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Structure and Absolute Configuration of (+)-Vitrenal, a Novel Carbon Skeletal Sesquiterpenoid having Plant-growth-inhibitory Activity, from the Liverwort *Lepidozia vitrea*

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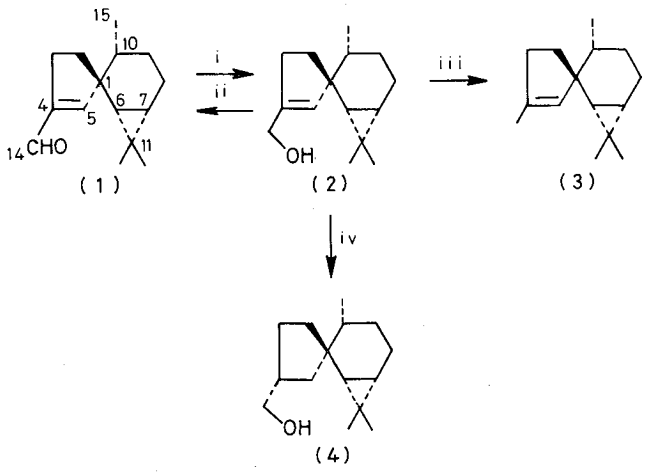
A novel carbon skeletal sesquiterpene aldehyde (+)-vitrenal displaying plant-growth-inhibitory properties has been isolated from the liverwort *Lepidozia vitrea*, and its structure and absolute configuration have been determined to be (1*R*,6*R*,7*S*,10*R*)-vitr-4-en-14-al (1) on the basis of chemical and spectral evidence as well as *X*-ray analysis.

In the preceding paper,[1] we reported the structure elucidation of two novel sesquiterpene aldehydes, (—)-isobicyclogermacrenal and (—)-lepidozenal, isolated from a methanol extract of the liverwort *Lepidozia vitrea* Steph., and displaying plant-growth-inhibitory properties. The sesquiterpenoids having *cis*- and *trans*-10,3-bicyclic nuclei are important compounds in the biogenetic sequence of liverwort sesquiterpenoids. From the same methanol extract we have now isolated an additional sesquiterpene aldehyde named (+)-vitrenal (1) with a novel carbon skeleton, and also exhibiting plant-growth-inhibitory activity. The structure and absolute configuration of this third plant-growth inhibitor (+)-vitrenal was determined as *ent*-vitr-4-en-14-al, or (1*R*,6*R*,7*S*,10*R*)-vitr-4-en-14-al (1).† In the present paper, we describe details of the chemical and spectral evidence as well as the results of an *X*-ray crystal structure analysis in support of the proposed structure.[2]

The ^{1}H n.m.r., i.r., and u.v. spectra characterized the structure of (+)-vitrenal (1), $C_{15}H_{22}O$, $[\alpha]_D$ +107°, as a tricarbocyclic sesquiterpenoid containing a cyclopropane ring [δ 0.7—0.8 (2 H, m)], a secondary methyl [δ 0.78 (3 H, d, *J* 5.5 Hz)] and two tertiary methyls [δ 0.96 and 1.19 (each 3 H, s); $\nu_{max.}$ 1 379 and 1 372 cm^{-1}] as well as an α,β-unsaturated aldehyde group conjugated with a trisubstituted double bond [δ 6.85 (1 H, br s), 9.75 (1 H, s); $\nu_{max.}$ 2 790, 2 695, 1 680, 1 613, and 853 cm^{-1}; $\lambda_{max.}$ 242 nm (ε 13 200)]. On reduction with lithium aluminium hydride the aldehyde (1) gave a primary alcohol (2), $C_{15}H_{24}O$ [$\nu_{max.}$ 3 610 and 3 310 cm^{-1}], which regenerated the original aldehyde by oxidation with manganese dioxide. The off-resonance ^{13}C n.m.r. spectrum of the alcohol (2) showed 15 signals for 3 quaternary carbons, 4 methine carbons, 5 methylene carbons, and 3 methyls which indicated the tricarbocyclic framework and the above partial structures.

In order to obtain information on the carbon skeleton, the alcohol (2) was converted by the pyridine–sulphur trioxide–lithium aluminium hydride reaction[3] into a sesquiterpene hydrocarbon (3), $C_{15}H_{24}$ (Scheme 1). The allylic alcohol (2) was also hydrogenated over Adams catalyst to give a saturated alcohol (4), $C_{15}H_{26}O$ [$\nu_{max.}$ 3 610 and 3 420 cm^{-1}]. The spectral properties of these compounds (1)—(4) were different from those of any of the known sesquiterpenoids,[4,5] suggesting a novel carbon skeleton for the compounds. An epoxide (5), $C_{15}H_{24}O_2$ [δ 3.32 (1 H, s), and 3.66 and 3.93 (each 1 H, d, *J* 12.0 Hz)],‡ produced by oxidation of the alcohol (2) with *m*-chloroperbenzoic acid (Scheme 2), was changed by treatment with lithium in ethylenediamine into two kinds of diol

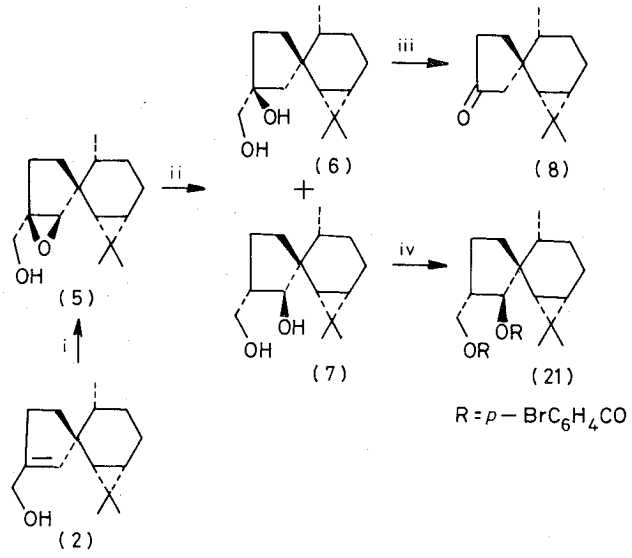


Scheme 1. *Reagents:* i, $LiAlH_4$; ii, MnO_2; iii, C_5H_5N–SO_3, $LiAlH_4$; iv, H_2–PtO_2

