

## Isolation and Characterisation of a Stable Ozonide during an Attempted Synthesis of Structural Analogues of Sarkomycin

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We describe the conversion of 2,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (1) into compounds resembling the antibiotic sarkomycin (3). An alternative synthetic pathway involving ozonolysis of (1) provided the crystalline ozonide (5), and the crystal structure of this compound showed that it existed in the envelope  $C_2$  conformation.

We have described<sup>1,2</sup> a number of methods for the preparation of 2,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (1), and its use in the synthesis of analogues of cocaine,<sup>1</sup> muscarine, and  $\alpha$ -multistriatin.<sup>3</sup> It occurred to us that this compound had the required structural features for elaboration into analogues of the cyclopentanoid antibiotics. This group includes methylenomycin A (2) and sarkomycin (3).<sup>4</sup> The former has demonstrated *in vitro* activity against both Gram-positive and Gram-negative organisms, while the latter has anti-tumour activity.

The bicyclic ketone (1) was easily converted into the  $\alpha$ -methylene ketones (4a) and (4b) *via* the  $\alpha$ -selenophenyl derivatives (lithium di-isopropylamide and phenylseleninyl chloride), with subsequent elimination of phenylseleninic acid upon addition of hydrogen peroxide.<sup>5</sup> Compound (4a) exhibited *in vitro* activity against the L1210 tumour cell line, and this encouraged us to prepare structures bearing a greater structural resemblance to sarkomycin.

Our strategy was to involve ozonolysis of (1), and this proved to be more interesting than we had anticipated. Ozonolysis in *n*-hexane led to the slow deposition of a crystalline product, the same compound being obtained by ozonolysis in dichloromethane and ethyl acetate followed by flash chromatography. The yields of pure product were good: 80% (from hexane), 65% ( $\text{CH}_2\text{Cl}_2$ ), and 66% (EtOAc). It gave a positive peroxide test (KI impregnated paper), and the  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectra were fully consistent with the simple ozonide (5). This was, however, surprisingly stable, being inert to oxidation with Jones reagent, and melting with decomposition at 107–110 °C. Further chemical evidence for the structure was obtained through reduction with hydrogen over 5% palladium on charcoal, which provided the symmetrical hemiacetal (6a). Finally, an X-ray crystal structure provided definitive proof of the structure (see Figure); the crystallographic data are discussed below.

We have also carried out the ozonolysis in methanol, and in this case the acetal (6b) was obtained in 45% yield, after flash chromatography, together with 11% of the ozonide (5). Treatment of (6b) with dimethyl sulphide<sup>6</sup> gave the hemiacetal (6c), oxidation of which with Jones' reagent yielded the lactone (7). Thus far, we have been frustrated in our efforts to convert this into  $\alpha$ -methylene derivatives due, in the main, to the base sensitivity of the lactone; we have also encountered similar difficulties with compounds (5) and (6c). Our present strategy involves selective ozonolysis<sup>7</sup> of the  $\alpha$ -methylene ketone (4a), and our initial efforts have been rewarded with the production of the desired cleavage product (8), albeit in low (25%) yield.

**Discussion of the Crystal Structure.**—The structure consists of discrete molecules of (5) and is shown in the Figure together with the atomic numbering scheme. This confirms the formation of the ozonide grouping between atoms C(1) and

