

The Dimerization of the Chromene, Precocene II

Braulio M. Fraga,* Victor P. García, Antonio G. González, and Melchor G. Hernandez
Instituto de Productos Naturales Orgánicos, CSIC, Carret. La Esperanza 2, La Laguna, Tenerife, Spain
 James R. Hanson and Peter B. Hitchcock
School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

The dimerization of precocene II with different Lewis acids has been studied. Besides $C_{22}H_{32}O_6$ dimeric products, two further dimers, containing a tetrahydrofuran ring, were isolated and their structures established by spectroscopic and X-ray analysis. Since the furans were formed in the presence of SiO_2-AgNO_3 or SiO_2-FeCl_3 and not with SiO_2-ZnBr_2 , it is possible that they arise by one-electron-transfer oxidation.

In the course of studies on the constituents of *Eupatorium sternbergianum* (Compositae),¹ the major component, precocene II² (ageratochromene³) (1) was isolated by chromatography on silica. Some fractions were contaminated with other products and were subjected to further chromatography on silica gel impregnated with silver nitrate (20%). This afforded three dimeric products (A, B, and C) which were shown in a separate experiment to have arisen by the action of silver nitrate-silica gel on precocene II. Their structure, stereochemistry and possible mode of formation, is the subject of this paper.

The first, least polar compound A, had analytical and high resolution mass spectral data (M^+ , 440.2191) corresponding to $C_{26}H_{32}O_6$. Its ¹H n.m.r. and u.v. data showed that it was identical with a compound previously obtained⁴⁻⁶ by Kasturi from *Ageratum conyzoides* and also obtained by the action of iodine in chloroform or sulphuric acid-acetic acid on ageratochromene. It had been tentatively assigned structure (3) on the basis of its ¹H n.m.r. data. However our ¹H n.m.r. data would not completely exclude isomeric structures and to overcome such ambiguity the structure was confirmed by an X-ray analysis (see Figure 1). The mass spectrum showed significant ions at m/z 221 and 219 corresponding to the monomeric fragments (5) and (6).

The second dimer, compound B, had mass spectral data (M^+ , 456.2183) corresponding to $C_{26}H_{32}O_7$. Its u.v. spectrum lacked the absorption (λ_{max} , 323 nm) typical of a chromene. The ¹H n.m.r. spectrum, which suggested structure (7), contained singlets at δ 6.98 and 7.11 (5-H and 5'-H), 6.52 and 6.54 (8-H and 8'-H) and doublets at δ 4.94 (J 7 Hz, 4-H) and 4.66 (J 11 Hz, 4'-H). Irradiation at δ 4.94 and 4.66 led to the collapse of signals at δ 2.52 (triplet, J 7 Hz) and 1.82 (quartet, J 7 and 11 Hz). Although the position of the resonances and the magnitude of the coupling constants could be accommodated by structure (7), they would not exclude isomeric tetrahydrofurans. Hence the structure was confirmed by an X-ray analysis (see Figure 2). The mass spectral fragmentation pattern can be accommodated in Scheme 1, in which the predominant fragmentation occurs adjacent to the ether linkage.

The third product, dimer C, was isomeric with compound B. Whilst their u.v. and mass spectra were almost identical, the ¹H n.m.r. spectrum of C showed that it was a substance of symmetrical structure. The aromatic signals (δ 6.4 and 6.8, each 2 H) were assigned to the C-8 and C-5 protons respectively, whilst the 3-H and 4-H resonances appeared as doublets (J 7 Hz) at δ 2.43 and 4.74 respectively. Whilst this could be accommodated in structure (8), there was a potential ambiguity in the orientation of the tetrahydrofuran ring, which was clarified by X-ray analysis (see Figure 3). Comparison of structures (7) and (8) (Figures 2 and 3) showed that (8) is a

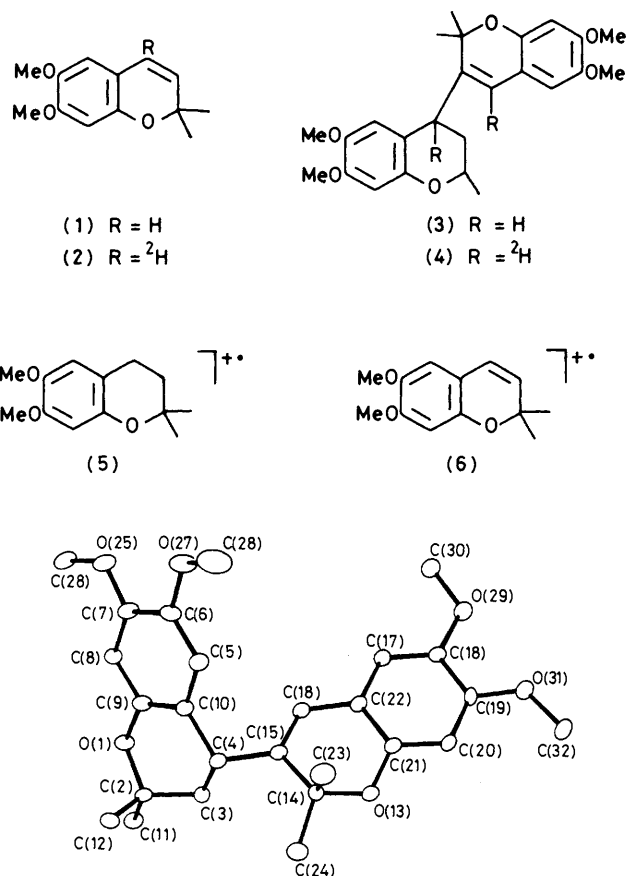


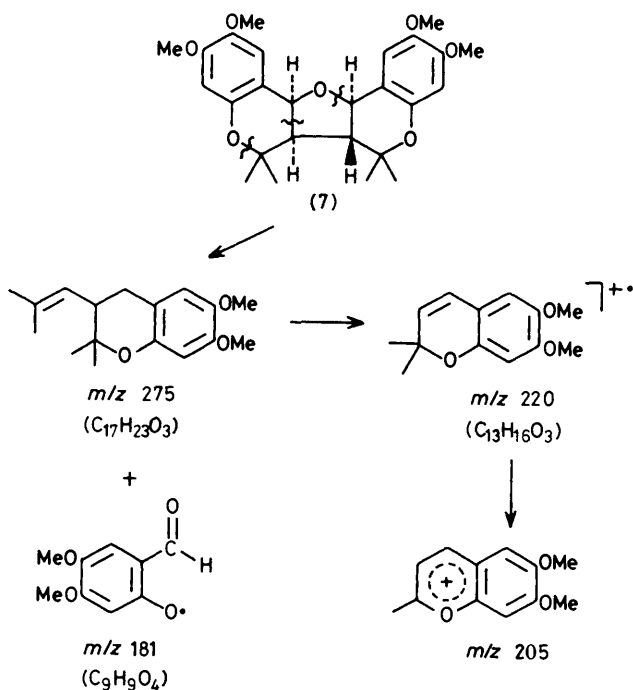
Figure 1. An ORTEP* drawing of dimer A

(* C. K. Johnson, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965).

more staggered structure in which the interactions between two of the methyl groups are reduced.

