

methoxybenzene (Rissanen, Valkonen & Knuutinen, 1987). The angle C(3)—O(3)—C(7), 114.7 (3)°, differs from the angles observed in coplanar methoxy groups, *viz.* 117.6 (2)° in 2,2',3,4',5'-pentachloro-4-methoxybiphenyl (Rissanen, Valkonen & Mannila, 1988) and 117.4 (1)° in 2,2',4,4',5,5'-hexamethoxybiphenyl (Chattopadhyay *et al.*, 1987). But it is close to the value found in a similarly oriented methoxy group in pentachloromethoxybenzene, 112.2 (9)° (Rissanen, Valkonen & Knuutinen, 1987). The distance between the phenyl rings [C(1)—C(1')], 1.490 (6) Å, and the narrowing of the endocyclic angle at C(1) and C(1'), indicating small inter-ring conjugation, have comparable values to those reported for similarly substituted biphenyls (Rissanen, Valkonen & Mannila, 1988; Chattopadhyay *et al.*, 1987). The twist angle between the phenyl rings, 82.72 (11)°, is caused by the three chlorine substituents occupying three *ortho* positions (2, 2' and 6) and is larger than the value found in 2,2',3,4',5'-pentachloro-4-methoxybiphenyl (two *ortho* chlorine substituents) (Rissanen, Valkonen & Mannila, 1988). The two larger methoxy substituents occupying the *ortho* positions in 2,2',4,4',5,5'-hexamethoxybiphenyl induce almost the same twist angle, 81.2 (1)° (Chattopadhyay *et al.*, 1987), as the present three smaller chlorine *ortho* substituents. The perpendicular orientation of the methoxy group inhibits π -electron overlap between adjacent molecules and the packing is maintained by van der Waals forces. There are three

intermolecular Cl—Cl distances shorter than the sum of the van der Waals radii: 3.456 (2), 3.418 (2) and 3.494 (2) Å for Cl(2)—Cl(5'), Cl(4')—Cl(6) and Cl(4)—Cl(5'), respectively.

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Acta Cryst. (1988). C44, 686–689

Structure of the Algal Metabolite *iso*-Strictaketal

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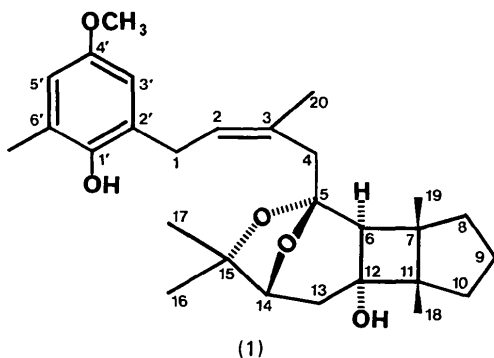
(Received 18 May 1987; accepted 18 November 1987)

Abstract. C₂₈H₄₀O₅·H₂O, *M_r* = 474.64, orthorhombic, *P*2₁2₁2₁, *a* = 7.907 (1), *b* = 17.351 (2), *c* = 19.843 (3) Å, *V* = 2722.2 (6) Å³, *Z* = 4, *D_x* = 1.16 g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.74$ cm⁻¹, *F*(000) = 1032, *T* = 296 K, *R* = 0.068 for 1890 inde-

pendent reflections. The X-ray study confirms that the structure of *iso*-strictaketal in the solid state is as deduced from spectroscopic evidence. The diterpenoid moiety of the molecule consists of four rings, which have the following conformations: cyclopentane distor-

ted boat; cyclobutane puckered; tetrahydropyran distorted chair; 1,3-dioxolane envelope. Crystal cohesion is due to van der Waals interactions and hydrogen bonds involving water molecules.

Introduction. As part of a programme directed towards the isolation of bioactive compounds from Mediterranean seaweeds, we have recently examined the brown alga *Cystoseira stricta*, from which a compound of mixed biogenesis, *iso*-strictaketol, has been obtained in crystalline form. The molecular formula $C_{28}H_{40}O_5$ was established by mass spectrometry and the chemical structure (1) proposed from spectroscopic studies (Amico, Cunsolo, Piattelli & Ruberto, 1987). The present investigation was undertaken to establish the three-dimensional structure and hence obtain information on the conformation of the unusual tetracyclic ring system more detailed than that inferred from nuclear Overhauser enhancement data (Abraham & Loftus, 1980).



