

Tests of the mode of coordination of (II) to bi- or trivalent metal ions (Cu^{II} , Fe^{III}) indicate sexidentate binucleating behavior, with a change from a chair to a boat conformation for the piperazine ring. Structural work on these compounds is in progress.

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The Absolute Configuration of the Tropane Alkaloid 6 β ,7 β -Epoxy-1 α H,5 α H-tropan-3 α -yl (–)-2,3-Dihydroxy-2-phenylpropionate from its *n*-Butylbromide

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Abstract. $\text{C}_{17}\text{H}_{21}\text{NO}_5 \cdot \text{C}_4\text{H}_9\text{Br}$, $M_r = 456.38$, orthorhombic, $P2_12_12_1$, $a = 7.215$ (1), $b = 12.974$ (2), $c = 22.466$ (2) Å, $Z = 4$, $D_c = 1.44$ Mg m $^{-3}$. Final $R = 0.027$ for 1978 observed reflexions. The tropane alkaloid is narrowly related to scopolamine with an additional OH group at the asymmetric atom of the tropic acid residue. The absolute configuration around this atom is *S*, which is the inverse of that around the corresponding atom in scopolamine.

Introduction. Moorhoff (1975) has separated a new alkaloid from extracts of leaves of *Datura sanguinea*, which he identified as 6 β ,7 β -epoxy-1 α H,5 α H-tropan-3 α -yl (–)-2,3-dihydroxy-2-phenylpropionate. It is narrowly related to scopolamine; instead of tropic acid (3-hydroxy-2-phenylpropionic acid) the new alkaloid contains 2,3-dihydroxy-2-phenylpropionic acid, which has an additional OH group at the asymmetric C atom. The main object of the present structure determination of the *n*-butylbromide of the new alkaloid was to establish the absolute configuration at the asymmetric centre of the 2,3-dihydroxy-2-phenylpropionic acid residue.

1978 reflexions with $2\theta \leq 130^\circ$ and intensities above the 2σ level were measured on a Nonius CAD-4 single-crystal diffractometer employing graphite-monochromatized Cu $K\alpha$ radiation. No absorption correction was applied (crystal dimensions $0.3 \times 0.3 \times 0.4$

Table 1. Fractional coordinates ($\times 10^5$ for Br, $\times 10^4$ for C,N,O) and equivalent isotropic thermal parameters ($\text{Å}^2 \times 10^3$) with e.s.d.'s in parentheses

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

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Br	5509 (6)	15143 (3)	19336 (2)	39.3 (1)
C(1)	5576 (4)	4611 (3)	3030 (2)	27 (1)
C(2)	5945 (5)	4778 (3)	2362 (2)	35 (1)
C(3)	5542 (5)	3824 (3)	1976 (2)	33 (1)
C(4)	5751 (5)	2763 (3)	2276 (2)	31 (1)
C(5)	5432 (5)	2796 (3)	2952 (2)	27 (1)
C(6)	3462 (5)	3183 (3)	3035 (2)	30 (1)
C(7)	3548 (5)	4300 (3)	3088 (2)	34 (1)
N(8)	6639 (4)	3645 (2)	3226 (2)	21 (1)
O(9)	3045 (4)	3680 (2)	3599 (2)	41 (1)
O(10)	3610 (4)	3860 (2)	1765 (2)	30 (1)
C(11)	3242 (5)	4543 (3)	1333 (2)	33 (1)
O(12)	4391 (5)	5107 (3)	1117 (2)	59 (1)
C(13)	1180 (5)	4556 (3)	1167 (2)	28 (1)
C(14)	545 (6)	5676 (3)	1203 (2)	41 (1)
O(15)	1173 (6)	6165 (3)	1731 (2)	57 (1)
O(16)	99 (4)	4009 (2)	1591 (2)	30 (1)
C(17)	922 (5)	4139 (3)	531 (2)	29 (1)
C(18)	2025 (7)	4494 (3)	71 (2)	46 (1)
C(19)	1769 (8)	4125 (4)	–511 (2)	57 (1)
C(20)	394 (9)	3407 (4)	–620 (2)	65 (2)
C(21)	–723 (11)	3084 (4)	–166 (2)	75 (2)
C(22)	–459 (7)	3434 (4)	413 (2)	50 (1)
C(23)	8615 (5)	3637 (3)	2998 (2)	30 (1)
C(24)	6796 (5)	3505 (3)	3910 (2)	33 (1)
C(25)	7982 (7)	4307 (4)	4219 (2)	49 (1)
C(26)	7887 (7)	4150 (4)	4899 (2)	53 (1)
C(27)	8786 (10)	3206 (5)	5135 (3)	81 (2)