When precocene II (1) was adsorbed on silica-silver nitrate for 20 days, the dimers A (3) and C (8) were formed in 22 and 64% yields respectively. The 3-nitrochromene (10) was also obtained in 10% yield. The formation of the dimer C (8) rather than B (7) with the extended reaction time is indicative of the relief of steric strain in (8) and the ease of fission of the benzylic furan oxygen-carbon bond inherent in structure (7).

The structure of the nitrochromene followed from its ¹H n.m.r. spectrum which showed singlet signals at δ 6.71 (5-H), 6.48 (8-H), and 7.68 (4-H) together with methyl



Scheme 1.

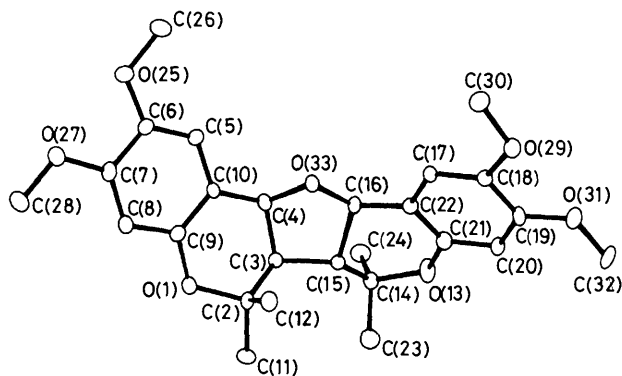


Figure 2. An ORTEP * drawing of dimer B. (* See reference given in caption to Figure 1)

signals at δ 1.75 and methoxy signals at 3.88 and 3.92. Conclusive evidence arose from the nitration of [4- 2H]precocene II (2) which was synthesized as follows. The chromanone (12) was obtained in accordance with the literature procedure.⁷ Reduction with lithium aluminium deuteride and dehydration of the resultant alcohol with acid afforded, after chromatography, [4- 2H]precocene II (2) and minor quantities of the corresponding deuteriated dimer A (4). When (2) was treated with silver nitrate-silica gel as in experiment 2b, the nitrochromene (11) retained the deuterium (M^+ , 266.1003; no 1H n.m.r. signal at δ 7.68) thus locating the nitro group at C-3 in accordance with the stability of benzylic carbocations in this series. This reaction also afforded the deuteriated dimer C (9).

The 1H n.m.r. spectra of the deuteriated dimers A (4) and C (9) lacked the signals at δ 3.52 (1 H) and 6.02 (1 H) in the first, and 4.74 (2 H) in the second, confirming the assignments in the unlabelled compounds.

Although column chromatography over silver nitrate-silica gel has been reported⁸ to lead to aromatic nitration,

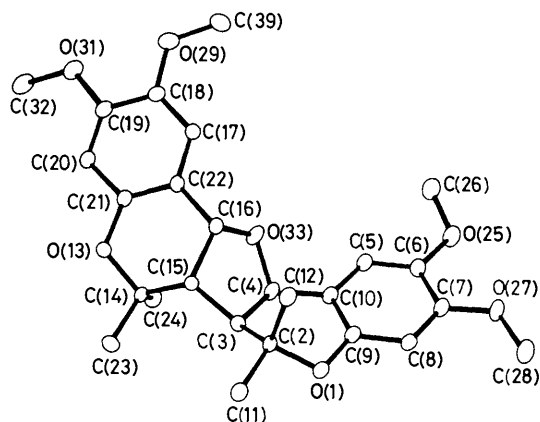
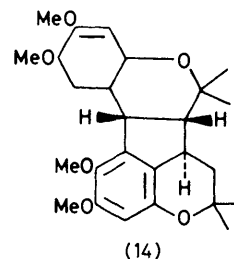
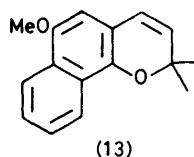
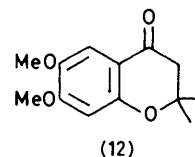
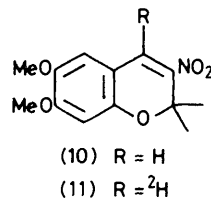
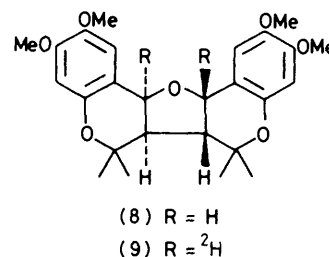


Figure 3. An ORTEP * drawing of dimer C. (* See reference given in caption to Figure 1)



this is the first time that it has been reported on a chromene double bond. Both the nitration and the formation of the dimers must be influenced by the presence of the methoxy group at C-7 which would stabilize a benzylic carbonium ion. Although unsubstituted chromenes also undergo dimerization on treatment with acid,⁹ the carbon skeleton of the products differs from that obtained with these substituted chromenes. Moreover lapachenole (13) dimerizes¹⁰ to give a product analogous to the dimer D (14) (*vide infra*).

Treatment of a solution of precocene II (1) in light petroleum with silver nitrate-silica gel (20%) gave the dimers B (7) and C (8). When the solution was more concentrated the dimer C (8), the nitrochromene (10) and two further inseparable minor dimers were obtained.

Ferric chloride was examined as an alternative Lewis acid. When a solution of precocene II (1) in light petroleum was treated with silica impregnated with ferric chloride (7.5%), the

dimers A (3) and C (8) were obtained in 20 and 48% yield respectively. Mazur *et al.* have used this supported reagent for the dehydration and rearrangement of *t*-alcohols,^{11,12} for the oxidation and coupling of aromatic methyl ethers,^{13,14} and the cleavage of benzyl ethers.¹⁵ When zinc bromide adsorbed on silica (7.5%) was used, only the dimers A (3) and D (14) were obtained. As expected for a reagent which is not a one-electron transfer oxidant, dimers of the tetrahydrofuran type related to B and C were not obtained. The dimer D (14) was identical with that reported by Kasturi⁶ as arising from the treatment of precocene II (1) with protic acids.

The formation of the dimers A (3), B (7) and C (8) can be rationalized in the following manner (see Scheme 2). Initial complex formation by the Lewis acid generates a benzylic C-4 carbocation (15) which may act as an electrophile to attack a second precocene II molecule. In forming the tetrahydrofurans, the initial carbocations (15) may react with water to generate the organometallic species (17) which could then undergo a one-electron transfer oxidation and coupling with a further molecule of (1) to afford (7). Alternatively the hydroxylated species (17) may react with a second carbocation (15) to give (18) from which the loss of silver leads to the formation of the new C-C bond.