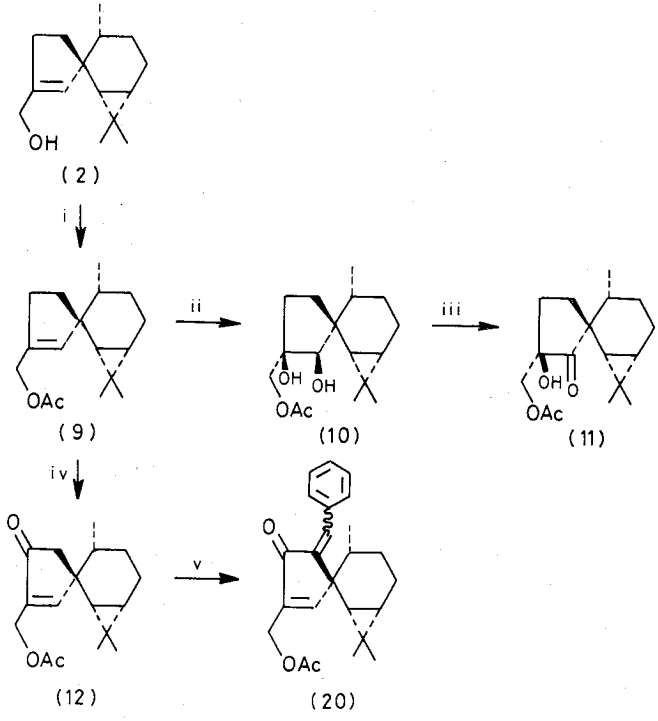
(6), $C_{15}H_{26}O_2$ [δ 3.53 (2 H, s)], and (7), $C_{15}H_{26}O_2$ [δ 3.6—3.9 (3 H, m)] in the ratio 1 : 3. They were, respectively, assigned as the 1,2-diol (6) and the 1,3-diol (7) on the basis of the numbers of the carbinyl protons in the ^{1}H n.m.r. spectra. The former vicinal diol (6) was, furthermore, oxidized with sodium periodate to yield a nor-ketone (8), $C_{14}H_{22}O$, which showed a characteristic i.r. band at $\nu_{max.}$ 1 740 cm^{-1} attributed to the cyclopentanone. Alternatively, acetylation of the alcohol (2) produced an acetate (9), $C_{17}H_{26}O_2$ [$\nu_{max.}$ 1 722 cm^{-1}], which was then oxidized with osmium tetraoxide to a glycol (10), $C_{17}H_{28}O_4$ [$\nu_{max.}$ 3 540 cm^{-1}]. The diol (10) was, furthermore, transformed by reaction with *N*-chlorosuccinimide and methyl sulphide into an α-hydroxycyclopentanone (11) (Scheme 3), $C_{17}H_{26}O_4$ [$\nu_{max.}$ 3 550, 3 450, and 1 738 cm^{-1}], which had no proton signals attributed to the adjacent positions of the carbonyl group in the ^{1}H n.m.r. spectrum. The acetate (9) was also oxidized with chromium trioxide to an α,β-unsaturated cyclopentenone (12), $C_{17}H_{24}O_3$ [$\nu_{max.}$ 1 710 cm^{-1}; $\lambda_{max.}$ 227 nm (ε 8 860); δ 7.49 (1 H, t, *J* 1.5 Hz)]. Since the ^{1}H n.m.r. spectrum of the cyclopentenone (12) exhibited a pair of AB type signals [δ 2.39 and 2.75 (each 1 H, d, *J* 18.5 Hz)] due to the methylene group adjacent to the carbonyl group, one of the two quaternary carbon atoms was certainly located at the β-position of the carbonyl group as a spiro-carbon atom. These chemical transformations indicated the formyl group of the original molecule (1) was attached to the cyclopentene ring at β-position of the quaternary carbon atom.

Furthermore, the primary alcohol (2) was ozonolysed to a biscarbocyclic hydroxy-keto-acid (13) (Scheme 4), $C_{15}H_{24}O_4$ [$\nu_{max.}$ 3 655, 3 500—2 500, 1 718, and 1 702 cm^{-1}]. Interestingly,

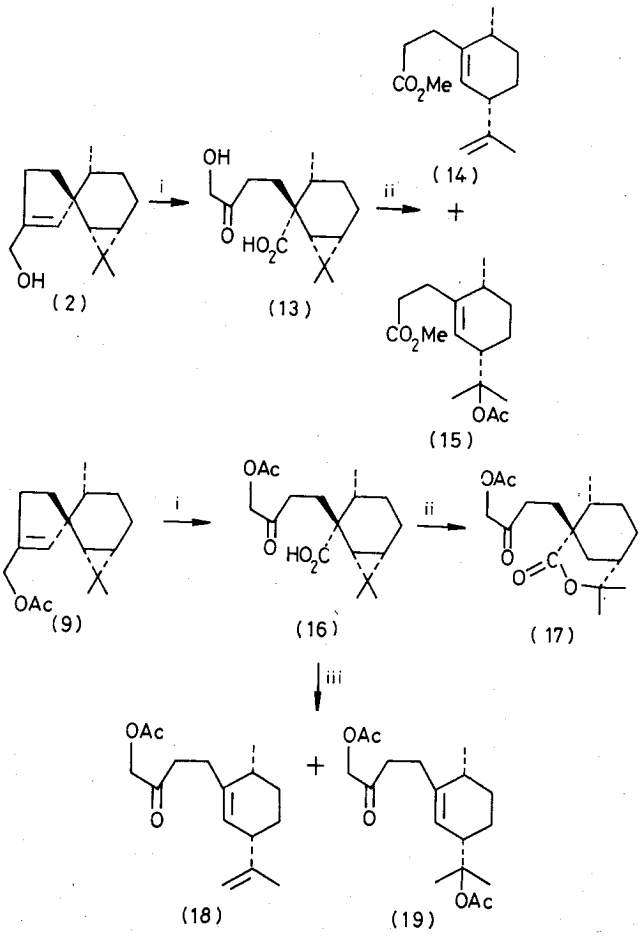
† We propose the name vitrane for the new carbon skeleton and suggest the numbering shown in the structure (1).
‡ Orientations of the epoxy ring of the epoxide (5) and of the hydroxy groups of the glycol (10) were assigned on the basis of the results of an *X*-ray analysis of the di-*p*-bromobenzoate (21).



Scheme 2. *Reagents:* i, *m*-$ClC_6H_4CO_3H$; ii, Li, $NH_2(CH_2)_2NH_2$; iii, $NaIO_4$; iv, *p*-BrC_6H_4COCl



Scheme 3. *Reagents:* i, Ac_2O, C_5H_5N; ii, OsO_4, Na_2SO_3; iii, $C_4H_4O_2NCl$, Me_2S; iv, CrO_3–C_5H_5N; v, PhCHO



Scheme 4. *Reagent:* i, O_3, H_2O_2; ii, $PbAc_4$; iii, AcOH

treatment of the hydroxy-keto-acid (13) with lead tetra-acetate followed by diazomethane afforded two kinds of monocarbocyclic esters, (14), $C_{14}H_{22}O_2$, and (15), $C_{16}H_{26}O_4$, in the ratio 1 : 1; these underwent oxidative cleavage of the 1,2-hydroxy-ketone moiety and decarboxylation accompanied by ring opening of the cyclopropane with the *gem*-dimethyl group.[6] These products had an isopropenyl group [$\nu_{max.}$ 890 cm^{-1}; δ 1.67 (3 H, *J* 1.0 Hz) and 4.64 (2 H, br s) for (14)] or an acetoxy-isopropyl group [δ 1.38 (6 H, s) and 1.94 (3 H, s) for (15)] together with a trisubstituted double bond [$\nu_{max.}$ 864 cm^{-1}; δ 5.20 (1 H, br, *w*/2 6.0 Hz) for (14)] and [$\nu_{max.}$ 872 cm^{-1}; δ 5.25 (1 H, br, *w*/2 5.0 Hz) for (15)], instead of the cyclopropane ring with the *gem*-dimethyl group in the original molecule, respectively. Otherwise, the acetate (9) was also converted into an acetoxy-keto-acid (16) by ozonolysis, and the biscarbocyclic acid (16) thus formed was heated with acetic acid to give an acetoxy-keto-lactone (17), $C_{17}H_{26}O_5$ [$\nu_{max.}$ 1 750, 1 735, and 1 705 cm^{-1}]; the ^1H n.m.r. spectrum of this showed the two methyl signals adjacent to the oxygen atom of the lactone ring [δ 1.43 (6 H, s)] * suggesting the formation of the lactone ring accompanied by ring opening of the cyclopropane substituted with the *gem*-dimethyl group. When the acetoxy-keto-acid (16) was treated with lead tetra-acetate it gave two monocarbocyclic compounds (18), $C_{16}H_{24}O_3$ ($\nu_{max.}$ 1 754 and 1 735 cm^{-1}), and (19), $C_{18}H_{28}O_5$ ($\nu_{max.}$ 1 754, 1 734, and 1 730 cm^{-1}), which suffered only the decarboxylation and ring opening reactions but had still the acetoxy-ketone unit.

The full structure was, therefore, deduced to be the structure (1) having the spiro[4.5]decane system as well as the cyclopropane ring substituted with the *gem*-dimethyl group to α,β-position of the spiro-carbon on the cyclohexane ring. Since a secondary methyl signal of a benzylidene derivative (20), $C_{22}H_{26}O_2$, produced from the α,β-unsaturated ketone (12) by treatment with benzaldehyde, resonated at high field [δ 0.50 (3 H, d, *J* 7.0 Hz)], the position of the methyl group was indicated as α to the spiro-carbon. This was

* The size of the lactone ring is not concluded but is tentatively assigned to δ-lactone.

