

Fig. 2. Composite difference electron-density synthesis: section through the methyl C atoms of the *tert*-butyl group. Solid lines: F_c without *tert*-butyl methyl C atom contributions; contours from $0.50 \text{ e } \text{Å}^{-3}$, at intervals of $0.20 \text{ e } \text{Å}^{-3}$. Dashed lines: F_c with the contributions of the C atoms located at the maxima in the previous difference synthesis. Contours from $0.30 \text{ e } \text{Å}^{-3}$, at intervals of $0.10 \text{ e } \text{Å}^{-3}$.

5 (1). In both cases one of the methyl C atoms is coplanar with the thiete ring, so that the rotational angle between the two conformations is nearly 60° . The electron-density distributions in the plane through the *tert*-butyl methyl C atoms were obtained by two consecutive difference syntheses and are displayed in a composite map shown in Fig. 2. Fig. 3 shows the Newman projections for both conformations along C(3)–C(4). The intermolecular packing is limited to van der Waals contacts.

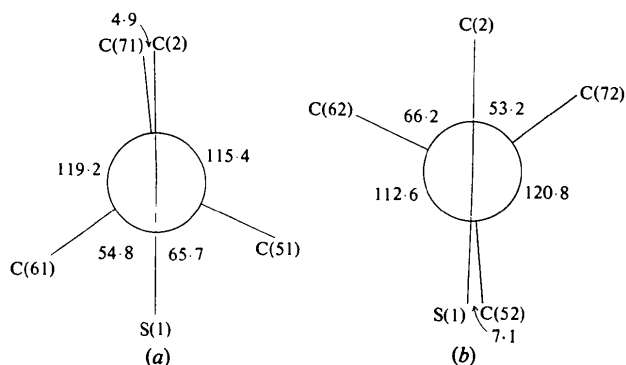


Fig. 3. Newman projections along C(3)–C(4). (a) Conformation with an occupancy factor of 0.84. (b) Conformation with an occupancy factor of 0.16. Since the positional parameters of the methyl C atoms were not included in the refinement no e.s.d.'s are given. (Torsion angles in deg.)

References

- BOS, H. J. T. & BOLEIJ, J. (1969). *Recl Trav. Chim. Pays-Bas*, **88**, 465–473.
- BROUWER, A. C. (1979). Thesis, Utrecht.
- BÜCHI, G., INMAN, C. G. & LIPINSKY, E. S. (1954). *J. Am. Chem. Soc.* **76**, 4327–4331.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1977). *MULTAN 77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain-la-Neuve, Belgium.
- STEWART, J. M. (1976). XRAY 76. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1980). **B36**, 486–489

The Structure of Dihydrnimbin*

BY C. R. NARAYANAN, N. N. DHANESHWAR, S. S. TAVALE AND L. M. PANT

National Chemical Laboratory, Pune, India

(Received 7 February 1979; accepted 9 October 1979)

Abstract. $\text{C}_{30}\text{H}_{38}\text{O}_9$, monoclinic, $P2_1$, $a = 16.24$ (1), $b = 7.61$ (1), $c = 11.47$ (2) Å, $\beta = 95.9$ (2)°, $\rho_o = 1.264$, $\rho_c = 1.278 \text{ Mg m}^{-3}$ for $Z = 2$. The structure was solved by direct methods with 1494 reflections. The molecular structure obtained from the present study is in agreement with the structures and stereochemistries deduced earlier for nimbin, nimbolide and

other related products from chemical, PMR and other studies.

Introduction. The crystalline bitter principle, nimbin, isolated from the seeds, bark and other parts of the neem tree (*Melia azadirachta*), has been shown to be a triterpenoid of the apoeuphol or tirucallol type with the unique feature that its C ring is oxidized and broken (Narayanan, Pachapurkar, Pradhan, Shah &

* NCL Communication No. 2405.

