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## The Structure of 6-(3-Hydroxy-4,5-dimethoxyphenyl)-3,7-dioxabicyclo[3.3.0]octan-2-one

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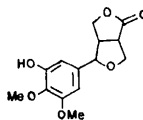
**Abstract.** C<sub>14</sub>H<sub>16</sub>O<sub>6</sub>, *M<sub>r</sub>* = 208.3, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 10.765 (4), *b* = 14.619 (5), *c* = 8.374 (4) Å, β = 98.02 (3)°, *V* = 1305 (2) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.43 Mg m<sup>-3</sup>, λ(Mo *Kα*) = 0.71073 Å, μ = 0.07 mm<sup>-1</sup>, *F*(000) = 592, *T* = 296 K, *R* = 0.058 for 807 reflections with *I* > 2σ(*I*). The bond lengths and angles are normal. In the dioxabicyclo group the five-membered rings are in unsymmetrical twist configurations. The dihedral angle between the best least-squares planes through these rings is 75 (1)°. Intermolecular hydrogen bonding occurs between the hydroxy and oxo groups.

**Introduction.** The term lignana was first introduced by Harworth (1942) to describe products from plants having a carbon skeleton formed by two *n*-propylbenzene moieties linked through their β positions. Later, Gottlieb (1972) proposed a biogenetic definition to include recently discovered structural types resulting from the association of two *n*-propylbenzenic residues, which did not fall into Harworth's structural classification.

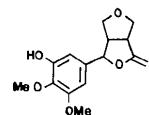
During a systematic chemical study of *Ormosia flava* (Ducke) Rudd, family Leguminosae, a white crystalline substance (hereafter named ormosalin) was isolated (melting point 418–420 K) whose infrared, ultraviolet and proton NMR spectra showed characteristic

features of lignanas of the type bicyclo[3.3.0]octanes. Its mass and <sup>13</sup>C NMR spectra indicated the absence of the second aromatic ring in the system C<sub>6</sub>–C<sub>3</sub>–C<sub>3</sub>–C<sub>6</sub> characteristic of these compounds (Böechat, 1984).

From the spectroscopic and chemical studies (Böechat, 1984), the isomeric structures (I) and (II) were proposed. To discriminate between these two possibilities and to determine the three-dimensional configuration of the molecule a crystal structure determination was undertaken.



(I)



(II)

**Experimental.** Prismatic transparent crystals, 0.12 × 0.14 × 0.30 mm, Nonius CAD-4 diffractometer; cell parameters by least squares on setting angles for 17 reflections, 6 < θ < 18°; intensities by ω–2θ scans for ω = (0.80 + 0.35 tan θ)° at ω speed of (1.9–6.7)° min<sup>-1</sup> min.–max.; range of *hkl*: –9 < *h* < 9, 0 < *k* < 17, 0 < *l* < 12, θ<sub>max</sub> = 25°; standard 040, varied ±3% of mean intensity over data collection; 2410 reflections measured, 2285 unique, *R*<sub>int</sub> = 0.020,

807 observed above  $2\sigma(I)$ ; Lp corrections. Structure solved by direct methods; H atoms located from difference map; full-matrix least-squares refinement minimizing  $\sum w(|F_o| - |F_c|)^2$  with  $w = [\sigma^2(F_o) + 0.001F_o^2]^{-1}$ ; 188 parameters refined: coordinates and anisotropic thermal parameters for non-hydrogen atoms, hydrogen atoms with common  $B = 5.9 \text{ \AA}^2$ , methyl hydrogens refined as rigid groups; excluding unobserved reflections  $R = 0.058$ ,  $wR = 0.059$ ; inspection of  $F_c$  and  $F_o$  values indicated a correction for secondary extinction required;\* max.  $\Delta/\sigma = 0.001$ ,  $\Delta\rho$  excursions within  $-0.26$  and  $0.38 \text{ e \AA}^{-3}$ ; scattering factors for non-hydrogen atoms from Cromer & Mann (1968) with corrections for anomalous dispersion from Cromer & Liberman (1970), for H from Stewart, Davidson & Simpson (1965); *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), *SHELX76* (Sheldrick, 1976) and *ORTEP* (Johnson, 1965) programs.

**Discussion.** Fig. 1 is a stereoscopic projection of the molecule showing the system of atom numbering. Final atomic coordinates and equivalent isotropic temperature factors (Hamilton, 1959) are given in Table 1.† Interatomic bond distances and angles are given in Table 2; all these values are within the expected range.

\*  $F_{\text{corr}} = F_c / [1.0 - 10^{-4} \chi F_c^2 / \sin\theta]$ , where  $\chi$  refined to 0.0051 in the final run.

