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(±)-*N*-Demethyl-*N*-formylmesembrenone

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Abstract. $C_{17}H_{19}NO_4$, monoclinic, $P2_1/a$, $a = 14{\cdot}698\,(9)$, $b = 9{\cdot}176\,(9)$, $c = 12{\cdot}161\,(9)$ Å, $\beta = 112{\cdot}17\,(3)^\circ$, $Z = 4$, $D_x = 1{\cdot}137$ g cm^{-3}. The orientation of the aromatic ring, such that the C(2′)–H(2′) bond is over the N(1)–C(2) bond and H(6′) is over C(4), differs substantially from the orientation of the aromatic ring in analogs containing a saturated C(4)–C(5) bond.

Introduction. Radioactive (±)-*N*-demethyl-*N*-formylmesembrenone (0·044 μCi/mg) (2) was isolated from *Sceletium strictum* after the feeding of [4′-OCT_3]-mesembrenone (1) to the plants (Karle, 1976) (see Fig. 1). Although presumably optically active in the plants, all of the mesembrine alkaloids containing a 6-keto-4-ene function have been isolated in racemic form (see discussion, Lettenbauer & Popelak, 1968; Jeffs, Capps, Johnson, Karle, Martin, & Rauckman, 1974). Because of insufficient material to assign unequivocally the structure of (2) by chemical and spectroscopic methods, a single-crystal X-ray analysis was undertaken to confirm the proposed structure. *N*-Demethyl-*N*-formylmesembrenone also represented the first mesembrine alkaloid containing an α,β-unsaturated ketone to be studied by X-ray analysis.

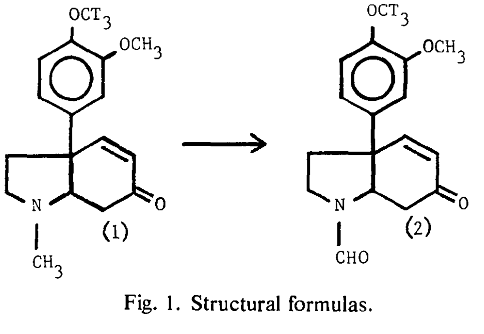

Fig. 1. Structural formulas.

The X-ray intensity data were collected from one crystal (plate, $CHCl_3$/EtOAc, 0·03 × 0·16 × 0·22 mm) on a four-circle automatic diffractometer using the θ–2θ technique with a $2{\cdot}0^\circ + 2\theta(\alpha_2) - 2\theta(\alpha_1)$ scan over 2θ with Cu $K\alpha$ radiation; 2112 reflections were scanned up to $2\theta = 115^\circ$. Only those reflections up to $2\theta = 100^\circ$ were used for the least-squares refinement. Unit-cell parameters were determined from a least-squares fit of the values θ, ψ, ω, and φ for 12 reflections which were individually centered on the diffractometer. The space group $P2_1/a$ was determined unequivocally from the extinctions $0k0$ (k = odd) and $h0l$ (h = odd). All intensities were corrected for Lorentz and polarization factors, and normalized structure factors, $|E|$, were derived. Phases for the structure factors were determined directly from the observed normalized structure factor magnitudes by means of the symbolic addition procedure (Karle & Karle, 1966). 487 phases for reflections with $|E| > 1{\cdot}1$ were used to compute a three-dimensional map.

Although the Σ_2 phase relationship does not hold for a number of the strong triples, a number of subsets of phases which were not connected with the original origin were correctly assigned. All the heavy atoms in the molecule appeared in the E map, but the molecule was too close to a symmetry equivalent and needed to be translated. The calculated translation function (Karle, 1972) contained one large peak at $x = 32/60$, $y = 0$, $z = 8/60$, which indicated the necessary translation of $\Delta x = -16/60$, $\Delta y = 0$, $\Delta z = -4/60$.

