Fig. 2. *ORTEP* drawing of 3-hydroxy-7-methoxy-3',4'-methylenedioxyflavan. Thermal ellipsoids are presented at the 50% probability level while H atoms are represented by spheres of arbitrary radius.

The methoxy methyl group bonded to C(7) is twisted slightly out of the plane as indicated by the C(6)C(7)-O(10)C(11) torsion angle of 10·4 (7)°. The five-membered ring is almost planar and a least-squares plane fitted to the atoms of the phenyl and methylenedioxy moieties shows a maximum deviation of 0·02 Å for O(7) and C(8). The conformation of the six-membered heterocyclic ring lies between the half-chair and 1,2-diplanar forms. The six C—C distances of the phenyl ring (4a–8a) average 1·387 (6) Å while the six C—C distances of the other phenyl ring average 1·370 (15) Å. The four $C(sp^2)$—$O(sp^3)$ distances average 1·378 (9) Å and the five $C(sp^3)$—$O(sp^3)$

distances 1·429 (11) Å. An intermolecular hydrogen bond is formed between the hydroxyl group bonded to C(3) and the O(10) methoxy O atom, O(9)···O(10) = 2·874 (5), O(9)—H(9) = 1·06 (9) and H(9)···O(10) = 1·87 (9) Å. The absolute configuration could not be assigned unambiguously from enantiomorph refinement and application of the Hamilton significance test.

References

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.
GOPALAKRISHNA, E. M., WATSON, W. H., PACHECO, P. & SILVA, M. (1976). *Cryst. Struct. Commun.* 5, 795–799.
GOPALAKRISHNA, E. M., WATSON, W. H., SILVA, M. & PACHECO, P. (1978). *Cryst. Struct. Commun.* 7, 41–46.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
PACHECO, P., SILVA, M., STEGLICH, W. & WATSON, W. H. (1978). *Rev. Latinoam. Quím.* 9, 28–32.
STEWART, J. M. (1976). The XRAY 76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
WATSON, W. H., TAIRA, Z., SILVA, M. & PACHECO, P. (1977). *Cryst. Struct. Commun.* 6, 797–801.
ZABEL, V., WATSON, W. H., PACHECO, P. & SILVA, M. (1979). *Cryst. Struct. Commun.* 8, 371–376.

N,O-Diacetyl-4-hydroxynornantenine

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Abstract. $C_{23}H_{23}NO_7$, M_r = 425·15, tetragonal, $P4_12_12$, a = 14·996 (4), c = 17·960 (4) Å, V = 4039 (2) Å^3, Z = 8, d_c = 1·398 Mg m^{-3}, μ = 0·744 mm^{-1}, λ(Cu $K\alpha$) = 1·54178 Å. Full-matrix least-squares refinement (nonhydrogen atoms anisotropic, H atoms isotropic) based on 1921 reflexions led to a final R of 0·045. 4-Hydroxynornantenine is a nor-aporphine-type alkaloid. The N and attached atoms

form a reasonably planar system which implies sp^2 hybridization of the N atom and conjugation with the carbonyl of the *N*-acetyl function.

Introduction. *Laurelia phillipiana* Looser (Atherospermataceae) is a Chilean tree which has yielded several aporphines and 7-oxoaporphines (Urzua, Cassels, Comin & Sanchez, 1975). A further study of

the minor bases led to the isolation for the first time of a 4-hydroxynoraporphine (Urzua & Cassels, 1978). The structure was postulated on the basis of spectroscopic properties and by comparison with known alkaloids. The relative configuration was established by a single-crystal X-ray diffraction study. We report here the structure of *rel*-(4*R*,6a*S*)-*N,O*-diacetyl-4-hydroxy-nornantenine (I).

