

## Structure of 2,8,11a-Trimethylpterocarpin

BY J. VIJAYALAKSHMI, S. S. RAJAN AND R. SRINIVASAN

Department of Crystallography and Biophysics,\* University of Madras, Guindy Campus, Madras 600 025, India

AND K. K. BALASUBRAMANIAN

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

(Received 22 August 1986; accepted 18 November 1986)

**Abstract.** 6a,11a-Dihydro-2,8,11a-trimethyl-6H-benzofuro[3,2-c]benzopyran,  $C_8H_{18}O_2$ ,  $M_r = 266.3$ , orthorhombic,  $Pbca$ ,  $a = 8.577(4)$ ,  $b = 13.279(3)$ ,  $c = 25.716(6)$  Å,  $V = 2928.9(17)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_m = 1.20(4)$ ,  $D_x = 1.208(1)$  Mg m<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.7107$  Å,  $\mu = 0.0834$  mm<sup>-1</sup>,  $F(000) = 1136$ ,  $T = 297$  K, final  $R = 0.063$ ,  $wR = 0.060$  for 938 reflections. The benzofuro and benzopyran ring systems have two asymmetric C atoms. The present structure has a *cis* junction between the pyran and furan rings and the torsion angle around the bond joining the asymmetric C atoms is  $25(4)^\circ$ . This unstrained *cis* junction is considered more likely in natural pterocarpan.

**Introduction.** Pterocarpan mostly occur in the heartwood and bark of the trees belonging to the tropical genera of the family 'Leguminosae', particularly of the subfamily 'Lotoidae'. Many of them are phytoalexins which are produced in plants during infection by fungus, bacteria or virus and subsequently act as protective agents for plants. Thus some pterocarpan have antifungal (Perrin & Cruickshank, 1969), antitubercular and oestrogenic activity. The pterocarpan are a group of heterocyclic compounds having a 6a,11a-dihydro-6H-benzopyran nucleus. Owing to the presence of asymmetric centres at the 6a and 11a positions, natural pterocarpan can show optical activity and have different geometry of fusion of the two hetero rings. NMR spectra show that all natural pterocarpan have the two hetero rings *cis* fused to each other. The absolute configuration for (–)-pterocarpan is 6aR,11aR, and that for (+)-pterocarpan is 6aS,11aS. The dextrorotatory pterocarpan, for example trifolirhizin (Kojima, Fukushima, Neno & Saiki, 1970), showed superior antitumour activity for laevorotatory forms. With the awareness of the importance of pterocarpan, an X-ray study of the present 11a-methyl-substituted pterocarpan was undertaken.

**Experimental.**  $D_m$  by flotation, white needles (from hot methanol)  $0.4 \times 0.5 \times 0.5$  mm, Enraf–Nonius CAD-4 diffractometer (at the Indian Institute of Technology, Madras),  $\omega/2\theta$  scan technique, Mo  $K\alpha$  radiation, cell parameters refined from 24 strong accurately centred reflections in the range  $18 \leq 2\theta \leq 32^\circ$ , Lp correction, absorption ignored, 2314 unique reflections with  $0 \leq h \leq 8$ ,  $0 \leq k \leq 15$ ,  $0 \leq l \leq 30$  and with  $0 \leq 2\theta \leq 50^\circ$ , 938 reflections with  $|F_o| \geq 1.0\sigma(|F_o|)$  considered observed. Two standard reflections showed no significant intensity variation. Structure solution using *SHELX76* (Sheldrick, 1976), reflections with  $|E| \geq 1.2$  for phase generation, H atoms located from  $\Delta\rho$  map. Full-matrix refinement (Gantzel, Sparks & Trueblood, 1961) with anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms. Final  $R = 0.063$ ,  $wR = 0.060$ , Cruickshank weighting scheme (Cruickshank, Bujosa, Lovell & Truter, 1961) with  $w = 1/\sigma^2$  where  $\sigma^2 = A + B|F_o| + C|F_o|^2$  and  $A = 24.0$ ,  $B = 1.0$  and  $C = 0.007$ . At the conclusion of the refinement, the final shifts in the positional parameters of non-H atoms were less than one-fifth of the e.s.d.'s in the parameters. The final difference synthesis showed no peaks either positive or negative exceeding  $0.4 e \text{ \AA}^{-3}$ . The scattering factors for non-H atoms were from *International Tables for X-ray Crystallography* (1974) and for H atoms from Stewart, Davidson & Simpson (1965).† All calculations were performed using the IBM 1130 at the University of Madras and the IBM 370 at the Indian Institute of Technology, Madras.