† Lists of structure factors, anisotropic thermal parameters and a complete list of atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42522 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

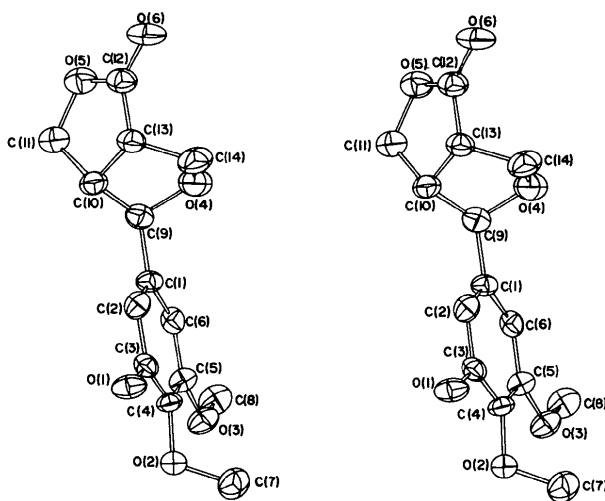


Fig. 1. Stereoscopic projection of the molecule (H atoms are omitted for clarity) showing the atom numbering.

The rather poor diffraction quality of the crystals prevented us from obtaining a good number of reflections per parameter ratio. As a result, the standard deviations for bond distances and angles are rather large, as expected after Cruickshank (1960).

The main result of the present study is that the conformation of ormosalin is unambiguously determined to be that of (I), as can be seen in Fig. 1.

The phenyl ring is planar to within experimental accuracy [ $\sigma_{\text{av}}$ , defined as  $(\sum_{i=1}^N d_i/N - 3)^{1/2}$ , is  $0.01 \text{ \AA}$ ] but the dioxabicyclic system is not, with a dihedral angle of  $75 (1)^\circ$  between the best least-squares planes through the five-membered rings. The conformations of

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors ( $\text{\AA}^2$ ) (Hamilton, 1959)

	x	y	z	$B_{\text{eq}}$
C(1)	0.3663 (7)	0.5913 (5)	0.1124 (9)	2.5 (3)
C(2)	0.4571 (7)	0.5811 (5)	0.2476 (9)	2.8 (3)
C(3)	0.5835 (7)	0.5936 (5)	0.233 (1)	2.7 (3)
C(4)	0.6189 (7)	0.6188 (5)	0.086 (1)	2.6 (3)
C(5)	0.5291 (7)	0.6306 (5)	-0.048 (1)	2.7 (3)
C(6)	0.4026 (7)	0.6161 (5)	-0.0355 (9)	2.7 (3)
C(7)	0.7909 (8)	0.7170 (6)	0.065 (1)	4.2 (3)
C(8)	0.4839 (8)	0.6612 (6)	-0.330 (1)	3.8 (3)
C(9)	0.2271 (7)	0.5766 (6)	0.117 (1)	3.4 (3)
C(10)	0.1947 (7)	0.5145 (6)	0.2542 (9)	2.9 (3)
C(11)	0.0835 (8)	0.4513 (6)	0.204 (1)	3.7 (3)
C(12)	0.0054 (8)	0.5659 (7)	0.351 (1)	3.3 (3)
C(13)	0.1450 (7)	0.5822 (6)	0.3736 (9)	3.1 (3)
C(14)	0.1733 (8)	0.6766 (7)	0.316 (1)	4.6 (4)
O(1)	0.6696 (5)	0.5768 (4)	0.3666 (7)	3.6 (2)
O(2)	0.7466 (5)	0.6249 (4)	0.0786 (7)	3.3 (2)
O(3)	0.5741 (5)	0.6530 (4)	-0.1871 (6)	3.5 (2)
O(4)	0.1656 (5)	0.6634 (4)	0.1382 (8)	5.0 (2)
O(5)	-0.0277 (5)	0.4955 (4)	0.2518 (7)	4.1 (2)
O(6)	-0.0719 (5)	0.6077 (4)	0.4079 (7)	4.5 (2)

Table 2. Interatomic bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

C(1)—C(2)	1.40 (1)	C(8)—O(3)	1.44 (1)
C(1)—C(6)	1.40 (1)	C(9)—C(10)	1.54 (1)
C(1)—C(9)	1.52 (1)	C(9)—O(4)	1.45 (1)
C(2)—C(3)	1.40 (1)	C(10)—C(11)	1.52 (1)
C(3)—C(4)	1.39 (1)	C(10)—C(13)	1.55 (1)
C(3)—O(1)	1.37 (1)	C(11)—O(5)	1.46 (1)
C(4)—C(5)	1.39 (1)	C(12)—C(13)	1.51 (1)
C(4)—O(2)	1.388 (9)	C(12)—O(5)	1.34 (1)
C(5)—C(6)	1.40 (1)	C(12)—O(6)	1.18 (1)
C(5)—O(3)	1.36 (1)	C(13)—C(14)	1.51 (1)
C(7)—O(2)	1.44 (1)	C(14)—O(4)	1.49 (1)
C(2)—C(1)—C(6)	119.7 (7)	C(10)—C(9)—O(4)	105.6 (6)
C(2)—C(1)—C(9)	123.1 (7)	C(9)—C(10)—C(11)	113.7 (6)
C(6)—C(1)—C(9)	117.2 (7)	C(9)—C(10)—C(13)	103.8 (6)
C(1)—C(2)—C(3)	119.7 (7)	C(11)—C(10)—C(13)	103.6 (6)
C(2)—C(3)—C(4)	120.3 (7)	C(10)—C(11)—O(5)	107.3 (6)
C(2)—C(3)—O(1)	117.5 (7)	C(13)—C(10)—O(5)	111.9 (7)
C(4)—C(3)—O(1)	122.2 (7)	C(13)—C(12)—O(6)	127.7 (8)
C(3)—C(4)—C(5)	120.3 (7)	O(5)—C(12)—O(6)	120.3 (8)
C(3)—C(4)—O(2)	116.9 (7)	C(10)—C(13)—C(12)	104.2 (6)
C(5)—C(4)—O(2)	122.6 (7)	C(10)—C(13)—C(14)	105.9 (6)
C(4)—C(5)—C(6)	119.9 (7)	C(12)—C(13)—C(14)	110.3 (7)
C(4)—C(5)—O(3)	115.5 (7)	C(13)—C(14)—O(4)	102.4 (7)
C(6)—C(5)—O(3)	124.6 (7)	C(4)—O(2)—C(7)	113.9 (6)
C(1)—C(6)—C(5)	120.1 (7)	C(5)—O(3)—C(8)	116.9 (6)
C(1)—C(9)—C(10)	115.4 (6)	C(9)—O(4)—C(14)	105.8 (6)
C(1)—C(9)—O(4)	110.3 (6)	C(11)—O(5)—C(12)	110.6 (6)