Experimental. Crystals suitable for X-ray analysis were obtained by recrystallization from hexane. A crystal of dimensions 0.15 × 0.12 × 0.10 mm was used for intensity-data collection at 296 K with a Siemens-Stoe four-circle diffractometer using graphite-monochromated Mo K α radiation.

Accurate unit-cell dimensions and crystal-orientation matrices were obtained from least-squares refinement of 2θ , ω , χ and ϕ values of 20 strong reflections in the range $14 < 2\theta < 25^\circ$. Crystal and electronic stability was confirmed by the constancy of three check reflections ($\bar{3}12$, $\bar{2}26$ and $\bar{2}\bar{3}0$) measured every 100 min of X-ray exposure. Of 1890 independent reflections measured by the $\omega/2\theta$ scan technique, in the range $3 < 2\theta \leq 46^\circ$ ($-9 \leq h \leq 0$, $-20 \leq k \leq 0$, $0 \leq l \leq 23$), 1016 ($R_{\text{int}} = 0.018$) having net intensity $I > 2.5\sigma(I)$ were used in the solution and refinement of the structure. Corrections for Lorentz and polarization effects were made, but not for absorption.

The structure was solved by direct methods with the MULTAN80 system (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); subsequent calculations were mainly carried out by the SHELX76

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for non-H atoms, with e.s.d.'s in parentheses

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}/U
O/W	3847 (14)	2317 (8)	723 (5)	89 (5)*
C28	5492 (31)	2572 (14)	5356 (9)	137 (10)*
O5	5601 (20)	3127 (6)	4835 (5)	118 (6)*
C27	4490 (26)	4030 (8)	2565 (8)	89 (7)*
O4	3775 (14)	2494 (5)	2207 (5)	69 (4)*
C1	4066 (18)	1213 (7)	3115 (6)	60 (5)*
C2	2346 (20)	943 (8)	3355 (6)	51 (5)*
C3	1100 (21)	641 (7)	3029 (7)	61 (6)*
C20	-555 (20)	407 (9)	3381 (7)	74 (6)*
C4	1108 (19)	470 (7)	2280 (6)	60 (6)*
C17	-1061 (21)	2481 (8)	2779 (6)	73 (6)*
C16	-278 (21)	3098 (8)	1672 (8)	79 (6)*
O1	560 (12)	2089 (6)	343 (4)	61 (3)*
C18	-2409 (28)	594 (11)	-179 (10)	122 (10)*
C19	-1053 (34)	-351 (9)	992 (9)	131 (10)*
C21	4404 (19)	2042 (8)	3307 (6)	59 (4)
C26	4909 (19)	2169 (8)	3996 (6)	60 (4)
C25	5240 (21)	2913 (8)	4184 (8)	73 (4)
C24	5035 (19)	3523 (7)	3719 (7)	66 (4)
C23	4568 (20)	3385 (7)	3078 (7)	66 (4)
C22	4214 (19)	2643 (7)	2866 (6)	52 (3)
C5	236 (17)	1059 (7)	1826 (6)	51 (4)
O2	-1493 (12)	1095 (5)	1962 (4)	59 (2)
O3	818 (10)	1840 (4)	1992 (3)	41 (2)
C15	-622 (20)	2326 (7)	2022 (6)	58 (4)
C14	-1984 (18)	1849 (8)	1710 (6)	50 (4)
C13	-2068 (20)	1784 (8)	944 (7)	63 (4)
C12	-450 (19)	1465 (7)	611 (6)	52 (4)
C11	-684 (25)	764 (9)	112 (7)	77 (5)
C10	578 (27)	761 (9)	-476 (8)	90 (5)
C9	2212 (30)	441 (12)	-189 (10)	116 (7)
C8	1620 (28)	-144 (11)	307 (10)	112 (6)
C7	105 (21)	232 (9)	651 (7)	72 (5)
C6	616 (16)	956 (6)	1076 (5)	40 (3)

* Refined anisotropically. U_{eq} values given.

(Sheldrick, 1976) and PARST (Nardelli, 1983) systems of programs on the IBM 4341 computer at the Centro di Calcolo dell'Università di Messina.

