KBr) 3 520, 3 050, 3 020, and 1 700 cm^{-1}; $\lambda_{max.}$ (EtOH) 200 nm (ε 5 600); δ 0.78 (3 H, s, 4α-Me), 0.87 (3 H, s, 4β-Me), 0.97 (3 H, s, 10-Me), 1.11 (3 H, s, 20-Me), 1.13 (3 H, s, 8-Me), 1.17 (6 H, s, $25-Me_2$), 3.2 (1 H, dd, $w_{\frac{1}{2}}$ 18 Hz, 3α-H), and 3.6 (1 H, dd, $w_{\frac{1}{2}}$ 13 Hz, 24-H) (Found: C, 75.9; H, 10.4. $C_{30}H_{48}O_4$ requires C, 76.2; H, 10.3%).

Sodium Borohydride Reduction of Compound (10).—A solution of the ketone (10) (0.05 g) in methanol containing sodium borohydride (0.045 g) was stirred for 3 h at room temperature. The usual work-up gave a mixture of alcohols (11) and (12) which was resolved by column chromatography with benzene–ethyl acetate (3 : 1) as eluant. The *alcohol* (11) (32 mg) had m.p. 215—218 °C; $[\alpha]_D$ +44° (*c*, 0.2); $\nu_{max.}$ (KBr) 3 400 and 3 070 cm^{-1}; δ 0.0 (1 H, m, 30-H), 0.78 (3 H, s, 4α-Me), 0.85 (3 H, s, 4β-Me), 0.98 (3 H, s, 10-Me), 1.20, 1.20, 1.11, and 1.08 (total 12 H, 4 × s, 8-, 20-, 25-, and 25-Me), 3.78 (1 H, dd, 24-H), and 4.2 (1 H, dd, $w_{\frac{1}{2}}$ 7 Hz, 16α-H) (Found: C, 75.7; H, 10.8. $C_{30}H_{50}O_4$ requires C, 75.9; H, 10.6) and the epimeric *alcohol* (12) (12 mg) had m.p. 209—211 °C; $[\alpha]_D$ +28° (*c*, 0.16); $\nu_{max.}$ (KBr) 3 530, 3 430, and 3 090 cm^{-1}; δ 0.6 (1 H, dd, 30-H), 0.78 (3 H, s, 4α-Me), 0.82 (3 H, s, 4β-Me), 0.97 (3 H, s, 10-Me), 1.36, 1.34, 1.26, and 1.25 (total 12 H, 4 × s, 8-, 20-, 25-, and 25-Me), 3.18 (1 H, dd, 3α-H), 3.77 (1 H, dd, 24-H), and 4.2 (1 H, dd, $w_{\frac{1}{2}}$ 14 Hz, 16β-H) (Found: C, 75.9; H, 10.8. $C_{30}H_{50}O_4$ requires C, 75.9; H, 10.6%).

Trevoagenin B (13).—This had m.p. 243—246 °C (acetone); $[\alpha]_D$ −31° (*c*, 0.2 in dioxan); *m/z* 490 (0.1%, M^+), 431 (18%, [b]), 389 (3%, [f]), 371 (3%, [f] − H_2O), 348 (2%, [e]), 207 (2%, [c]), 203 (2%, [d]), 189 (4%, [c] − H_2O), 143 (100%, [a]), 125 (15%, [a] − H_2O), 109.2 (m^*; 143 ⟶ 125), and 107 (9%, [a] − $2H_2O$); $\nu_{max.}$ (KBr) 3 420 and 1 730 cm^{-1} (Found: C, 73.2; H, 10.5. $C_{30}H_{50}O_5$ requires C, 73.4; H, 10.3%).

Acetylation of compound (13) with acetic anhydride and pyridine at room temperature gave a *diacetate* (14) which was crystallized from n-hexane, m.p. 155—157 °C; $[\alpha]_D$ −20° (*c*, 0.2); $\nu_{max.}$ (KBr) 3 480 and 1 720 cm^{-1}; δ 0.86 (6 H, s, 4β- and 4α-Me), 0.93 (3 H, s, 10-Me), 1.11 (total 6 H, 8- and 25-Me), 1.19 (3 H, s, 25-Me), 1.29 (3 H, s, 20-Me), 1.98 (3 H, s, 30-OAc), 2.04 (3 H, s, 3-OAc), 3.79 (1 H, dd, $w_{\frac{1}{2}}$ 16 Hz, 20-H), 4.33 and 4.56 (total 2 H, AB system, *J* 12 Hz, $30-H_2$), and 4.5 (1 H, m, 3α-H) (Found: C, 71.3; H, 9.8. $C_{34}H_{54}O_7$ requires C, 71.1; H, 9.5%).