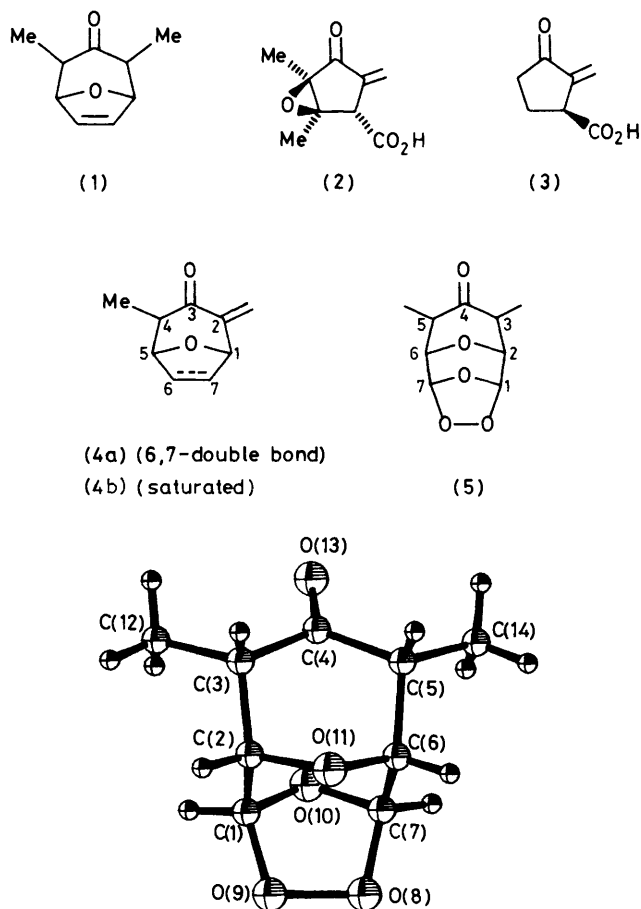
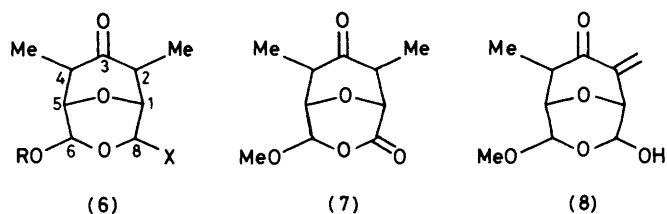
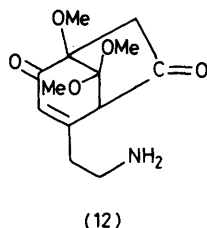
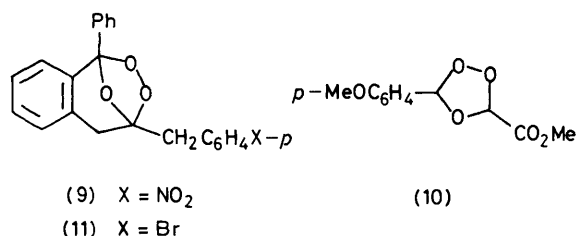


Figure. Structure and atomic numbering scheme of the ozonide (5)



- a; X = OH, R = H  
 b; X = OOH, R = Me  
 c; X = OH, R = Me

C(7). There have been few structural studies of the geometry of the ozonide group. Several simple ozonides have been studied *via* their microwave spectrum<sup>8</sup> *viz* ethylene ozonide,



propylene ozonide and fluoroethylene ozonide. The dimensions of all three molecules are similar with C-O-O-C torsion angles of 49.4, 49.2, and 46.0° respectively. Other dimensions include O-O bonds of *ca.* 1.46 Å and angles C-O-O 99.2–101.1, O-C-O 104.6–107.6, and C-O-C 104.6–105.5°. These dimensions are rather different from those observed in crystal structures where the molecules are more complex.

We searched the Cambridge Data Centre files<sup>9</sup> and found only four structures containing this five-membered ring. The torsion angles vary considerably ranging from 0 to 15°. Thus in 1,4-epoxy-4-(4-nitrophenylmethyl)-1-phenyl-1*H*-2,3-benzodioxepin-5(4*H*)-one (9),<sup>10</sup> the torsion angle is -1.0°. In 3-methoxycarbonyl-5-*p*-methoxyphenyl-1,2,4-trioxacyclopentane (10),<sup>11</sup> the five-membered ring is disordered and no conclusions can be drawn as to its conformation. In 4-*p*-bromobenzyl-1,4-epoxy-1-phenyl-1*H*-2,3-benzodioxepin-5(4*H*)-one (11),<sup>12</sup> the torsion angle is 15°. In the related compound 4-(2-aminoethyl)-1,8,8-trimethoxybicyclo[3.2.1]oct-3-ene-2,6-dione (12),<sup>13</sup> the angle is 5°. It is particularly interesting that the two similar compounds (9), (11) which only differ *via* a 4-bromo- or 4-nitro-group which is well away from the ozonide grouping<sup>10,12</sup> have torsion angles of 1 and 15°. This must be a consequence of intermolecular packing effects. But intermolecular forces cannot account for the major difference between the low O-C-C-O torsion angle in these compounds and the 46–49° found in the sample ozonides.

