The Structures of 2,3-Dimethyl-4aβ,5,8,8aβ-tetrahydro-1-naphthoquin-4α-ol and 6,7-Dimethyl-4aβ,5,8,8aβ-tetrahydro-1-naphthoquin-4α-ol*

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Abstract

Crystals of 2,3-dimethyl-4aβ,5,8,8aβ-tetrahydro-1-naphthoquin-4α-ol, $C_{12}H_{16}O_2$, $M_r = 192.3$, are orthorhombic, space group $P2_12_12_1$, $h00$, $h = 2n + 1$, $0k0$, $k = 2n + 1$, $00l$, $l = 2n + 1$ absent, with $a = 5.148$ (1), $b = 12.269$ (2), $c = 16.478$ (3) Å, $V = 1040.8$ (4) Å^3, $Z = 4$, $D_c = 1.226$ g cm^{-3}, μ(Mo $K\alpha$) = 0.764 cm^{-1}, $\lambda = 0.71073$ Å. 6,7-Dimethyl-4aβ,5,8,8aβ-tetrahydro-1-naphthoquin-4α-ol, $C_{12}H_{16}O_2$, $M_r = 192.3$, is monoclinic, space group $P2_1/c$, $h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$ absent, with $a = 9.242$ (3), $b = 22.724$ (3), $c = 5.139$ (2) Å, $\beta = 102.7$ (1)°, $V = 1052.8$ (5) Å^3, $Z = 4$, $D_c = 1.213$ g cm^{-3}, μ(Mo $K\alpha$) = 0.756 cm^{-1}, $\lambda = 0.71073$ Å. A CAD-4 X-ray diffractometer was used for data collection. Both structures were solved by direct methods and refined to $R = 0.031$ (671 reflections) and $R = 0.036$ (626 reflections) for the 2,3-dimethyl and 6,7-dimethyl compounds respectively. Molecules in the two crystals adopt a twisted conformation and are joined by O(4)–H⋯O(4) hydrogen bonds. The solid-state photochemistry is explained on the basis of the structural data obtained.

## Introduction

In an attempt to resolve the photoreactivity differences between tetrahydronaphthoquinols in solution and in the solid state, the structures of the title compounds were investigated. Further confirmation of the geometric requirements leading to the established naphthoquinol reaction patterns was sought from the structural data.

Experimental

Preparation of the title compounds involved sodium borohydride reduction of the appropriate Diels–Alder

adducts resulting from the thermal reactions between butadiene and 2,3-dimethylbenzoquinone, and between 2,3-dimethylbutadiene and benzoquinone, which yielded the 2,3- (I) and 6,7-dimethyl-4aβ,5,8,8aβ-tetrahydro-1-naphthoquin-4α-ols (II) respectively. Crystals of the individual compounds were afforded by slow evaporation of petroleum ether/ethanol solutions and were shown to be better than 98% pure by gas-chromatography analysis. Mass-spectral data confirmed the assigned chemical formulae $C_{12}H_{16}O_2$. All crystals exhibited acicular habits and those chosen for data collection were cut from larger crystals to measure 0.1 × 0.3 × 0.5 and 0.4 × 0.2 × 0.1 mm for the 2,3- and 6,7-dimethyl compounds, respectively.

(I)   (II)
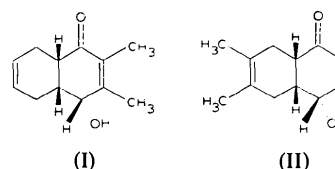
Final cell constants for both structures were obtained by least-squares fit of the $2 \sin \theta/\lambda$ values for 25 centered reflections.

In the following, quantities in square brackets refer to the 6,7-dimethyl compound. Parameters after which no brackets follow are to be regarded as the same for both title compounds.