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mm; $\mu = 3.14 \text{ mm}^{-1}$). The Br coordinates were derived from an E^2 Patterson synthesis. A Patterson minimum function based on the positions of the four Br atoms in the unit cell revealed the remaining non-H atoms. Block-diagonal least-squares refinement, anisotropic for C, N, O and Br and isotropic for the H atoms, which were located in a ΔF synthesis, reduced R to 0.027. In this refinement a weighting scheme $w = (2.0 + F_o + 0.006F_o^2)^{-1}$ and an extinction correction $F_c^{\text{corr}} = F_c(1 + 2.2 \times 10^{-6} F_c^2)^{-1/2}$ were applied. The anomalous scattering of Br was taken into account. A similar refinement with the inverted structure resulted in $R = 0.038$. This establishes the correctness of the original structure, the final coordinates of which are listed in Table 1.* The calculations were carried out with XRAY 76 (Stewart, 1976).

Discussion. A stereoscopic picture of the molecule is given in Fig. 1. The atomic numbering and the bond distances and angles are indicated in Fig. 2. The latter compare very well with those in the related compounds scopolamine *N*-oxide (SNO) (Huber, Fodor & Mandava, 1971) and *N*-*n*-butylscopolamine bromide (NBS) (Leger, Gadret & Carpy, 1978). The conformation of the tropine skeleton is the same in all three compounds and in scopolamine hydrobromide (Pauling & Petcher, 1969); the piperidine ring is in the chair form with the *N*-methyl group and O(10) axially attached. As pointed

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36215 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

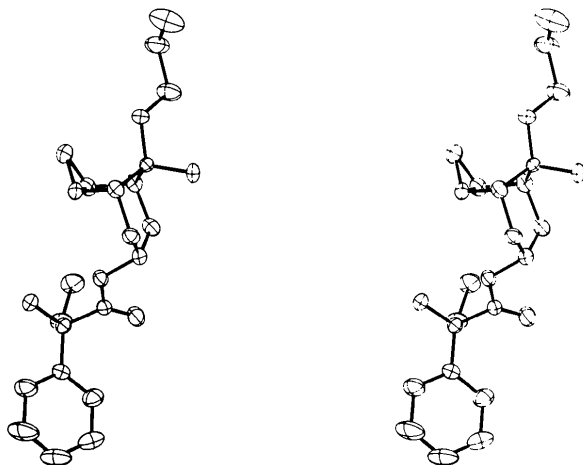


Fig. 1. Stereoview (Johnson, 1965) of the molecule.