the five-membered rings may be described, following the notation of Altona & Sundaralingam (1972), as <sup>3</sup>T<sub>2</sub> with O(4)-endo and C(14)-exo and <sup>3</sup>T<sub>4</sub> with C(10)-endo and C(11)-exo. Atoms O(1) and O(6) are involved in intermolecular hydrogen bonding as indicated by the following parameters: O(1)⋯O(6)(x + 1, y, z) = 2.793 (8) Å, O(1)–H(O1) = 1.05715 Å, H(O1)⋯O(6) = 1.779 (6) Å and angle O(1)–H(O1)–O(6) = 159.2 (3)°.

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## Structure of 4-Hydroxy-3,3,4-trimethyl-5-methylene-1-phenyl-2-pyrrolidinone

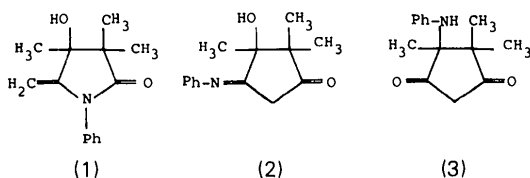
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**Abstract.** C<sub>14</sub>H<sub>17</sub>NO<sub>2</sub>, *M<sub>r</sub>* = 231.3, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 7.187 (1), *b* = 13.531 (1), *c* = 13.357 (1) Å, β = 93.75 (1)°, *V* = 1296.2 (2) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.185 Mg m<sup>-3</sup>, λ(Cu *Kα*) = 1.54178 Å, μ = 0.599 mm<sup>-1</sup>, *F*(000) = 496, *T* = 296 K, *R* = 0.084 for 1069 observed reflections. The five-membered ring has a conformation midway between envelope and twist and forms a dihedral angle with the planar six-membered ring of 83.4 (3)°. The distances and angles in the two rings are normal. The cohesion of the crystal is stabilized by hydrogen bonds, O⋯O 2.750 (7) Å, O–H⋯O 159°.

**Introduction.** In the reaction of the monoimine of diacetyl and aniline with the lithium enolate derived from methyl isobutyrate, in molar ratio 1:2 (Pérez-Ossorio, Alcaide, Plumet & López-Mardomingo, 1985), a compound was obtained that from analytical and spectroscopic data (IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectra) and on account of the mechanistic possibilities for the above reaction could be considered as either structure (1), (2) or (3).



The spectroscopic structural assignment becomes complex since both (2) and (3) can exist as enolic tautomers, some of which are favoured by intramolecular chelation. Structure (1) is related to some enamides used as intermediates in some syntheses of various corrins such as vitamin B<sub>12</sub>. The present investigation was undertaken to clarify which is the true structure.

**Experimental.** Colourless, prismatic, single crystal (0.06 × 0.09 × 0.14 mm) used for X-ray analysis. Cell parameters from setting angles of 53 reflections (θ < 40.7°) by least-squares refinement from a Philips PW 1100 computer-controlled four-circle diffractometer, graphite-monochromated Cu *Kα* radiation. Intensity measurement performed up to θ = 63°, ω–2θ scan technique; range of *hkl* –9 to 9, 0 to 16 and 0 to 16. Two standard reflections (002, 00 $\bar{2}$ ) measured every 90 min, no significant change in intensities. Total of 2093 independent reflections collected, 1069 for which *I* > 2σ(*I*) used in further calculations; *R*<sub>int</sub> = 0.014. Lorentz–polarization factors applied but no absorption correction. Structure solved by direct methods using *MITHRIL83* (Gilmore, 1983). *E* map calculated from the set with the highest figure of merit revealed all non-H atoms. H atoms from a difference synthesis and included in the calculation with a fixed isotropic temperature factor. A further refinement cycle gave a final *R* = 0.084, *wR* = 0.069, (*Δ*/*σ*)<sub>max</sub> = 0.04, *S* =