(20S)-3β,30-*Diacetoxy*-16-*oxo*-24,25,26,27-*tetranor-dammarane*-23,20-*carbolactone* (16).—A solution of trevoagenin B diacetate (14) (50 mg) in acetone (10 ml) was oxidized with Jones' reagent as described in the preparation of compound (6). Work-up gave the desired *lactone* (16) (30 mg) which was crystallized from acetone, m.p. 248—253 °C; $[\alpha]_D$ −28° (*c*, 0.17); $\nu_{max.}$ (KBr) 1 770, 1 740, and 1 730 cm^{-1}; δ 0.86 (6 H, s, 4α- and 4β-Me), 1.11 (3 H, s, 8-Me), 1.49 (3 H, s, 20-Me), 1.97 (3 H, s, 30-OAc), 2.03 (3 H, s, 3-OAc), 4.38 and 4.58 (total 2 H, AB system, *J* 12 Hz, $30-H_2$), and 4.5 (1 H, m, 3α-H) (Found: C, 70.0; H, 8.8. $C_{31}H_{48}O_7$ requires C, 69.9; H, 9.1%).

Trevoagenin C (17).—This had m.p. 267—269 °C (acetone); $[\alpha]_D$ −36° (*c*, 0.2 in dioxan); $\nu_{max.}$ (KBr) 3 420 and 1 730 cm^{-1} (Found: C, 73.2; H, 10.6. $C_{30}H_{50}O_5$ requires C, 73.4; H, 10.3%).

Acetylation of compound (17) with acetic anhydride and pyridine at room temperature gave a *diacetate* (18) which was crystallized from n-hexane, m.p. 171—173 °C; $[\alpha]_D$ −40° (*c*, 0.21); $\nu_{max.}$ (KBr) 3 520 and 1 730 cm^{-1}; δ 0.86 (6 H, s, 4α- and 4β-Me), 0.96 (3 H, s, 10-Me), 1.09 (3 H, s, 30-OAc), 2.05 (3 H, s, 3-OAc), 4.32 and 4.56 (total 2 H, AB system, *J* 12 Hz, $30-H_2$), and 4.5 (1 H, m, 3α-H) (Found: C, 71.3; H, 9.7. $C_{34}H_{54}O_7$ requires C, 71.1; H, 9.5%).

Oxidation of Trevoagenin C 3,30-*Diacetate* (18).—Jones' reagent was added to a solution of trevoagenin C 3,30-diacetate (18) in acetone as described for the preparation of compound (6). Work-up afforded the lactone (16), m.p. 248—253 °C (acetone); $[\alpha]_D$ −26° (*c*, 0.17), which was identical with a sample obtained from the oxidation of trevoagenin B 3,20-diacetate (14) (see above).

Trevoagenin B (13) *from Trevoagenin A* (1).—To a solution of trevoagenin A (1) (0.25 g) in ethanol (5.7 ml) was added aqueous hydrochloric acid [concentrated HCl (2 ml) in water (1.5 ml)] and the mixture was refluxed for 2 h. After the addition of water, the solution was neutralized with aqueous $NaHCO_3$ and was extracted with ethyl acetate. The extract was washed with water, dried (Na_2SO_4), and evaporated to dryness under reduced pressure. Column chromatography of the residue [benzene–ethyl acetate (7 : 3) as eluant] afforded unchanged trevoagenin A (1) (0.04 g) and trevoagenin B (13) (0.045 g), both identical with the respective natural product. Trevoagenin B (13) was also transformed into trevoagenin A (1) by identical acid treatment.

