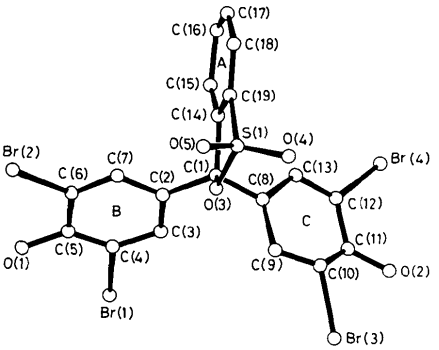

Fig. 1. A perspective view of the molecule.

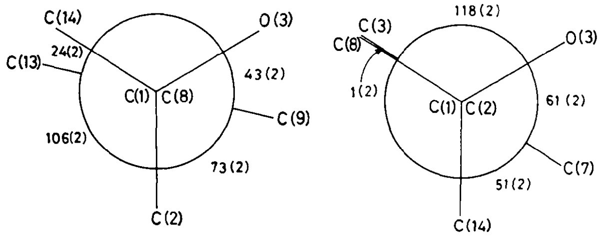

Fig. 2. Conformation of the molecule about the C(1)—C(2) and C(1)—C(8) bonds. The relevant torsion angles (°) are indicated.

are inclined with respect to each other at 73°, are oriented with respect to the sulfonphthalein system at 85 and 68° respectively. The dispositions of the rings are controlled by rotations about the C(1)—C(2) and C(1)—C(8) single bonds. The conformations about these bonds are given in Fig. 2. The orientations of the two rings are clearly different. One lies in a plane defined by C(2), C(1) and C(8) while the other lies approximately in the plane of C(14), C(1) and C(8).

The crystal structure of the compound is shown in Fig. 3. The molecules aggregate into helical columns around 2_1 screw axes. These columns are presumably stabilized by van der Waals interactions. It is interesting to note that the interior of each column is made up of the non-polar regions of the molecules whereas the polar regions consisting of O and Br atoms are distributed on its surface. This arrangement is reminiscent of hydrophobic association in macromolecular systems. The columns which run parallel to the b axis are held together by a network of O—H···O hydrogen bonds. The hydroxyl O atoms belonging to the dibromophenol rings are the donors in the two crystallographically non-equivalent hydrogen bonds. The acceptor atom in one of the hydrogen bonds is the ring O atom O(3) while that in the other is O(5). The O(1)···O(3) and O(2)···O(5) distances are 2·97 (3) and 2·96 (3) Å respectively. The dimerization of the molecules across inversion centres facilitated by the O(1)···O(3) hydrogen bond and its symmetry equivalent is somewhat similar to that found in the crystal structures of some carboxylic acids (Leiserowitz, 1976).

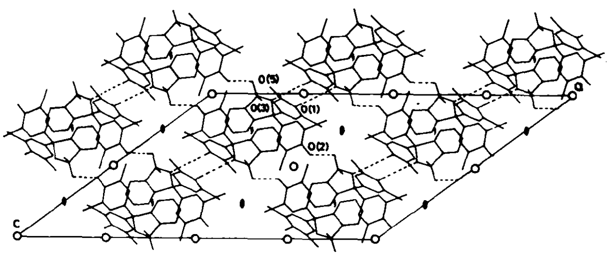

Fig. 3. The crystal structure as seen along the b axis. The broken lines represent hydrogen bonds. Only atoms involved in hydrogen bonds are numbered.

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The Structure of *transoid*-(1*RS*, 3*SR*, 6*RS*, 9*RS*)-7-Hydroxyimino-9-methyl-1-(2-methylpropyl)tricyclo[4.2.1.$0^{3,9}$]nonan-8-one, $C_{14}H_{21}NO_2$