It seems obvious that the most stable form of the ozonide ring has a torsion angle of *ca.* 45°. The low torsion angle and envelope conformation in (5) and the other crystal structures must be a consequence of the fused ring system on the carbon atoms C(1) and C(7) (using our numbering scheme). In all these structures the single oxygen O(11) is the unique atom in the envelope conformation. (It is perhaps worthy of note that structure (10) with the disordered ring<sup>11</sup> has no such fused rings and therefore no such steric strain. Many of the earlier studies of ozonide rings by electron diffraction also indicated disordered structures.)

The bond lengths and angles in the five-membered rings are also dissimilar in the simple molecules and the crystal structures. For example, the C-O-O angles are larger *viz* 103.3, 104.5° in (5) and C-O-C is smaller [98.8 in (5)]. Again we read little significance into these values which could be a consequence of the different ring conformation and possible intramolecular forces.

As far as the present structure is concerned there is a close

intramolecular contact of 2.66 Å between C(4) and O(10). This suggests that one reason for the envelope conformation of the ozonide ring is the need to maximise this distance. Indeed the structure as a whole has C<sub>s</sub> symmetry within experimental error (though without crystallising in *P2<sub>1</sub>/m*). The other ring conformations are as expected. As shown in Table 3 (p. 170), they are distorted chairs. There are no intermolecular contacts less than the sum of van der Waals radii.

### Experimental

I.r. spectra were recorded with a Perkin-Elmer 157 double-beam grating spectrophotometer (liquid films for oils and Nujol mulls for solids); <sup>1</sup>H n.m.r. spectra were recorded with a Varian T-60 (60 MHz) or Varian HA 100 (100 MHz) instruments (tetramethylsilane as internal standard); <sup>13</sup>C n.m.r. spectra were recorded at the City of London Polytechnic on a Jeol FX90Q (90 MHz) instrument; and mass spectra were recorded on an A.E.I. MS12 spectrometer. Kieselgel GF<sub>254+354</sub> (Merck) was used for analytical t.l.c., and flash chromatography was performed with Merck silica gel (230–400 mesh). Organic solvents were distilled from calcium hydride when required anhydrous.

**2,4-Dimethyl-2-selenophenyl-8-oxabicyclo[3.2.1]oct-6-en-3-one.**—Lithium di-isopropylamide (*ca.* 8 mmol) was prepared from di-isopropylamine (1.2 ml) and *n*-butyl-lithium (5.3 ml of a 1.55*M*-solution in hexane) in dry THF (7 ml) during 20 min at -78 °C. To this was added 2,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (1) (1.01 g, 6.7 mmol; prepared as previously described<sup>1</sup>) in THF (7 ml), and the resultant solution was stirred under nitrogen at -78 °C for 40 min. The enolate thus formed was treated with phenylseleninyl chloride (1.89 g, *ca.* 10 mmol) in THF (7 ml) by dropwise addition of the reagent over a period of 20 min. The mixture was then stirred for an hour at -78 °C, and then allowed to warm to room temperature during the next 2 h. The reaction was quenched by addition of HCl (40 ml of 0.5*M*), and the product was extracted into ether. This ethereal extract was then washed with brine, dried, and concentrated to yield an orange solid. Flash chromatography with dichloromethane–light petroleum (b.p. 40–60 °C) (4 : 1) provided a pale yellow solid (1.49 g, 73%). A small sample was recrystallised from light petroleum to give white crystals, m.p. 146–148 °C; *v*<sub>max</sub>, 1 692 (C=O), 1 045, 940, 851, and 836 cm<sup>-1</sup>;  $\delta$  (100 MHz, CDCl<sub>3</sub>) 1.0 and 1.03 (6 H, d and s respectively, 2 × Me), 3.75 (1 H, dq, *J* 7 and 4.5 Hz, 4-H), 4.85 (1 H, dd, *J*<sub>4,5</sub> 4.5 Hz, and *J*<sub>5,6</sub> 1.5 Hz, 5-H), 4.93 (1 H, d, *J* 1.5 Hz, 1-H), 6.35 and 6.45 (2 H, s × dd, *J* 1.5 and 6 Hz, 6-H and 7-H), 7.2–7.6 (5 H, phenyl ring). The compound was relatively unstable and was not characterised further.