A least-squares refinement of the coordinates and isotropic thermal factors for the C, N, and O atoms was followed by refinement with anisotropic thermal factors for all data with $2\theta < 100^\circ$ (1586 reflections). Difference maps at this stage revealed all the H atoms except those on the *O*-methyl groups which were assigned calculated coordinates. The assumption was made that two H atoms of the *O*-methyl groups straddled the neighboring H atoms on the phenyl ring. The H coordinates listed in Table 2 have not been refined. One more cycle of refinement with anisotropic thermal factors and the inclusion of the H atoms with constant parameters resulted in an R $(= \Sigma||F_o| - |F_c||/\Sigma|F_o|)$ of 7·8% for 1586 reflections. The function minimized was $\Sigma\omega(|F_o| - |F_c|)^2$ where $\omega = 1/\sigma^2$, and the weights were calculated according to the procedure outlined by Gilardi (1973). The restricted set of data was used in the refinement since the intensities of the reflections beyond $2\theta > 100^\circ$ were very weak; that is, there were only 31 reflections with $|F_o| > 10$ among 528 reflections ($2\theta > 100$), and the remainder were mainly

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Table 1. *Fractional coordinates* (×10⁴) *and thermal parameters for the non-hydrogen atoms*

Standard deviations are in parentheses. The thermal parameters are expressed in the form:
$T = \exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}hlb^*c^*)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N(1)	4914 (5)	7952 (7)	550 (5)	3·3 (4)	2·9 (3)	2·0 (3)	0·2 (3)	1·0 (3)	0·3 (3)
C(2)	5972 (6)	7648 (9)	732 (7)	2·7 (4)	6·0 (5)	2·9 (4)	1·0 (4)	1·0 (4)	0·4 (4)
C(3)	6523 (6)	7893 (9)	2112 (7)	4·4 (5)	5·8 (5)	3·2 (4)	0·2 (4)	2·1 (4)	0·2 (4)
C(3a)	5733 (6)	7407 (8)	2610 (7)	3·4 (5)	2·7 (4)	2·8 (4)	0·2 (4)	1·4 (4)	0·2 (3)
C(4)	5693 (7)	5739 (9)	2550 (6)	5·2 (6)	3·5 (5)	2·2 (4)	0·7 (4)	1·0 (4)	0·3 (4)
C(5)	4876 (7)	4950 (9)	2061 (7)	4·2 (5)	3·6 (5)	3·2 (4)	−0·4 (5)	0·6 (4)	−0·8 (4)
C(6)	3905 (7)	5643 (10)	1550 (7)	3·3 (6)	4·1 (5)	3·0 (4)	−0·7 (5)	1·2 (4)	−0·4 (4)
C(7)	3844 (6)	7267 (8)	1680 (7)	2·7 (4)	2·6 (4)	3·7 (4)	−0·2 (4)	1·5 (4)	0·5 (4)
C(7a)	4755 (6)	8074 (8)	1698 (6)	3·6 (4)	2·5 (4)	2·7 (4)	0·3 (4)	1·6 (4)	0·1 (3)
C(1′)	5980 (6)	7980 (8)	3868 (6)	3·3 (5)	2·4 (4)	2·3 (4)	0·5 (4)	1·0 (4)	0·4 (3)
C(2′)	6105 (6)	9503 (9)	4089 (7)	3·6 (5)	3·1 (5)	2·0 (4)	0·2 (4)	1·1 (4)	0·4 (4)
C(3′)	6353 (6)	10023 (9)	5225 (7)	3·8 (5)	1·9 (4)	3·0 (4)	0·1 (4)	1·2 (4)	0·5 (4)
C(4′)	6478 (6)	9114 (9)	6192 (7)	3·0 (5)	2·7 (5)	3·5 (4)	0·2 (4)	1·0 (4)	0·4 (4)
C(5′)	6326 (6)	7629 (9)	5970 (7)	4·6 (5)	3·9 (5)	3·8 (4)	0·6 (4)	2·6 (4)	1·2 (4)
C(6′)	6075 (6)	7060 (9)	4795 (6)	3·4 (5)	2·8 (4)	2·7 (4)	−0·3 (4)	0·9 (4)	−0·3 (4)
C(8)	4271 (6)	8425 (9)	−491 (7)	4·9 (6)	3·0 (4)	2·6 (4)	−0·7 (4)	0·8 (4)	−0·1 (4)
O(9)	4440 (4)	8475 (6)	−1417 (5)	0·1 (4)	4·9 (4)	2·8 (3)	0·5 (3)	1·4 (3)	0·3 (3)
O(10)	3155 (5)	4912 (7)	1105 (5)	4·9 (4)	4·7 (4)	5·9 (4)	−1·3 (3)	1·7 (3)	1·0 (3)
O(11)	6749 (4)	9725 (6)	7292 (4)	5·0 (3)	3·6 (3)	2·1 (3)	−0·5 (3)	0·8 (3)	−0·7 (3)
C(12)	6949 (7)	8790 (10)	8304 (6)	8·4 (6)	4·7 (5)	1·9 (4)	1·1 (5)	1·9 (4)	1·3 (4)
O(13)	6499 (4)	11480 (6)	5533 (4)	6·0 (4)	2·6 (3)	3·3 (3)	−0·5 (3)	1·5 (3)	−0·5 (3)
C(14)	6318 (7)	12555 (9)	4595 (7)	6·9 (6)	3·1 (4)	4·0 (4)	0·4 (4)	1·9 (4)	1·6 (4)