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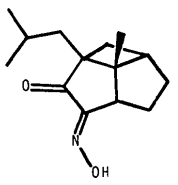
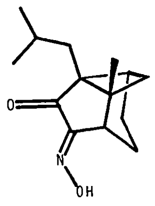
Abstract. $M_r = 235{\cdot}33$, monoclinic, $P2_1/c$, $a = 7{\cdot}3367\,(9)$, $b = 7{\cdot}9791\,(9)$, $c = 23{\cdot}298\,(2)$ Å, $\beta = 103{\cdot}207\,(7)°$, $V = 1327{\cdot}8\,(2)$ Å^3, $Z = 4$, $D_m = 1{\cdot}172\,(3)$, $D_x = 1{\cdot}177$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}732$ cm^{-1}, $F(000) = 128$, $T = 298$ K, $R = 0{\cdot}0647$ for 1254 independent reflections with $F^2 > 3\sigma(F^2)$. The crystal structure determines the configuration of an intermediate in an ongoing formal total

synthesis of the sesquiterpene alkaloid dendrobine. The nitrogen is intermolecularly hydrogen bonded to the oxime oxygen.

Introduction. Dendrobine is the major alkaloid of the Chinese drug 'Chin-Shih-Hu' with biological activities similar to the convulsant picrotoxin (Inubushi, Kikuchi, Ibuka, Tanaka, Saji & Tokane, 1972; Kende, Bentley, Mader & Ridge, 1974; Roush, 1978; Yamada *et al.*, 1972). The title compound is an intermediate in an ongoing effort by Dr Clayton Heathcock and Mr Peter Connolly to develop a more efficient total synthesis of dendrobine. The previous reaction in the synthetic sequence could have led to either (1) or (2). The infrared spectrum and ^{13}C- and ^{1}H-NMR data did not permit assignment of the configuration of $C_{14}H_{21}NO_2$, which has been determined by X-ray crystallography to be (1).



(1)



(2)

Experimental. Pale yellow rectangular prisms, recrystallized from hexane, kindly provided by Mr Peter Connolly and Dr Clayton Heathcock; D_m by flotation in salt (KI, NaCl) water; crystal $0.32 \times 0.18 \times 0.40$ mm; precession photographs, monoclinic symmetry and systematic absences $0k0$ for k odd and $h0l$ for l odd; Enraf–Nonius CAD-4 diffractometer; unit cell: least-squares on 24 high-angle reflections; graphite-monochromatized Mo $K\alpha$, θ–2θ scans; 2051 intensities in quadrant $+h$ $+k$ $\pm l$ ($h = 0$–7, $k = 0$–8, $l = -25$–24), $2 < 2\theta < 45°$; no decrease in intensity in 3 intensity standards nor did crystal orientation need to be redetermined during data collection; data correction for background, scan speed, Lorentz, and polarization factors (Frenz, 1982), absorption negligible; systematically absent reflections and redundant data rejected yielding 1568 data, 1254 of which had $F^2 > 3\sigma(F^2)$. Structure solved by direct methods; first run of *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) unambiguously yielded positions of nitrogen atom and eleven of the fourteen carbon atoms; subsequent least-squares refinements and Fourier syntheses yielded positions of the two oxygen atoms and remaining carbon atoms; majority of hydrogen atoms located following full anisotropic refinement of non-hydrogen atoms. C(5) and C(6) had very large elongated thermal ellipsoids, owing to the flexible nature of their positions within a five-membered ring. Hydrogen atoms were not included for these carbons, but all other hydrogen atoms except the hydroxyl hydrogen were assigned idealized coordinates, with C—H 0·95 Å. Hydrogen atoms were assigned thermal factors $B = 6{\cdot}0$ to $10{\cdot}0$ Å^2, based on the magnitude of the thermal parameters of their parent carbons. The hydroxyl hydrogen was found to be intermolecularly hydrogen bonded to the nitrogen atom of a symmetry-related molecule, explaining the moderately high density found for this compound. The intermolecular distance between the hydroxyl oxygen and the nitrogen is 2·824 (2) Å. This oxygen proton was assigned the coordinates of its associated peak in the difference Fourier map. C(5) and C(6) were removed from the least-squares calculations to determine if four distinct positions could be observed in the difference Fourier, allowing for a disordered model, but only one large peak could be observed for each carbon. The large thermal motion causes an unrealistic shortening of the C(5)—C(6) bond as an artifact. There are no abnormally short intermolecular distances. Examination of the most intense, low-angle reflections indicated no secondary extinction. $w = [4F_o^2/\sigma^2(F_o^2)]$, $\sigma^2(F_o^2) = \{\sigma_0^2(F_o^2) + (pF^2)^2\}$, $p = 0{\cdot}04$, $\sum w(\Delta F)^2$ minimized; in final least-squares cycle $R = 6{\cdot}47$, $R_w = 9{\cdot}46\%$; nine largest $\Delta\rho$ excursions in final difference Fourier, 0·437 to 0·163 e Å^{-3}, associated with C(5) and C(6); none of the 20 largest peaks within 1·90 Å of C(8), GOF with 154 variables was 3·826; atomic scattering factors of C, N, O and H atoms and f' and f'' values taken from *International Tables for X-ray Crystallography* (1974).*

