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A NEW CLASS OF TRICYCLIC DITERPENES FROM EREMOPHILA GEORGII DIELS (MYOPORACEAE)[+]

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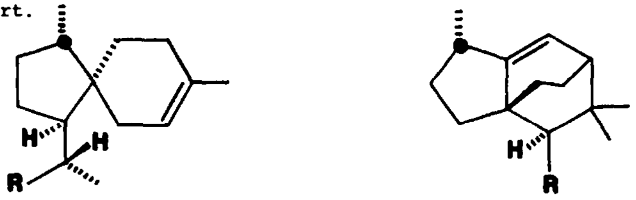
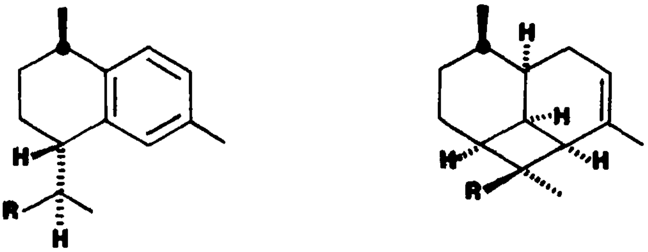
Abstract - A diterpene hydroxy acid, representing a new class of tricyclic diterpenes, has been isolated from Eremophila georgii Diels (Myoporaceae). Chemical and X-ray crystallographic evidence shows it to be an isoprenologue of 2-epi-(-)-α-cedrene.

Species of the Eremophila genus elaborate a range of unusual diterpenes including cembranes with cis-double bonds,[1] eremolactone,[2] decipianes,[3] viscidanes[4] and serrulatanes.[5,6] A notable feature of the bicyclic and tricyclic diterpenes from Eremophila is that they contain a C5-extended sesquiterpene skeleton, the terminal C5 unit not being involved in cyclization (see Scheme). Thus the viscidane and serrulatane skeletons are isoprenologues of the acorane and calamenene sesquiterpenes, whereas the eremane and decipianes are isoprenologues of as yet unknown classes of sesquiterpenes. In continuation of our work on the phytochemistry of Eremophila we have examined the resin of a form of E. georgii and have isolated a new tricyclic diterpene acid which contains a C5-extended cedrene skeleton. The evidence for the structure and absolute configuration of this compound is the subject of this report.



VISCIDANE EREMANE



SERRULATANE DECIPIANE

SCHEME. Classes of diterpenes (R = $(CH_2)_3CH(CH_3)_2$) found in Eremophila

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[+] The Chemistry of Eremophila spp XXIV. Part XXIII. Phytochemistry, 1985 (submitted).