**4-Methyl-2-methylene-8-oxabicyclo[3.2.1]oct-6-en-3-one (4a).**—The above compound (2.25 g, 7.4 mmol) in THF (40 ml) containing acetic acid (1.65 ml) was held at 0 °C during the addition of hydrogen peroxide (5.0 ml of a 30% solution). The mixture was then stirred at the same temperature for 1 h, prior to addition of saturated aqueous sodium hydrogen carbonate (80 ml). The product was extracted into ether, and this extract was washed with brine, dried, and concentrated to yield an oil. Flash chromatography of this with ether–light petroleum (1 : 1) as eluant provided a clear oil (0.88 g, 80%), which was pure by t.l.c. analysis, *v*<sub>max</sub>, 3 090 (=CH), 1 700 (C=O), 1 631 (C=C), 1 341, 1 141, 1 059, 935, 915, and 814 cm<sup>-1</sup>;  $\delta$  (100 MHz, CDCl<sub>3</sub>) 1.05 (3 H, d, *J* 7 Hz, 4-Me), 2.8 (1 H, dq, *J* 7 Hz, and *J*<sub>4,5</sub> 5 Hz, 4-H), 4.9 (1 H, d, *J* 5 Hz, 5-H), 5.1 (1 H, d, *J* 1 Hz, exocyclic CH=), 5.21 (1 H, s, 1-H), 5.85

(1 H, d,  $J$  1 Hz, exocyclic CH=), 6.33 (2 H, s, 6-H and 7-H);  $m/z$  (%)  $M^+$  150.0688 (95) ( $C_9H_{10}O_2$  requires  $M$ , 150.0681), 121 (100), 107 (42), 94 (50), 81 (52), 79 (42), 77 (48), 66 (44), and 65 (46).

**4-Methyl-2-methylene-8-oxabicyclo[3.2.1]octan-3-one (4b).**—This compound was prepared from 2,4-dimethyl-8-oxabicyclo[3.2.1]octan-3-one (prepared as previously described<sup>1</sup>) via the  $\alpha$ -selenophenyl derivative exactly as described for compound (4a) in an overall yield for the two steps of 66%. It was a colourless oil homogeneous by t.l.c.;  $\nu_{\max}$  1 700 (C=O), 1 629 (C=C), 1 378, 1 155, 1 050, 945, 895, and 798  $cm^{-1}$ ;  $\delta$  ( $CDCl_3$ , 100 MHz) 1.06 (3 H, d,  $J$  7 Hz, 4-Me), 1.7—2.3 (4 H, m, 6-H and 7-H), 2.8 (1 H, m, 4-H), 4.51 (1 H, m, 5-H), 4.98 (1 H, m, 1-H), 5.1 (1 H, dd,  $J$  0.75 Hz and 1.2 Hz, exocyclic CH=), and 5.8 (1 H, dd,  $J$  0.75 Hz and 1.5 Hz, exocyclic CH=);  $m/z$  (100%),  $M^+$  152.0839 (52) ( $C_9H_{12}O_2$  requires  $M^+$  152.0837), 134 (42), 124 (65), 123 (85), 109 (66), 95 (74), 67 (74), 56 (58), 55 (54), and 41 (100).