Table 1. *Final atomic parameters and their estimated standard deviations (in parentheses)*

The atoms of the furan ring have isotropic B values; C(21) 10.2, O(7) 12.4, C(22) 6.9 and C(23) 7.8 Å². Atom O(5) has $b = 7.0$ Å² and for all other atoms B is in the range 2.5–5.0 Å².

	x	y	z
(a) Non-hydrogen atoms ($\times 10^4$)			
C(1)	2481 (8)	-3742 (19)	-4301 (10)
C(2)	3331 (9)	-4161 (20)	-4558 (12)
C(3)	3773 (10)	-2458 (28)	-4851 (12)
C(4)	3883 (8)	-1193 (19)	-3810 (10)
C(5)	3270 (7)	-1629 (17)	-2843 (9)
C(6)	3197 (6)	-256 (17)	-1913 (10)
C(7)	2759 (6)	-939 (16)	-842 (9)
C(8)	1914 (6)	-1832 (16)	-1180 (9)
C(9)	1969 (5)	-3086 (15)	-2286 (8)
C(10)	2382 (7)	-2249 (19)	-3386 (9)
C(11)	1094 (7)	-3887 (18)	-2580 (10)
C(12)	1102 (6)	-5646 (17)	-3062 (9)
C(13)	1422 (8)	-3178 (18)	797 (10)
C(14)	1907 (6)	-2869 (18)	-41 (8)
C(15)	2769 (6)	-3416 (17)	285 (9)
C(16)	2804 (7)	-3486 (19)	1694 (10)
C(17)	1912 (8)	-3926 (20)	1889 (10)
C(18)	498 (7)	-2739 (25)	868 (12)
C(19)	1863 (8)	-862 (22)	-4020 (12)
C(20)	1749 (9)	-5834 (20)	1968 (10)
C(21)	1769 (16)	-7001 (24)	1142 (15)
C(22)	1598 (13)	-6781 (26)	2952 (12)
C(23)	1449 (15)	-8396 (24)	2768 (13)
C(28)	4782 (8)	-1353 (19)	-3312 (11)
C(29)	3765 (10)	659 (22)	-4308 (12)
C(30)	1224 (7)	-473 (18)	-1373 (10)
C(31)	5786 (8)	-3092 (25)	-2245 (13)
C(32)	4099 (7)	1978 (21)	-1168 (12)
C(33)	5005 (8)	2313 (25)	-845 (16)
C(34)	247 (8)	-7677 (20)	-4712 (12)
O(1)	1890 (6)	-4265 (15)	-4834 (8)
O(2)	4940 (5)	-2828 (14)	-2708 (8)
O(3)	5317 (6)	-3470 (15)	-3401 (9)
O(4)	4010 (4)	246 (0)	-1506 (7)
O(5)	3515 (7)	2889 (17)	-1139 (13)
O(6)	3283 (4)	-2160 (12)	-180 (6)
O(7)	1587 (11)	-8551 (24)	1499 (13)
O(8)	1602 (5)	-6716 (14)	-2833 (9)
O(9)	360 (5)	-5978 (12)	-3705 (7)

	x	y	z
(b) Hydrogen atoms ($\times 10^3$)			
H(2)	370 (7)	-441 (16)	-397 (10)
H'(2)	332 (7)	-507 (18)	-511 (10)
H(3)	430 (8)	-249 (21)	-511 (11)
H'(3)	352 (8)	-212 (21)	-557 (11)
H(5)	359 (6)	-287 (16)	-235 (8)
H(6)	285 (6)	94 (16)	-228 (8)
H(7)	257 (6)	11 (15)	-29 (8)
H(9)	240 (6)	-388 (16)	-209 (8)
H(11)	84 (6)	-427 (16)	-187 (9)
H'(11)	68 (6)	-308 (17)	-322 (9)
H(15)	295 (6)	-441 (15)	-13 (8)
H(16)	285 (6)	-249 (16)	177 (8)
H'(16)	330 (6)	-399 (16)	195 (8)
H(17)	180 (7)	-316 (18)	269 (9)

Narasimhan, 1964*a,b*). The elucidation of the structure and stereochemistry of this complex molecule was based on chemical and, to a large extent, PMR spectral studies of the compound and several of its derivatives. The stereochemistries of the protons at C(15) and C(17) of nimbin were assigned by considering all the

possible configurations at these points and the effects of their possible coupling patterns on the C(16) protons and then comparing these values with those actually observed (Narayanan & Pachapurkar, 1965).