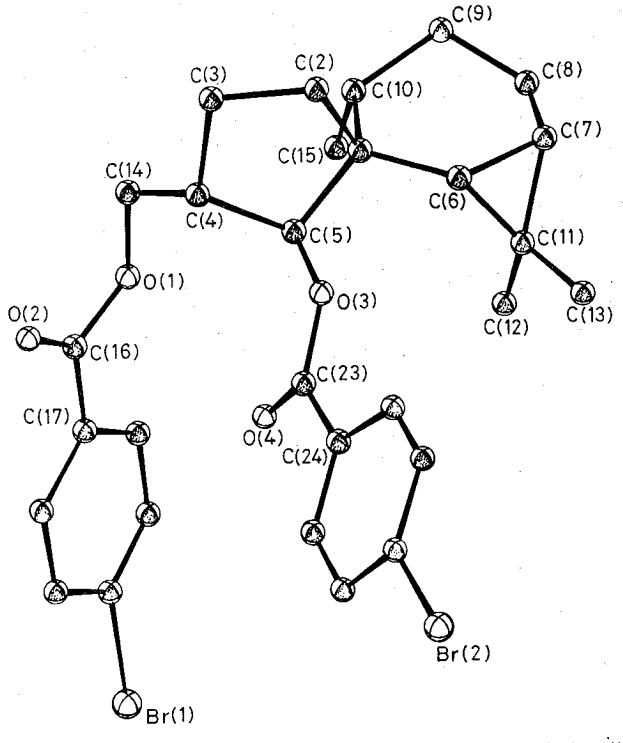


Figure. A computer-generated perspective drawing of the di-*p*-bromobenzoate (21) derived from (+)-vitrenal (1). Hydrogen atoms have been omitted for clarity

Table 1. Atomic co-ordinates (× 10^4) for non-hydrogen atoms, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Br(1)	1 803(2)	−896(2)	3 804(1)
Br(2)	3 452(2)	6 685(2)	1 166(1)
O(1)	−340(15)	4 420(12)	4 715(4)
O(2)	1 955(15)	4 831(13)	4 744(6)
O(3)	−657(12)	6 272(11)	3 393(5)
O(4)	348(13)	4 476(11)	3 436(4)
C(1)	−2 813(16)	6 758(14)	3 820(7)
C(2)	−2 261(17)	7 989(14)	4 025(6)
C(3)	−1 246(20)	7 684(15)	4 498(6)
C(4)	−645(17)	6 494(17)	4 357(6)
C(5)	−1 507(18)	6 003(12)	3 876(6)
C(6)	−3 314(19)	6 946(16)	3 223(6)
C(7)	−4 849(19)	6 908(17)	3 059(7)
C(8)	−5 862(18)	6 429(17)	3 510(8)
C(9)	−5 418(21)	6 814(17)	4 049(7)
C(10)	−3 951(19)	6 349(19)	4 228(6)
C(11)	−3 735(19)	6 054(15)	2 832(6)
C(12)	−3 332(19)	6 420(13)	2 243(6)
C(13)	−3 686(21)	4 734(15)	2 905(6)
C(14)	−643(21)	5 628(16)	4 861(5)
C(15)	−4 064(18)	4 947(16)	4 339(6)
C(16)	1 025(25)	4 132(21)	4 664(8)
C(17)	1 181(23)	2 886(19)	4 486(7)
C(18)	2 551(21)	2 517(20)	4 354(8)
C(19)	2 692(21)	1 378(21)	4 153(7)
C(20)	1 540(25)	650(15)	4 086(6)
C(21)	228(21)	968(19)	4 234(8)
C(22)	50(19)	2 119(18)	4 417(7)
C(23)	190(21)	5 421(18)	3 223(7)
C(24)	954(19)	5 719(19)	2 714(6)
C(25)	2 015(18)	5 006(16)	2 534(7)
C(26)	2 762(18)	5 252(15)	2 074(8)
C(27)	2 451(16)	6 305(16)	1 812(6)
C(28)	1 410(21)	7 080(13)	1 971(6)
C(29)	688(18)	6 764(19)	2 422(8)

also suggested by the biogenetic isoprene rule[7] and by the similarity with respect to the secondary methyl of ^{1}H n.m.r. and i.r. spectra of the degradation products (14) and (15) to those of the corresponding epimers which had been obtained as intermediates from (−)-*trans*-caran-2-one in the organic synthesis of cubebane type sesquiterpenoids.[8] Furthermore, the n.O.e. value (4.6%) between the secondary methyl and the vinyl proton in the α,β-unsaturated cyclopentenone (12) suggested the configuration of the C(10)-secondary methyl to be the α-configuration.

For confirmation of the structure including the absolute configuration and to establish the molecular conformation, several kinds of *p*-bromobenzoates were prepared for carrying out *X*-ray crystallographic analysis. A di-*p*-bromobenzoate (21), $C_{29}H_{34}Br_2O_4$, which was derived by treatment of the 1,3-diol (7) with *p*-bromobenzoyl chloride, formed crystals suitable for the purpose.

The molecular model of the di-*p*-bromobenzoate (21) obtained by the *X*-ray crystal structure analysis is shown in the Figure. The atomic co-ordinates for non-hydrogen atoms and for hydrogen atoms are listed in Tables 1 and 2, respectively. Thus, the structure, including the absolute configuration, of (+)-vitrenal should be represented by structure (1) consisting of the unique spiro[4.5]decane skeleton with the cyclopropane ring. Bond lengths and bond angles of the molecule (21) are, respectively, given in Tables 3 and 4, and the selected torsion angles in Table 5. The C–C bond lengths are widely distributed between 1.471 and 1.611 Å with a mean value of 1.546 Å. The cyclopentane ring has a conformation somewhere between a half-chair and an envelope form based on the torsion angles and the displacements of C(1) and C(2) atoms from the C(3)–C(5) plane [−0.327 and 0.288 Å]. The cyclohexane ring has a deformed chair form based on its torsion angles. The fusion of the cyclopropane ring causes the distortion of the conformation in the cyclohexane ring present. A mean bond angle of the cyclohexane ring is 114.0°. Ring angles at the positions of C(1), C(6), C(7), and C(9) are enlarged to a mean value of 117.9° owing to the strain caused by fusion with the cyclopropane ring. Although the cyclopropane ring is almost perpendicular to the cyclohexane ring, it is tilted a little (1.35°) toward the C(10) atom by non-bonded repulsion between the axial secondary methyl group and the C(5) atom [C(15) · · · C(5), 2.954 Å]. This is evident from the enlargement of the angles of C(15)–C(10)–C(1) (116.7°) and C(5)–C(1)–C(6) (114.5°).

From the chemical and spectral evidence and the results of the *X*-ray analysis mentioned above, the structure, including the absolute configuration, of (+)-vitrenal was determined as structure (1). This enantiomeric structure agrees with the result that most of the liverworts elaborate enantiomeric sesquiterpenoids.[9] The carbon framework of (+)-vitrenal (1) is presumably constructed by Wagner-Meerwein type migration of the C(5)–C(6) bond to the C(1)–C(6) bond in the *ent*-aromadendrane structure which, as described in the preceding paper, may be formed *via* an anti-Markownikoff type cyclization of *ent*-isobicyclogermacrene.[1] (+)-Vitrenal (1) inhibits completely the growth of leaves and roots of rice seedlings at a concentration of 25 p.p.m. (1.1×10^{-4} M) and the concentration for 50% growth inhibition (I_{50}) is 18 p.p.m. It may be acting as allomone, together with (−)-isobicyclogermacrenal, the other constituent of this liverwort, in ecological systems. Details of the biological activity will be reported in a separate paper.