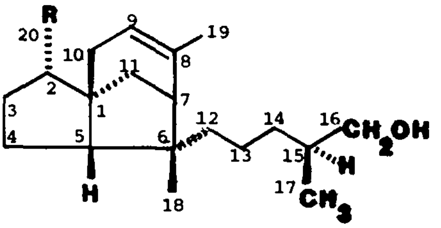
Extraction of a sample of *E. georgii* and isolation of the acidic components yielded a complex mixture in which one compound predominated. Normal chromatographic procedures provided fractions enriched with this compound (80%) which from ^{1}H-NMR analysis appeared to contain a trisubstituted double bond whereas the contaminant showed the presence of a disubstituted double bond. Selective hydrogenation (Pd/C) of the impurity followed by reverse phase HPLC afforded a pure sample of a crystalline diterpene acid (1), $C_{20}H_{32}O_3$. The ^{13}C-NMR spectrum of (1) included signals for three sp^2-hybridized carbons, δ 179.9 (s), 140.7 (s) and 120.1 (d) attributable to a carboxylic acid,and a trisubstituted double bond and at δ 68.3 (t) for a hydroxymethyl carbon so the compound must be a tricyclic hydroxy acid. Other signals included two singlets, four doublets, seven triplets and three quartets. The ^{1}H-NMR spectrum showed signals for a secondary methyl group (δ 0.91, d, J 6.7 Hz), and a tertiary methyl group (δ 0.97, s). A doublet (J 1.2 Hz) at δ 1.69 was assigned to an olefinic methyl group which was shown to be coupled to a vinylic proton at δ 5.23. This in turn showed coupling to two other mutually coupled protons resonating at δ 2.67 (dt, J_d 16.2 Hz, $J_t \sim 1$ Hz) and δ 1.80 (partly obscured). A small long-range coupling ($\sim$ 1 Hz) was observed between the proton at δ 2.67 and the B part of an ABX spin system (δ_A 1.22, $J_{A,B}$ 10.6 Hz; δ_B 1.70, $J_{A,B}$ 10.6 Hz; J_{BX} 3.3 Hz; δ_X 1.99, J_{AX} 3.3 Hz), the chemical shift of the X proton indicating it to be allylic. This information suggested the presence of a 1-methyl-4,4,6-trisubstituted cyclohexene moiety, a feature which is not present in the two other tricyclic diterpene skeletons, eremanes and decipianes (Scheme) previously isolated from *Eremophila* species. Conversion of (1) to its parent hydrocarbon (3), was achieved by reduction to the diol (2) and treatment of the corresponding ditosylate derivative with lithium aluminium hydride. On the assumption that (1), like other bicyclic and tricyclic diterpenes from *Eremophila* species, contained a 6-carbon atom side chain and from biogenetic considerations, the ^{13}C-NMR spectrum of the hydrocarbon (3) was compared with that[7] of α-cedrene (4). A good correlation was observed with 12 of the 15 carbon chemical shifts of cedrene (Table 1). Two notable exceptions involved C-6 and C-7, δ 48 (s) and 55 (d) respectively, which in (3) appeared at δ 51.5 (s) and δ 48.2 (d) supporting the presence of an alkyl chain at C-6 in (3). Thus the structure of (1) appeared to contain a skeleton which could be considered an isoprenologue of a cedrene. Evidence for the structure and the relative stereochemistry of (1) was obtained by a combination of X-ray diffraction analysis and ^{13}C-NMR spectroscopy. Hydrogenation of the diol (2) over platinum oxide gave the dihydrodiol (5), as a single isomer, which was found suitable for X-ray analysis. The results described below show that the structure and stereochemistry of the dihydrodiol are shown in (5). Evidence for the relative location of the carboxylic acid and primary alcohol groups in (1) comes from a consideration of the $^{-3}$C-NMR spectra of (1), (2) and hydrocarbon (3). In the spectrum of (1) the presence of a 2-methyl-3-hydroxypropan-1-yl group is indicated from the chemical shift of a doublet at δ 35.8, a quartet at δ 16.7 and a triplet at δ 34.4 compared with signals at 28.1 (d), 27.7 (q), 40.1 (t) for the same carbons in the hydrocarbon (3). These shifts reflect β-deshielding and γ-shielding effects predicted for a hydroxyl group. The chemical shifts assigned to the carbons on the side chain in (1) correspond closely with a set observed in the spectrum of the diol (2) indicating no change in functionality on the side chain. Indeed the only major differences in the spectra of (1) and (2) (Table 1) involve a doublet (δ 53.9 *v* 49.8), a triplet (δ 29.9 *v* 30.9) and a singlet (δ 54.6 *v* 53.3) consistent with the change from a carboxylic acid to a primary alcohol group at position 2.

Given the structure and relative stereochemistry of the hydroxy acid (1) determination of its absolute configuration was simplified by reference to the known chemistry of α-cedrene. Hydroboration of α-cedrene (4) produces isocedranol (6) in which the carbinol carbon has been shown[8] to have the *S*-configuration by application of Horeau's method. A similar sequence on hydrocarbon (3) yielded the alcohol (7) which was shown to have the 9*S*-configuration. Thus the absolute configuration of the hydroxy acid from *E. georgii* is as shown in structure (1).

It is worthwhile noting that the proton chemical shift of the secondary methyl group at C-2 is sensitive to changes in orientation. Thus the ^{1}H-NMR spectrum of the hydrocarbon (3) shows the

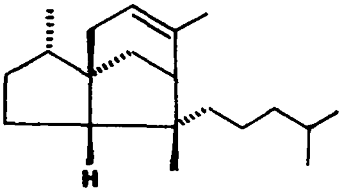
C-2 methyl protons resonating at δ 0.95 compared with δ 0.83 in the spectrum of α-cedrene (4).