Experimental

M.p.s are determined with a Kofler hot-plate apparatus and are uncorrected. I.r. spectra were taken for solutions in CHCl_3 , u.v. spectra for solutions in ethanol, and ^1H n.m.r. spectra were determined for solutions in CDCl_3 . Silica gel Merck (0.05–0.2 mm) was used for column chromatography and as a support. Unless noted the precocene II and the inorganic reagents were commercial samples used without purification.

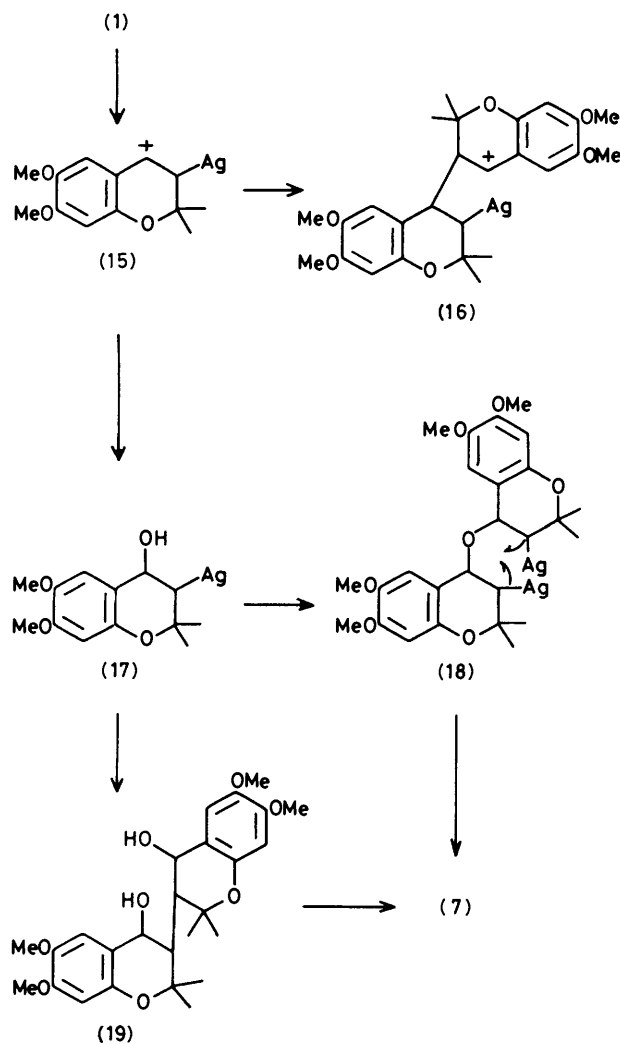
Preparation of Iron(III) Chloride, Zinc Bromide, or Silver Nitrate Coated Silica Gel.—A solution of iron(III) chloride or zinc bromide (1.5 g) in acetone (20 ml) and chromatographic grade silica gel (18 g) was stirred in a rotatory evaporator until dry and then heated for 1 h at 120 °C. Silica gel–20% silver nitrate was prepared in the same way, using water as a solvent, and heated for 12 h to 150 °C.

Treatment of Precocene II (1) with Silica Gel–20% Silver Nitrate.—1a. A concentrated solution of precocene II (1) (240 mg) in light petroleum was placed on top of a chromatographic column (internal diam. 10 mm) filled with silica gel (to 25 cm) impregnated with silver nitrate (20%) and eluted with light petroleum (200 ml). After 10 days, the column was eluted with light petroleum–ethyl acetate (1 : 1) and a mixture of compounds (225 mg) was obtained. The mixture was chromatographed over silica gel and eluted with light petroleum–ethyl acetate (8 : 2) giving in order of increasing polarity: starting material (1) (124 mg), dimer A (3) (16 mg), dimer B (7) (35 mg), and dimer C (8) (40 mg).

1b. Precocene II (1) (300 mg) was chromatographed as above but was left on the column for 20 days. In this way the nitro-chromene (10) (35 mg), dimer A (3) (65 mg) and dimer C (8) (200 mg) were obtained, but no starting material was detected.

2a. Precocene II (1) (100 mg) in light petroleum (30 ml) and silica gel–silver nitrate (20%) (1 g) was stirred at room temperature in the dark and under argon, for 24 h. The products were recovered by filtration and dimer B (7) (60 mg) and dimer C (8) (30 mg) were obtained after silica gel chromatography.

2b. A mixture of precocene II (1) (500 mg), light petroleum (30 ml), and silica gel–silver nitrate (20%) (10 g) was treated



Scheme 2.

as in (2a). The products were identified as the nitro-chromene (10) (30 mg), dimer C (8) (400 mg), and two further inseparable minor dimers.

Reaction of Precocene II (1) with Iron(III) Chloride–Silica Gel.—To a solution of precocene II (1) (100 mg) in light petroleum (30 ml) iron(III) chloride–silica gel reagent (10 g) was added and kept with stirring, under argon in the dark, for 4 h at room temperature. After filtration and chromatography using light petroleum–ethyl acetate (20%), the dimers A (3) (20 mg) and C (8) (50 mg) were obtained.

Treatment of Precocene II (1) with Zinc Bromide–Silica Gel.—A solution of precocene II (1) was treated as above, but with zinc bromide–silica gel instead of iron(III) chloride–silica gel. In this way the dimers A (3) (73 mg) and D (15 mg) were obtained.

Dimer A (3) had m.p. 160–161 °C (from light petroleum–ethyl acetate) (lit.,⁴ 154–155.5 °C) (Found: M^+ , 440.2191. Calc. for $\text{C}_{26}\text{H}_{32}\text{O}_6$: M , 440.2198); $[\alpha]_D -3^\circ$ (*c* 0.5 in CHCl_3) (lit.,⁴ $[\alpha]_D -7^\circ$), λ_{max} 296 and 326 nm; δ_{H} (60 MHz) 1.27, 1.42, 1.51, and 1.59 (each 3 H, s), 1.89 (2 H, m, 3-H), 3.52 (1 H, m, 4-H), 3.72, 3.78, and 3.85 (each 3 H, s), 6.02 (1 H, s, 4'-H), 6.42 (1 H, s), 6.47 (2 H, s), and 6.62 (1 H, s); m/z 440 (M^+ , 73%), 425(100), 409(35), 221(32), and 185(25).

Dimer B (7) had m.p. 184—187 °C (from light petroleum-ethyl acetate) (Found: M^+ , 456.2183. $C_{26}H_{32}O_7$ requires M , 456.2148), ν_{\max} . 2 840, 1 620, 1 510, 1 470, 1 200, 1 145, and 860 cm^{-1} ; λ_{\max} . 232 and 294; δ_H (90 MHz) 1.16, 1.50, 1.58, and 1.60 (each 3 H, s), 1.92 (1 H, q, J 7 and 11 Hz, 3-H), 2.52 (1 H, t, J 7 Hz, 3'-H), 3.86, 3.88, 3.90, and 3.96 (each 3 H, s), 4.66 (1 H, d, J 11 Hz, 4-H), 4.94 (1 H, d, J 7 Hz, 4'-H), 6.52 and 6.54 (each 1 H, s, 8-H and 8'-H), and 6.98 and 7.11 (each 1 H, s, 5-H and 5'-H), irradiation at 1.92 caused the doublet at 4.66 to collapse to a singlet and irradiation at 2.52 caused the doublet at 4.94 to collapse to a singlet; m/z 456 (M^+ , 13%), 275(68), 259(19), 220(2), 205(8), 192(8), 181(3), 167(10), 97(22), and 69(15).