Table 2. Hydrogen atom atomic co-ordinates (× 10^4), labelled according to their bonded carbon atoms

Atom	*x*	*y*	*z*
H(2a)	−938	625	4 167
H(2b)	−1 017	2 455	4 524
H(3a)	−1 861	7 704	4 867
H(3b)	−503	8 388	4 545
H(4)	387	6 516	4 303
H(5)	−1 817	5 069	3 933
H(6)	−2 500	7 500	3 125
H(7)	−5 313	6 250	3 229
H(8a)	−6 848	6 640	3 450
H(8b)	−5 777	5 478	3 428
H(9a)	−6 264	5 972	4 241
H(9b)	−5 469	7 642	4 158
H(10)	−3 627	6 598	4 626
H(12a)	−3 750	5 938	1 979
H(12b)	−4 063	7 188	2 396
H(12c)	−2 188	5 938	2 188
H(13a)	−2 500	4 063	2 917
H(13b)	−4 327	4 264	2 642
H(13c)	−4 093	4 530	3 314
H(14a)	−1 563	5 938	4 688
H(14b)	−365	5 640	5 258
H(15a)	−5 000	4 688	4 583
H(15b)	−4 105	4 363	3 972
H(15c)	−3 125	5 000	4 583
H(18)	3 470	3 079	4 448
H(19)	3 762	1 048	4 018
H(21)	−1 563	8 438	3 750
H(22)	−3 438	8 438	4 167
H(25)	2 311	4 166	2 785
H(26)	3 614	4 634	1 915
H(28)	1 213	7 874	1 751
H(29)	−1 996	7 311	2 570

Table 3. Bond lengths (Å) with estimated standard deviations in parentheses for the di-*p*-bromobenzoate (21)

Br(1)–C(20)	1.898(17)	C(8)–C(9)	1.471(25)
Br(2)–C(27)	1.915(16)	C(9)–C(10)	1.563(27)
O(1)–C(14)	1.441(22)	C(10)–C(15)	1.611(28)
O(1)–C(16)	1.352(28)	C(11)–C(12)	1.566(20)
O(2)–C(16)	1.206(28)	C(11)–C(13)	1.502(24)
O(3)–C(5)	1.480(20)	C(16)–C(17)	1.483(32)
O(3)–C(23)	1.326(23)	C(17)–C(18)	1.414(30)
O(4)–C(23)	1.202(23)	C(17)–C(22)	1.396(29)
C(1)–C(2)	1.572(23)	C(18)–C(19)	1.386(32)
C(1)–C(5)	1.519(23)	C(19)–C(20)	1.385(31)
C(1)–C(6)	1.570(23)	C(20)–C(21)	1.356(31)
C(1)–C(10)	1.557(24)	C(21)–C(22)	1.387(29)
C(2)–C(3)	1.563(23)	C(23)–C(24)	1.498(25)
C(3)–C(4)	1.502(25)	C(24)–C(25)	1.371(26)
C(4)–C(5)	1.553(23)	C(24)–C(29)	1.408(29)
C(4)–C(14)	1.588(23)	C(25)–C(26)	1.376(25)
C(6)–C(7)	1.525(25)	C(26)–C(27)	1.387(24)
C(6)–C(11)	1.457(23)	C(27)–C(28)	1.384(24)
C(7)–C(8)	1.577(25)	C(28)–C(29)	1.363(25)
C(7)–C(11)	1.543(25)		

Experimental

For general experimental details see ref. 1. The aldehyde (+)-vitrenal (1) was isolated as a gum in a yield of 2% from the ethereal extract as described in the preceding paper.

(+)-*Vitrenal* [(1R,6R,7S,10R)-*vitr*-4-*en*-14-*al*] (1): $[\alpha]_D$ +107° (*c*, 1.55) (Found: M^+, 218.1673. $C_{15}H_{22}O$ requires *M*, 218.1669); $\lambda_{max.}$ 242 nm (ε 13 200); $\nu_{max.}$ 3 040, 2 790, 2 695, 1 680, 1 613, 1 379, 1 372, 1 175, 1 148, 884, and 853 cm^{-1}; δ_H 0.7—0.8 (2 H, m), 0.78 (3 H, d, *J* 5.5 Hz), 0.96 and 1.19 (each 3 H, s), 6.85 (1 H, t, *J* 1.5 Hz), and 9.75 (1 H, s); *m/z* 218.1673 (M^+, $C_{15}H_{22}O$ requires *M*, 218.1669, 19%), 203,1427 ($C_{14}H_{19}O$ requires 203.1434, 7), 189.1644 ($C_{14}H_{21}$ requires 189.1642, 8), 176.1233 ($C_{12}H_{16}O$ requires 176.1200, 19), 175.1171 ($C_{12}H_{15}O$ requires 175.1220, 9), 161.0961 ($C_{11}H_{18}O$ requires 161.0965, 20), 147 (20), 136 (21), 133 (23), 119 (24), 105 (50), 91 (79), 77 (63), 67 (61), 55 (86), and 41 (100).

Table 4. Bond angles (°) with estimated standard deviations in parentheses for the di-*p*-bromobenzoate (21)

C(14)–O(1)–C(16)	116.5(15)	C(7)–C(11)–C(12)	110.2(13)
C(5)–O(3)–C(23)	116.5(13)	C(7)–C(11)–C(13)	126.7(15)
C(2)–C(1)–C(5)	100.9(13)	C(12)–C(11)–C(13)	111.5(13)
C(2)–C(1)–C(6)	106.8(13)	O(1)–C(16)–O(2)	122.7(20)
C(2)–C(1)–C(10)	106.6(13)	O(1)–C(16)–C(17)	110.7(18)
C(5)–C(1)–C(6)	114.5(13)	O(2)–C(16)–C(17)	126.6(20)
C(5)–C(1)–C(10)	110.4(14)	C(16)–C(17)–C(18)	116.2(18)
C(6)–C(1)–C(10)	116.1(14)	C(16)–C(17)–C(22)	123.2(18)
C(1)–C(2)–C(3)	104.9(13)	C(18)–C(17)–C(22)	120.5(18)
C(2)–C(3)–C(4)	105.1(13)	C(17)–C(18)–C(19)	116.5(19)
C(3)–C(4)–C(5)	107.2(14)	C(18)–C(19)–C(20)	121.1(19)
C(3)–C(4)–C(14)	111.5(14)	C(19)–C(20)–C(21)	123.2(19)
C(5)–C(4)–C(14)	112.8(14)	Br(1)–C(20)–C(19)	119.0(15)
C(1)–C(5)–C(4)	107.9(13)	Br(1)–C(20)–C(21)	117.8(15)
O(3)–C(5)–C(1)	105.2(12)	C(20)–C(21)–C(22)	116.7(19)
O(3)–C(5)–C(4)	104.9(12)	C(17)–C(22)–C(21)	121.8(18)
C(1)–C(6)–C(7)	122.9(14)	O(3)–C(23)–O(4)	125.5(17)
C(1)–C(6)–C(11)	128.3(15)	O(3)–C(23)–C(24)	113.9(16)
C(7)–C(6)–C(11)	62.3(12)	O(4)–C(23)–C(24)	120.7(17)
C(6)–C(7)–C(8)	114.3(14)	C(23)–C(24)–C(25)	120.3(17)
C(6)–C(7)–C(11)	56.7(11)	C(23)–C(24)–C(29)	122.3(17)
C(8)–C(7)–C(11)	118.0(14)	C(25)–C(24)–C(29)	117.3(17)
C(7)–C(8)–C(9)	111.6(15)	C(24)–C(25)–C(26)	122.5(17)
C(8)–C(9)–C(10)	114.7(15)	C(25)–C(26)–C(27)	116.8(16)
C(1)–C(10)–C(9)	110.1(14)	C(26)–C(27)–C(28)	124.2(16)
C(1)–C(10)–C(15)	116.7(14)	Br(2)–C(27)–C(26)	118.5(12)
C(9)–C(10)–C(15)	108.6(14)	Br(2)–C(27)–C(28)	117.2(12)
C(6)–C(11)–C(7)	61.0(11)	C(27)–C(28)–C(29)	115.7(16)
C(6)–C(11)–C(12)	111.8(14)	C(24)–C(29)–C(28)	123.5(18)
C(6)–C(11)–C(13)	126.7(15)		