The diterpenes from *E. georgii* are isoprenologues of the 2-*epi*-cedrenes which have been found in the terpenes of lac resin.[9] Their presence in *Eremophila* resin is interesting from a biogenetic point of view. The bicyclic and tricyclic diterpenes from *Eremophila* form two series with respect to the configuration of the carbon carrying the secondary methyl group (labelled in the Scheme). At this carbon the *S*-configuration holds for the viscidanes and eremanes, whereas the serrulatanes and decipianes have the *R*-configuration. The 2-*epi*-cedrene isoprenologue (1) belongs to the first group in this respect. Furthermore, the *trans*-1,4-disubstitution observed for the viscidanes when compared to the *cis*-1,4-disubstitution for (1) suggests that the two skeletons do not arise from the same bicyclic intermediate and that the stereochemical differentiation may have been made before formation of the second ring from a C5 extended bisabolonium cation, a putative intermediate in the biosynthesis of the bicyclic and tricyclic diterpenes of *Eremophila*. *E. georgii* Diels is part of a wide ranging complex and several other varieties are under investigation. A different variety studied previously has been shown to contain a cembrene diterpene[10] and sesquiterpenes.[11]



1 R = CO_2H

2 R = CH_2OH



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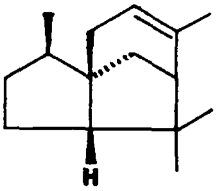

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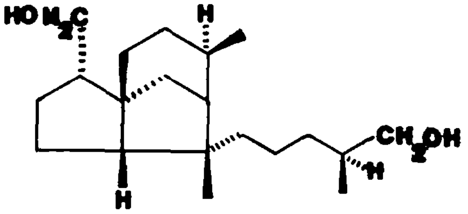

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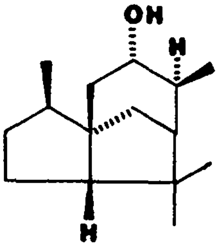

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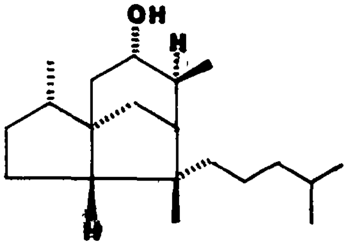

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Table 1. ^{13}C-NMR spectra of compounds (1-7). Chemical shifts (δ) in ppm relative to TMS[a]

Carbon	1	2	3	4[b]	5	7	6[b]
1	54.6	53.3	54.6	53.8	54.6	56.3	55.1
2	53.9	49.8	41.6	41.6	50.8	42.2[c]	41.9[c]
3	29.9	30.9	35.9	36.2	30.7[c]	38.7[d]	36.8
4	23.3	23.4	23.3	24.9	23.7	23.8	25.8
5	60.9	61.5	60.6	59.0	59.2	58.9	58.5
6	51.3	51.1	51.5	48.0	47.4	47.9	44.0
7	48.5	48.5	48.2	55.0	48.4	47.9	55.3
8	140.6	140.7	141.0	140.1	38.5	46.5[c]	46.4[c]
9	120.1	120.1	120.4	119.0	38.8[d]	76.6	73.2
10	42.3	42.8	41.7	38.9	40.0[d]	47.4	47.0
11	35.8	35.9	35.1	40.7	38.9[d]	39.4[d]	44.0
12	34.2	33.9	33.9	25.7	30.3[c]	34.4	28.9
13	22.5	22.5	22.9		22.9	23.1	
14	34.9	34.4	40.4		34.5	40.3	
15	35.8	35.9	28.1		35.9	28.1	
16	68.3	68.4	22.8		68.5	22.7	
17	16.7	16.7	22.8		16.7	22.7	
18	24.2[c]	24.2[c]	24.4[c]	27.7[c]	24.1	25.1	28.0
19	24.6[c]	24.6[c]	24.6[c]	24.8[c]	21.6	17.8	17.9
20	179.9	64.4	13.8	15.5	64.7	14.2	15.5

a. ($CDCl_3$; 20.1 MHz) Multiplicities of signals were determined by SFORD and GASPE techniques and are consistent with assignments.

b. For ease of comparison the numbering system for the diterpenes has been used for the cedrane derivatives.

c-d Values in any one column may be interchanged.

CRYSTALLOGRAPHY

Crystal data. $C_{20}H_{36}O_2$, M = 308.5, Orthorhombic, space group $I222$ (D_2^8, No. 23), a = 28.45 (1), b = 13.629(4), c = 10.127(3) Å, U = 3926(2) Å^3. D_m = 1.04(1), D_c (Z = 8) = 1.04 g cm^{-3}. $F(000)$ = 1376. Monochromatic Mo $K\alpha$ radiation, λ = 0.71069 Å, μ = 0.70 cm^{-1}, specimen: 0.25 x 0.40 x 0.38 mm. T = 295 K.