Dimer C (8) had m.p. 86—88 °C (from light petroleum) (Found: M^+ , 456.2152. $C_{26}H_{32}O_7$ requires M , 456.2148), ν_{\max} . 2 480, 1 620, 1 510, 1 470, 1 200, 1 140, 1 130, 1 015, 885, and 860 cm^{-1} ; λ_{\max} . 233 and 294 nm; δ_H (90 MHz) 1.36 and 1.46 (each 6 H, s), 2.43 (2 H, d, J 7 Hz, 3-H and 3'-H), 3.86 (12 H, s), 4.74 (2 H, d, J 7 Hz, 4-H and 4'-H), 6.41 (2 H, s, 8-H and 8'-H), and 6.85 (2 H, s, 5-H and 5'-H); m/z 456 (M^+ , 100%), 441(2), 275(94), 259(11), 220(5), 219(3), 205(18), 192(12), 181(5), 167(13), 97(38), and 69(22).

Dimer D (14) had m.p. 200—204 °C (from light petroleum) (lit.,⁶ 198—199 °C) (Found: M^+ , 440.2186. Calc. for $C_{26}H_{32}O_6$: M , 440.2198), 1H n.m.r. and mass spec. identical with those reported.⁶

6,7-Dimethoxy-2,2-dimethyl-3-nitrochromene (10) had m.p. 107—108 °C (from light petroleum) (Found: C, 59.05; H, 5.75; N, 5.3%. $C_{13}H_{15}NO_5$ requires C, 58.86; H, 5.70; N, 5.28%), ν_{\max} . 1 630, 1 610, 1 565, 1 505, 1 150, 1 035, 1 010, and 850 cm^{-1} ; λ_{\max} . 269, 326, and 433 nm; δ_H (90 MHz) 1.75 (6 H, s), 3.88 and 3.92 (each 3 H, s), 6.48 and 6.71 (each 1 H, s, 8-H and 5-H), and 7.68 (1 H, s, 3-H); m/z 265 (M^+ , 75%), 250(100), 219(41), 189(14), 175(21), and 69(16).

6,7-Dimethoxy-2,2-dimethylchroman-4-one (12).—This compound was prepared by the literature⁷ method and purified by chromatography over silica gel, eluted with light petroleum-ethyl acetate (8 : 2).

6,7-Dimethoxy-2,2-dimethyl[4- 2H]chromene (2).—The chromanone (12) (1.47 g) in dry THF (33 ml) was treated with lithium aluminium deuteride (180 mg) with stirring. After 5 min drops of ethyl acetate were added. The solution was acidified with 4M-hydrochloric acid and stirred for 1 h and then extracted with ethyl acetate. The solvent was evaporated and the residue chromatographed with light petroleum-ethyl acetate (8 : 2) as eluant to afford the [4- 2H]precocene II (2) (1.32 g), δ_H (60 MHz) 1.38 (6 H, s), 3.78 and 3.80 (each 3 H, s), 5.47br (1 H, s, 3-H), 6.42 (1 H, s, 8-H), and 6.54 (1 H, s, 5-H); m/z 221 (M^+ , 23%), 206(100), 190(17), and 162(9). Further elution gave the [4,4'- 2H]-dimer A (4) (45 mg), δ_H (90 MHz) 1.27, 1.42, 1.51, and 1.59 (each 3 H, s), 1.80 and 2.08 (each 1 H, d, J 12 Hz), 3.74 and 3.80 (each 3 H, s), 3.87 (6 H, s), and 6.44, 6.47, 6.49, and 6.66 (each 1 H, s); m/z 442 (M^+ , 36%), 427(100), 411(19), 236(10), 222(26), 221.5(1), 221(14), and 206(9).

6,7-Dimethoxy-2,2-dimethyl-3-nitro-[4- 2H]chromene (11).—The [4- 2H]precocene II (10) (640 mg) was treated as in experiment 2b. In this way the deuterated nitrochromene (11) (40 mg) was obtained (Found: M^+ , 266.1003. $C_{13}H_{13}^2HNO_5$ requires M^+ , 266.1012), δ_H (60 MHz) 1.70 (6 H, s), 1.84 and 1.89 (each 3 H, s), 6.47 (1 H, s, 8-H), and 6.70 (1 H, s, 5-H); m/z 266 (M^+ , 38%), 251(100), 222(22), 206(8), 205(7), and 204(7). Further elution gave the [4,4'- 2H]-dimer C (12) (470 mg), δ_H (60 MHz) 1.34 and 1.42 (each 6 H, s), 2.40 (2 H, s, 3-H and 3'-H), 3.82 (12 H, s), 6.41 (2 H, s, 8-H and 8'-H), and

6.86 (2 H, s, 5-H and 5'-H); m/z 458 (M^+ , 74%), 276(100), 206(35), 192(16), 168(19), 97(59), 83(41), and 70(39).

Crystallographic Data for the Dimer A (3).— $C_{26}H_{32}O_6$, $M = 440.54$, monoclinic, $a = 9.845(1)$, $b = 24.740(4)$, $c = 10.313(3)$ Å, $\beta = 110.81(2)^\circ$, $U = 2348.0$ Å³, $Z = 4$, $D_c = 1.25$ g cm^{-3} , $F(000) = 944$, Mo- K_α radiation, $\lambda = 0.71069$ Å, $\mu = 1.0$ cm^{-1} . Space group $P2_1/n$ from systematic absences of $0k0$ for k odd and $h0l$ for $h + 1$ odd.

All data were measured on an Enraf-Nonius CAD4 diffractometer. The data crystal was a clear, stout prism *ca.* 0.20 × 0.20 × 0.15 mm. Preliminary cell dimensions were found by the SEARCH and INDEX routines of the CAD4. Final cell dimensions were calculated from the setting angles for 25 strong reflections with $\theta > 15^\circ$. Intensities for $hk \pm 1$ with $2 < \theta < 20^\circ$ were measured by a $\theta/2\theta$ scan with a scan width of $\Delta\theta = (0.8 + 0.35 \tan\theta)$ and monochromated Mo- K_α . Two standard reflections were monitored every hour and showed no significant variation. After correction for Lorentz and polarisation (Lp) effects but not for absorption equivalent data were averaged and 1 357 reflections with $|F^2| > (F^2)$ were used in the structure analysis. The values of $\sigma(F^2)$ were calculated as $[\sigma^2(I) + (0.06I)^2]^{1/2}/Lp$.