Table 2. *Approximate coordinates* (×10³) *for the H atoms*

$B = 4·5$ Å² for all atoms.

	x	y	z
H(2α)	598	661	51
H(2β)	628	828	20
H(3α)	681	733	197
H(3β)	664	883	216
H(4)	635	538	315
H(5)	495	389	172
H(7α)	330	769	102
H(7β)	364	754	241
H(7a)	471	912	195
H(2′)	599	1019	340
H(5′)	638	692	662
H(6′)	597	598	466
H(8)	362	857	−43
H(C12)	753	810	837
H′(C12)	638	817	823
H″(C12)	716	936	906
H(C14)	561	1249	402
H′(C14)	675	1234	412
H″(C14)	646	1355	491

$0 \leq |F_o| \leq 5$. Atomic coordinates and thermal parameters are given in Tables 1 and 2.*

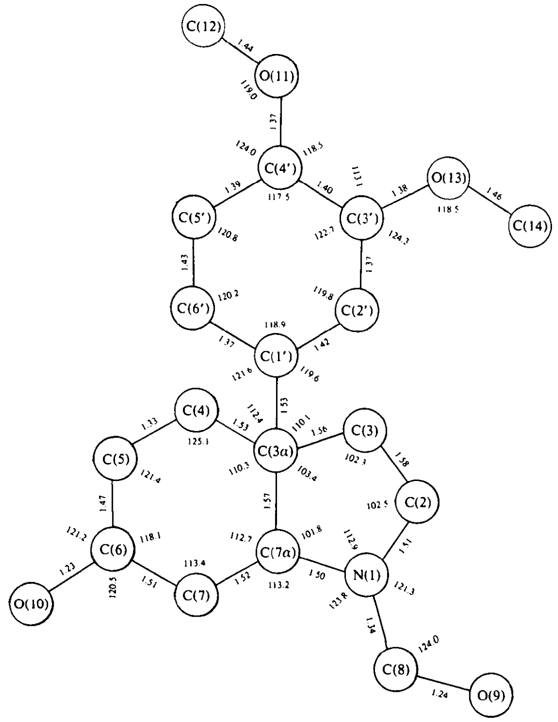

Fig. 2. Bond distances and angles. Standard deviations are of the order of 0·01 Å for the bond lengths and 0·8° for the bond angles. Also, C(1′)–C(3a)–C(7a) is 112·4° and C(3)–C(3a)–C(4) is 106·7°.