Data collection proceeded on an Enraf–Nonius CAD-4 diffractometer in the θ range 0.0–27.5° [0.0–25.0°] using graphite-monochromatized Mo $K\alpha$ radiation. An ω–2(4/6)θ [ω–2θ] scan was employed with an ω-scan angle of (0.75 + 0.35 tan θ)° [(0.55 + 0.35 tan θ)°]. Each scan was extended 25% on both sides of the peak to allow for background measurement. The horizontal slit width was varied according to the θ-dependent relationship (2.00 + 1.00 tan θ) mm [(2.50 + 1.00 tan θ)] mm while the vertical slit remained open at a constant 4 mm. The setting angles of three reference reflections were checked periodically to ensure proper crystal orientation throughout data collection. Three other reflections were chosen as intensity controls and monitored every 3600 s of X-ray

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exposure time. Processing of the data which included application of Lorentz and polarization corrections, showed little or no decay in the check reflections' intensities. Of the 1413 [1834] reflections collected, 671 [626], or 47·5% [34·1% (55% for $0° < \theta \leq 20°$)] were classified as observed having $I \geq 3\sigma(I)$, where $\sigma^2(I)$ is defined as $S + 2B + [0·04(S - B)]^2$; S is the total peak count and B the background. The linear absorption coefficients indicated that absorption corrections were not warranted.

Solution and refinement

2,3-*Dimethyl*-4aβ,5,8,8aβ-*tetrahydro*-1-*naphthoquin*-4a-*ol*

The structure was solved by direct methods using the 156 largest E values which were derived using a K-curve normalization (Karle, 1975). The acentric E distribution was consistent with the previously assigned non-centrosymmetric space group. The E map obtained from the solution with the highest figure of merit in *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) clearly indicated the positions of the 14 non-H atoms. After two anisotropic cycles of full-matrix least-squares refinement a Fourier difference map revealed the positions of the 16 H atoms. Convergence was reached at $R = 0·031$ and $R_w = 0·036$ where $R = \sum||F_o| - k|F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - k|F_c|)^2/\sum w|F_o|^2]^{1/2}$. For the complete data set $R = 0·103$ and $R_w = 0·036$. The function minimized throughout refinement was $\sum w(|F_o| - k|F_c|)^2$ using the weighting scheme $w = 1/\sigma^2(F)$ where $\sigma^2(F)$ is derived from the previously defined $\sigma^2(I)$. A weighting analysis confirmed the suitability of the chosen weights by showing uniform average values of $w(|F_o| - k|F_c|)^2$ over ranges of $|F_o|$. A difference synthesis, following refinement, showed random fluctuations with the highest peak corresponding to 0·15 e Å^{-3}. In the final cycle of refinement 191 parameters were varied using 671 observed data and no parameter shift exceeded 0·39σ. The standard deviation in an observation of unit weight was 1·210.

6,7-*Dimethyl*-4aβ,5,8,8aβ-*tetrahydro*-1-*naphthoquin*-4a-*ol*

MULTAN yielded the positional parameters for the 14 non-H atoms. Following full-matrix least-squares refinement of the non-H atoms, the coordinates of the 16 H atoms were obtained from a difference Fourier map. Refinement proceeded with anisotropic thermal parameters for C and O and isotropic thermal parameters for H until the refinement converged. The difference Fourier map, calculated after convergence, indicated the largest peak, corresponding to excess

Table 1. *Final positional* ($\times 10^4$, *for* H $\times 10^3$) *and isotropic thermal parameters* ($U \times 10^3$ Å^2) *with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}$ trace of the diagonalized anisotropic temperature factor matrix.