The C and O atoms were located by direct methods using the MULTAN¹⁵ program and refined by full-matrix least-squares. The hydrogen atoms were included at calculated positions (C-H 1.08 Å) and held fixed with a common isotropic temperature factor of $B = 5.0$ Å². The refinement converged at $R = 0.049$, $R' = 0.061$, where the weighting scheme was $w = 1/\sigma^2(F)$ and the maximum shift/error was 0.3. A final difference map was everywhere featureless.

The structure solution and refinement was done on a

Table 1. Dimer A (3)

(a) Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	5 809(3)	5 065(1)	2 800(3)
C(2)	7 191(4)	4 789(2)	3 087(5)
C(3)	7 420(5)	4 397(2)	4 264(5)
C(4)	6 221(5)	3 963(2)	3 949(4)
C(5)	3 451(4)	3 986(2)	3 219(5)
C(6)	2 125(4)	4 246(2)	2 679(5)
C(7)	2 059(5)	4 776(2)	2 199(5)
C(8)	3 309(4)	5 028(2)	2 220(4)
C(9)	4 639(4)	4 759(2)	2 794(4)
C(10)	4 751(4)	4 243(2)	3 317(4)
C(11)	8 302(5)	5 245(2)	3 504(5)
C(12)	7 170(5)	4 526(2)	1 745(5)
O(13)	7 852(3)	3 034(1)	7 085(3)
C(14)	7 275(5)	3 134(2)	5 601(5)
C(15)	6 378(4)	3 657(2)	5 275(4)
C(16)	5 707(4)	3 810(2)	6 127(4)
C(17)	5 069(5)	3 629(2)	8 231(4)
C(18)	5 326(4)	3 357(2)	9 448(4)
C(19)	6 456(5)	2 982(2)	9 906(5)
C(20)	7 273(5)	2 867(2)	9 088(5)
C(21)	6 983(5)	3 136(2)	7 846(5)
C(22)	5 900(4)	3 522(2)	7 395(4)
C(23)	6 304(6)	2 666(2)	4 891(6)
C(24)	8 628(5)	3 146(2)	5 228(5)
O(25)	714(3)	5 009(1)	1 730(3)
C(26)	632(5)	5 558(2)	1 288(6)
O(27)	819(3)	4 018(1)	2 593(4)
C(28)	686(6)	3 498(2)	2 675(8)
O(29)	4 544(3)	3 430(1)	10 309(3)
C(30)	3 342(5)	3 786(2)	9 827(5)
O(31)	6 669(4)	2 757(1)	11 167(3)
C(32)	7 684(6)	2 327(2)	11 621(5)

Table 1 (continued)

(b) Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

Bonds			
O(1)-C(2)	1.455(5)	O(1)-C(9)	1.376(5)
C(2)-C(3)	1.506(6)	C(2)-C(11)	1.523(6)
C(2)-C(12)	1.523(6)	C(3)-C(4)	1.543(6)
C(4)-C(10)	1.526(6)	C(4)-C(15)	1.523(6)
C(5)-C(6)	1.383(6)	C(5)-C(10)	1.401(6)
C(6)-C(7)	1.394(6)	C(6)-O(27)	1.378(5)
C(7)-C(8)	1.372(6)	C(7)-O(25)	1.366(5)
C(8)-C(9)	1.398(6)	C(9)-C(10)	1.376(6)
O(13)-C(14)	1.451(5)	O(13)-C(21)	1.375(5)
C(14)-C(15)	1.535(6)	C(14)-C(23)	1.513(6)
C(14)-C(24)	1.512(6)	C(15)-C(16)	1.328(6)
C(16)-C(22)	1.443(6)	C(17)-C(18)	1.367(6)
C(17)-C(22)	1.408(6)	C(18)-C(19)	1.395(6)
C(18)-O(29)	1.379(5)	C(19)-C(20)	1.386(6)
C(19)-O(31)	1.361(5)	C(20)-C(21)	1.380(6)
C(21)-C(22)	1.383(6)	O(25)-C(26)	1.425(5)
O(27)-C(28)	1.297(6)	O(29)-C(30)	1.416(5)
O(31)-C(32)	1.420(5)		
Angles			
C(2)-O(1)-C(9)	117.6(3)	O(1)-C(2)-C(3)	109.1(3)
O(1)-C(2)-C(11)	103.6(3)	O(1)-C(2)-C(12)	107.8(3)
C(3)-C(2)-C(11)	111.2(4)	C(3)-C(2)-C(12)	114.0(4)
C(11)-C(2)-C(12)	110.5(4)	C(2)-C(3)-C(4)	113.2(4)
C(3)-C(4)-C(10)	108.2(4)	C(3)-C(4)-C(15)	109.4(3)
C(10)-C(4)-C(15)	112.8(3)	C(6)-C(5)-C(10)	121.7(4)
C(5)-C(6)-C(7)	119.9(4)	C(5)-C(6)-O(27)	124.1(5)
C(7)-C(6)-O(27)	116.1(4)	C(6)-C(7)-C(8)	119.5(4)
C(6)-C(7)-O(25)	116.1(4)	C(8)-C(7)-O(25)	124.4(5)
C(7)-C(8)-C(9)	119.4(4)	O(1)-C(9)-C(8)	113.5(4)
O(1)-C(9)-C(10)	123.9(4)	C(8)-C(9)-C(10)	122.6(4)
C(4)-C(10)-C(5)	122.0(4)	C(4)-C(10)-C(9)	121.4(4)
C(5)-C(10)-C(9)	116.7(4)	C(14)-O(13)-C(21)	118.7(3)
O(13)-C(14)-C(15)	110.8(4)	O(13)-C(14)-C(23)	108.9(4)
O(13)-C(14)-C(24)	102.8(4)	C(15)-C(14)-C(23)	108.8(4)
C(15)-C(14)-C(24)	114.7(4)	C(23)-C(14)-C(24)	110.7(4)
C(4)-C(15)-C(14)	118.9(4)	C(4)-C(15)-C(16)	122.4(4)
C(14)-C(15)-C(16)	118.6(4)	C(15)-C(16)-C(22)	121.4(4)
C(18)-C(17)-C(22)	120.7(4)	C(17)-C(18)-C(19)	120.2(4)
C(17)-C(18)-O(29)	124.2(4)	C(19)-C(18)-O(29)	115.5(4)
C(18)-C(19)-C(20)	119.7(4)	C(18)-C(19)-O(31)	115.4(4)
C(20)-C(19)-O(31)	124.9(4)	C(19)-C(20)-C(21)	119.5(4)
O(13)-C(21)-C(20)	118.4(4)	O(13)-C(21)-C(22)	119.8(4)
C(20)-C(21)-C(22)	121.7(4)	C(16)-C(22)-C(17)	122.9(4)
C(16)-C(22)-C(21)	118.9(4)	C(17)-C(22)-C(21)	118.1(4)
C(7)-O(25)-C(26)	116.9(4)	C(6)-O(27)-C(28)	121.1(4)
C(18)-O(29)-C(30)	116.4(3)	C(19)-O(31)-C(32)	118.3(4)

PDP11/34 computer using the Enraf-Nonius Structure Determination Package. Scattering factors for neutral atoms were taken from ref. 2. Final atoms positions are listed in Table 1 and lists of temperature factors, hydrogen atom position and final structure factors have been deposited as Supplementary Publication No. SUP 23693 (38 pp.).*

Crystallographic Data for the Dimer B (5).— $C_{26}H_{32}O_7$, $M = 456.5$, triclinic, $a = 9.882(1)$, $b = 10.510(4)$, $c = 13.277(2)$ Å, $\alpha = 69.80(2)$, $\beta = 66.54(1)$, $\gamma = 70.89(3)^\circ$, $U = 1157.9$ Å³, $Z = 2$, $D_c = 1.31$ g cm⁻³, $F(000) = 488$. Mo- K_α radiation, $\lambda = 0.71069$ Å, $\mu = 1.0$ cm⁻¹. Space group $P\bar{1}$ from successful structure refinement.