**3,5-Dimethyl-8,9,10,11-tetraoxatricyclo[5.2.1.1<sup>2,6</sup>]undecan-4-one (5).**—Ozone was passed into a solution of 2,4-dimethyl-oxabicyclo[3.2.1]oct-6-en-3-one (1) (1.01 g, 6.66 mmol) dissolved in ethyl acetate (110 ml) held at 0 °C. After ca. 20 min the reaction was judged to be complete since ozone began issuing from the exit tube of the flask. The solvent was removed under reduced pressure and the product was purified by flash chromatography using ether–dichloromethane as eluant. A white crystalline material was obtained (885 mg, 66%), m.p. 107—110 °C,  $\nu_{\max}$  1 707 (C=O), 1 178, 1 088, 1 062, 939, 891, and 867  $cm^{-1}$ ;  $\delta_H$  ( $CDCl_3$ , 60 MHz), 1.16 (6 H, d,  $J$  7 Hz, 2 Me), 2.8—3.1 (2 H, m 3-H and 5-H), 4.1 (2 H, dt,  $J$  6 and 1 Hz, 2-H and 6-H), 5.7 (2 H, m, H-1 and H-7).  $\delta_C$  ( $CDCl_3$ ), 9.48 (dq,  $J$  128.18 and 4.88 Hz, 2  $\times$  Me), 45.67 (d,  $J$  126.95, C-3 and C-5), 77.09 (d,  $J$  152.58, C-2 and C-6), 99.90 (dm,  $J$  172.11 and 4.88 Hz, C-1 and C-7), 207.22 (s, C-4) (Found: C, 54.4; H, 6.15.  $C_9H_{12}O_5$  requires C, 54.00; H, 6.04%); mass spectrum unobtainable due to decomposition.

**6,8-Dihydroxy-2,4-dimethyl-7,9-dioxabicyclo[3.3.1]nonan-3-one (6a).**—The ozonide (5) (1.195 g, 5.98 mmol) dissolved in dichloromethane (40 ml) was reduced to the diol (6a) using 10% palladium on charcoal at room temperature. After filtration through Hyflo, the solution was concentrated to yield a viscous oil which crystallised upon standing; yield 1.06 g (87%). T.l.c. using ether–methanol (98 : 2) showed one pure component,  $R_F$  0.24, m.p. 140—146 °C;  $\nu_{\max}$  3 440 (OH), 1 707 (C=O), 1 181, 1 171, 1 106, 1 049, 1 000, 972, 890, and 845  $cm^{-1}$ ;  $\delta$  ( $CDCl_3$ ) 1.0 (6 H, d,  $J$  7 Hz, 2  $\times$  Me), 2.75—3.2 (2 H, m, 2-H and 4-H), 4.2 (2 H, d,  $J$  Hz, 1-H and 5-H), 4.95br (4 H, s, exchanges with  $D_2O$  to give 2 H, s, 2  $\times$  OH and 6-H and 8-H);  $m/z$  184 ( $M^+$  —  $H_2O$ ), 155, 127, 109, 97, 85, 71, 69, 57, 55, and 43 (Found: C, 53.45; H, 6.9.  $C_9H_{14}O_5$  requires C, 53.46; H, 6.98%).

**8-Hydroperoxy-6-methoxy-2,4-dimethyl-7,9-dioxabicyclo[3.3.1]nonan-3-one (6b).**—Ozonolysis of (1) (2.02 g, 13.25 mmol) in methanol (110 ml) at 0 °C was judged to be complete after 45 min, and after removal of the solvent under reduced pressure, flash chromatography with diethyl ether– $CH_2Cl_2$  (9 : 1) as eluant provided the ozonide (6a) (0.28 g) and the hydroperoxide (6b) (1.28 g). The latter was a white crystalline solid after recrystallisation from diethyl ether–hexane, m.p. 100—101 °C (decomp.);  $\nu_{\max}$  3 335 (OOH), 1 720 (C=O), 1 185, 1 068, 941, 919, and 855  $cm^{-1}$ ;  $\delta$  ( $CDCl_3$ ) 1.08 (6 H, d, 7 Hz, 2  $\times$  Me), 2.8—3.2 (2 H, m, 2-H and 4-H), 3.62 (3 H, s, OMe), 4.2 (1 H, d,  $J$  6.5 Hz, 5-H), 4.35 (1 H, d,

$J$  6.5 Hz, 1-H), 4.5 (1 H, s, 6-H), 5.01 (1 H, s, 8-H), 9.25br (1 H, s, exchanged with  $D_2O$ , OOH);  $m/z$  214 ( $M^+$  —  $H_2O$ ), 199, 196, 168, 155, 125, 111, 109, 101, 85, 71, 69, 57, 55, and 41 (Found: C, 51.75; H, 7.0.  $C_{10}H_{16}O_6$  requires C, 51.72; H, 6.94%).