	x	y	z	U_{eq}/U_{iso}
Compound (I)				
C(1)	3659 (8)	31 (3)	1937 (2)	41 (2)
C(2)	3612 (7)	−161 (3)	1055 (2)	41 (2)
C(21)	1863 (11)	−1062 (4)	770 (4)	63 (3)
C(3)	5099 (7)	441 (3)	550 (2)	40 (2)
C(31)	5222 (12)	238 (5)	−351 (3)	67 (3)
C(4)	6849 (7)	1340 (3)	862 (2)	38 (2)
C(4a)	6156 (7)	1739 (3)	1706 (2)	34 (2)
C(5)	3753 (9)	2472 (3)	1728 (2)	40 (2)
C(6)	2729 (7)	2621 (3)	2571 (2)	44 (2)
C(7)	3430 (9)	2024 (3)	3193 (2)	49 (2)
C(8)	5332 (10)	1113 (4)	3142 (2)	52 (3)
C(8a)	5790 (7)	754 (3)	2268 (2)	39 (2)
O(1)	2076 (5)	−400 (3)	2386 (2)	59 (2)
O(4)	7017 (6)	2225 (2)	292 (2)	47 (2)
H1(21)	279 (14)	−166 (5)	65 (3)	130 (25)
H2(21)	45 (18)	−129 (7)	108 (5)	205 (41)
H3(21)	102 (16)	−93 (6)	21 (4)	165 (29)
H1(31)	499 (11)	−46 (4)	−48 (3)	103 (20)
H2(31)	432 (11)	77 (4)	−67 (3)	106 (22)
H3(31)	712 (14)	43 (5)	−54 (4)	139 (24)
H(4)	866 (7)	103 (2)	86 (2)	30 (8)
H(4a)	765 (7)	218 (3)	190 (2)	40 (10)
H1(5)	229 (8)	212 (3)	135 (2)	67 (12)
H2(5)	422 (7)	318 (3)	150 (2)	38 (10)
H(6)	155 (8)	323 (3)	262 (2)	47 (10)
H(7)	287 (8)	216 (3)	377 (2)	58 (11)
H1(8)	479 (9)	46 (4)	346 (3)	78 (15)
H2(8)	694 (9)	129 (3)	340 (2)	68 (13)
H(8a)	727 (7)	39 (2)	221 (2)	24 (9)
H(O4)	570 (12)	245 (5)	19 (3)	98 (22)
Compound (II)				
C(1)	9123 (4)	9440 (2)	11056 (9)	40 (3)
C(2)	10502 (5)	9195 (2)	12635 (10)	43 (3)
C(3)	11047 (5)	8693 (2)	11972 (9)	43 (3)
C(4)	10357 (4)	8349 (2)	9557 (9)	41 (3)
C(4a)	8717 (4)	8487 (2)	8612 (9)	36 (3)
C(5)	7760 (5)	8233 (2)	10396 (11)	42 (3)
C(6)	6200 (5)	8485 (2)	9884 (9)	46 (3)
C(61)	5168 (8)	8153 (3)	11252 (18)	72 (5)
C(7)	5818 (4)	8964 (2)	8411 (9)	49 (3)
C(71)	4264 (7)	9215 (4)	7818 (21)	84 (5)
C(8)	6897 (5)	9311 (2)	7226 (11)	50 (3)
C(8a)	8499 (4)	9152 (2)	8387 (9)	37 (3)
O(1)	8540 (3)	9864 (1)	11858 (6)	58 (2)
O(4)	10627 (3)	7735 (1)	10149 (8)	53 (2)
H(2)	1094 (4)	942 (2)	1423 (9)	60 (14)
H(3)	1196 (4)	854 (1)	1281 (7)	31 (10)
H(4)	1091 (4)	846 (1)	809 (7)	42 (11)
H(4a)	841 (3)	833 (1)	682 (8)	31 (10)
H1(5)	822 (4)	830 (1)	1240 (9)	49 (13)
H2(5)	767 (4)	779 (2)	1018 (7)	48 (12)
H1(61)	417 (8)	830 (3)	1075 (13)	139 (26)
H2(61)	538 (6)	776 (3)	1120 (12)	119 (25)
H3(61)	533 (8)	819 (3)	1304 (17)	163 (40)
H1(71)	407 (7)	935 (3)	602 (15)	126 (31)
H2(71)	421 (8)	957 (3)	848 (16)	158 (34)
H3(71)	350 (7)	895 (3)	809 (13)	143 (28)
H1(8)	667 (4)	924 (2)	526 (10)	64 (14)
H2(8)	680 (4)	974 (2)	745 (8)	60 (13)
H(8a)	913 (4)	931 (1)	739 (7)	31 (11)
H(O4)	1059 (5)	757 (2)	879 (10)	57 (18)

density of $0 \cdot 12$ e Å^{-3}, was in the immediate vicinity of O(1). The mean and maximum parameter shifts on the final cycle of refinement were $0 \cdot 020$ and $0 \cdot 20\sigma$ respectively. The weights used in the refinement, $w = 1/\sigma^2(F)$ (see above), gave uniform average values of $w(|F_o| - k|F_c|)^2$ over ranges of $|F_o|$. The final R value was $0 \cdot 032$ and $R_w = 0 \cdot 037$ for the 191 parameters and 626 observations (where R and R_w are as defined above), whereas for the complete data set $R = 0 \cdot 167$ and $R_w = 0 \cdot 037$. The standard deviation in an observation of unit weight was $1 \cdot 193$.