(I)
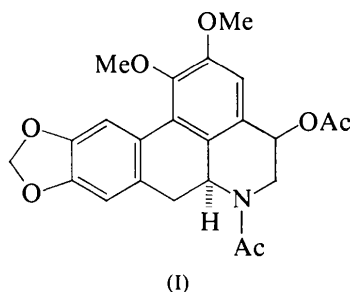
A crystal of dimensions 0·5 × 0·5 × 0·44 mm was used to collect intensity data on a Syntex $P2_1$ diffractometer system by the θ:2θ scanning technique using a variable scan speed and a graphite mono-chromator. Room-temperature lattice parameters were refined by a least-squares procedure utilizing 15 reflexions whose angles were measured by a centering routine associated with the Syntex diffractometer. Systematic absences were consistent with space group $P4_12_12$ or $P4_32_12$. A periodically monitored reflexion showed no significant change in intensity. Of the 2029 independent reflexions measured, 99 had intensities less than $2\sigma(I)$ and were not used in the refinement. Nine additional reflexions showed significant secondary extinction and were dropped from the final refinement. Lorentz and polarization corrections were applied, but no absorption corrections were made.

The direct-methods program *MULTAN* (Germain, Main & Woolfson, 1971) was used to calculate phases for the 300 $|E|$ values greater than 1·7. The phase set with the largest combined figure of merit was selected, and the E map calculated with these phases revealed the positions of 29 nonhydrogen atoms. Alternate least-squares refinements and difference Fourier calculations yielded the coordinates of the two missing heavy atoms and all H atoms. Least-squares refinement was terminated at a final R of 0·045 where $R = \sum \|F_o| - |F_c\|/\sum |F_o|$. The function minimized in the refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = [1/\sigma(F_o)]^2$ was determined from counting statistics. H atom thermal parameters were refined isotropically.

A final difference map showed no peak larger than 0·2 e Å^{-3}. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Atomic positional parameters are given in Table 1

while interatomic distances, valence and torsion angles are presented in Table 2.*

Table 1. *Positional parameters* ($\times 10^4$, *for* H $\times 10^3$) *for N,O-diacetyl-4-hydroxynornantenine*

	x	y	z
C(1)	8307 (2)	6170 (2)	8031 (1)
C(2)	9093 (2)	6631 (2)	7870 (1)
C(3)	9835 (2)	6177 (2)	7628 (1)
C(3a)	9800 (2)	5253 (2)	7539 (1)
C(4)	10611 (2)	4721 (2)	7308 (1)
C(5)	10586 (2)	3832 (2)	7709 (2)
N(6)	9802 (2)	3376 (1)	7437 (1)
C(6a)	8947 (2)	3788 (2)	7601 (2)
C(7)	8509 (2)	3404 (2)	8279 (2)
C(7a)	7597 (2)	3797 (2)	8353 (1)
C(8)	6890 (2)	3253 (2)	8582 (2)
C(9)	6061 (2)	3620 (2)	8592 (2)
C(10)	5914 (2)	4496 (2)	8413 (1)
C(11)	6582 (2)	5053 (2)	8181 (1)
C(11a)	7457 (2)	4700 (2)	8156 (1)
C(11b)	8253 (2)	5234 (2)	7957 (1)
C(11c)	9021 (2)	4788 (2)	7692 (1)
O(12)	7567 (1)	6654 (1)	8235 (1)
C(13)	7540 (2)	6925 (3)	8983 (2)
O(14)	9055 (1)	7526 (1)	7979 (1)
C(15)	9802 (2)	8037 (2)	7738 (2)
O(16)	11416 (1)	5201 (1)	7498 (1)
C(17)	12160 (2)	4895 (2)	7156 (2)
C(18)	12974 (2)	5384 (3)	7388 (2)
O(19)	12154 (1)	4296 (2)	6718 (1)
C(20)	9821 (2)	2641 (2)	6990 (2)
C(21)	10716 (3)	2223 (3)	6856 (3)
O(22)	9136 (2)	2340 (2)	6727 (2)
O(23)	5273 (1)	3214 (2)	8792 (1)
C(24)	4614 (2)	3883 (3)	8751 (2)
O(25)	5013 (1)	4680 (2)	8459 (1)
H(3)	1040 (3)	643 (2)	762 (2)
H(4)	1055 (3)	464 (3)	673 (2)
H(5α)	1111 (3)	355 (3)	772 (2)
H(5β)	1069 (4)	385 (4)	833 (3)
H(6α)	861 (2)	366 (2)	712 (2)
H(7α)	856 (2)	269 (3)	818 (2)
H(7β)	889 (3)	345 (3)	863 (3)
H(8)	699 (2)	271 (3)	872 (2)
H(11)	641 (2)	573 (2)	812 (2)
H(13α)	694 (4)	715 (4)	892 (3)
H(13β)	804 (4)	734 (4)	907 (3)
H(13γ)	761 (4)	654 (4)	927 (3)
H(15α)	996 (3)	779 (3)	712 (2)
H(15β)	1032 (3)	775 (3)	798 (2)
H(15γ)	962 (3)	865 (3)	801 (2)
H(18α)	1283 (4)	592 (4)	768 (3)
H(18β)	1326 (7)	524 (6)	688 (6)
H(18γ)	1339 (5)	481 (4)	763 (4)
H(21α)	1101 (3)	265 (3)	661 (2)
H(21β)	1117 (4)	212 (5)	736 (4)
H(21γ)	1054 (3)	173 (3)	636 (2)
H(24α)	412 (3)	375 (3)	837 (2)
H(24β)	420 (5)	397 (5)	931 (4)