Structure determination. - A unique data set was measured to $2\theta_{max}$ = 50° using a Syntex $P\bar{1}$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode. 1968 independent reflections were measured, 1070 with $I > 3\sigma(I)$ being considered 'observed' and used in the full matrix least squares refinement without absorption correction after solution of the structure by direct methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x,y,z)_H$ were included at idealized values. Residuals on $|F|$ at convergence were R = 0.056, R' = 0.052 (statistical weights). Neutral complex scattering factors were used;[13] computation used the XTAL 83 program system implemented by S.R. Hall on a Perkin-Elmer 3240 computer.[14] Results are presented in the Figure and Tables; the Figure shows the non-hydrogen atom numbering. Material deposited comprises structure factor amplitudes, thermal and hydrogen parameters.*

Molecular geometry is substantially as expected. Hydrogen-bonding is evidenced by the intermolecular contacts O(16)...O(20) $(x, y-1, z)$, 2.661(6), O(16)...O(16) $(\bar{x}, y, 1-z)$, 2.590(7) and O(20)...O(20) $(\bar{x}, \bar{y}, z)$, 2.696(6) Å.

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*Copies available on application to the Editorial Office.

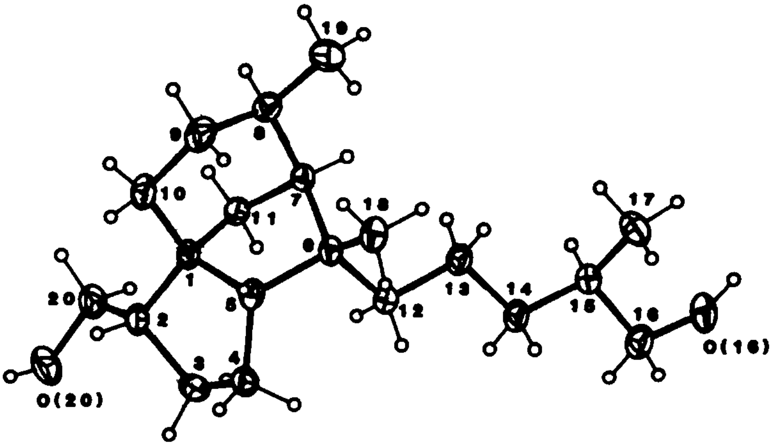

FIGURE 1. Projection of the single molecule of (5). 20% probability thermal ellipsoids are shown for the non-hydrogen atoms together with skeletal numbering. Hydrogen atoms have an arbitrary radius of 0.1Å

Table 2. Non-hydrogen atom coordinates

Atom	x	y	z	Atom	x	y	z
C(1)	0.1389(2)	0.1341(4)	0.7876(7)	C(12)	0.1072(2)	0.3807(4)	0.8111(7)
C(2)	0.0964(2)	0.0670(4)	0.8057(7)	C(13)	0.1159(2)	0.4744(4)	0.7338(7)
C(3)	0.0590(2)	0.1355(5)	0.8628(7)	C(14)	0.0746(2)	0.5447(4)	0.7406(8)
C(4)	0.0863(2)	0.1996(5)	0.9585(6)	C(15)	0.0787(2)	0.6363(4)	0.6539(6)
C(5)	0.1357(2)	0.2123(4)	0.8978(6)	C(16)	0.0350(2)	0.6985(5)	0.6700(8)
C(6)	0.1501(2)	0.3130(4)	0.8335(7)	O(16)	0.0339(2)	0.7801(3)	0.5853(5)
C(7)	0.1709(2)	0.2805(4)	0.6988(7)	C(17)	0.1224(2)	0.6957(5)	0.6853(8)
C(8)	0.2215(2)	0.2383(5)	0.6925(8)	C(18)	0.1838(2)	0.3680(5)	0.9258(7)
C(9)	0.2277(2)	0.1537(5)	0.7909(9)	C(19)	0.2611(2)	0.3147(6)	0.7077(9)
C(10)	0.1863(2)	0.0800(4)	0.7890(8)	C(20)	0.0808(3)	0.0115(5)	0.6847(8)
C(11)	0.1381(2)	0.1967(4)	0.6616(6)	O(20)	0.0410(2)	-0.0498(3)	0.7126(6)