All non-H scattering factors were taken from Cromer & Mann (1968) whereas those for H were from Stewart, Davidson & Simpson (1965). Final atomic coordinates for (I) and (II) are given in Table 1.*

Discussion

Molecules of (I) and (II) assume a conformation which is similar to that found in other tetrahydronaphtho-quinols (Greenhough & Trotter, 1980; Secco & Trotter, 1982). Bridgehead torsion angles, C(5)–C(4a)–C(8a)–C(1), of $66 \cdot 6$ (3) for (I) and $67 \cdot 3$ (5)° for (II), indicate the degree of twist in this conformation which consists of a half-chair cyclohexene ring *cis* fused to a second half-chair cyclohexenone moiety (Fig. 1). The hydroxyl group in both structures occupies the less stereochemically hindered pseudo-equatorial position in the cyclohexenone ring. Relatively short distances between the β-enone carbon, C(3), and H1(5), and between the α-enone carbon, C(2), and C(5) are a result of this conformation. Such molecular geometry makes H1(5) abstraction by C(3) and subsequent collapse of the ensuing biradical [C(2)$\cdots$C(5)] highly favorable upon ultraviolet irradiation. This sequence is observed for both the 2,3- and 6,7-dimethyl compounds in which the C(3) to H1(5) distances are $2 \cdot 84$ (4) and $2 \cdot 82$ (3) Å respectively. Both these values are less than the suggested (Dzakpasu & Scheffer, 1977) van der Waals radii sum limit of $2 \cdot 90$ Å for hydrogen abstraction by carbon. A list of other parameters involved in the abstraction reaction is given in Table 2.

A further consequence of this twisted conformation in the solid state, exhibited by naphthoquinols in which the hydroxyl group is *anti* to the bridgehead substituents, is the geometrically suitable position of the β-hydrogen, H(8), to oxygen abstraction. Although this
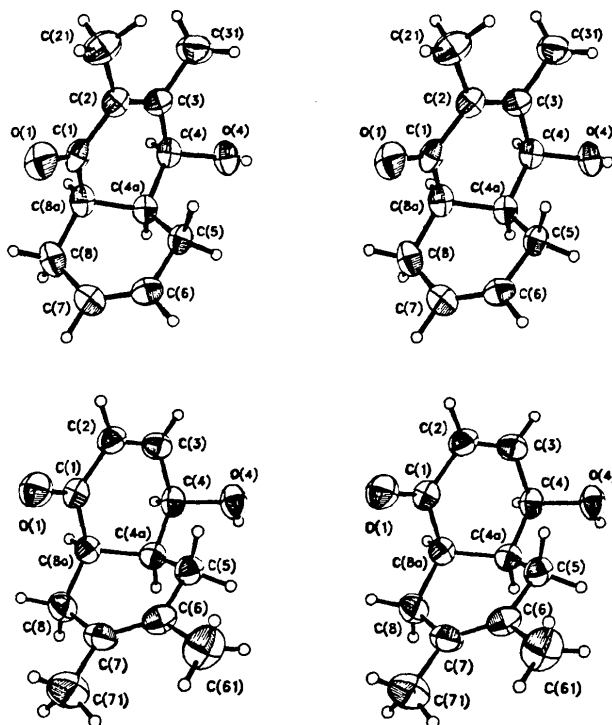
* A list of structure factors, anisotropic thermal parameters, bond distances and angles involving H atoms, torsion angles and a packing diagram have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36561 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 1. Stereodiagrams of 2,3-dimethyl-4aβ,5,8,8aβ-tetrahydro-1-naphthoquin-4α-ol (top) and 6,7-dimethyl-4aβ,5,8,8aβ-tetrahydro-1-naphthoquin-4α-ol. Thermal ellipsoids are at 50% probability. H1(5) is the upper hydrogen on C(5).

Table 2. *Geometrical parameters in the β-enone abstraction reaction*

τ_C = angle between C(3)$\cdots$H1(5) vector and the plane of the C(2)=C(3) double bond.