Discussion. The final atomic parameters are listed in Table 1. Bond distances and angles are listed in Table 2.

The molecular structure is shown in Fig. 1 along with the crystallographic-numbering scheme. This and the data in Table 2 establish the structure of the compound unequivocally as isomer (1). As previously noted, the large thermal motion of C(5) and C(6) results in their having an artificially short bond distance. All other bond distances and angles are consistent with literature values.

This structure determination was undertaken as part of a course in X-ray crystallography taught by the Chemistry Department at the University of California, Berkeley. We wish to thank Dr F. J. Hollander and the instructors of this course, Dr K. N. Raymond, Dr S.-H. Kim and Mr R. C. Scarrow, for their assistance. Equipment used was funded in part by the National Science Foundation, Grant CHE79-007027.

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* Lists of structure factors, anisotropic thermal parameters and hydrogen-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38991 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and their e.s.d.'s*

	x	y	z	B_{eq}(Å^2)*
O(1)	0·5304 (4)	−0·1396 (3)	0·9213 (1)	6·89 (7)
O(2)	0·9368 (3)	0·1995 (3)	1·0045 (1)	6·11 (7)
N	0·8147 (4)	0·0757 (4)	0·9753 (1)	4·87 (7)
C(1)	0·3658 (4)	0·1088 (4)	0·8750 (1)	3·62 (7)
C(2)	0·5169 (4)	0·0113 (4)	0·9149 (1)	4·21 (8)
C(3)	0·6583 (4)	0·1335 (4)	0·9476 (1)	3·93 (7)
C(4)	0·5871 (5)	0·3073 (4)	0·9393 (1)	4·61 (8)
C(5)	0·7031 (6)	0·4269 (6)	0·9096 (3)	9·9 (1)
C(6)	0·6084 (8)	0·4498 (7)	0·8502 (2)	13·9 (1)
C(7)	0·4250 (6)	0·3528 (5)	0·8378 (2)	6·2 (1)
C(8)	0·4283 (5)	0·1694 (4)	0·8185 (1)	4·93 (9)
C(9)	0·3923 (5)	0·2956 (4)	0·8974 (1)	3·79 (7)
C(10)	0·2430 (6)	0·3813 (6)	0·9208 (2)	7·9 (1)
C(11)	0·1685 (5)	0·0375 (4)	0·8648 (1)	4·62 (8)
C(12)	0·1300 (5)	−0·1421 (4)	0·8428 (2)	5·52 (9)
C(13)	−0·0748 (7)	−0·1799 (6)	0·8336 (2)	7·9 (1)
C(14)	0·1959 (8)	−0·1802 (5)	0·7871 (2)	7·7 (1)

* B_{eq} is defined as $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta) \times B(1,3) + bc(\cos\alpha)B(2,3)]$.