* For details of the Supplementary publications scheme see Instructions for Authors (1983), *J. Chem. Soc., Perkin Trans. 1*, 1983, Issue 1.

Table 2. Dimer B (7)

(a) Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

	x	y	z
O(1)	7 067(3)	4 474(3)	15(2)
C(2)	7 391(5)	5 585(4)	-1 019(3)
C(3)	6 188(4)	6 917(4)	-807(3)
C(4)	6 053(4)	7 254(4)	278(3)
C(5)	6 410(5)	6 202(4)	2 198(3)
C(6)	6 780(5)	5 080(4)	3 019(3)
C(7)	7 280(5)	3 746(4)	2 819(3)
C(8)	7 410(5)	3 574(4)	1 801(3)
C(9)	7 008(5)	4 730(4)	986(3)
C(10)	6 528(4)	6 047(4)	1 155(3)
C(11)	7 243(5)	5 058(4)	-1 882(4)
C(12)	9 023(5)	5 677(5)	-1 301(4)
O(13)	6 292(3)	10 397(3)	-3 167(2)
C(14)	5 689(5)	9 121(4)	-2 541(3)
C(15)	6 600(4)	8 253(4)	-1 736(3)
C(16)	6 502(5)	9 201(4)	-1 040(3)
C(17)	8 454(5)	10 642(4)	-1 556(3)
C(18)	9 266(5)	11 584(4)	-2 366(3)
C(19)	9 069(5)	12 123(4)	-3 436(4)
C(20)	8 086(5)	11 716(4)	-3 683(3)
C(21)	7 284(5)	10 752(4)	-2 864(3)
C(22)	7 444(5)	10 217(4)	-1 805(3)
C(23)	5 948(6)	8 445(5)	-3 464(4)
C(24)	4 030(5)	9 598(5)	-1 977(4)
O(25)	6 681(4)	5 125(3)	4 066(2)
C(26)	6 260(6)	6 449(5)	4 300(4)
O(27)	7 667(4)	2 690(3)	3 678(2)
C(28)	8 305(6)	1 343(5)	3 475(4)
O(29)	10 298(3)	12 064(3)	-2 221(2)
C(30)	10 359(5)	11 692(5)	-1 107(4)
O(31)	9 953(3)	13 043(3)	-4 187(2)
C(32)	9 816(6)	13 558(6)	-5 293(4)
O(33)	6 979(3)	8 266(3)	-107(2)

(b) Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

Bonds			
O(1)-C(2)	1.463(4)	O(1)-C(9)	1.382(4)
C(2)-C(3)	1.538(4)	C(2)-C(11)	1.506(4)
C(2)-C(12)	1.532(4)	C(3)-C(4)	1.544(4)
C(3)-C(15)	1.561(4)	C(4)-C(10)	1.488(4)
C(4)-O(33)	1.457(3)	C(5)-C(6)	1.364(4)
C(5)-C(10)	1.405(4)	C(6)-C(7)	1.407(4)
C(6)-O(25)	1.371(4)	C(7)-C(8)	1.375(4)
C(7)-O(27)	1.369(4)	C(8)-C(9)	1.387(4)
C(9)-C(10)	1.374(4)	O(13)-C(14)	1.483(4)
O(13)-C(21)	1.385(4)	C(14)-C(15)	1.530(4)
C(14)-C(23)	1.519(4)	C(14)-C(24)	1.498(5)
C(15)-C(16)	1.535(4)	C(16)-C(22)	1.479(4)
C(16)-O(33)	1.430(4)	C(17)-C(18)	1.370(4)
C(17)-C(22)	1.401(4)	C(18)-C(19)	1.403(4)
C(18)-O(29)	1.376(4)	C(19)-C(20)	1.362(4)
C(19)-O(31)	1.373(4)	C(20)-C(21)	1.384(4)
C(21)-C(22)	1.376(4)	O(25)-C(26)	1.422(4)
O(27)-C(28)	1.421(4)	O(29)-C(30)	1.415(4)
O(31)-C(32)	1.424(4)		
Angles			
C(2)-O(1)-C(9)	115.8(2)	O(1)-C(2)-C(3)	108.0(2)
O(1)-C(2)-C(11)	103.1(2)	O(1)-C(2)-C(12)	106.6(3)
C(3)-C(2)-C(11)	111.8(3)	C(3)-C(2)-C(12)	115.1(2)
C(11)-C(2)-C(12)	111.3(3)	C(2)-C(3)-C(4)	112.1(2)
C(2)-C(3)-C(15)	113.1(2)	C(4)-C(3)-C(15)	102.0(2)
C(3)-C(4)-C(10)	115.7(3)	C(3)-C(4)-O(33)	105.4(2)
C(10)-C(4)-O(33)	110.3(2)	C(6)-C(5)-C(10)	121.0(3)
C(5)-C(6)-C(7)	119.4(3)	C(5)-C(6)-O(25)	125.2(3)
C(7)-C(6)-O(25)	115.3(3)	C(6)-C(7)-C(8)	120.4(3)

Table 2 (continued)