Table 2. *Interatomic distances* (Å), *valence angles* (°)
and selected torsion angles (°)

Table 2 (cont.)

C(1)–C(2)	1·397 (4)	C(11)–C(11a)	1·415 (4)	
C(2)–C(3)	1·376 (4)	C(11a)–C(7a)	1·417 (4)	
C(3)–C(3a)	1·395 (4)	C(11a)–C(11b)	1·481 (3)	
C(3a)–C(11c)	1·387 (3)	C(9)–O(23)	1·377 (4)	
C(11c)–C(11b)	1·415 (3)	O(23)–C(24)	1·412 (5)	
C(1)–C(11b)	1·413 (3)	C(24)–O(25)	1·436 (5)	
C(3a)–C(4)	1·513 (3)	C(10)–O(25)	1·381 (3)	
C(4)–C(5)	1·516 (4)	C(1)–O(12)	1·377 (3)	
C(5)–N(6)	1·445 (4)	O(12)–C(13)	1·404 (4)	
N(6)–C(6a)	1·454 (3)	C(2)–O(14)	1·357 (3)	
C(6a)–C(11c)	1·513 (4)	O(14)–C(15)	1·425 (4)	
C(6a)–C(7)	1·500 (4)	C(4)–O(16)	1·447 (3)	
C(7)–C(7a)	1·495 (4)	O(16)–C(17)	1·353 (3)	
C(7a)–C(8)	1·399 (4)	C(17)–C(18)	1·482 (4)	
C(8)–C(9)	1·359 (4)	C(17)–O(19)	1·195 (4)	
C(9)–C(10)	1·370 (4)	N(6)–C(20)	1·364 (4)	
C(10)–C(11)	1·369 (4)	C(20)–C(21)	1·500 (5)	
C(3)–H(3)	0·93 (4)	C(20)–O(22)	1·216 (4)	
C(4)–H(4)	1·06 (4)	C(15)–H(15α)	1·19 (4)	
C(5)–H(5α)	0·89 (5)	C(15)–H(15β)	0·99 (5)	
C(5)–H(5β)	1·13 (6)	C(15)–H(15γ)	1·07 (4)	
C(6a)–H(6a)	1·01 (3)	C(18)–H(18α)	0·98 (6)	
C(7)–H(7α)	1·08 (4)	C(18)–H(18β)	1·04 (10)	
C(7)–H(7β)	0·86 (5)	C(18)–H(18γ)	1·15 (7)	
C(8)–H(8)	0·86 (4)	C(21)–H(21α)	0·90 (4)	
C(11)–H(11)	1·06 (3)	C(21)–H(21β)	1·15 (7)	
C(13)–H(13α)	0·97 (6)	C(21)–H(21γ)	1·19 (4)	
C(13)–H(13β)	0·99 (6)	C(24)–H(24α)	1·03 (5)	
C(13)–H(13γ)	0·78 (6)	C(24)–H(24β)	1·18 (7)	