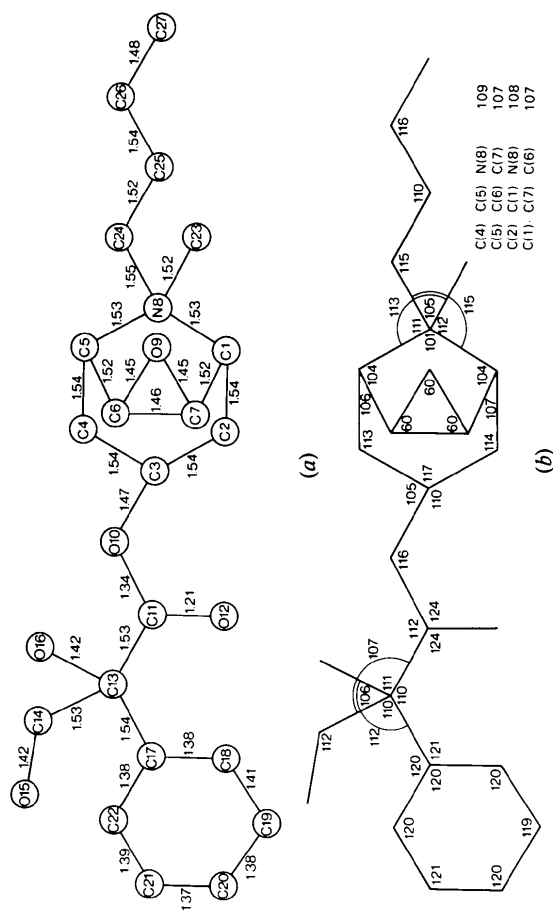


Fig. 2. (a) Numbering of the atoms and bond distances (Å). (b) Bond angles ($^{\circ}$). Calculated standard deviations are 0.005–0.009 Å. (c) Calculated standard deviations are 0.3–0.6 $^{\circ}$.

out by Pauling & Petcher (1969), the *N*-methyl group in scopolamine is axial instead of equatorial as in tropine (Visser, Manassen & de Vries, 1954), pseudotropine (Schenk, MacGillavry, Skolnik & Laan, 1967) and cocaine (Gabe & Barnes, 1963), because of the presence of the epoxy group on the ethylene bridge. The axially attached O(10) requires the epoxy group to be at the opposite side of the bridge. This in turn makes the equatorial attachment of the *N*-methyl group, although not sterically impossible, less favourable than the axial one. As a result the last entered *n*-butyl group, both in the title compound and in NBS, is not in the axial position as Fodor's rule (Fodor, 1955) would require, but in the equatorial one.

The configuration about C(13) is *S* in the Cahn, Ingold & Prelog (1956) convention. This is inverse with respect to the configuration about the corresponding atom in scopolamine so far as the common carboxyl, phenyl and hydroxymethyl groups are concerned. So if the title compound has been formed from scopolamine the introduction of the additional OH group has been accompanied by inversion of the configuration.

The carboxylic ester group has the usual conformation with C(3), O(10), C(11), O(12) and C(13) approximately in one plane (largest deviation 0.03 Å) and O(10)—C(3) *syn* with respect to C(11)—O(12) about the bond O(10)—C(11). The benzene ring is planar within the limits of accuracy with an average C—C distance of 1.386 Å. The terminal bond of the *n*-butyl group is rather short (1.48 Å) probably due to the extra large thermal motion of the terminal methyl group.

The packing is effected by normal van der Waals interactions.

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(2*E*,4*E*)-2-Cyano-4-methyl-5-thiocyanato-2,4-hexadienoic Acid Ethyl Ester

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Abstract. C₁₁H₁₂N₂O₂S, monoclinic, *P*2₁/*c*, *a* = 4.551 (3), *b* = 19.846 (13), *c* = 13.358 (8) Å, β = 90.49 (5)°, *D*_o = 1.32, *D*_c = 1.300 Mg m⁻³, *Z* = 4; *R* = 0.046 for 1178 reflections with *I* > 2σ(*I*). The most important feature of the structure is the presence of a substituted (*E*)-*s-trans*-(*E*)-1,3-butadiene.

Introduction. In continuation of our research on β-thiocyanatovinylcarbonyl compounds (Mühlstädt, Brämer & Schulze, 1976; Schulze, Brämer, Kleinpeter & Mühlstädt, 1976), we prepared 2-cyano-4-methyl-5-thiocyanato-2,4-hexadienoic acid ethyl ester (CMTHCE) by reaction of (*E*)-α-methyl-β-thiocy-

anacrotonaldehyde with ethyl cyanoacetate in the presence of piperidine acetate (Schulze, Mühlstädt, Baldauf & Brämer, 1977). We previously suggested the existence of an (*E*)-*s-trans*-(*E*) conformation for the possible stereoisomeric forms of CMTHCE on the basis of ¹H NMR spectroscopy from the H(3) proton chemical shift, the Eu(fod)₃[†]-produced paramagnetic signal shifts of the ¹H resonances and UV spectroscopy. However, according to the fragment behaviour in the mass spectrum (Herzschuh, Schulze & Mühlstädt, 1981) other isomers are possible. Therefore, an X-ray structure analysis was undertaken to confirm the spectroscopic assignment of the stereochemistry.

[†] Tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)-europium(III).

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