Angles			
C(6)-C(7)-O(27)	115.2(3)	C(8)-C(7)-O(27)	124.4(3)
C(7)-C(8)-C(9)	119.0(3)	O(1)-C(9)-C(8)	116.0(3)
O(1)-C(9)-C(10)	122.1(3)	C(8)-C(9)-C(10)	121.8(3)
C(4)-C(10)-C(5)	121.4(3)	C(4)-C(10)-C(9)	120.1(3)
C(5)-C(10)-C(9)	118.3(3)	C(14)-O(13)-C(21)	122.5(2)
O(13)-C(14)-C(15)	106.6(2)	O(13)-C(14)-C(23)	104.1(3)
O(13)-C(14)-C(24)	106.4(3)	C(15)-C(14)-C(23)	113.4(3)
C(15)-C(14)-C(24)	115.2(3)	C(23)-C(14)-C(24)	110.3(3)
C(3)-C(15)-C(14)	123.1(3)	C(3)-C(15)-C(16)	102.8(2)
C(14)-C(15)-C(16)	106.9(2)	C(15)-C(16)-C(22)	107.4(3)
C(15)-C(16)-O(33)	104.4(2)	C(22)-C(16)-O(33)	116.2(3)
C(18)-C(17)-C(22)	119.7(3)	C(17)-C(18)-C(19)	119.7(3)
C(17)-C(18)-O(29)	124.8(3)	C(19)-C(18)-O(29)	115.5(3)
C(18)-C(19)-C(20)	120.8(3)	C(18)-C(19)-O(31)	114.8(3)
C(20)-C(19)-O(31)	124.3(3)	C(19)-C(20)-C(21)	119.1(3)
O(13)-C(21)-C(20)	116.1(3)	O(13)-C(21)-C(22)	122.6(3)
C(20)-C(21)-C(22)	121.3(3)	C(16)-C(22)-C(17)	126.7(3)
C(16)-C(22)-C(21)	113.9(3)	C(17)-C(22)-C(21)	119.3(3)
C(6)-O(25)-C(26)	118.1(3)	C(7)-O(27)-C(28)	117.2(3)
C(18)-O(29)-C(30)	116.4(2)	C(19)-O(31)-C(32)	115.7(3)
C(4)-O(33)-C(16)	100.8(2)		

Data were measured on an Enraf-Nonius CAD4 diffractometer using a crystal of size *ca.* 0.20 × 0.20 × 0.13 mm. Preliminary cell dimensions were found using the SEARCH and INDEX routines of the CAD4 and final values were calculated from the setting angles for 25 reflections with $\theta < 15^\circ$. Intensities for $h \pm k \pm l$ reflections with $2 < \theta < 20^\circ$ were measured by a $\theta/2\theta$ scan with a scan width of $\Delta\theta = (0.8 + 0.35 \tan \theta)^\circ$. The scan rate for each reflection was determined by a rapid pre-scan at $10^\circ \text{ min}^{-1}$ in θ at which point any reflection with $I < \sigma(I)$ was coded as unobserved. The remaining reflections were re-scanned at a such speed as to give a minimum value of $\sigma(I)/I$ of 0.5 subject to a maximum scan time of 120 s. Two standard reflections monitored every hour showed no significant variation. Data were corrected for Lorentz polarisation (Lp) effects but not for absorption, and after averaging any equivalent reflections 1570 reflections with $|F^2| > \sigma(F^2)$ were used in the structure refinement. The values of (F^2) were taken as $|\sigma^2(I) + (0.02I)^2|/Lp$. The structure was solved by direct methods using the MULTAN¹⁵ program. Refinement of non-hydrogen atoms with anisotropic temperature factors was by full-matrix least-squares. Hydrogen atoms were located on a low angle difference map and held fixed with a common isotropic temperature factor of $B = 5.0 \text{ \AA}^2$. Refinement converged at $R = 0.054$, $R' = 0.065$, when the maximum shift/error was 0.01 and the weighting scheme was $w = 1/\sigma^2(F)$. A final difference map was everywhere featureless.

The structure solution and refinement was done on a PDP 11/34 computer using the Enraf-Nonius Structure Determination Package. Scattering factors for neutral atoms were taken from ref. 16. Final atom co-ordinates are listed in Table 2, and lists of temperature factors, hydrogen atom positions, and final structure factors have been deposited as Supplementary Publication No. SUP 23693 (38 pp.).*

Crystallographic Data for the Dimer C (6).— $\text{C}_{26}\text{H}_{32}\text{O}_7$, CH_4O , $M = 488.6$, triclinic, $a = 8.952(2)$, $b = 14.904(2)$, $c = 9.341(2) \text{ \AA}$, $\alpha = 90.16(2)$, $\beta = 99.90(2)$, $\gamma = 89.37(2)^\circ$, $U = 1227.6 \text{ \AA}^3$, $Z = 2$, $D_c = 1.32 \text{ g cm}^{-3}$, $F(000) = 524$. Mo- K_α radiation, $\lambda = 0.71069 \text{ \AA}$, $\mu = 1.04 \text{ cm}^{-1}$. Space

* For details of the Supplementary publications scheme see Instructions for Authors (1983), *J. Chem. Soc., Perkin Trans. I*, 1983, Issue 1.

Table 3. Dimer C (8)

(a) Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

	x	y	z
O(1)	7 207(2)	829(1)	5 405(2)
C(2)	6 647(3)	1 189(2)	6 672(3)
C(3)	4 906(3)	1 258(2)	6 287(3)
C(4)	4 325(3)	1 714(2)	4 812(3)
C(5)	5 232(3)	2 344(2)	2 621(3)
C(6)	6 294(3)	2 419(2)	1 730(3)
C(7)	7 667(3)	1 935(2)	2 057(3)
C(8)	7 954(3)	1 417(2)	3 290(3)
C(9)	6 867(3)	1 362(2)	4 193(3)
C(10)	5 506(3)	1 817(2)	3 872(3)
C(11)	7 104(4)	495(2)	7 839(3)
C(12)	7 451(3)	2 067(2)	7 093(3)
O(13)	1 984(2)	2 052(1)	8 549(2)
C(14)	2 686(3)	1 404(2)	7 700(3)
C(15)	4 169(3)	1 808(2)	7 375(3)
C(16)	3 946(3)	2 730(2)	6 674(3)
C(17)	2 382(3)	4 142(2)	6 605(3)
C(18)	1 254(4)	4 645(2)	7 034(3)
C(19)	352(3)	4 267(2)	7 960(3)
C(20)	608(3)	3 400(2)	8 435(3)
C(21)	1 755(3)	2 903(2)	7 972(3)
C(22)	2 642(3)	3 255(2)	7 064(3)
C(23)	3 040(4)	625(2)	8 743(4)
C(24)	1 531(3)	1 162(2)	6 377(4)
O(25)	6 117(3)	2 948(2)	516(2)
C(26)	4 999(4)	3 632(3)	419(4)
O(27)	8 644(2)	2 034(2)	1 110(2)
C(28)	10 067(4)	1 589(3)	1 443(4)
O(29)	877(3)	5 511(1)	6 627(3)
C(30)	1 749(5)	5 936(2)	5 716(4)
O(31)	-763(2)	4 806(1)	8 304(3)
C(32)	-1 826(4)	4 423(3)	9 086(4)
O(33)	3 709(3)	2 572(2)	5 127(2)
O(S)	7 898(6)	6 490(3)	7 262(5)
C(S)	6 326(39)	5 405(19)	6 587(18)

(b) Intramolecular distances (\AA) and angles ($^\circ$) with estimated standard deviations in parentheses