C(1)C(2)C(3)	120·1 (2)	C(9)O(23)C(24)	105·8 (3)
C(2)C(3)C(3a)	119·9 (2)	O(23)C(24)O(25)	108·6 (3)
C(3)C(3a)C(11c)	120·5 (2)	C(24)O(25)C(10)	105·3 (2)
C(3a)C(11c)C(11b)	121·0 (2)	O(25)C(10)C(9)	109·6 (2)
C(11c)C(11b)C(1)	117·0 (2)	C(10)C(9)O(23)	110·3 (2)
C(11b)C(1)C(2)	121·4 (2)	C(11b)C(1)O(12)	120·2 (2)
C(3a)C(4)C(5)	108·3 (2)	C(2)C(1)O(12)	118·3 (2)
C(4)C(5)N(6)	106·0 (2)	C(1)O(12)C(13)	115·5 (2)
C(5)N(6)C(6a)	116·6 (2)	C(1)C(2)O(14)	115·1 (2)
N(6)C(6a)C(11c)	112·2 (2)	C(3)C(2)O(14)	124·7 (2)
C(6a)C(11c)C(3a)	122·6 (2)	C(2)O(14)C(15)	117·0 (2)
C(11c)C(3a)C(4)	117·8 (2)	C(3a)C(4)O(16)	110·1 (2)
C(6a)C(7)C(7a)	108·8 (2)	C(5)C(4)O(16)	110·3 (2)
C(7)C(7a)C(11a)	119·4 (2)	C(4)O(16)C(17)	114·4 (2)
C(7a)C(11a)C(11b)	117·2 (2)	O(16)C(17)C(18)	112·6 (3)
C(11a)C(11b)C(11c)	118·9 (2)	O(16)C(17)O(19)	123·2 (2)
C(11b)C(11c)C(6a)	116·4 (2)	C(18)C(17)O(19)	124·3 (2)
C(11c)C(6a)C(7)	109·0 (2)	C(5)N(6)C(20)	124·4 (2)
C(7a)C(8)C(9)	117·4 (3)	C(6a)N(6)C(20)	118·8 (2)
C(8)C(9)C(10)	122·2 (3)	N(6)C(20)C(21)	116·7 (3)
C(9)C(10)C(11)	122·6 (2)	N(6)C(20)O(22)	120·8 (3)
C(10)C(11)C(11a)	117·4 (2)	C(21)C(20)O(22)	122·5 (3)
C(11)C(11a)C(7a)	119·1 (2)	N(6)C(6a)C(7)	112·8 (2)
C(11a)C(7a)C(8)	121·2 (2)	C(7)C(7a)C(8)	119·3 (2)
C(1)C(11b)C(11a)	124·1 (2)	C(8)C(9)O(23)	127·5 (3)
C(11)C(11a)C(11b)	123·6 (2)	C(11)C(10)O(25)	127·7 (3)