**Discussion.** Figs. 1(a) and 1(b) show perspective views of the molecule with the bond lengths and angles respectively; Fig. 2 shows an *ORTEP* plot. Table 1

† Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bonds and angles involving H atoms and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43578 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

\* Contribution No. 695 from the Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Madras 600 025, India.

gives the atomic coordinates with equivalent thermal parameters for non-H atoms. Table 2 lists the torsion angles around various bonds in the furan and pyran rings. In the present structure, the torsion angles *viz.* 13.8 and 17.5° respectively around C(11a)—C(12) and C(6a)—C(11a) have values different from the corresponding angles in related structures [bromoedunol (Leipoldt, Rall, Roux & Bretenbach, 1977), phaseolin (Demartinis, Mackay & Poppleton, 1978), pisatin (Demartinis, Mackay & Perrin, 1978)]. This may be due to the presence of a methyl group at C(11a) in this structure. Ring *B* is skew with O(5), C(11a), C(12) and C(13) being roughly planar within  $\pm 0.03 \text{ \AA}$  [ $\sum(\Delta/\sigma)^2$

$= 52.19$ ] and C(6) and C(6a) having deviations of 0.860 (8) and 0.227 (6) Å respectively from the plane. Ring *C* is an envelope with O(11), C(14), C(15) and C(6a) forming a plane within 0.002 Å [ $\sum(\Delta/\sigma)^2 = 0.52$ ] and C(11a) lies 0.297 (6) Å away from the plane. Ring *A* is planar [ $\sum(\Delta/\sigma)^2 = 18.56$ ] within 0.02 Å and ring *D* is planar [ $\sum(\Delta/\sigma)^2 = 9.91$ ] with a maximum deviation of 0.012 Å for C(7).

The junction between pyran ring *B* and furan ring *C* is *cis* with the torsion angle C(17)—C(11a)—C(6a)—H(C6a) being 25 (4)°. The NMR spectra of related compounds show evidence for the *cis* configuration (Pachler & Underwood, 1967; Sugimoto & Iwada, 1962).

The bond lengths and bond angles in this structure are almost normal. Average bond lengths and bond angles in ring *A* are 1.39 (2) Å and 120 (2)° respectively, and for ring *D* the values are 1.390 (6) Å and 120 (3)° respectively. The C(2)—C(18) distance of 1.502 Å compares well with the C(*sp*<sup>2</sup>)—C(*sp*<sup>3</sup>) distance of 1.503 Å (Bastiansen & Trætteberg, 1962). The C(6a)—C(11a) single bond is larger than the

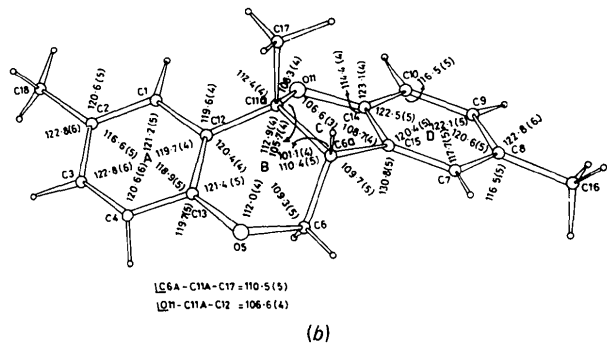
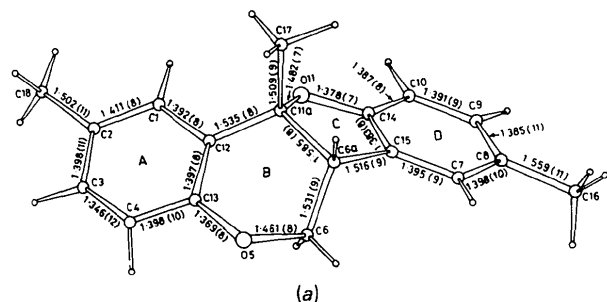


Fig. 1. Perspective views of the molecule showing (a) bond lengths (Å) and (b) angles (°).