**6-Methoxy-2,4-dimethyl-7,9-dioxabicyclo[3.3.1]nonane-3,8-dione (7).**—The hydroperoxide (6b) was reduced to the hemiacetal (6c) using dimethyl sulphide in methanol, and yielded a white crystalline solid (m.p. 125—127 °C) after flash chromatography using diethyl ether–ethyl acetate (1 : 1) as eluant. This compound (3.47 g, 16.07 mmol) was dissolved in diethyl ether– $CH_2Cl_2$  (9 : 1; 75 ml), and treated with Jones' reagent at 0 °C until oxidation was judged to be complete. The aqueous layer was separated and extracted with ether. The combined organic extract was washed with water, 10% aqueous  $KHCO_3$  and brine, and then dried and concentrated to yield a solid which was purified by flash chromatography using ether as eluant; yield 1.42 g (41%) of a white crystalline solid, which could be recrystallised from hexane–diethyl ether to provide an analytical sample, m.p. 133—134 °C;  $\nu_{\max}$  1 758 (lactone C=O), 1 711 (ketone C=O), 1 195, 1 122, 1 086, 1 060, 1 021, 977, and 940  $cm^{-1}$ ;  $\delta$  ( $CDCl_3$ ) 1.1 (6 H, t,  $J$  7 Hz, 2  $\times$  Me), 2.8—3.3 (2 H, m, 2-H and 4-H), 3.58 (3 H, s, OMe), 4.3 (1 H, d,  $J$  7 Hz, 5-H), 4.65 (1 H, d,  $J$  6.5 Hz, 1-H), and 5.09 (1 H, s, 6-H) (Found: C, 56.05; H, 6.65.  $C_{10}H_{14}O_5$  requires C, 56.07; H, 6.59%).

**8-Hydroxy-6-methoxy-4-methyl-2-methylene-7,9-dioxabicyclo[3.3.1]nonan-3-one (8).**—Compound (4a) (410 mg, 2.7 mmol) was dissolved in methanol (40 ml) and a trace of Fat Red 7B dye was added. The solution was cooled to –78 °C and ozone was passed through until the colour changed to yellow (7.5 min). T.l.c. analysis showed the presence of a trace of (4a), and the appearance of a new u.v. positive compound of lower  $R_F$  value. Dimethyl sulphide (0.25 ml, 3.3 mmol) was added, and the solution was allowed to warm to room temperature. The solvent was removed under reduced pressure, and the product was purified by flash chromatography with ether as eluant. A crystalline product was obtained (157 mg, 27%), and this could be further purified by recrystallisation from  $CHCl_3$ –diethyl ether–light petroleum mixtures; it had m.p. 126—130 °C;  $\nu_{\max}$  3 440 (OH), 1 700 (C=O), 1 635 (C=C), 1 182, 1 117, 1 044, 1 020, 980, 953, 931, 849, and 841  $cm^{-1}$ ;  $\delta$  ( $CDCl_3$ ) 1.16 (3 H, d, 7 Hz,  $CH_3$ ), 2.8—3.1 (1 H, m, 4-H), 3.56 (3 H, s, OMe), 4.16 (1 H, d,  $J$  7 Hz, 5-H), 4.35 (1 H, s, 6-H), 4.45 (1 H, d,  $J$  Hz, exchanges with  $D_2O$ , OH), 4.6 (1 H, s, 1-H), 4.9 (1 H, d,  $J$  Hz, 8-H), 5.28 (1 H, m,  $J$  1 and 0.75 Hz, C=CH), and 6.03 (1 H, m, C=CH) (Found: C, 56.0; H, 6.65.  $C_{10}H_{14}O_5$  requires C, 56.07; H, 6.59%).