Discussion. Fig. 2 contains the bond lengths and angles for the non-hydrogen atoms. Fig. 3 shows the conformation of the molecule. Most of the bond lengths and angles are within normal ranges. The somewhat shorter C(5)–C(6) bond demonstrates a small amount of double-bond character. Compared to the structure of mesembrine alkaloids containing

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31965 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Fig. 3. Stereo diagram of *N*-demethyl-*N*-formylmesembrenone drawn by *ORTEP* (Johnson, 1965). The atoms O, N, C, and H are represented by spheres of decreasing radii.

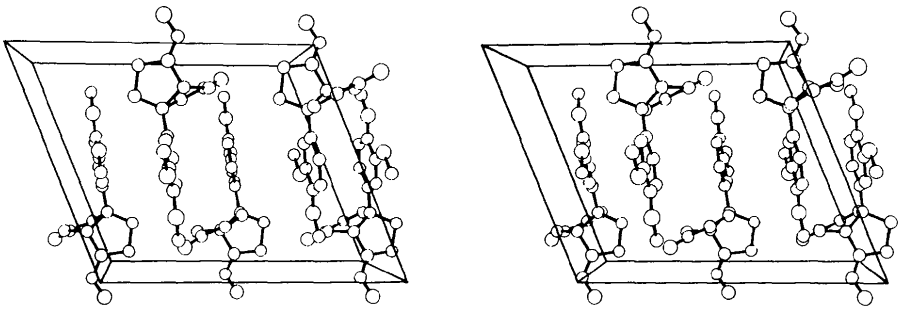

Fig. 4. Packing diagram. The view is seen looking down **b** with **a** → and **c** ↑ .

Table 3. *Deviations of atoms* (Å) *from least-squares planes*

Atoms marked with an asterisk have not been included in the calculation of the plane.

Plane I	C(1′) 0·011, C(2′) 0·017, C(3′) 0·008, C(4′) –0·024, C(5′) –0·072, C(6′) –0·053, C(3a) 0·062, O(11) 0·004, C(12) 0·068, O(13) 0·024, C(14) –0·044
Plane II	C(7a) –0·039, N(1) 0·063, C(2) –0·059, C(3) 0·035, C(3a)* –0·623
Plane III	C(3a) –0·035, C(4) 0·032, C(5) 0·008, C(6) –0·045, C(7) 0·039, C(7a)* –0·568

an *N*-methyl group in place of the *N*-formyl group (Jeffs, Luhan, McPhail & Martin, 1971; Luhan & McPhail, 1972, 1973) in which the bonds around the N atom are 1·46–1·47 (2) Å, the N(1)–C(2) and N(1)–C(7a) bonds in (2) are slightly longer at 1·50–1·51 (1) Å, and the N(1)–C(8) bond is significantly shorter at 1·34 (1) Å. The C(3a)–C(4)–C(5) angle has been stretched to 125·1 (8)°.

The displacements of atoms from various least-squares planes are given in Table 3. Plane I demonstrates the approximate coplanarity of the phenyl ring, the methoxyl groups, and C(3a). Plane II illustrates the envelope conformation of the five-membered ring with C(3a) 0·633 Å below the average plane of the other four atoms. A 172° torsion angle for C(7a)–N(1)–C(8)–O(9) shows the substantial planarity of the *N*-formyl group. Because of three sp^2 C atoms in the six-membered ring, the ring is also nearly planar with only C(7a) deviating significantly (0·568 Å) from the average plane of the other five atoms (see plane III).