Bonds			
O(1)-C(2)	1.461(2)	O(1)-C(9)	1.373(2)
C(2)-C(3)	1.541(2)	C(2)-C(11)	1.507(2)
C(2)-C(12)	1.519(3)	C(3)-C(4)	1.543(2)
C(3)-C(15)	1.535(2)	C(4)-C(10)	1.495(2)
C(4)-O(33)	1.437(2)	C(5)-C(6)	1.373(2)
C(5)-C(10)	1.395(2)	C(6)-C(7)	1.405(3)
C(6)-O(25)	1.368(2)	C(7)-C(8)	1.374(3)
C(7)-O(27)	1.356(2)	C(8)-C(9)	1.396(2)
C(9)-C(10)	1.375(2)	O(13)-C(14)	1.453(2)
O(13)-C(21)	1.379(2)	C(14)-C(15)	1.542(2)
C(14)-C(23)	1.512(3)	C(14)-C(24)	1.515(3)
C(15)-C(16)	1.520(2)	C(16)-C(22)	1.493(2)
C(16)-O(33)	1.443(2)	C(17)-C(18)	1.366(2)
C(17)-C(22)	1.396(2)	C(18)-C(19)	1.404(3)
C(18)-O(29)	1.388(2)	C(19)-C(20)	1.370(3)
C(19)-O(31)	1.355(2)	C(20)-C(21)	1.387(2)
C(21)-C(22)	1.367(2)	O(25)-C(28)	1.413(2)
O(27)-C(28)	1.417(3)	O(29)-C(30)	1.406(3)
O(31)-C(32)	1.421(3)		
Angles			
C(2)-O(1)-C(9)	113.6(1)	O(1)-C(2)-C(3)	107.8(1)
O(1)-C(2)-C(11)	104.5(1)	O(1)-C(2)-C(12)	108.0(1)
C(3)-C(2)-C(11)	110.2(1)	C(3)-C(2)-C(12)	115.2(1)
C(11)-C(2)-C(12)	110.4(2)	C(2)-C(3)-C(4)	113.9(1)
C(2)-C(3)-C(15)	114.1(1)	C(4)-C(3)-C(15)	104.0(1)
C(3)-C(4)-C(10)	114.2(1)	C(3)-C(4)-O(33)	106.7(1)
C(10)-C(4)-O(33)	110.9(2)	C(6)-C(5)-C(10)	121.3(2)

Table 3 (continued)

Angles			
C(5)-C(6)-C(7)	119.5(2)	C(5)-C(6)-O(25)	124.2(2)
C(7)-C(6)-O(25)	116.3(2)	C(6)-C(7)-C(8)	119.8(2)
C(6)-C(7)-O(27)	115.9(2)	C(8)-C(7)-O(27)	124.4(2)
C(7)-C(8)-C(9)	119.7(2)	O(1)-C(9)-C(8)	117.3(2)
O(1)-C(9)-C(10)	121.4(2)	C(8)-C(9)-C(10)	121.2(2)
C(4)-C(10)-C(5)	121.0(2)	C(4)-C(10)-C(9)	120.5(2)
C(5)-C(10)-C(9)	118.5(2)	C(14)-O(13)-C(21)	116.2(1)
O(13)-C(14)-C(15)	108.1(1)	O(13)-C(14)-C(23)	102.5(1)
O(13)-C(14)-C(24)	107.9(1)	C(15)-C(14)-C(23)	110.0(2)
C(15)-C(14)-C(24)	115.3(1)	C(23)-C(14)-C(24)	112.2(2)
C(3)-C(15)-C(14)	113.7(1)	C(3)-C(15)-C(16)	103.4(1)
C(14)-C(15)-C(16)	113.2(1)	C(15)-C(16)-C(22)	114.2(1)
C(15)-C(16)-O(33)	105.7(1)	C(22)-C(16)-O(33)	109.9(2)
C(18)-C(17)-C(22)	120.9(2)	C(17)-C(18)-C(19)	119.5(2)
C(17)-C(18)-O(29)	125.9(2)	C(19)-C(18)-O(29)	114.7(2)
C(18)-C(19)-C(20)	120.2(2)	C(18)-C(19)-O(31)	115.5(2)
C(20)-C(19)-O(31)	124.3(2)	C(19)-C(20)-C(21)	119.0(2)
O(13)-C(21)-C(20)	115.4(2)	O(13)-C(21)-C(22)	122.6(2)
C(20)-C(21)-C(22)	121.8(2)	C(16)-C(22)-C(17)	120.5(2)
C(16)-C(22)-C(21)	120.8(2)	C(17)-C(22)-C(21)	118.5(2)
C(6)-O(25)-C(26)	116.4(1)	C(7)-O(27)-C(28)	117.3(2)
C(18)-O(29)-C(30)	117.7(2)	C(19)-O(31)-C(32)	117.8(2)
C(4)-O(33)-C(16)	110.7(1)		

group $P\bar{1}$ from successful refinement. Data were measured on an Enraf-Nonius CAD4 diffractometer using a crystal of size *ca.* 0.30 × 0.25 × 0.25 mm. Preliminary cell dimensions were found using the SEARCH and INDEX routines of the CAD4 and final values were calculated from the setting angles for 25 reflections with $\theta = 15^\circ$. Intensities for $h \pm k \pm l$ reflections with $2 < \theta < 25^\circ$ were measured by a $\theta/2\theta$ scan with a scan width of $\Delta\theta = (1.0 + 0.35 \tan\theta)^\circ$. The scan rate for each reflection was determined by a rapid pre-scan at $10^\circ \text{ min}^{-1}$ in θ at which point any reflection with $I < \sigma(I)$ was coded as unobserved. The remaining reflections were re-scanned at such a speed as to give a minimum value of $\sigma(I)/I$ of 0.05 subject to a maximum scan time of 120 s. Two standard reflections monitored every hour showed no significant variation. Data were corrected for Lorentz polarisation effects but not for absorption and after averaging any equivalent reflections. 2 897 Reflections with $|F^2| > \sigma(F^2)$ were used in the structure refinement. The values of $\sigma(F^2)$ were taken as $|\sigma^2(I) + (0.02I)^2|^{1/2}/Lp$. The structure was solved by routine direct methods using the MULTAN¹⁵ programs. A

* For details of the Supplementary publications scheme see Instructions for Authors (1983), *J. Chem. Soc., Perkin Trans. 1*, 1983, Issue 1.

difference map after isotropic refinement of the dimer C showed two poorly defined peaks not connected to the dimer which were assigned as a molecule of methanol solvent. Refinement of non-hydrogen atoms with anisotropic temperature factors was by full-matrix least-squares. All hydrogen atoms of the dimer were located on a difference map and held fixed with a common isotropic temperature factor of $B = 5.0 \text{ e \AA}^{-3}$. Refinement converged at $R = 0.057$, $R' = 0.072$, when the maximum shift/error was 0.3 except for the solvent atoms and the weighting scheme was $w = 1/\sigma^2(F)$. A final difference map was featureless. The structure solution and refinement was done on a PDP 11/34 computer using the Enraf-Nonius Structure Determination Package. Scattering factors for neutral atoms were taken from ref. 16. Final atom co-ordinates are listed in Table 3, and lists of temperature factors, hydrogen atom positions, and final structure factors have been deposited as Supplementary Publication No. SUP 23693 (38 pp.)*

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Received 28th March 1983; Paper 3/485