**Structure Determination.**—Crystals of (5) were obtained as described above.

**Crystal data.**  $C_9H_{12}O_5$ ,  $M = 200.1$ , Monoclinic,  $a = 7.702(7)$ ,  $b = 5.538(8)$ ,  $c = 11.012(12)$  Å,  $\beta = 98.2(1)^\circ$ ,  $U = 464.9$  Å<sup>3</sup>,  $Z = 2$ ,  $F(000) = 212$ ,  $D_m = 1.42$ ,  $D_c = 1.42$  g  $cm^{-3}$ ,  $\mu$  (Mo- $K\alpha$ ) = 1.26  $cm^{-1}$ . Space group  $P2_1$  from systematic absences  $0k0$ ,  $k = 2n + 1$  and the successful structure determination. The crystal of approximate size 0.03  $\times$  0.03  $\times$  0.04 mm was mounted on a Stoe STADI2 diffractometer and data was collected via variable width  $\omega$  scans. Background counts were 20 s and the scan rate of 0.033°/s was applied to a width of  $(1.5 + \sin \mu / \tan \theta)$ . 910 Independent reflections were measured with a  $2\theta$  maximum of 40° using Mo- $K\alpha$  radiation. Absorption and extinction corrections were not applied. The structure was solved using Multan78.<sup>14</sup> The carbon and oxygen atoms were then refined anisotropically. The hydrogen

**Table 1.** Atomic co-ordinates ( $\times 10^4$ ) with estimated standard deviations in parentheses

Atom	x	y	z
O(8)	8 517(11)	2 197(19)	5 271(7)
O(9)	6 805(11)	3 444(21)	5 313(7)
O(10)	8 014(9)	4 839(15)	3 738(7)
O(11)	6 268(11)	285(0)	3 404(7)
O(13)	7 222(14)	4 943(23)	746(8)
C(1)	6 368(14)	4 382(24)	4 102(11)
C(2)	5 367(15)	2 514(23)	3 282(10)
C(3)	5 115(17)	3 293(23)	1 923(11)
C(4)	6 880(19)	3 419(27)	1 448(11)
C(5)	8 078(18)	1 256(25)	1 841(12)
C(6)	8 051(17)	654(22)	3 188(11)
C(7)	8 834(16)	2 587(23)	4 074(11)
C(12)	4 072(19)	5 667(28)	1 716(13)
C(14)	9 928(22)	1 656(33)	1 533(16)

**Table 2.** Molecular dimensions in (1)

C(2)-C(1)	1.511(16) Å
C(2)-C(3)	1.543(16)
C(3)-C(4)	1.526(17)
C(3)-C(12)	1.540(18)
C(5)-C(4)	1.536(19)
C(5)-C(14)	1.527(17)
C(6)-C(5)	1.523(16)
C(6)-C(7)	1.515(16)
O(9)-C(1)	1.426(14)
O(8)-C(7)	1.391(14)
O(13)-C(4)	1.198(15)
O(11)-C(6)	1.441(14)
O(11)-C(2)	1.413(13)
O(10)-C(1)	1.406(13)
O(10)-C(7)	1.423(13)
O(9)-O(8)	1.495(11)
O(10)-C(1)-C(2)	110.9(9)°
O(10)-C(1)-O(9)	103.3(7)
C(2)-C(1)-O(9)	110.0(9)
O(11)-C(2)-C(3)	109.2(9)
O(11)-C(2)-C(1)	109.9(8)
C(3)-C(2)-C(1)	111.8(9)
C(2)-C(3)-C(4)	110.5(9)
C(2)-C(3)-C(12)	111.9(10)
C(4)-C(3)-C(12)	112.4(10)
C(3)-C(4)-O(13)	122.8(13)
C(3)-C(4)-C(5)	113.3(10)
O(13)-C(4)-C(5)	123.5(12)
C(6)-C(5)-C(4)	110.8(9)
C(6)-C(5)-C(14)	113.0(12)
C(4)-C(5)-C(14)	111.5(11)
O(11)-C(6)-C(7)	107.2(9)
O(11)-C(6)-C(5)	109.7(10)
C(7)-C(6)-C(5)	114.4(9)
O(10)-C(7)-C(6)	109.3(9)
O(10)-C(7)-O(8)	104.5(8)
C(6)-C(7)-O(8)	113.1(10)
O(9)-O(8)-C(7)	103.4(7)
O(8)-O(9)-C(1)	103.3(7)
C(1)-O(10)-C(7)	98.8(7)
C(6)-O(11)-C(2)	109.1(7)

atoms were placed in tetrahedral positions. The hydrogen atoms on the two methyl groups were located by rigid body refinement. Three thermal parameters were refined for the hydrogen atoms, one for the six non-methyl hydrogens and for each set of three in a methyl group. We were unable to distinguish between possible enantiomorphs by reversing co-