Structures of related natural products, such as deacetylnimbin (Narayanan & Iyer, 1967), nimbolide (Ekong, 1967), vepinin (Narayanan, Pachapurkar, Sawant & Wadia, 1969), salanin (Henderson, McCrindle, Malera & Overton, 1968), vilasinin (Pachapurkar, Kornule & Narayanan, 1974) and azadirachtin (Zanno, Muira, Nakanishi & Elder, 1975), which have many features in common with nimbin, were elucidated largely by PMR spectral analysis and by considering their evident relationship to nimbin. Hence it was considered desirable to perform an X-ray structure determination of a derivative of the parent compound nimbin, so that the structures of all these compounds would stand on a firmer basis. In the present paper, we report the structure analysis of dihydronimbin.

Cell dimensions were determined with the help of high-angle reflexions in zero-layer Weissenberg photographs with the films mounted in the Straumanis arrangement.

Data were collected with unfiltered Cu radiation from equi-inclination Weissenberg photographs ($h0l-h6l$); the crystal used for data collection had a cross-section 0.4×0.5 mm and length 1.7 mm. The intensities were measured visually using extended spots in higher-layer photographs, and were corrected for L_p factors as well as for the effect of spot extension; absorption was neglected. The intensities were scaled layerwise by Wilson's method. 1494 reflexions were observed; unobserved reflexions were excluded from all calculations.

The structure was determined by direct methods using the program *MULTAN* (Germain, Main &

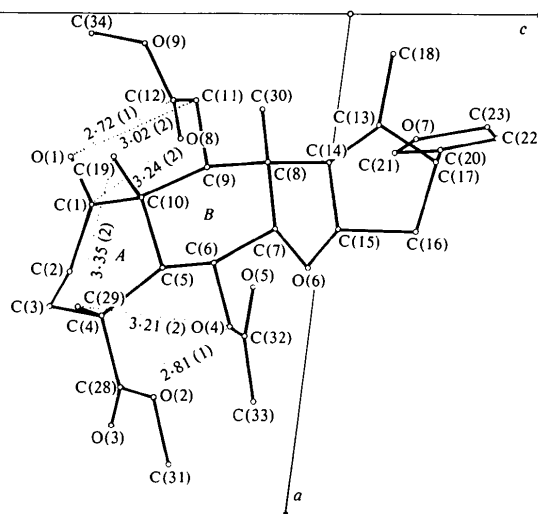


Fig. 1. Molecule projected along [010].

Table 2. *Intramolecular bond lengths (Å) and angles (°) and their standard deviations (in parentheses)*