All the H atoms were found from the difference Fourier map. However, only the H atoms involved in hydrogen bonds were actually refined, the others were added at calculated positions (C-H distance 0.98 Å) and included in the structure-factor calculation with a common thermal parameter ($U = 0.08 \text{ \AA}^2$). The structure was isotropically and anisotropically refined on F by the full-matrix least-squares method.

The final R value was 0.068 and $wR = 0.074$. The weighting scheme used in the last refinement cycle was $w = 1.5569/[\sigma^2(F_o) + 0.003188F_o^2]$, $S = 5.226$. Final difference-map peaks were in the range 0.27, -0.24 e \AA^{-3} ; max. $\Delta/\sigma = 0.11$. Scattering factors for the non-H atoms were taken from Cromer & Mann (1968) and for H atoms from Stewart (1970).

Discussion. The final atomic parameters are given in Table 1.* Fig. 1 shows the molecular conformation of

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44560 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(1) and explains the numbering scheme. Bond distances and angles are listed in Table 2. The packing is shown in Fig. 2.

Table 2. Intramolecular bond lengths (Å) and angles (°) with *e.s.d.*'s in parentheses

C1-C2	1.51 (2)	C12-C13	1.54 (2)
C1-C21	1.51 (2)	C12-O1	1.43 (1)
C2-C3	1.29 (2)	C13-C14	1.53 (2)
C3-C4	1.51 (2)	C14-C15	1.49 (2)
C3-C20	1.54 (2)	C14-O2	1.45 (1)
C4-C5	1.53 (2)	C15-C16	1.53 (2)
C5-C6	1.53 (2)	C15-C17	1.57 (2)
C5-O2	1.39 (1)	C15-O3	1.42 (1)
C5-O3	1.47 (1)	C21-C22	1.37 (2)
C6-C7	1.56 (2)	C21-C26	1.44 (2)
C6-C12	1.54 (2)	C22-C23	1.38 (2)
C7-C8	1.53 (2)	C22-O4	1.38 (1)
C7-C11	1.54 (2)	C23-C24	1.35 (2)
C7-C19	1.52 (2)	C23-C27	1.51 (2)
C8-C9	1.49 (2)	C24-C25	1.41 (2)
C9-C10	1.52 (2)	C25-C26	1.37 (2)
C10-C11	1.53 (2)	C25-O5	1.37 (2)
C11-C12	1.58 (2)	C28-O5	1.41 (2)
C11-C18	1.51 (2)		
C1-C2-C3	131 (1)	C10-C11-C12	114 (1)
C1-C21-C26	116 (1)	C10-C11-C18	107 (2)
C1-C21-C22	123 (1)	C11-C7-C19	117 (1)
C2-C1-C21	112 (1)	C11-C12-C13	116 (1)
C2-C3-C4	125 (1)	C11-C12-O1	114 (1)
C2-C3-C20	122 (1)	C12-C11-C18	120 (1)
C3-C4-C5	116 (1)	C12-C13-C14	114 (1)
C4-C3-C20	113 (1)	C13-C12-O1	110 (1)
C4-C5-C6	114 (1)	C13-C14-C15	119 (1)
C4-C5-O2	111 (1)	C13-C14-O2	107 (1)
C4-C5-O3	110 (1)	C14-C15-C16	115 (1)
C5-C6-C7	124 (1)	C14-C15-C17	109 (1)
C5-C6-C12	114 (1)	C14-C15-O3	103 (1)
C5-O2-C14	104 (1)	C15-C14-O2	99 (1)
C5-O3-C15	108 (1)	C16-C15-C17	109 (1)
C6-C5-O2	113 (1)	C16-C15-O3	111 (1)
C6-C5-O3	105 (1)	C17-C15-O3	109 (1)
C6-C7-C8	112 (1)	C21-C22-C23	119 (1)
C6-C7-C19	117 (1)	C21-C26-C25	117 (1)
C6-C7-C11	90 (1)	C21-C22-O4	119 (1)
C6-C12-C11	90 (1)	C22-C21-C26	121 (1)
C6-C12-C13	114 (1)	C22-C23-C24	120 (1)
C6-C12-O1	110 (1)	C22-C23-C27	118 (1)
C7-C8-C9	105 (1)	C23-C22-O4	121 (1)
C7-C6-C12	90 (1)	C23-C24-C25	121 (1)
C7-C11-C10	105 (1)	C24-C23-C27	121 (1)
C7-C11-C12	89 (1)	C24-C25-C26	120 (1)
C7-C11-C18	121 (1)	C24-C25-O5	116 (1)
C8-C7-C11	105 (2)	C26-C25-O5	123 (1)
C8-C7-C19	113 (1)	C28-O5-C25	119 (1)
C8-C9-C10	103 (2)	O3-C5-O2	103 (1)
C9-C10-C11	106 (1)		