**Table 3.** Torsion angles in (1)

(a) Ozonide ring		
C(1)-O(9)-O(8)-C(7)	0.4	
O(9)-O(8)-C(7)-O(10)	29.9	
O(8)-C(7)-O(10)-C(1)	-49.3	
C(7)-O(10)-C(1)-O(9)	48.7	
O(10)-C(1)-O(9)-O(8)	-30.7	
(b) Other rings		
C(1)-C(2)-O(11)-C(6)	-53.6	
C(2)-O(11)-C(6)-C(7)	55.7	
O(11)-C(6)-C(7)-O(10)	-68.6	
C(6)-C(7)-O(10)-C(1)	72.1	
C(7)-O(10)-C(1)-C(2)	-69.1	
O(10)-C(1)-C(2)-O(11)	63.8	
C(2)-C(3)-C(4)-C(5)	44.1	
C(3)-C(4)-C(5)-C(6)	-43.8	
C(4)-C(5)-C(6)-O(11)	54.6	
C(5)-C(6)-O(11)-C(2)	-69.1	
C(6)-O(11)-C(2)-C(3)	69.3	
O(11)-C(2)-C(3)-C(4)	-56.2	

**Table 4.** Least-squares planes for (1) (distances of atoms from the planes are given in Å). Atoms marked with an asterisk do not contribute to the plane

Plane 1: O(10) -0.00, O(11) 0.00, O(13) 0.00, C(4) -0.01.  
 Plane 2: O(8) -0.00, O(9) 0.00, C(1) -0.00, C(7) 0.00, O(10)\* 0.69.  
 Plane 3: C(1) -0.02, C(2) 0.02, C(6) -0.02, C(7) 0.02, O(10)\* -0.82, O(11)\* 0.64.  
 Plane 4: C(2) -0.00, C(3) -0.00, C(6) 0.00, C(5) 0.00, C(4)\* 0.55, O(11)\* -0.73.  
 Plane 5: C(3) -0.01, C(4) 0.03, C(5) -0.01, C(12)\* 0.27, O(13) -0.01, C(14)\* 0.28.

Angles between planes: 1 and 2 89.6, 1 and 3 89.2, 1 and 4 89.4, 1 and 5 89.2, 2 and 3 68.6, 2 and 4 1.8, 2 and 5 36.0, 3 and 4 67.1, 3 and 5 75.4, 4 and 5 37.5

ordinates. The structure was refined by full-matrix least-squares using Shelx76.<sup>15</sup> 577 Data with  $I > 2\sigma(I)$  were used. The weighting scheme was chosen to give equivalent values of  $\omega\Delta^2$  over ranges of  $F_0$  and  $\sin\theta/\lambda$ . This was  $\omega = 1/[\sigma^2(F) + 0.003 F^2]$  where  $\sigma(F)$  was taken from counting statistics. All non-hydrogen atoms were refined anisotropically. Scattering factors were taken from International Tables.<sup>16</sup> Calculations were made using Shelx76 on the CDC 7600 computer at the University of Manchester Computer Centre. The final  $R$  value was 0.083. Atomic co-ordinates are listed in Table 1. Details of interatomic distances and angles are listed in Table 2 and torsion angles and least-squares planes in Tables 3 and 4 respectively. The anisotropic thermal parameters, observed and calculated structure factors and hydrogen atom positions are given in a Supplementary Publication [SUP No. 23442 (6 pp.)].†

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† For details of the Supplementary publications scheme, see Notice to Authors No. 7, *J. Chem. Soc., Perkin Trans. 1*, 1981, Index Issue.

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