C(1)–C(2)	1.48 (2)	C(2)–C(3)	1.54 (2)	O(2)–C(31)	1.44 (2)	C(6)–O(4)	1.41 (1)
C(3)–C(4)	1.53 (2)	C(4)–C(5)	1.60 (2)	O(4)–C(32)	1.38 (2)	C(32)–C(33)	1.50 (2)
C(5)–C(10)	1.58 (2)	C(10)–C(1)	1.57 (2)	C(32)–O(5)	1.18 (2)	C(13)–C(18)	1.55 (2)
C(5)–C(6)	1.51 (2)	C(6)–C(7)	1.57 (2)	C(8)–C(30)	1.52 (2)	C(9)–C(11)	1.55 (2)
C(7)–C(8)	1.54 (2)	C(8)–C(9)	1.60 (1)	C(11)–C(12)	1.45 (2)	C(12)–O(8)	1.16 (1)
C(9)–C(10)	1.62 (2)	C(7)–O(6)	1.43 (1)	C(12)–O(9)	1.37 (1)	O(9)–C(34)	1.73 (2)
O(6)–C(15)	1.41 (1)	C(15)–C(14)	1.47 (2)	C(10)–C(19)	1.49 (2)	C(2)–H(2)	0.88 (11)
C(14)–C(8)	1.53 (2)	C(15)–C(16)	1.61 (2)	C(2)–H'(2)	0.94 (12)	C(3)–H(3)	0.93 (14)
C(16)–C(17)	1.53 (2)	C(17)–C(13)	1.52 (2)	C(3)–H'(3)	0.92 (14)	C(5)–H(5)	1.19 (10)
C(13)–C(14)	1.32 (2)	C(17)–C(20)	1.48 (2)	C(6)–H(6)	1.13 (11)	C(7)–H(7)	1.09 (10)
C(20)–C(21)	1.30 (3)	C(21)–O(7)	1.29 (3)	C(15)–H(15)	0.95 (11)	C(16)–H'(16)	0.91 (11)
O(7)–C(23)	1.50 (3)	C(23)–C(22)	1.27 (3)	C(16)–H(16)	0.77 (11)	C(17)–H(17)	1.11 (12)
C(20)–C(22)	1.38 (2)	C(1)–O(1)	1.15 (2)	C(9)–H(9)	0.94 (10)	C(11)–H(11)	0.99 (11)
C(4)–C(29)	1.53 (2)	C(4)–C(28)	1.52 (2)	C(11)–H'(11)	1.12 (11)		
C(28)–O(3)	1.17 (2)	C(28)–O(2)	1.33 (2)				
C(1)–C(2)–C(3)	109 (1)	C(2)–C(3)–C(4)	112 (1)	C(4)–C(28)–O(2)	113 (1)	O(2)–C(28)–O(3)	119 (1)
C(3)–C(4)–C(5)	112 (1)	C(4)–C(5)–C(10)	113 (1)	C(28)–O(2)–C(31)	116 (1)	C(5)–C(6)–O(4)	106 (1)
C(5)–C(10)–C(1)	109 (1)	C(10)–C(1)–C(2)	117 (1)	C(7)–C(6)–O(4)	108 (1)	C(6)–O(4)–C(32)	115 (1)
C(5)–C(10)–C(9)	104 (1)	C(10)–C(9)–C(8)	116 (1)	O(4)–C(32)–C(33)	108 (1)	O(4)–C(32)–O(5)	121 (1)
C(9)–C(8)–C(7)	110 (1)	C(8)–C(7)–C(6)	114 (1)	O(5)–C(32)–C(33)	132 (1)	C(5)–C(10)–C(19)	115 (1)
C(7)–C(6)–C(5)	114 (1)	C(6)–C(5)–C(10)	111 (1)	H'(2)–C(2)–H(2)	109 (11)	C(1)–C(2)–H'(2)	110 (7)
C(7)–C(8)–C(14)	96 (1)	C(8)–C(14)–C(15)	106 (1)	C(1)–C(2)–H(2)	118 (8)	C(3)–C(3)–C(2)	117 (7)
C(14)–C(15)–O(6)	107 (1)	C(15)–O(6)–C(7)	107 (1)	C(3)–C(2)–H(2)	93 (8)	H(3)–C(3)–C(2)	121 (9)
O(6)–C(7)–C(8)	108 (1)	C(15)–C(14)–C(13)	113 (1)	H(3)–C(3)–H'(3)	94 (12)	H'(3)–C(3)–C(4)	122 (9)
C(14)–C(13)–C(17)	111 (1)	C(13)–C(17)–C(16)	103 (1)	C(4)–C(3)–H(3)	103 (9)	H'(3)–C(3)–C(2)	105 (9)
C(17)–C(16)–C(15)	103 (1)	C(16)–C(15)–C(14)	101 (1)	H(5)–C(5)–C(6)	106 (5)	H(5)–C(5)–C(4)	103 (5)
C(13)–C(17)–C(20)	110 (1)	C(20)–C(21)–O(7)	112 (1)	C(10)–C(5)–H(5)	106 (5)	H(6)–C(6)–C(5)	112 (5)
C(21)–O(7)–C(23)	107 (2)	O(7)–C(23)–C(22)	101 (2)	H(6)–C(6)–C(7)	108 (5)	O(4)–C(6)–H(6)	108 (5)
C(23)–C(22)–C(20)	115 (2)	C(22)–C(20)–C(21)	105 (2)	C(6)–C(7)–H(7)	113 (5)	O(6)–C(7)–H(7)	111 (5)
C(18)–C(13)–C(17)	118 (1)	C(18)–C(13)–C(14)	131 (1)	H(7)–C(7)–C(8)	100 (5)	O(6)–C(15)–H(15)	97 (6)
C(30)–C(8)–C(14)	114 (1)	C(30)–C(8)–C(9)	113 (1)	C(16)–C(15)–H(15)	120 (6)	H(15)–C(15)–C(14)	116 (6)
C(8)–C(11)–C(11)	106 (1)	C(10)–C(9)–C(11)	115 (1)	H(9)–C(9)–C(10)	95 (6)	H(9)–C(9)–C(8)	107 (6)
C(9)–C(11)–C(12)	114 (1)	C(11)–C(12)–O(8)	127 (1)	H(9)–C(9)–C(11)	117 (6)	C(9)–C(11)–H(11)	113 (6)
C(11)–C(12)–O(9)	110 (1)	O(8)–C(12)–O(9)	123 (1)	H(11)–C(11)–H'(11)	115 (8)	H'(11)–C(11)–C(12)	107 (6)
C(12)–O(9)–C(34)	122 (1)	C(9)–C(10)–C(19)	114 (1)	H'(11)–C(11)–C(9)	113 (6)	H(11)–C(11)–C(12)	93 (6)
C(1)–C(10)–C(19)	106 (1)	C(1)–C(10)–C(9)	108 (1)	C(15)–C(16)–H'(16)	106 (7)	H(16)–C(16)–H'(16)	108 (10)
C(1)–C(10)–O(1)	118 (1)	C(2)–C(1)–O(1)	124 (1)	H(16)–C(16)–C(17)	106 (8)	H'(16)–C(16)–C(17)	133 (7)
C(5)–C(4)–C(29)	113 (1)	C(29)–C(4)–C(28)	107 (1)	H(16)–C(16)–C(15)	94 (8)	C(16)–C(17)–H(17)	104 (6)
C(28)–C(4)–C(3)	106 (1)	C(3)–C(4)–C(29)	107 (1)	C(20)–C(17)–H(17)	115 (6)	H(17)–C(17)–C(13)	111 (6)
C(5)–C(4)–C(28)	111 (1)	C(4)–C(28)–O(3)	128 (1)				