Table 3. Non-hydrogen interatomic distances (Å)

Atoms	Distance (Å)	Atoms	Distance (Å)
C(1)-C(2)	1.527(8)	C(7)-C(8)	1.552(8)
C(1)-C(5)	1.546(9)	C(7)-C(11)	1.522(8)
C(1)-C(10)	1.538(8)	C(8)-C(9)	1.534(11)
C(1)-C(11)	1.535(9)	C(8)-C(19)	1.543(10)
C(2)-C(20)	1.508(10)	C(9)-C(10)	1.546(9)
C(2)-C(3)	1.530(9)	C(12)-C(13)	1.518(8)
C(3)-C(4)	1.520(9)	C(13)-C(14)	1.518(8)
C(4)-C(5)	1.544(9)	C(14)-C(15)	1.530(9)
C(5)-C(6)	1.572(8)	C(15)-C(16)	1.514(9)
C(6)-C(7)	1.551(9)	C(15)-C(17)	1.517(9)
C(6)-C(12)	1.546(8)	C(16)-O(16)	1.404(8)
C(6)-C(18)	1.536(9)	C(20)-O(20)	1.435(8)

Table 4. Interatomic non-hydrogen angles (degrees)

Atoms	Angle (degrees)	Atoms	Angle (degrees)
C(2)-C(1)-C(5)	106.3(5)	C(7)-C(6)-C(18)	115.8(5)
C(2)-C(1)-C(10)	114.0(5)	C(12)-C(6)-C(18)	106.9(5)
C(2)-C(1)-C(11)	114.9(5)	C(6)-C(7)-C(8)	119.8(5)
C(5)-C(1)-C(10)	112.0(5)	C(6)-C(7)-C(11)	101.4(5)
C(5)-C(1)-C(11)	102.5(4)	C(8)-C(7)-C(11)	106.2(5)
C(10)-C(1)-C(11)	106.7(5)	C(7)-C(8)-C(9)	111.0(5)
C(1)-C(2)-C(3)	103.4(5)	C(7)-C(8)-C(19)	115.0(5)
C(1)-C(2)-C(20)	115.9(6)	C(9)-C(8)-C(19)	111.1(6)
C(3)-C(2)-C(20)	114.1(6)	C(8)-C(9)-C(10)	113.1(6)
C(2)-C(3)-C(4)	103.6(5)	C(1)-C(10)-C(9)	110.9(5)
C(3)-C(4)-C(5)	106.1(5)	C(1)-C(11)-C(7)	101.7(5)
C(1)-C(5)-C(4)	105.3(5)	C(6)-C(12)-C(13)	116.7(5)
C(1)-C(5)-C(6)	106.7(5)	C(12)-C(13)-C(14)	112.4(5)
C(4)-C(5)-C(6)	119.9(5)	C(13)-C(14)-C(15)	115.4(5)
C(5)-C(6)-C(7)	102.4(4)	C(14)-C(15)-C(16)	109.4(5)
C(5)-C(6)-C(12)	112.2(5)	C(14)-C(15)-C(17)	112.3(5)
C(5)-C(6)-C(18)	109.7(5)	C(16)-C(15)-C(17)	110.5(5)
C(7)-C(6)-C(12)	110.0(5)	C(15)-C(16)-O(16)	113.3(3)
		C(2)-C(20)-O(20)	111.4(6)

Table 5. Ring dihedral angles (degrees)

Atoms are denoted by number only.

Atoms	Angle (degrees)	Atoms	Angle (degrees)
5-1-2-3	148.8	4-5-6-7	-48.7
10-1-2-3	24.9	5-6-7-8	-101.8
11-1-2-3	-98.6	5-6-7-11	141.9
1-2-3-4	-140.3	6-7-8-9	127.3
2-3-4-5	146.7	11-7-8-9	-118.9
3-4-5-1	-166.1	7-8-9-10	134.8
3-4-5-6	73.8	8-9-10-1	-134.9
2-1-5-4	-169.2	9-10-1-2	-8.3
2-1-5-6	-40.7	9-10-1-5	-129.1
10-1-5-4	-44.1	9-10-1-11	119.5
10-1-5-6	84.4	6-7-11-1	-129.2
11-1-5-4	69.9	8-7-11-1	104.9
11-1-5-6	-161.6	7-11-1-2	22.7
1-5-6-7	-168.0	7-11-1-5	137.5
		7-11-1-10	-104.7