Table 5. Selected torsion angles (°) for the di-*p*-bromobenzoate (21)

C(5)–C(1)–C(2)–C(3)	−37.4
C(1)–C(2)–C(3)–C(4)	30.4
C(2)–C(3)–C(4)–C(5)	−11.0
C(3)–C(4)–C(5)–C(1)	−13.1
C(4)–C(5)–C(1)–C(2)	30.9
C(10)–C(1)–C(6)–C(7)	8.4
C(1)–C(6)–C(7)–C(8)	−43.0
C(6)–C(7)–C(8)–C(9)	12.2
C(7)–C(8)–C(9)–C(10)	−10.8
C(8)–C(9)–C(10)–C(1)	39.0
C(9)–C(10)–C(1)–C(6)	−14.3

Lithium Aluminium Hydride Reduction of (+)-*Vitrenal* (1).—A solution of the aldehyde (1) (170 mg) in dry ether (5 ml) was added to a suspension of lithium aluminium hydride (30 mg) in dry ether (5 ml), and the mixture was stirred at 0 °C for 1 h. The excess of hydride was decomposed by addition of ice-water (0.1 ml) and 10% aqueous sodium hydroxide (0.1 ml) and work-up afforded (+)-*vitrenol* [(1R,6R,7S,10R)-*vitr*-4-*en*-14-*ol*] (2) as needles (110 mg): m.p. 60.5—61.5 °C (from MeOH); $[\alpha]_D$ +76.6° (*c*, 0.35) (Found: C, 81.9; H, 11.25. $C_{15}H_{24}O$ requires C, 81.76; H, 10.98%); $\nu_{max.}$ 3 610, 3 310, 3 035, 1 040, 1 012, 945, and 850 cm^{-1}; δ_H 0.5—0.7 (2 H, m), 0.74 (3 H, d,

J 5.5 Hz), 0.96 and 1.16 (each 3 H, s), 4.21 (2 H, s), and 5.63 (1 H, br s); δ_C 17.1 (q), 18.0 (q), 18.8 (s), 20.4 (q), 20.6 (t), 30.0 (t), 30,7 (t), 31.5 (d), 34.2 (d), 37.5 (d), 43.5 (t), 51.3 (s), 62.4 (t), 128.9 (d), and 143.0 (s); *m/z* 220 (M^+, 23%), 202 (7), 189 (9), 177 (14), 159 (9), 147 (21), 137 (51), 119 (23), 105 (42), 81 (54), 79 (46), 67 (53), 55 (56), and 41 (100).

Oxidation of the Alcohol (2) *with Manganese Dioxide.*—To a solution of the alcohol (2) (90 mg) in dry ether (10 ml) was added manganese dioxide (350 mg) with stirring, and the mixture was stirred at room temperature for 3 h. The reaction product was filtered through a column packed with silica gel to afford, upon work-up, the aldehyde (1) as a gum (55 mg). The spectral properties and optical rotation were identical with those of the natural aldehyde (1).

Pyridine–Sulphur Trioxide–Lithium Aluminium Hydride Reduction of the Alcohol (2).[3]—Pyridine–sulphur trioxide complex (170 mg) was added to the alcohol (2) (110 mg) in dry tetrahydrofuran (10 ml) at —25 °C and the suspension stirred at 0 °C for 12 h under nitrogen. Addition of lithium aluminium hydride (200 mg) in tetrahydrofuran at −25 °C was followed by stirring at 0 °C for 1 h and at room temperature for 4 h. Work-up, after decomposition of excess of hydride by addition of water and 10% aqueous sodium hydroxide, gave a crude reaction product which was separated by p.l.c. into the hydrocarbon (+)-vitrene (3) (27 mg) and recovered alcohol (2) (40 mg).

(+)-*Vitrene* [(1R,6R,7S,10R)-*vitr*-4-*ene*] (3): $[\alpha]_D$ +67.1° (*c*, 0.97); $\nu_{max.}$ 3 040, 1 655, 1 117, 1 010, 985, 948, and 847 cm^{-1}; δ_H 0.70 (3 H, d, *J* 5.5 Hz), 0.95 and 1.14 (each 3 H, s), 1.73 (3 H, br s), and 5.31 (1 H, br s); *m/z* 204 (M^+, 13%), 147 (46), 133 (32), 121 (54), 119 (57), 105 (82), 91 (100), 79 (75), 67 (46), 55 (64), and 43 (38).

Catalytic Hydrogenation of the Allylic Alcohol (2).—The allylic alcohol (2) (31 mg) in ethyl acetate (5 ml) was hydrogenated over Adams catalyst (5 mg) at room temperature for 2 h. Work-up afforded (+)-*vitranol* [(1R,4R,6R,7S,10R)-*vitran*-14-*ol*] (4) as crystals (24 mg): m.p. 54—55 °C (from MeOH); $[\alpha]_D$ +38.5° (*c*, 1.87); $\nu_{max.}$ ($CHCl_3$) 3 610, 3 420, 1 238, 1 010, and 906 cm^{-1}; δ_H 0.5—0.8 (2 H, m), 0.83 (3 H, d, *J* 5.0 Hz), 0.97 and 1.12 (each 3 H, s), 2.53 (1 H, s, exchangeable with D_2O), and 3.54 (2 H, d, *J* 6.0 Hz); *m/z* 222 (M^+, 4%), 191 (3), 179 (7), 161 (6), 140 (6), 135 (6), 121 (11), 107 (15), 93 (27), 82 (100), 67 (28), 55 (30), and 43 (15).

Epoxidation of the Alcohol (2).—To a solution of the alcohol (2) (120 mg) in chloroform (4 ml) was added *m*-chloroperbenzoic acid (150 mg) in chloroform (5 ml) with stirring at 0 °C; the mixture was then further stirred at 0—5 °C for 1 h. After decomposition of the peracid with potassium iodide, (+)-*epoxyvitranol* [(1R,4R,5R,6R,7S,10R)-4,5-*epoxyvitran*-14-*ol*] (5) was obtained as a gum (115 mg): $[\alpha]_D$ +118° (*c*, 1.34) (Found: C, 75.9; H, 10.4. $C_{15}H_{24}O_2$ requires C, 76.22; H, 10.24%); $\nu_{max.}$ 3 460, 3 000, 1 235, 1 074, 1 042, 945, 935, and 845 cm^{-1}; δ_H 0.4—0.7 (2 H, m), 0.83 (3 H, d, *J* 5.5 Hz), 1.04 and 1.25 (each 3 H, s), 3.32 (1 H, s), and 3.66 and 3.93 (each 1 H, d, *J* 12.0 Hz); *m/z* 236 (M^+, 1%), 218 (2), 205 (5), 189 (3), 175 (3), 163 (4), 149 (11), 126 (100), 121 (11), 105 (21), 93 (20), 79 (19), 67 (18), 55 (24), and 43 (17).

Reduction of the Epoxide (5) *with Lithium in Ethylenediamine.*—To a solution of the epoxide (5) (300 mg) in ethylenediamine (12 ml), lithium (200 mg) was added at room temperature with stirring. The mixture was stirred at 50 °C under nitrogen. In 1.5 h a persistent blue colour appeared and the reaction mixture was cooled. Water (10 ml) was added to destroy excess of reagent after which the reaction mixture was extracted with chloroform and purified by column chromatography to yield the 1,2-diol (6) (25 mg) and the 1,3-diol (7) (80 mg).