Woolfson, 1971) with the help of 224 normalized structure factors. Block-diagonal least-squares refinement using anisotropic temperature factors (but excluding H atoms) gave an *R* value of 0.118. At this stage 14 H atoms were positioned assuming normal stereochemistry; no attempt was made to locate the methyl and furan ring H atoms. Final refinement (using isotropic *B* factors for H atoms) gave an *R* value of 0.107.

The atomic parameters along with their e.s.d.'s are given in Table 1, and intramolecular bond lengths and angles in Table 2.*

Discussion. The results of the present study are in complete agreement with the structures and stereochemistries deduced earlier for nimbin, nimbolide and

other related products from chemical, PMR and other studies. The *A* ring of dihydronimbin (Fig. 1) is in a slightly distorted boat conformation whereas ring *B* is in a chair conformation. Instead of a chair-like conformation (Narasimhan, 1966), a boat-like conformation for ring *A* of nimbin was proposed by Narayanan & Pachapurkar (1966) from the CD measurements of its enone system and from PMR studies of some derivatives of nimbin and cedrelone (Grant, Hamilton, Hamor, Robertson & Sim, 1963; Hodges, McGeachin & Raphael, 1963).

The intramolecular distances are C(29)–C(19) 3.35 (2), C(29)–O(4) 3.21 (2) and C(28)–O(4) 2.81 (1) Å in dihydronimbin and the corresponding distances in cedrelone, which also has a boat-like *A* ring, are 3.65, 3.15 and 2.81 Å respectively.

The intramolecular distances O(1)–C(11) and O(1)–C(12) are 3.02 (2) and 2.72 (1) Å respectively. The opposite dipoles of the carbonyl O(1) atom and the carboxyl C(12) atom would keep them close together and thus protect the C(1) ketone from attack by ketonic reagents and hence cause sluggishness in its

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34834 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