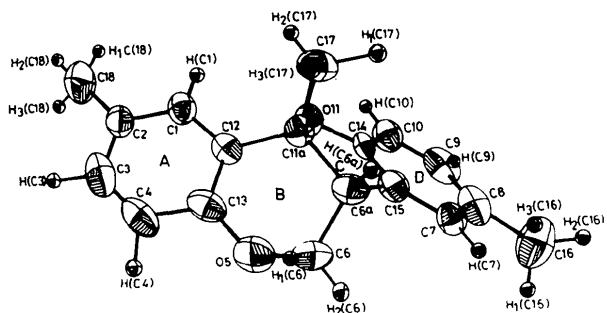


Fig. 2. ORTEP (Johnson, 1965) plot of the molecule with 50% probability.

Table 1. Fractional positional parameters ( $\times 10^4$ ) of the non-H atoms with *e.s.d.*'s in parentheses and their equivalent isotropic thermal parameters

The arithmetic mean of the principal axes of the thermal ellipsoid:  
 $B_{eq}^* = \frac{1}{3} \sum_i \sum_j B_{ij} a_i \cdot a_j$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{Å}^2)$
C(1)	1653 (7)	4499 (5)	1644 (2)	3.5
C(2)	978 (8)	4327 (5)	2136 (2)	4.0
C(3)	1130 (11)	3356 (7)	2340 (3)	5.7
C(4)	1887 (9)	2612 (6)	2090 (3)	5.2
O(5)	3196 (6)	1989 (3)	1334 (2)	5.1
C(6)	2959 (9)	2053 (5)	772 (3)	4.8
C(6a)	3800 (8)	2985 (4)	562 (2)	3.3
C(7)	3518 (7)	2690 (5)	-451 (3)	4.0
C(8)	2825 (8)	3068 (6)	-903 (2)	4.5
C(9)	1857 (8)	3902 (6)	-881 (3)	4.5
C(10)	1573 (8)	4416 (5)	-419 (2)	4.0
O(11)	2050 (5)	4435 (3)	513 (1)	3.5
C(11a)	3227 (7)	3965 (4)	858 (2)	3.1
C(12)	2397 (7)	3729 (4)	1372 (2)	3.1
C(13)	2498 (9)	2769 (4)	1592 (2)	3.9
C(14)	2280 (7)	4035 (4)	24 (2)	3.2
C(15)	3253 (7)	3204 (4)	13 (3)	3.6
C(16)	3119 (11)	2465 (7)	-1414 (3)	7.3
C(17)	4556 (9)	4697 (5)	927 (3)	4.6
C(18)'	121 (12)	5154 (6)	2414 (4)	7.0

\* Hamilton (1959).

Table 2. Torsion angles (°) around the bonds in rings *B* and *C*

C(17)—C(11a)—C(6a)—H(C6a)	25 (4)	C(11a)—C(12)—C(13)—O(5)	-6.8 (9)
C(12)—C(13)—O(5)—C(6)	-33.8 (8)	C(6a)—C(11a)—O(11)—C(14)	-18.5 (5)
C(13)—O(5)—C(6)—C(6a)	65.8 (7)	C(11a)—O(11)—C(14)—C(15)	12.5 (8)
O(5)—C(6)—C(6a)—C(11a)	-55.8 (7)	O(11)—C(14)—C(15)—C(6a)	-0.5 (7)
C(6)—C(6a)—C(11a)—C(12)	17.5 (7)	C(14)—C(15)—C(6a)—C(11a)	-10.7 (6)
C(6a)—C(11a)—C(12)—C(13)	13.8 (8)	C(15)—C(6a)—C(11a)—O(11)	17.4 (6)

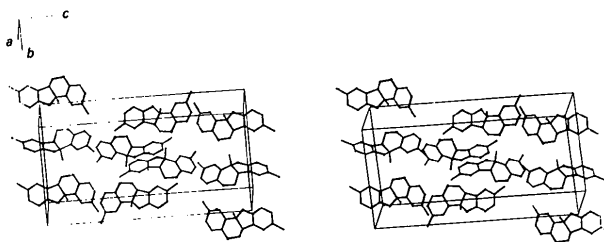


Fig. 3. Stereo packing diagram of the molecules.

expected value in related structures and C(11a)—C(17) is shorter than the expected value. The C(8)—C(16) bond [ $C(sp^2_{\text{aryl}})$ — $C(sp^3_{\text{methyl}})$ ] is unusually long. The large value may be due to the fact that this bond involves a methyl C atom which has high thermal vibration ( $B_{\text{eq}} = 7.3 \text{ \AA}^2$ ). Such lengthening is not unusual with the presence of methyl C atoms. In fact lengths of 1.586 and 1.592  $\text{\AA}$  for C( $sp^3$ )—C( $sp^3$ ) bonds have been observed (Pajunen & Pajunen, 1979) as compared with the C—C single-bond distance of 1.544  $\text{\AA}$  (Pauling, 1960).