EXPERIMENTAL

General experimental details have been described.[12]

Isolation of metabolites from E. georgii. Leaves and outer branches (519.2 g) of a sample of the plant, collected at 22km east of Meekatharra in Western Australia, were extracted with acetone and the extract (64.9 g) was partitioned into $NaHCO_3$ soluble (22.4 g), 10% aq. NaOH soluble (29.5 g) and neutral (2.0 g) fractions. The NaOH soluble fraction was fractionated by rapid silicic acid filtration (RSF) using gradient elution (light petroleum to ethyl acetate) to give two major fractions. The more polar fraction was partially decolourised with charcoal and the light green oil obtained was subjected to RSF as before to give a fraction (4.94 g) of a mixture containing the hydroxy acid (1) and the corresponding exocyclic double bond isomer (4:1) which could not be resolved by normal chromatographic procedures. An analytical sample of (1) was obtained as follows. A portion of this mixture (280 mg) in EtOH (5 ml) was stirred over 10% Pd-C (20 mg) under an atmosphere of H_2 for 2 hr. The product recovered was subjected to semi-preparative HPLC (C_{18} column, 30% H_2O-MeOH) to give the hydroxy acid (1) (108 mg) which crystallized from ether-pentane as a white microcrystalline material, m.p. 90-91°, $[\alpha]_D$ -83.8° (*c*, 0.3; $CHCl_3$) (Found: C, 75.04; H, 10.28. $C_{20}H_{32}O_3$ requires: C, 74.94; H, 10.07%). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 0.91 (d, J 6.7 Hz, $(H17)_3$); 0.97 (s, $(H18)_3$); 1.22 (d, J 10.6 Hz, $H11_b$); 1.69 (d, J 1.2 Hz, $(H19)_3$); 1.70 (dd, $J_{11a,11b}$ 10.6 Hz, $J_{11a,7}$ 3.3 Hz, $H11_a$); 1.76-1.95 (m, $H3_b$, $H10_b$, $H10_a$); 1.99 (d, J 3.3 Hz, H7); 2.37 (X part of ABX, $J_{2,3a}$ + $J_{2,3b}$ 17.4 Hz, H2); 2.67 (ddq, $J_{10a,10b}$ 16.2 Hz, $J_{10a,9}$ and $J_{10a,19}$ $\sim$ 1 Hz each, $H10_a$); 3.38-3.54 (AB part of ABX, $(H16)_2$); 5.23 (br s, H9). ^{13}C-NMR: (see Table 1). MS: m/z 320 (M^+, 16%), 302 (60), 274 (10), 233 (11), 219 (11), 202 (17), 192 (26), 191 (100), 174 (41), 173 (40), 150 (32), 145 (62), 131 (50), 105 (81).

Conversion of (1) to the hydrocarbon (3). A portion (200 mg) of the mixture, containing (1) and its double bond isomer, in ether (10 ml) was treated with $LiAlH_4$ (200 mg) and heated under reflux for 3 hr. The product recovered was hydrogenated with 10% Pd/C in EtOH (3 ml) for 2 hr and the mixture obtained was chromatographed on 10% $AgNO_3$-alumina (neutral-act III). Elution with 40% EtOAc-CH_2Cl_2 gave the *diol* (2) as an oil, b.p. 170-175° (bath)/0.15 mm, $[\alpha]_D$ -62.5° (c, 1.4; $CHCl_3$) (Found: C, 78.59; H, 11.00. $C_{20}H_{34}O_2$ requires C, 78.36; H, 11.19%). ^1H-NMR (80 MHz, $CDCl_3$): δ 0.94 (d, J 7.4 Hz, $(H17)_3$); 0.99 (s, $(H18)_3$); 1.67 (br s, $(H19)_3$); 1.84 (2 x OH); 2.00 (d, J 3.4 Hz, H7); 3.29-3.67 (AB part of ABX, $(H16)_2$); 3.67-3.75 (AB part of ABX, $(H20)_2$); 5.24 (br s, H9). ^{13}C-NMR: see Table 1. MS: m/z 306 (M^+, 27%), 288 (12), 276 (22), 275 (19), 258 (5), 189 (18), 177 (25), 159 (77), 145 (59), 105 (100).