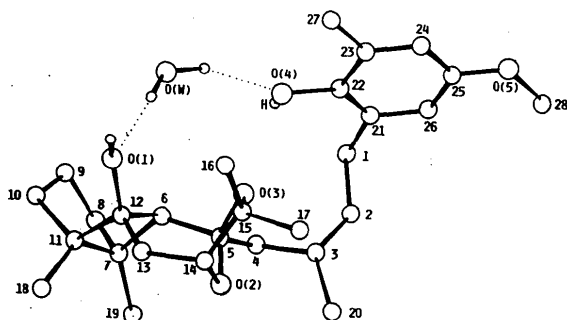


Fig. 1. A perspective view of the molecular structure with crystallographic numbering scheme. Numbers are for C atoms unless indicated otherwise. The H atoms are omitted for clarity. Hydrogen bonds are marked with dotted lines.

The aromatic ring has normal geometry (1.385 Å and 120° for the average bond length and average internal angle), with the methoxy group almost coplanar [the torsion angle C26-C25-O5-C28 is -6(2)°]. The C2-C3 double bond has standard length [1.29 (2) Å] and *Z* configuration; the torsion angle C1-C2-C3-C4 is 1(2)°.

As regards the tetracyclic system, the cyclobutane ring [C-C lengths within the range 1.54 (2) and 1.58 (2) Å and mean values of the internal angles 90°] is puckered with C11, C6, C12 and C7 respectively 0.10 (1), 0.04 (1), -0.06 (1) and -0.07 (1) Å out of the mean plane through the ring.

This ring is fused with a *cis* junction to the cyclopentane ring, which adopts a distorted boat conformation; the distortion of both carbocycles is reflected in the values of the angles C10-C11-C12 [114 (1)°] and C6-C7-C8 [112 (1)°] as well as those of the torsion angles C6-C12-C11-C10 [-96 (1)°] and C8-C7-C11-C12 [-123 (1)°].

The tetrahydropyran ring has a slightly distorted chair conformation, as atoms O2 and C12 are displaced from the opposite side of the plane through C5, C6, C13 and C14 by -0.80 (1) and 0.27 (1) Å respectively. The 1,3-dioxolane ring adopts an envelope conformation and the C-O distances as one proceeds from C14 to C15 through O2, C5 and O3 alternate: 1.45 (1), 1.39 (1), 1.47 (1) and 1.42 (1) Å.

The molecular packing is essentially due to van der Waals interactions as well as to *intermolecular* hydrogen bonds which connect the *iso*-strictaketol and water molecules in a three-dimensional network. The O...O

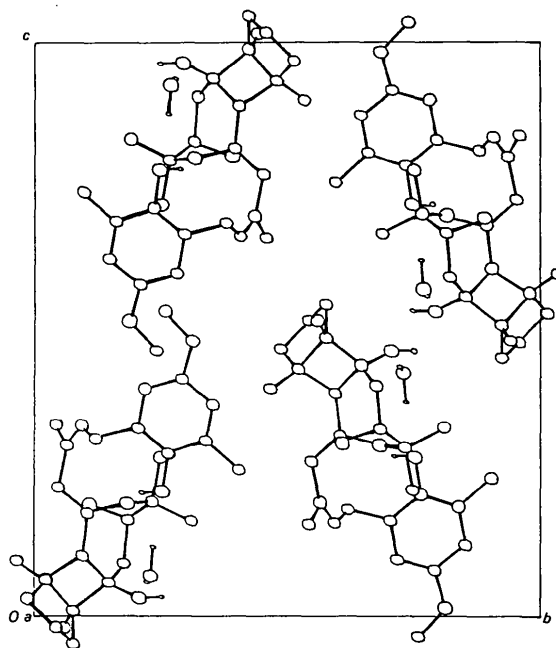


Fig. 2. Molecular packing for *iso*-strictaketol (1) viewed down the *a* axis.

distances are $OW\cdots O1$ 2.73 (2), $OW\cdots O4$ 2.96 (2) and $OW\cdots O1'$ $[(i)\frac{1}{2} + x, \frac{1}{2} - y, -z]$ 2.72 (2) Å.