(+)-*Vitrane*-4,14-*diol* [(1R,4S,6R,7S,10R)-4.14-*dihydroxyvitrane*] (6): m.p. 58—59 °C (from MeOH); $[\alpha]_D$ +6.6° (*c*, 0.31); $\nu_{max.}$ ($CHCl_3$) 3 575, 3 400, 1 074, and 1.028 cm^{-1}; δ_H (0.6—0.7 (2 H, m), 0.81 (3 H, d, *J* 6.5 Hz), 1.06 and 1.22 (each 3 H, s), and 3.53 (2 H, s); *m/z* 238 (M^+, 2%), 220 (11), 207 (6), 189 (21), 177 (9), 159 (8), 149 (35), 133 (14), 121 (19), 107 (42), 91 (54), 82 (100), 67 (67), 55 (85), and 43 (59). (+)-*Vitrane*-5,14-*diol* [(1R,4S,5S,6R,7S,10R)-5,14-*dihydroxyvitrane*] (7): m.p. 83.5—84.5 °C (from MeOH); $[\alpha]_D$ +13.7° (*c*, 1.95); $\nu_{max.}$ ($CHCl_3$) 3 580, 3 425, 1 082, and 1 020 cm^{-1}; δ_H 0.34 (1 H, d, *J* 10.0 Hz), 0.97 (3 H, d, *J* 6.5 Hz), 1.08 and 1.26 (each 3 H, s), 3.6—3.9 (3 H, m); *m/z* 238 (M^+, 3%), 220 (5), 205 (3), 189, (9), 177 (6), 159 (10), 149 (11), 135 (18), 121 (20), 107 (47), 91 (74), 79 (76), 67 (81), 55 (100), and 43 (78).

Oxidation of the 1,2-*Diol* (6) *with Sodium Metaperiodate.*—A solution of sodium metaperiodate (120 mg) in water (1 ml) was added to a solution of the 1,2-diol (20 mg) in methanol (5 ml), and the mixture was stirred at room temperature for 24 h. Work-up gave (−)-4-*oxo*-14-*norvitrane* [(1R,6R,7S,10R)-14-*norvitran*-4-*one*] (8) as a gum (10 mg): $[\alpha]_D$ −63.0° (*c*, 0.46) (Found: M^+, 206.1658. $C_{14}H_{22}O$ requires *M*, 206.1668); $\nu_{max.}$ 1 740, 1 410, 1 378, 1 372, 1 242, and 1 147 cm^{-1}; δ_H 0.5—0.7 (2 H, m), 0.79 (3 H, d, *J* 6.0 Hz), and 0.96 and 1.10 (each 3 H, s); δ_H (C_6H_6) 0.57 (3 H, d, *J* 5.5 Hz), and 0.87 and 0.97 (each 3 H, s); *m/z* 206.1658 (M^+, $C_{14}H_{22}O$ requires *M*, 206.1688, 6%), 191 (2), 177 (3), 163.1119 ($C_{11}H_{15}O$ requires 161.1121, 8), 150.1408 ($C_{11}H_{18}$ requires 150.1408, 16), 135.1177 ($C_{10}H_{15}$ requires 135.1173, 37), 123.0783 ($C_8H_{11}O$ requires 123.0809, 24), 107.0860 (C_8H_{11} requires 107.0860, 60), 91.0558 (C_7H_7 requires 91.0547, 96), 79 (100), 67 (89), 53 (83), and 47 (33).

Acetylation of the Alcohol (2).—A mixture of the alcohol (2) (140 mg), dry pyridine (1 ml), and acetic anhydride (3.5 ml) was allowed to react overnight at room temperature. Work-up afforded (+)-*vitrenoyl acetate* [(1R,6R,7S,10R)-14-*acetoxyvitr*-4-*ene*] (9) as a gum (90 mg): $[\alpha]_D$ +62.7° (*c*, 1.35) (Found: C, 77.95; H, 10.25. $C_{17}H_{26}O_2$ requires C, 77.82; H, 9.99%); $\nu_{max.}$ ($CHCl_3$) 3 015, 1 722, 1 250, 1 023, 957, 905, and 853 cm^{-1}; δ_H 0.5—0.7 (2 H, m), 0.72 (3 H, d, *J* 5.5 Hz), 0.93 and 1.12 (each 3 H, s), 2.06 (3 H, s), 4.63 (2 H, s), and 5.66 (1 H, br s); *m/z* 262 (M^+, 6%), 220 (3), 219 (3), 202 (22), 187 (8), 179 (14), 159 (30), 145 (35), 131 (25), 119 (87), 105 (31), 91 (44), 79 (25), 69 (24), 55 (27), and 43 (100).

Oxidation of the Acetate (9) *with Osmium Tetraoxide.*—To a solution of the acetate (9) (68 mg) in dry pyridine (3 ml) was added osmium tetraoxide (40 mg) with cooling in an ice-bath; the reaction mixture was then allowed to stand at room temperature for 5 d. The solvent was distilled out, the residual substance dissolved in ethanol (3 ml), and the solution mixed with a solution of sodium sulphite (250 mg) in water (5 ml). The mixed solution was heated under reflux for 2 h, and the resulting precipitates were filtered off and the filtrate extracted with chloroform. Work-up gave [(1R,4R,5R,6R,7S,10R)-14-*acetoxyvitrane*-4,5-*diol*] (10) as a gum (43 mg): $[\alpha]_D$ +13.5° (*c*, 1.85); $\nu_{max.}$ ($CHCl_3$) 3 540, 1 733, 1 245, 1 092, 1 080, 1 035, 972, and 840 cm^{-1}; δ_H 0.3—0.9 (2 H, m), 0.97 (3 H, d, *J* 6.5 Hz), 1.06 and 1.26 (each 3 H, s), 2.13 (3 H, s), 2.56 (1 H, d, *J* 8.0 Hz, exchangeable with D_2O), 3.17 (1 H, s, exchangeable with D_2O), 3.64 (1 H, d, *J* 8.0 Hz, singlet by addition of D_2O), and 4.06 (2 H, s); *m/z* 296 (M^+, 3%), 278 (35), 236 (13), 218 (43), 205 (62), 189 (13), 178 (41), 163 (46), 150 (97), 149 (100), 135

(55), 123 (47), 121 (48), 107 (76), 93 (65), 82 (72), 69 (51), 55 (65), and 41 (90).

Oxidation of the Glycol (10) *with* N-*Chlorosuccinimide and Methyl Sulphide*.—To a solution of *N*-chlorosuccinimide (55 mg) in toluene (2 ml) was added methyl sulphide (0.1 ml) at 0 °C under nitrogen. A white precipitate appeared immediately after addition of the sulphide. The mixture was cooled to −25 °C, and a solution of the glycol (10) (35 mg) in toluene (0.5 ml) was added dropwise. The mixed solution was stirred for 3 h at −25 °C, and then a solution of trimethylamine (60 mg) in toluene (0.3 ml) was added dropwise. The cooling bath was removed and after 5 min, ether (4 ml) was added. Work-up gave (1R,4R,6R,7S,10R)-14-*acetoxy*-4-*hydroxyvitran*-4-*one* (11) as crystals (29 mg): m.p. 137.5—138.5 °C (from MeOH); $[\alpha]_D$ +60.8° (*c*, 1.53) (Found: M^+, 294.1888. $C_{17}H_{20}O_4$ requires *M*, 294.1830); $\nu_{max.}$ ($CHCl_3$) 3 550, 3 450, 1 738, 1 235, 1 117, 1 040, 1 018, and 897 cm^{-1}; δ_H 0.3—0.7 (2 H, m), 0.80 (3 H, d, *J* 5.5 Hz), 0.97 and 1.03 (each 3 H, s), 2.08 (3 H, s), and 3.95 and 4.19 (each 1 H, d, *J* 11.5 Hz); *m/z* 294.1888 (M^+, $C_{17}H_{26}O_4$ requires 294.1830, 16%), 234.1566 ($C_{15}H_{22}O_2$ requires 234.1618, 10), 221.1502 ($C_{14}H_{21}O_2$ requires 221.1539, 100), 203 (7), 178.1339 ($C_{12}H_{18}O$ requires 178.1356, 64), 163.1123 ($C_{11}H_{15}O$ requires 163.1122, 21), 150.1400 ($C_{11}H_{18}$ requires 150.1407, 69), 135.1149 ($C_{10}H_{15}$ requires 135.1172, 64), 121 (23), 107 (50), 93 (36), 79 (31), 67 (23), 55 (30), and 43 (81).