Δ_C = H1(5)$\cdots$C(3)=C(2) angle.

	Δ_C	τ_C	C(3)$\cdots$H1(5)	C(2)$\cdots$C(5)
(I)	79·7 (8)°	54·1°	2·84 (4) Å	3·416 (5) Å
(II)	80·9 (7)	56·7	2·82 (3)	3·353 (6)

reaction is observed in substituted naphthoquinones (Dzakpasu & Scheffer, 1977; Phillips & Trotter, 1977), its absence in the photoreactivity of naphthoquinols has been rationalized on the basis of the following two points (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980). First, in the quinone systems, the carbonyl group aids in stabilizing the biradical resulting from intramolecular β-hydrogen abstraction, whereas the quinols lack this possibility of π-electron delocalization. Secondly, any charge-transfer interaction (which may be required for β-hydrogen abstraction) between the cyclohexene double bond and the excited ene-one chromophore is facilitated by the 2-ene-1,4-dione moiety which is a better electron acceptor than the 2-ene-1-one chromophore.

While the 2,3-dimethylnaphthoquinol (I) exhibits no oxygen-abstraction photoreactivity, the 6,7-dimethyl compound yields a second solid-state photoproduct which results from the unprecedented tetrahydronaphthoquinol reaction, oxygen abstraction of a β-hydrogen. The pertinent geometrical factors in the abstraction process are τ_O, the angle subtended by the oxygen to β-hydrogen vector and its projection on the plane of the carbonyl double bond, and Δ_O, the $C(1)-O(1)\cdots\beta$-H angle. These angles are 1 and 81 (1)° respectively which are close to the ideal abstraction angles of $\tau_O = 0$ and $\Delta_O = 90°$.

Further investigation of the unsubstituted and other substituted tetrahydronaphthoquinols reveals that the oxygen-abstraction photoprocess occurs only in the systems in which the 2 and 3 positions on the cyclohexenone moiety are unsubstituted (Scheffer & Walsh, unpublished results). This suggests that once conformational control is established, methyl substitution (or lack thereof) on the enone double bond plays a critical role in determining the photochemical reaction pathway in the solid state. In view of these recent findings, the previous rationale (see above) used in explaining the lack of oxygen abstraction in tetrahydronaphthoquinols becomes less general.

Irradiation in solution, where conformational equilibration is facile, affords mainly intramolecular 2 + 2 cycloadducts (Appel, Herbert, Jiang, Scheffer & Walsh, 1981) owing to the presence of higher-energy conformers which place the two intramolecular double bonds parallel to each other and within reacting distance. The absence of intramolecular cycloaddition products in the solid-state photolysis of (I) and (II) is due mainly to the inability of the reactant molecules to undergo the extensive conformational rearrangement required to attain the reacting geometry. In the ground state, the C=C double bonds are non-parallel with $C(2)\cdots C(7)$ and $C(3)\cdots C(6)$ separations of 4·427 (5) and 4·442 (5) Å respectively for (I), and 4·427 (6) and 4·397 (6) Å for (II).

Generally, bond lengths and angles (Table 3) correspond to accepted values (Sutton, 1965). However, angles involving the methyl groups deviate from the normal values, reflecting the steric interaction between adjacent substituents.

Molecules of (I) are linked in the crystal by $O(4)-H\cdots O(4)$ hydrogen bonds to form chains running along a. The $O(4)-H\cdots O(4)$ angle is 166 (6)° with an $H\cdots O(4)$ distance of 2·09 (6) Å. Similarly, $O(4)-H\cdots O(4)$ interactions join molecules of (II) in the crystal forming a linkage along the c axis. The hydrogen-bond angle and distance are 171 (5)° and 2·00 (5) Å respectively. All other intermolecular contacts correspond to normal van der Waals distances.