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Acta Cryst. (1988). **C44**, 689–691

Structure of 1,12-Dinitrododecane – an Alkane with Terminal Dipolar Substituents

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(Received 14 August 1986; accepted 7 December 1987)

Abstract. $C_{12}H_{24}N_2O_4$, $M_r = 260.336$, monoclinic, $P2_1/n$, $a = 5.322$ (1), $b = 24.496$ (10), $c = 5.631$ (2) Å, $\beta = 100.36$ (2)°, $V = 722.2$ Å³, $Z = 2$, $D_x = 1.197$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 6.54$ cm⁻¹, $F(000) = 284$, $T = 293$ K, $R = 0.041$, $wR = 0.043$ for 939 observed reflections. In the molecule, which lies on a centre of symmetry and has a fully extended *trans* configuration, the nitro group is oriented such that its plane is approximately orthogonal [78 (1)°] to that of the C_n skeleton; the molecules are arranged in the lattices such that the intermolecular $O\cdots N$ attractions are maximized whilst the $O\cdots O$ repulsions are minimized.

Introduction. This paper presents the initial structural results from a program to investigate the properties of novel materials arising from ionic and highly dipolar substituted alkanes having negligible homologous dispersion. This work is an extension of previous studies of the electrical and mechanical properties of alkanes of known crystal structures (Belmont, 1985; Belmont, Hooper & Amechi, 1985). The basic starting material in the synthesis, 12-bromododecanol, $\text{Br}(\text{CH}_2)_{12}\text{OH}$, was prepared following the route described in Bidd, Kelly, Ottley, Paynter, Simmonds & Whiting (1983), and converted to 1,12-dinitrododecane, $\text{O}_2\text{N}(\text{CH}_2)_{12}\text{NO}_2$ (Ainscow, Belmont, Henshall, Hooper & Simmonds, 1987), using modified procedures based on standard methods of functional-group conversion (Blatt, 1959; Johnson, 1954). This particular method

allows very precise control of the chain length, with negligible contamination by homologues.

Experimental. Elongated rhombohedral crystals of the compound were prepared by slow evaporation of a diethyl ether solution. Single crystal $0.6 \times 0.45 \times 0.25$ mm. CAD-4 diffractometer, Ni-filtered $\text{Cu } K\alpha$ radiation, cell dimensions from setting angles for 25 automatically centred reflections, $30 < \theta < 35^\circ$. 1227 reflections measured ($3.0 < \theta < 60^\circ$, $h: 0 \rightarrow 14$; $k: 0 \rightarrow 5$; $l: -6 \rightarrow 6$), $\omega/2\theta$ scan, ω width $0.95^\circ + 0.15^\circ \tan\theta +$ background, data corrected for absorption empirically using ψ scan curves. Three standard reflections, no intensity variation. Structure solved by direct methods (*SHELXS84*, Sheldrick, 1984) and refined by full-matrix least squares (*SHELX76*, Sheldrick, 1976), minimizing $\sum w(|F_o| - |F_c|)^2$. Non-H atoms refined anisotropically, H atoms isotropically. 130 parameters, 939 observed data [$I > 1.5\sigma(I)$], weights $w = 1/[\sigma^2(F_o) + 0.00005(F_o)^2]$ with $\sigma(F_o)$ from counting statistics, $R = 0.041$, $wR = 0.043$, max. $\Delta/\sigma = 0.135$, max./min. peaks in ΔF map $+0.15, -0.2$ e Å⁻³. Coefficients for atomic scattering factor calculation as in *SHELX76*. All calculations made on a DEC VAX 11/750 computer. Final atomic fractional coordinates are given in Table 1.†

† Lists of structure factors, anisotropic thermal parameters and intra- and intermolecular non-bonded distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44599 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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