Allylic Oxidation of the Acetate (9) *with Chromium Trioxide* (*Sarett Oxidation*).—Chromium trioxide (2.5 g) was added to dry pyridine (8 ml) at −5 °C under nitrogen and the mixture was stirred for 20 min. To the stirred slurry, the acetate (9) (110 mg) in dry dichloromethane (12 ml) was added and refluxed at 60 °C for 10 h. The mixture was filtered through an alumina column and the solution was washed with water and 5% hydrochloric acid. Evaporation of the solvent left the crude product which was submitted to p.l.c. to isolate the recovered acetate (9) (40 mg) and (1R,6R,7S,10R)-14-*acetoxyvitr*-4-*en*-3-*one* (12) (20 mg): $[\alpha]_D$ +46.4° (*c*, 1.51) (Found: C, 73.6; H, 8.85. $C_{17}H_{24}O_3$ requires C, 73.88; H, 8.75%); $\lambda_{max.}$ 227 nm (ε 8 860); $\nu_{max.}$ 1 748, 1 711, 1 643, 1 226, 1 022, and 967 cm^{-1}; δ_H 0.5—0.8 (2 H, m), 0.68 (3 H, d, *J* 6.0 Hz), 0.96 and 1.25 (each 3 H, s), 2.09 (3 H, s), 2.39 and 2.75 (each 1 H, d, *J* 18.5 Hz), 4.77 (2 H, d, *J* 1.5 Hz), and 7.49 (1 H, t, *J* 1.5 Hz); *m/z* 276 (M^+, 6%), 234 (15), 216 (73), 201 (15), 191 (26), 174 (55), 159 (28), 145 (21), 134 (55), 121 (19), 105 (21), 95 (36), 83 (43), 67 (28), 55 (36), and 43 (100).

Ozonolysis of the Alcohol (2).—Ozonized oxygen gas was passed through a solution of the alcohol (2) (500 mg) in ethyl acetate (40 ml) at −70 °C for 40 min. The solvent was evaporated under reduced pressure and the residue heated at 50—60 °C with water (20 ml) and 35% hydrogen peroxide (0.3 ml) for 2 h. Work-up gave (1R,6R,7S,10R)-14-*hydroxy*-4-*oxo*-4,5-*secovitran*-5-*oic acid* (13) as a gum (380 mg): $[\alpha]_D$ +36.7° (*c*, 2.98); $\nu_{max.}$ ($CHCl_3$) 3 655, 3 500—2 500, 1 718, 1 702, 1 404, 1 267, 1 073, 1 017, and 940 cm^{-1}; δ_H 0.4—0.8 (2 H, m), 1.02 (3 H, s), 1.03 (3 H, d, *J* 7.0 Hz), 1.05 (3 H, s), and 4.30 (2 H, s); *m/z* 268 (M^+, 5%), 250.1614 ([*M* − 18]$^+$, $C_{15}H_{22}O_3$ requires 250.1567, 6), 235.1429 ($C_{14}H_{19}O_3$ requires 235.1333, 5), 222.1581 ($C_{14}H_{22}O_2$ requires 222.1617, 14), 209.1544 ($C_{13}H_{21}O_2$ requires 209.1540, 9), 195.1369 ($C_{12}H_{19}O_2$ requires 195.1383, 16), 181.1231 ($C_{11}H_{17}O_2$ requires 181.1228, 11), 168.0791 ($C_9H_{12}O_3$ requires 168.0786, 14), 161.1333 ($C_{12}H_{17}$ requires 161.1330, 17), 161.0955 ($C_{11}H_{13}O$ requires 161.0965, 6), 149.1238 ($C_{11}H_{17}$ requires 149.1329, 37), 135.1104 ($C_{10}H_{15}$ requires 135.1104, 26), 121 (19), 107 (43), 93 (52), 83 (100), 67 (30), 51 (44), 43 (72), and 41 (73).

Transformation of the Hydroxy-keto-acid (13) *into the Monocarbocyclic Esters* (14) *and* (15).—A mixture of the hydroxy-keto-acid (13) (380 mg), lead tetra-acetate (700 mg), dry benzene (10 ml) and pyridine (1.2 ml) was stirred at 0—5 °C for 1 h under nitrogen. The reaction mixture was filtered through a silica gel column followed by washing with water, and extraction with chloroform. After evaporation of the solvent, the extract was dissolved in methanol (4 ml) and treated with ethereal diazomethane. The solvent was distilled off and the residue was subjected to column chromatography to provide the two esters; the less polar compound (14) (25 mg) and the more polar ester (15) (22 mg).

(1R,4S)-2-(2-*Methoxycarbonylethyl*)-p-*mentha*-2,8-*diene* (14): $[\alpha]_D$ −29.8° (*c*, 1.04) (Found: M^+, 222.1644. $C_{14}H_{22}O_2$ requires *M*, 222.1619); $\nu_{max.}$ ($CHCl_3$) 3 060, 1 730, 1 659, 1 642, 1 260, 1 227, 1 155, 890, and 864 cm^{-1}; δ (CCl_4) 1.04 (3 H, d, *J* 7.0 Hz), 1.67 (3 H, d, *J* 1.0 Hz), 3.59 (3 H, s), 4.64 (2 H, br s), and 5.20 (1 H, br s); *m/z* 222.1644 (M^+, $C_{14}H_{22}O_2$ requires *M*, 222.1619, 55%), 196 (16), 191 (8), 175 (7), 162.1388 ($C_{12}H_{18}$ requires 162.1406, 20), 148.1187 ($C_{11}H_{16}$ requires 148.1250, 100), 135.1135 ($C_{10}H_{15}$ requires 135.1172, 54), 119 (41), 105 (62), 93 (58), 83 (45), 67 (17), 55 (35), and 41 (48).

(1R,4S)-8-*Acetoxy*-2-(2-*methoxycarbonylethyl*)-p-*menth*-2-*ene* (15): $[\alpha]_D$ +31.5° (*c*, 0.73) (Found: C, 67.75; H, 9.25. $C_{16}H_{26}O_4$ requires C, 68.05; H, 9.28%); $\nu_{max.}$ ($CHCl_3$) 3 015, 1 735, 1 268, 1 127, 1 015, 947, and 872 cm^{-1}; δ_H (CCl_4) 1.05 (3 H, d, *J* 7.0 Hz), 1.38 (6 H, s), 1.94 (3 H, s), 3.63 (3 H, s), and 5.25 (1 H, br s); *m/z* 222 ([*M* − 60]$^+$, 83%), 207 (8), 191 (15), 181 (24), 162 (17), 149 (34), 135 (31), 119 (13), 107 (33), 93 (25), 79 (15), 59 (26), and 43 (100).

Ozonolysis of the Acetate (9).—To a solution of the acetate (9) (275 mg) in ethyl acetate (30 ml) ozonized oxygen gas was passed at −70 °C for 35 min. The solvent was removed under reduced pressure and the residue heated with water (10 ml) and hydrogen peroxide (0.3 ml) at 50—60 °C for 2 h. Work-up gave (1R,6R,7S,10R)-14-*acetoxy*-4-*oxo*-4,5-*secovitran*-5-*oic acid* (16) as a gum (195 mg): δ_H 1.02 and 1.04 (each 3 H, s), 2.18 (3 H, s), 4.68 (2 H, s), and 7.93 (1 H, br, exchangeable with D_2O).