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

C(1)—C(2)	1·492 (2)	C(7)—C(8)	1·533 (3)
C(2)—O(1)	1·215 (2)	C(7)—C(9)	1·531 (3)
C(2)—C(3)	1·499 (2)	C(8)—C(1)	1·567 (2)
C(3)—N	1·268 (2)	C(9)—C(1)	1·576 (2)
N—O(2)	1·401 (2)	C(9)—C(10)	1·496 (3)
C(3)—C(4)	1·479 (2)	C(1)—C(11)	1·522 (3)
C(4)—C(5)	1·543 (3)	C(11)—C(12)	1·526 (3)
C(4)—C(9)	1·538 (3)	C(12)—C(13)	1·499 (3)
C(5)—C(6)	1·412 (4)	C(12)—C(14)	1·516 (3)
C(6)—C(7)	1·522 (4)		
C(1)—C(2)—O(1)	128·42 (16)	C(4)—C(9)—C(10)	113·12 (16)
C(1)—C(2)—C(3)	107·89 (15)	C(4)—C(9)—C(1)	107·09 (14)
O(1)—C(2)—C(3)	123·70 (16)	C(8)—C(7)—C(9)	89·93 (13)
C(2)—C(3)—N	117·58 (16)	C(7)—C(8)—C(1)	91·11 (14)
C(3)—N—O(2)	113·24 (15)	C(7)—C(9)—C(1)	90·87 (12)
C(2)—C(3)—C(4)	111·12 (15)	C(1)—C(9)—C(10)	120·50 (16)
N—C(3)—C(4)	131·26 (16)	C(8)—C(1)—C(2)	111·42 (14)
C(3)—C(4)—C(5)	115·09 (18)	C(8)—C(1)—C(9)	87·05 (12)
C(3)—C(4)—C(9)	105·99 (14)	C(2)—C(1)—C(9)	105·61 (13)
C(9)—C(4)—C(5)	106·33 (16)	C(8)—C(1)—C(11)	115·71 (14)
C(4)—C(5)—C(6)	108·75 (21)	C(2)—C(1)—C(11)	116·60 (14)
C(5)—C(6)—C(7)	109·54 (22)	C(9)—C(1)—C(11)	116·49 (15)
C(6)—C(7)—C(8)	117·9 (3)	C(1)—C(11)—C(12)	120·00 (17)
C(6)—C(7)—C(9)	107·20 (18)	C(11)—C(12)—C(13)	109·86 (20)
C(7)—C(9)—C(10)	118·27 (18)	C(11)—C(12)—C(14)	113·85 (16)
C(4)—C(9)—C(7)	103·97 (16)	C(13)—C(12)—C(14)	110·00 (18)

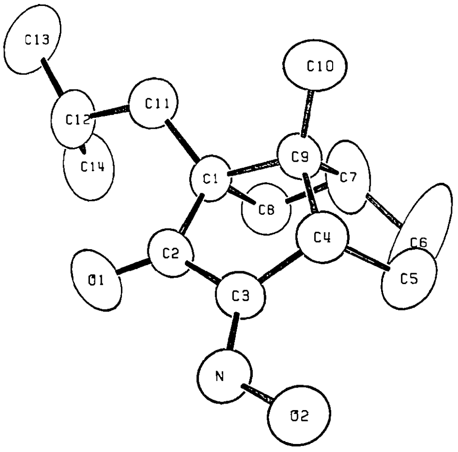

Fig. 1. View of the $C_{14}H_{21}NO_2$ molecule with the crystallographic-numbering scheme.

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(*E*)- and (*Z*)-2,3-Bis(2-methoxyphenyl)-2-butene, $C_{18}H_{20}O_2$

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Abstract. (*E*)-Isomer, $M_r = 268·4$, monoclinic, $C2/c$, $a = 21·096$ (5), $b = 7·473$ (2), $c = 10·247$ (2) Å, $\beta = 110·41$ (2)°, $V = 1514$ (1) Å^3, $Z = 4$, $D_x = 1·177$ (1) g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·81$ cm^{-1}, $F(000) = 576$, $T = 298$ K, final $R = 0·042$ for 461 observations. The molecule has $\bar{1}$ symmetry, with a dihedral angle of 68·6° between the aromatic plane and the plane of the double bond. (*Z*)-Isomer, orthorhombic, $P2_12_12_1$, $a = 8·307$ (3), $b = 11·053$ (3), $c = 16·854$ (3) Å, $V = 1547$ (1) Å^3, $Z = 4$, $D_x =$

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