Table 3. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

	(I)	(II)
C(1)–C(2)	1·471 (5)	1·463 (6)
C(1)–C(8a)	1·512 (5)	1·514 (6)
C(1)–O(1)	1·221 (4)	1·219 (4)
C(2)–C(21)	1·502 (6)	–
C(2)–C(3)	1·351 (5)	1·321 (5)
C(3)–C(31)	1·506 (6)	–
C(3)–C(4)	1·514 (5)	1·487 (6)
C(4)–C(4a)	1·518 (5)	1·519 (6)
C(4)–O(4)	1·438 (4)	1·437 (5)
C(4a)–C(5)	1·530 (5)	1·521 (6)
C(4a)–C(8a)	1·533 (5)	1·525 (5)
C(5)–C(6)	1·497 (5)	1·520 (6)
C(6)–C(61)	–	1·506 (7)
C(6)–C(7)	1·310 (5)	1·327 (5)
C(7)–C(71)	–	1·514 (7)
C(7)–C(8)	1·489 (6)	1·501 (6)
C(8)–C(8a)	1·525 (6)	1·514 (5)
C(2)–C(1)–C(8a)	117·5 (3)	116·7 (4)
C(2)–C(1)–O(1)	121·2 (3)	120·6 (4)
C(8a)–C(1)–O(1)	121·3 (3)	122·6 (4)
C(1)–C(2)–C(21)	115·9 (4)	–
C(1)–C(2)–C(3)	120·8 (3)	121·4 (5)
C(21)–C(2)–C(3)	123·3 (4)	–
C(2)–C(3)–C(31)	122·7 (4)	–
C(2)–C(3)–C(4)	121·8 (3)	123·5 (4)
C(31)–C(3)–C(4)	115·5 (4)	–
C(3)–C(4)–C(4a)	113·9 (3)	111·9 (4)
C(3)–C(4)–O(4)	111·3 (3)	108·1 (4)
C(4a)–C(4)–O(4)	111·7 (3)	112·5 (3)
C(4)–C(4a)–C(5)	113·6 (3)	113·6 (4)
C(4)–C(4a)–C(8a)	109·2 (3)	109·6 (3)
C(5)–C(4a)–C(8a)	110·5 (3)	109·7 (4)
C(4a)–C(5)–C(6)	112·2 (3)	114·1 (4)
C(5)–C(6)–C(61)	–	113·8 (5)
C(5)–C(6)–C(7)	124·1 (3)	122·0 (4)
C(61)–C(6)–C(7)	–	124·1 (5)
C(6)–C(7)–C(71)	–	123·1 (5)
C(6)–C(7)–C(8)	123·9 (4)	123·0 (4)
C(71)–C(7)–C(8)	–	113·9 (5)
C(7)–C(8)–C(8a)	111·8 (4)	113·2 (4)
C(1)–C(8a)–C(4a)	109·5 (3)	110·0 (3)
C(1)–C(8a)–C(8)	113·4 (3)	113·5 (4)
C(4a)–C(8a)–C(8)	111·2 (3)	111·6 (4)

References

APPEL, W. K., GREENHOUGH, T. J., SCHEFFER, J. R., TROTTER, J. & WALSH, L. (1980). *J. Am. Chem. Soc.* **102**, 1158–1160.

APPEL, W. K., HERBERT, D., JIANG, Z. Q., SCHEFFER, J. R. & WALSH, L. (1981). In preparation.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

DZAKPASU, A. A. & SCHEFFER, J. R. (1977). *J. Am. Chem. Soc.* **100**, 2163–2173.

GREENHOUGH, T. J. & TROTTER, J. (1980). *Acta Cryst.* B36, 1831–1835.

KARLE, I. L. (1975). Summer School on Crystallographic Computing, Prague. Published as *Crystallographic Computing Techniques* (1976), edited by F. R. AHMED, pp. 27–70. Copenhagen: Munksgaard.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

PHILLIPS, S. E. V. & TROTTER, J. (1977). *Acta Cryst.* B33, 996–1003.

SECCO, A. S. & TROTTER, J. (1982). *Acta Cryst.* B38, 1229–1232.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.

SUTTON, L. E. (1965). Editor, *Tables of Interatomic Distances and Configuration in Molecules and Ions.* Spec. Publ. No. 18. London: The Chemical Society.