A stereoview of the molecular packing is shown in Fig. 3. It was obtained with projection down the  $a$  axis with  $4^\circ$ ,  $20^\circ$  and  $5^\circ$  rotations around the plotter  $x$ ,  $y$  and  $z$  directions using the molecular plotting program of Radhakrishnan (1982). Packing results from normal van der Waals contacts and the crystal is thus a molecular crystal.

*Acta Cryst.* (1987). **C43**, 907–909

## Neutron Refinement of Telluric Acid–Glycine (1/2) Monohydrate

BY D. TRAN QUI AND B. LAMBERT-ANDRON

*Laboratoire de Cristallographie, Centre National de la Recherche Scientifique, Laboratoire associé à l'USMG, 166X, 38042 Grenoble CEDEX, France*

AND J. X. BOUCHERLE

*Service de Physique/MDN, CENG, 85X, 38041 Grenoble CEDEX, France*

(Received 16 January 1986; accepted 29 September 1986)

**Abstract.**  $\text{Te}(\text{OH})_6 \cdot 2\text{C}_2\text{H}_5\text{NO}_2 \cdot \text{H}_2\text{O}$ ,  $M_r = 397.8$ , monoclinic,  $P2_1/n$ ,  $a = 7.981$  (3),  $b = 12.286$  (5),  $c = 7.154$  (2)  $\text{\AA}$ ,  $\beta = 110.51$  (3) $^\circ$ ,  $V = 657 \text{ \AA}^3$ ,  $Z = 2$ ,  $D_x = 2.01 \text{ g cm}^{-3}$ ,  $\lambda = 1.18 \text{ \AA}$ ,  $\mu = 2.5 \text{ cm}^{-1}$ , room temperature, final  $wR = 0.05$  for 1214 independent reflections. The H-atom positions confirm the zwitterion form of the glycine species and the role of H bonds in linking the glycine molecule to the  $\text{Te}(\text{OH})_6$  group. Te—O distances and O—Te—O angles indicate substan-

tial distortion of  $\text{Te}(\text{OH})_6$  groups from ideal octahedral coordination.

**Introduction.** The crystal structure of  $\alpha$ -glycine–telluric acid has been recently and independently determined at room temperature and at 120 K by X-ray diffraction studies (Anderson, Lindqvist & Moret, 1983; Tran Qui, Vicat & Durif, 1984). In this structure, despite the presence of the heavy Te atom, the H-atom positions in

### References

- BASTIANSEN, O. & TRÆTTEBERG, M. (1962). *Tetrahedron*, **17**, 147–154.
- CRUICKSHANK, D. W. J., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). *Computing Methods and Phase Problems in Structure Analysis*, edited by R. PEPINSKY & J. M. ROBERTSON. New York: Pergamon Press.
- DEMARTINIS, C., MACKAY, M. F. & PERRIN, D. R. (1978). *J. Cryst. Mol. Struct.* **8**, 247.
- DEMARTINIS, C., MACKAY, M. F. & POPPLETON, B. J. (1978). *Tetrahedron*, **34**, 1849–1852.
- GANTZEL, P. K., SPARKS, R. A. & TRUEBLOOD, K. N. (1961). *UCLALS1*. Univ. of California, Los Angeles.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KOJIMA, R., FUKUSHIMA, S., NENO, A. & SAIKI, Y. (1970). *Chem. Pharm. Bull. Jpn.* **18**, 2555–2563.
- LEIPOLDT, J. G., RALL, G. J. H., ROUX, D. G. & BRETENBACH, J. C. (1977). *J. Chem. Soc. Chem. Commun.* pp. 349–350.
- PACHLER, K. G. R. & UNDERWOOD, W. G. E. (1967). *Tetrahedron*, **23**, 1817–1826.
- PAJUNEN, A. & PAJUNEN, S. (1979). *Acta Cryst.* **B35**, 3058–3060.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, p. 232. Cornell Univ. Press.
- PERRIN, D. R. & CRUICKSHANK, I. A. M. (1969). *Phytochemistry*, **8**, 971–978.
- RADHAKRISHNAN, R. (1982). *J. Appl. Cryst.* **15**, 135–136.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- SUGINOME, H. & IWADARE, T. (1962). *Experientia*, **18**, 163–164.