Treatment of the Acetoxy-keto-acid (14) *with Acetic Acid*.—A solution of the acid (16) (30 mg) in acetic acid (0.5 ml) was heated at 190 °C for 1 h, to give, in the customary fashion, (1S,7S,10R)-14-*acetoxy*-4-*oxo*-4,5:6,11-*disecovitrane*-5,11-*carbolactone* (17) as a gum (21 mg): $[\alpha]_D$ −36.4° (*c*, 1.86); $\nu_{max.}$ ($CHCl_3$) 1 750, 1 735, 1 705, 1 415, 1 390, 1 375, 1 220, 1 131, and 1 099 cm^{-1}; δ_H 0.93 (3 H, d, *J* 5.5 Hz), 1.43 (6 H, s), 2.16 (3 H, s), and 4.66 (2 H, s); δ_C 16.3 (q), 20.5 (q), 26.3 (q), 27.7 (t), 28.6 (t), 29.4 (t), 30.2 (q), 32.3 (t), 33.9 (t), 35.9 (d), 41.5 (d), 45.4 (s), 67.9 (t), 85.2 (s), 170.3 (s), 172.9 (s), and 203.6 (s); *m/z* 310 (M^+, 4%), 295 (7), 262 (7), 250 (6), 237 (100), 224 (7), 209 (42), 191 (20), 163 (7), 150 (46), 135 (9), 108 (23), 95 (9), 81 (9), and 47 (88).

Decarboxylation of the Acetoxy-keto-acid (16) *with Lead Tetra-acetate*.—To a solution of the acetoxy-keto-acid (16) (190 mg) in dry benzene (5 ml) and pyridine (0.3 ml) was added lead tetra-acetate (350 mg), and the reaction mixture was stirred at 20 °C for 2 h under nitrogen. The same procedures as for the hydroxy-keto-acid (13) gave the menthadiene (18) (34 mg) and the acetoxymenthene (19) (25 mg).

(1R,4S)-2-(4-*Acetoxy*-3-*oxobutyl*)-p-*mentha*-2,8-*diene* (18): $[\alpha]_D$ −29.3° (*c*, 1.38); $\nu_{max.}$ 3 060, 1 754, 1 735, 1 658, 1 642, 1 414, 1 227, 1 058, and 890 cm^{-1}; δ_H 1.04 (3 H, d, *J* 7.0 Hz), 1.71 (3 H, d, *J* 1.0 Hz), 2.16 (3 H, s), 4.66 (4 H, br s), and 5.24 (1 H, d, *J* 3.0 Hz); *m/z* 264 (M^+, 1%), 222 (3), 191 (2), 148 (18), 133

(8), 119 (7), 105 (10), 91 (13), 79 (14), 67 (6), 55 (10), and 43 (100).

(1R,4S)-8-*Acetoxy*-2-(4-*acetoxy*-3-*oxobutyl*)-p-*menth*-2-*ene* (19): $[\alpha]_D$ +17.6° (*c*, 1.45); $\nu_{max.}$ 1 754, 1 734, 1 730, 1 658, 1 413, 1 253, 1 223, 1 132, 1 057, and 1 014 cm^{-1}; δ_H 1.03 (3 H, d, *J* 7.5 Hz), 1.39 and 1.43 (each 3 H, s), 2.00 and 2.18 (each 3 H, s), 4.67 (4 H, s), and 5.26 (1 H, br s); *m/z* 263 ($[M - 61]^+$, 2%), 221 (1), 204 (1), 161 (14), 148 (10), 133 (7), 119 (8), 105 (15), 91 (13), 79 (12), 67 (8), 55 (16), and 43 (100).

Claisen-Schmidt Reaction of the α,β-*Unsaturated Ketone* (12) *with Benzaldehyde.*—To a solution of sodium hydroxide (23 mg) in water (0.3 ml) and methanol (1 ml) was added the α,β-unsaturated ketone (12) (235 mg) with stirring. Benzaldehyde (53 mg) was added to the solution at 0 °C, and the mixture stirred at 0 °C for 1 h and a further 12 h at room temperature. Work-up gave (1R,6R,7S,10R)-14-*acetoxy*-2-*benzylidenevitr*-4-*en*-3-*one* (20) as a gum (16 mg): $[\alpha]_D$ +229° (*c*, 0.80); $\lambda_{max.}$ 229 and 309 nm (ε 7 450 and 11 600); $\nu_{max.}$ ($CHCl_3$) 3 675, 3 510, 1 712, 1 643, 1 526, 1 408, 1 390, 1 382, 1 020, 960, and 905 cm^{-1}; δ_H 0.50 (3 H, d, *J* 7.0 Hz), 1.02 and 1.38 (each 3 H, s), 4.58 (2 H, d, *J* 1.5 Hz), and 7.3—8.2 (7 H, m); *m/z* 322 (M^+, 16%), 304 (5), 291 (4), 279 (4), 261 (5), 249 (4), 239 (6), 219 (4), 207 (6), 191 (6), 178 (8), 165 (8), 152 (5), 141 (5), 131 (5), 108 (21), 91 (28), 83 (100), 79 (26), 67 (9), 55 (15), 47 (43), and 41 (24).

Preparation of the Di-p-*bromobenzoate Derivative* (21) *of the* 1,3-*Diol* (7).—*p*-Bromobenzoyl chloride (80 mg) was added to the 1,3-diol (7) (40 mg) in dry pyridine (1 ml) and the mixture was refluxed at 90 °C for 8 h with stirring under nitrogen. The product, recovered in the usual way, was purified by p.l.c. to give (1R,4S,5S,6R,7S,10R)-*vitrane*-5,14-*diyl di*-p-*bromobenzoate* (21) (30 mg), m.p. 114—115 °C (from MeOH and chloroform, 2 : 1); $[\alpha]_D$ +8.5° (*c*, 1.18) (Found: C, 57.7; H, 5.45. $C_{29}H_{34}Br_2O_4$ requires C, 57.44; H, 5.65%); $\nu_{max.}$ ($CHCl_3$) 3 040, 1 712, 1 589, 1 483, 1 282, 1 270, 1 126, 1 110, 1 077, 1 019, and 852 cm^{-1}; δ_H 0.3—0.8 (2 H, m), 0.88 and 0.98 (each 3 H, s), 0.98 (3 H, d, *J* 7.0 Hz), 4.42 (2 H, d, *J* 8.0 Hz), 5.53 (1 H, d, *J* 4.0 Hz), 7.54 (2 H, d, *J* 9.0 Hz), 7.58 (2 H, d, *J* 9.0 Hz), and 7.94 (4 H, d, *J* 9.0 Hz); *m/z* 608, 606, and 604 (M^+, 1, 2, and 1%), 404 (4), 402 (4), 219 (12), 202 (100), 183 (54), 173 (7), 159 (29), 146 (16), 133 (12), 120 (20), 105 (17), 91 (14), 82 (20), 67 (13), 55 (17), and 41 (18).

Crystal Structure Determination of the Di-p-*Bromobenzoate* (21).—*Crystal data.* $C_{29}H_{34}Br_2O_4$, *M* = 606.5, Orthorhombic, *a* = 9.568(3), *b* = 11.290(1), *c* = 24.814(11) Å, *U* = 2681.5 $Å^3$, D_c = 1.50 g cm^{-3}, *Z* = 4, *F*(000) = 1 240, μ(Mo-K_α) = 32.4 cm^{-1}, space group $P2_12_12_1$.

The intensity data were collected on a Syntex R3 four-circle diffractometer using monochromated Mo-K_α radiation (λ = 0.7107 Å). The reflections of 1 170 were judged to be observed after correction for the Lorentz, polarization, and background effects. The positions of the two bromine atoms were determined from the Patterson synthesis. The subsequent electron density synthesis revealed the non-hydrogen atom skeleton, and the 34 hydrogen atoms were located using the difference electron density synthesis. Refinement by the full-matrix least-squares, using the anisotropic temperature factors, converged to a current *R* value of 0.073. At this stage, the anomalous scattering factor corrections for the bromine atoms were introduced into the structure-factor calculations to establish the absolute configuration. For the configuration (21), the *R* value was 0.070 whereas for the inverted configuration it was 0.081.[10] Further full-matrix least-squares iterations reduced the *R* factor to 0.067 for 1 170 reflections. The anisotropic thermal parameters, and the observed and calculated structure factors have been listed in Supplementary Publication No. 23774 (25 pp.).*

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* For details of the Supplementary Publications scheme, see Instructions for Authors (1984), *J. Chem. Soc., Perkin Trans. 1*, 1984, Issue 1.