Trevoagenin B 3-*Acetate* (15).—A solution of trevoagenin B 3,30-diacetate (14) (100 mg) in methanol (50 ml) was treated with sodium carbonate as previously described for the preparation of compound (4). Work-up afforded the *monoacetate*

(15) (60 mg) which was crystallized from acetone, m.p. 214—216 °C; $[\alpha]_D$ −10° (*c*, 0.22); $\nu_{max.}$ (KBr) 3 430 and 1 720 cm^{-1}; δ 0.86 (total 9 H, s, 4α-, 4β-, and 10-Me), 1.08 (3 H, s, 25-Me), 1.12 (3 H, s, 8-Me), 1.21 (3 H, s, 25-Me), 1.24 (3 H, s, 20-Me), 2.04 (3 H, s, 3-OAc), 3.84 (1 H, m, 24-H), 4.0 (2 H, dd, $w_{\frac{1}{2}}$ 4 Hz, 30-H_2), and 4.48 (1 H, m, $w_{\frac{1}{2}}$ 18 Hz, 3α-H) (Found: C, 72.1; H, 10.1. $C_{32}H_{52}O_6$ requires C, 72.1; H, 9.8%).

Ocotillol (21) *from Compound* (15).—To a mixture of pyridine (0.3 g), dry methylene dichloride (10 ml), and chromium trioxide (0.25 g) was added a solution of compound (15) (0.1 g) in methylene dichloride (5 ml). The resulting mixture was stirred at room temperature for 1 h and was then thoroughly extracted with diethyl ether. The combined extracts were washed in turn with aqueous sodium hydroxide (10%), aqueous hydrochloric acid (10%), and saturated aqueous NaCl, dried (Na_2SO_4), and evaporated to dryness under reduced pressure. The residue, the crude aldehyde (19) (80 mg), was reduced, without purification, by the Huang-Minlon method as follows: a mixture of the crude product (19), hydrazine hydrate (98%; 2 ml), and diethylene glycol (8 ml) was refluxed for 1.5 h, potassium hydroxide (0.5 g) was then added, and the mixture was refluxed at 190 °C for a further 3 h. The usual work-up gave, after column chromatography [benzene–ethyl acetate (8 : 2) as eluant], ocotillol (21) (45 mg) which was crystallized from n-hexane–ethyl acetate, m.p. 196—198 °C; $[\alpha]_D$ +28° (*c* 0.18) (lit.,[8] m.p. 198—200 °C; $[\alpha]_D$ +28°); δ 0.78 (3 H, s, 4α-Me), 0.85 (3 H, s, 4β-Me), 0.87 (3 H, s, 14-Me), 0.97 (total 6 H, s, 8- and 10-Me), 1.13 (6 H, s, 25-Me_2), 3.18 (1 H, m, $w_{\frac{1}{2}}$ 18 Hz, 3α-H), and 3.73 (1 H, m, $w_{\frac{1}{2}}$ 16 Hz, 24-H) (Found: C, 77.9; H, 11.6. Calc. for $C_{30}H_{52}O_3$: C, 78.2; H, 11.4%). This compound was found to be identical (i.r. and n.m.r. spectra, m.p. and mixed m.p., t.l.c.) with an authentic reference sample.

3β,25-*Dihydroxy*-(20R,24R)-*epoxydammaran*-16-*one* (23).—Lithium (30 mg) was added to liquid ammonia (15 ml) at −33 °C and the mixture was stirred until the metal had dissolved. A solution of the cyclopropyl ketone (10) (50 mg) in dioxan (3 ml) was then added to the lithium amide solution *via* a syringe. After being stirred for 40 min at reflux temperature, the mixture was quenched with solid NH_4Cl (1 g), and the ammonia was evaporated off at room temperature. The resulting residue was partitioned between ethyl acetate and saturated aqueous NaCl. The organic phase was dried (Na_2SO_4), concentrated under reduced pressure, and chromatographed [benzene–ethyl acetate (7 : 3) as eluant] to give compounds (23) (23 mg) and (24) (15 mg). The *title ketone* (23) was crystallized from n-hexane–diethyl ether, m.p. 238—240 °C; $[\alpha]_D$ −45° (*c*, 0.2); *m/z* 474 (0.1%, M^+), 459 (3%), 456 (2%), 415 (60%), 397 (20%), 373 (10%), 355 (10%), 332 (5%), 143 (100%, [a]), 125 (25%, [a] − H_2O), and 107 (12%, [a] − $2H_2O$); $\nu_{max.}$ (KBr) 3 520 and 1 725 cm^{-1}; δ 0.78 (3 H, s, 4α-Me), 0.88 (3 H, s, 4β-Me), 0.97 and 0.96 (together 6 H, s, 8- and 10-Me), 1.08, 1.10, 1.13, and 1.17 (total 12 H, 4 × s, 14-, 20-, 25-, and 25-Me), 3.2 (1 H, 3α-H), and 3.65 (1 H, 24-H) (Found: C, 75.8; H, 10.7. $C_{30}H_{50}O_4$ requires C, 75.9; H, 10.6%).