The diol (2) (350 mg) in dry pyridine (10 ml) and toluene-p-sulphonyl chloride (700 mg) were left at room temperature for 18 hr. The product (370 mg) in ether was treated with $LiAlH_4$ (700 mg) and heated under reflux for 16 hr. The product obtained was adsorbed on a column of 10% $AgNO_3$-silica (60-120 mesh) and elution with light petroleum gave the *hydrocarbon* (3) (71 mg) as an oil, b.p. 76-78° (bath)/0.05 mm, $[\alpha]_D$ -96.9° (c, 0.4; $CHCl_3$) (Found: C, 87.52; H, 12.52. $C_{20}H_{34}$ requires C, 87.51; H, 12.49%). ^1H-NMR (90 MHz, $CDCl_3$): δ 0.88 (d, 6H, J 6.5 Hz, $(H16)_3$ and $(H17)_3$); 0.92 (s, $(H18)_3$); 0.95 (d, J 6.0 Hz, $(H20)_3$); 1.66 (br d, J 1.5 Hz, $(H19)_3$); 1.98 (d, J 3.4 Hz, H7); 2.34 (br d, J 16 Hz, H10); 5.24 (br s, H9). ^{13}C-NMR: see Table 1. MS: m/z 274 (M^+, 19%), 217 (7), 203 (3), 189 (4), 161 (22), 119 (100), 105 (20).

Hydrogenation of (2). The diol (2) (30 mg) in EtOH (2 ml) was stirred at room temperature with PtO_2 (10 mg) under H_2 for 18 hr. Recovery of the product yielded the *dihydrodiol* (5) which crystallized from ether as needles, m.p. 112-113°, $[\alpha]_D$ -17.2° (c 0.4; $CHCl_3$) (Found: C, 77.81; H, 11.59. $C_{20}H_{36}O_2$ requires C, 77.85; H, 11.77%). ^1H-NMR (80 MHz, $CDCl_3$): δ 0.93 (d, J 6.0 Hz, $(H17)_3$); 1.00 (d, J 6.0 Hz, $(H19)_3$); 1.10 (s, $(H18)_3$); 1.78 (bs, 2 x OH); 3.39-3.72 (2 x AB part of ABX systems, $(H17)_2$ and $(H20)_2$). ^{13}C-NMR: see Table 1. MS: m/z 290 (M^+ -18, 2%), 207 (42), 189 (100), 161 (22), 147 (15), 133 (18).

Hydroboration of (3). The hydrocarbon (3) (290 mg) in ether (10 ml) at 0° under N_2 was treated with excess $BH_3.(CH_3)_2S$ (0.5 ml). The solution was allowed to warm to room temperature and left for 3 hr. After cooling to 0° EtOH (0.1 ml) was added followed by 30% NaOH solution (1 ml) and 30% H_2O_2 (1 ml). The mixture was stirred at 40° for 1 hr then diluted with H_2O and extracted with ether. The product recovered (333 mg) crystallized from ether-pentane as needles of the *alcohol* (7), m.p. 103-104°, $[\alpha]_D$ -19.6° (c, 0.5; $CHCl_3$) (Found: C, 82.38; H, 12.12. $C_{20}H_{36}O$ requires C, 82.11; H, 12.41%). ^1H-NMR (90 MHz; $CDCl_3$): δ 0.88 (d, J 6.0 Hz, $(H17)_3$); 1.12 (d, J 7.2 Hz, $(H20)_3$); 1.15 (d, J 7.5 Hz, $(H19)_3$); 1.18 (s, $(H18)_3$); 3.81 (m, $W_{h/2}$ 26.5 Hz, H9). ^{13}C-NMR: see Table 1. MS: m/z 292 (M^+, 23%), 274 (2), 220 (8), 207 (96), 189 (100), 161 (63), 138 (45), 119 (47), 109 (42).

Horeau determination. The alcohol (7) (51.2 mg; 0.175 mmol) in dry pyridine (0.87 ml) was treated with phenybutyric anhydride (108.7 mg; 0.351 mmol) for 44 hr. The excess anhydride was hydrolyzed with H_2O and the mixture was titrated with 0.106M NaOH (4.76 ml) using phenolphthalein as indicator. The solution was extracted with $CHCl_3$ (twice) to give 60 mg of esters. The aqueous solution was acidified with 10% HCl and extracted with $CHCl_3$ (twice) to give the acids (75.1 mg), $[\alpha]_D$ -9.07° (benzene). Chemical yield 100%; optical yield 28%.

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