The conformation of the aromatic ring in which the C(2′)–H(2′) bond is above the N(1)–C(2) bond and H(6′) is over C(4) differs from the conformation of the aromatic ring in the mesembrine alkaloids previously studied: sceletium A_4 (Jeffs *et al.*, 1971; Luhan & McPhail, 1972), mesembranol (Luhan & McPhail, 1973), and 6-epimesembranol methiodide (Coggin, Farrier, Jeffs & McPhail, 1970), in which the C(2′)–H(2′) bond points over the C(7)–C(7a) bond and H(6′) is sandwiched between H atoms on C(3) and C(4). In other words, the torsion angle C(2′)–C(1′)–C(3a)–C(7a) is –59° for (2) whereas the same torsion angle in the other alkaloids is near +5 to +10°. Unlike the mesembrine alkaloids previously studied, (2) contains no axial H atoms on C(4) or C(5) to interact with H atoms on the aromatic ring.

The packing diagram, illustrated in Fig. 4, is dominated by the parallel stacking of the dimethoxyphenyl groups.

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Chlorides with the Chrysoberyl Structure: Na_2CoCl_4 and Na_2ZnCl_4

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Abstract. Na_2CoCl_4: *Pnma*, $a = 13{\cdot}713$ (2), $b = 8{\cdot}073$ (1), $c = 6{\cdot}4277$ (6) Å, $Z = 4$; and Na_2ZnCl_4: *Pnma*, $a = 13{\cdot}695$ (1), $b = 8{\cdot}0528$ (7), $c = 6{\cdot}4017$ (8) Å. Structure refinements based on neutron diffraction powder diagrams establish the chrysoberyl structure for both compounds.

Introduction. As part of a research programme on the structural relations of compounds in the systems NaCl–TCl_2 and LiCl–TCl_2 (where T represents a first-row transition or alkaline-earth metal) we investigated the crystal structure of Na_2CoCl_4 and Na_2ZnCl_4. Li_2ZnCl_4 was also prepared and its X-ray pattern indexed.

Detailed information about the background to the investigations can be obtained from some earlier papers (van Loon & Verschoor, 1973; van Loon, 1974; van Loon & IJdo, 1975; van Loon & de Jong, 1975).

The compounds Na_2ZnCl_4 and Li_2ZnCl_4 had been reported to have the chrysoberyl structure (Eysel, 1971) with the following structural data. Na_2ZnCl_4: space group *Pnam*; $a = 13{\cdot}72$, $b = 6{\cdot}42$, $c = 8{\cdot}09$ Å; Li_2ZnCl_4: space group $P2_122_1$; $a = 12{\cdot}78$, $b = 6{\cdot}12$, $c = 7{\cdot}43$ Å. The crystal structure of Na_2CoCl_4 has not previously been reported.

NaCl and LiCl were dried in vacuum at 200 and 400 °C respectively. $CoCl_2$ was obtained by dehydrating $CoCl_2.6H_2O$ in a vacuum in steps up to 400°C, followed by melting in dry HCl gas. $ZnCl_2$ was melted in dry HCl gas after dehydration in a vacuum at 200 °C.

Stoichiometric amounts of the starting materials were evacuated up to 10^{-5} torr and fused together in a dry HCl atmosphere; the products were annealed for one week in a dry N_2 atmosphere just below the melting point. While Na_2ZnCl_4 could be cooled in the normal way, Na_2CoCl_4 had to be quenched in the liquid N_2. The latter compound has been investigated by DTA (by means of a Mettler Vacuum Thermal Analyzer TA1) and appears to be unstable below 367 °C.

The prepared samples were pulverized in a glove-box filled with dry N_2, again heated for a week just below their respective melting points (Na_2CoCl_4: 380; Na_2ZnCl_4: 400 °C) and cooled as before. Because of the extremely hygroscopic nature of the compounds, all handling was carried out in N_2- or Ar-filled glove-boxes.

An elemental analysis* was carried out for Na_2ZnCl_4 with the following results (wt %): Zn, obs. 25·38, calc. 25·82; Cl, obs. 56·83, calc. 56·02.

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* This analysis was carried out under the supervision of W. J. Buis at the Micro-Analytical Department of the Institute for Organic Chemistry, TNO, Utrecht, The Netherlands.