The triol (24) * was crystallized from chloroform–n-hexane, m.p. 216—218 °C; $[\alpha]_D$ +31° (*c*, 0.17); $\nu_{max.}$ (KBr) 3 400 cm^{-1}; δ 0.78 (3 H, s, 4α-Me), 0.82 (3 H, s, 4β-Me), 0.97 (3 H, s, 10-Me), and 0.92, 1.11, 1.11, 1.18, and 1.20 (total 15 H, 5 × s, 8-, 14-, 20-, 25-, and 25-Me) (Found: C, 75.8; H, 10.7. $C_{30}H_{52}O_4$ requires C, 75.6; H, 11.0%).

(20R,24R)-*Epoxydammaran*-3β,25-*diol* (25).—The ketone (23) (100 mg) was reduced by the Huang–Minlon method, as previously described for the preparation of compound (21), to give the *diol* (25) (40 mg) which was crystallized from n-hexane, m.p. 155—158 °C; $[\alpha]_D$ +14° (*c*, 0.21); $\nu_{max.}$ (KBr) 3 560 and 3 360 cm^{-1}; δ 0.78 (3 H, s, 4α-Me), 0.86 (total 6 H, s, 4β- and 14-Me), 0.97 (total 6 H, s, 8- and 10-Me), 1.11, 1.13, and 1.19 (total 9 H, 3 × s, 20-, 25-, and 25-Me), 3.2 (1 H, m, $w_{\frac{1}{2}}$ 15 Hz, 3α-H), and 3.69 (1 H, m, $w_{\frac{1}{2}}$ 17 Hz, 24-H) (Found: C, 78.4; H, 11.6. $C_{30}H_{52}O_3$ requires C, 78.2; H, 11.4%).

(20R, 24R)-*Ocotillone* (26).—To a solution of the diol (25) (28 mg) in dry methylene dichloride (5 ml) was added an excess of chromium trioxide–pyridine complex. The usual work-up gave the ketone (26) (15 mg) which was crystallized from acetonitrile, m.p. 203—205 °C; $[\alpha]_D$ +56° (*c*, 0.18) (lit.,[11b] m.p. 204—206 °C; $[\alpha]_D$ +54°); $\nu_{max.}$ (KBr) 3 575, 3 545, and 1 702 cm^{-1}; δ 0.88 (3 H, s, 14-Me), 0.94 (3 H, s, 4α-Me), 1.00 (3 H, s, 8-Me), 1.03 (3 H, s, 4β-Me), 1,08 (3 H, s, 10-Me), and 1.10, 1.14, and 1.19 (total 9 H, 3 × s, 20-, 25-, and 25-Me). The product was identical (i.r. and n.m.r. spectra, m.p. and mixed m.p., t.l.c.) with an authentic reference sample.[11b]

Crystallographic Data for Trevoagenin A (1).—The cell parameters, determined on a Philips PW1100 four-circle automatic diffractometer, were: a = 37.467, b = 11.124, c = 6.604 Å; orthorhombic, space group $P2_12_12_1$. The data were collected with Cu-K_α radiation (λ = 1.5418 Å) monochromatized by graphite. 2 433 Intensities were collected up to 2θ = 120°, 2 210 of which were found to have $I > 2\sigma(I)$. Lorentz and polarization factors were applied, but no absorption corrections were made. The structure was solved using the multi-solution method.[21] On the *E*-map corresponding to the highest figures of merit were observed 20 peaks which were used in a recycling Fourier procedure to develop the complete set of atomic co-ordinates. The refinements were carried out with isotropic, then anisotropic, thermal parameters to a final $R = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|} = 6.7\%$. Hydrogen atoms were located by difference Fourier syntheses and were introduced with an isotropic thermal factor equal to that of the carbon to which they were bonded, but their co-ordinates were not refined. Lists of structure factors are given in Supplementary Publication No. 23531 (11 pp.).†

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