Delphinifoline: a Lycoctonine Alkaloid with Configuration 1α-OH

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Abstract

Delphinifoline, $C_{23}H_{37}NO_7$, orthorhombic, $P2_12_12_1$, $a = 15·750$ (5), $b = 16·356$ (6), $c = 8·415$ (2) Å, $V = 2166·4$ Å³, $D_c = 1·347$ Mg m⁻³, $Z = 4$, μ(Mo $K\alpha$) = 0·1062 mm⁻¹; $F(000) = 952$; $R = 0·038$ for 1154 contributing reflections. The substitution pattern is 1α-OH, 4β-CH_2OCH_3, 6β-OH, 7α-OH, 8β-OH, 14α-OH, 16β-OCH_3, N-ethyl. The presence of an oxygenated functional group at C(7) established delphinifoline as a member of the lycoctonine family of alkaloids. The α configuration observed at C(1) is unexpected and calls into question the structural assignments of all alkaloids of this class.

Introduction

Delphinifoline was isolated as a minor alkaloid from *Aconitum delphinifolium* DC (Aiyar, Codding, Kerr, Benn & Jones, 1981) by chromatography on neutral alumina. Recrystallization from methanol yielded colourless needles, m.p. 491–493 K. The crystal chosen for analysis had dimensions 0·15 × 0·10 × 0·20 mm and was mounted about the *c* axis. Data were collected on a Picker FACS-I diffractometer operated in the $\theta/2\theta$ scan mode with a scan width $\Delta 2\theta = (1·4 + 0·692 \times \tan \theta)°$ and a scan rate of 1° min⁻¹. Background was measured for 20 s at either end of the scan. Of the 1642 reflections accessible with $2\theta < 45°$, 852 had intensities $I > 3\sigma(I)$ where $\sigma(I) = [T + S^2B + 0·02I^2]^{1/2}$, T is the

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Table 1. *Positional parameters* $(\times 10^4)$ *and equivalent isotropic thermal parameters* $(\times 10^3)$ *for non-hydrogen atoms in delphinifoline*

$U_{eq} = \frac{1}{3}$ trace $\tilde{U}$ where $\tilde{U}$ is the diagonalized U_{ij} matrix. The e.s.d. for U_{eq} is $\sim 5 \times 10^{-3}$ Å².

	x	y	z	U_{eq} (Å²)
C(1)	8147 (4)	3654 (5)	29 (9)	38
C(2)	7577 (5)	4329 (5)	−573 (9)	46
C(3)	6669 (5)	4039 (5)	−798 (9)	53
C(4)	6319 (5)	3549 (5)	636 (9)	38
C(5)	6929 (4)	3619 (4)	2118 (8)	32
C(6)	6611 (4)	3026 (4)	3417 (9)	35
C(7)	7194 (4)	2270 (4)	3265 (8)	28
C(8)	7905 (4)	2247 (5)	4530 (8)	34
C(9)	8376 (4)	3074 (5)	4554 (8)	30
C(10)	8512 (4)	3423 (4)	2897 (8)	26
C(11)	7812 (4)	3272 (4)	1626 (8)	26
C(12)	9402 (4)	3084 (5)	2353 (9)	34
C(13)	9700 (4)	2537 (4)	3714 (9)	32
C(14)	9291 (4)	2979 (4)	5100 (9)	32
C(15)	8509 (5)	1515 (4)	4326 (8)	32
C(16)	9371 (4)	1671 (4)	3527 (9)	32
C(17)	7581 (4)	2361 (4)	1591 (8)	28
C(18)	5449 (5)	3900 (5)	1062 (10)	52
C(19)	6204 (5)	2658 (5)	233 (9)	38
C(20)	6878 (5)	1346 (5)	−212 (10)	49
C(21)	7672 (6)	843 (5)	−406 (13)	69
C(22)	4745 (5)	5095 (5)	1902 (11)	69
C(23)	9877 (5)	274 (5)	3721 (12)	58
N	7016 (4)	2215 (3)	177 (7)	35
O(1)	8288 (3)	3041 (3)	−1177 (6)	47
O(2)	5523 (4)	4741 (3)	1502 (8)	61
O(3)	6620 (3)	3392 (3)	4997 (5)	41
O(4)	6705 (3)	1532 (2)	3365 (5)	40
O(5)	7482 (3)	2096 (3)	6040 (5)	41
O(6)	9429 (3)	2549 (3)	6564 (6)	47
O(7)	9998 (3)	1121 (3)	4172 (6)	43