|			
3a–4–5–N(6)	64·1 (3)	5–N(6)–20–21	7·8 (4)
4–5–N(6)–6a	−63·7 (3)	5–N(6)–20–22	−173·3 (3)
5–N(6)–6a–11c	27·3 (4)	6a–N(6)–20–22	0·6 (4)
N(6)–6a–11c–3a	7·7 (4)	6a–N(6)–20–21	−178·3 (3)
6a–11c–3a–4	−2·9 (3)	3–2–14–15	8·1 (3)
11c–3a–4–5	−33·2 (3)	12–1–2–14	3·9 (3)
6a–7–7a–11a	−36·3 (3)	1–2–14–15	−172·6 (2)
7–7a–11a–11b	−6·2 (3)	2–1–12–13	−80·9 (3)
7a–11a–11b–11c	24·4 (3)	3a–4–16–17	−164·4 (2)
11a–11b–11c–6a	2·6 (3)	11b–1–12–13	101·7 (3)
11b–11c–6a–7	−45·5 (3)	5–4–16–17	76·1 (3)
11c–6a–7–7a	60·7 (3)	4–16–17–18	−177·8 (2)
9–23–24–25	5·1 (3)	4–16–17–19	2·1 (4)
23–24–25–10	−6·6 (3)	1–11b–11a–11	23·7 (3)
24–25–10–9	5·6 (3)		
25–10–9–23	−2·6 (3)		
10–9–23–24	−1·6 (3)		
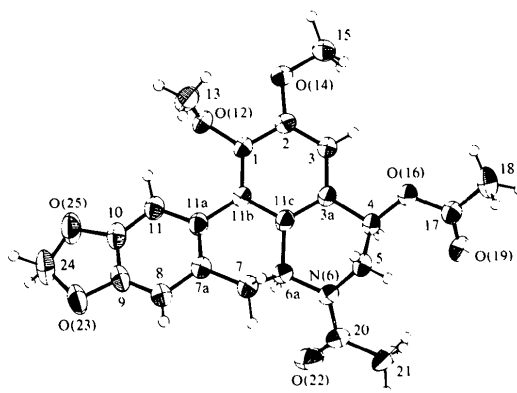
Fig. 1. *ORTEP* drawing of *N,O*-diacetyl-4-hydroxynornantenine. Thermal ellipsoids drawn at 50% probability are shown. H atoms are represented by circles of arbitrary size.

Discussion. Fig. 1 is an *ORTEP* drawing (Johnson, 1965) of *N,O*-diacetyl-4-hydroxynornantenine. The phenyl ring, C(1)C(2)C(3)C(3a)C(11c)C(11b), is reasonably planar; however, a least-squares plane fitted to this ring and the five attached atoms show deviations from the plane of 0·02–0·08 Å for the substituents. The phenyl ring with the attached methylenedioxy group

shows deviations of 0·01–0·09 Å for the substituent atoms. The six-membered heterocyclic ring exhibits a slightly distorted 1,2-diplanar conformation. The atoms C(5)N(6)C(6a)C(20)C(21)O(22) form an almost planar system as indicated by the associated torsion angles. This indicates a high degree of sp^2 hybridization at the N and conjugation with the carbonyl of the acetyl group. The C(5)N(6)C(6a) angle of 116·6 (2)° and the N(6)–C(20) and C(20)–O(22) lengths of 1·364 (4) and 1·216 (4) Å are consistent with this observation. The C(20)–O(22) bond is significantly longer than the C(17)–O(19) bond of 1·195 (4) Å. The remaining six-membered ring exhibits a 1,3-diplanar conformation due to the attachment of two phenyl rings. The five-membered ring exhibits a very flattened envelope conformation.

The C(13) methyl is twisted out of the plane of the phenyl ring as indicated by the 2−1−12−13 torsion angle of −80·9 (3)° while the C(15) methyl is almost

coplanar with 3–2–14–15 = 8·1 (3)°. The two phenyl rings make a dihedral angle of about 24° while the methylenedioxy group is coplanar with the attached phenyl ring. Least-squares enantiomorph refinement indicates a slight preference for the (4R,6aS) configuration; however, the statistics are not unequivocal.

References

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
URZUA, A. & CASSELS, B. K. (1978). *Tetrahedron Lett.* pp. 2649–2652.
URZUA, A., CASSELS, B. K., COMIN, J. & SANCHEZ, E. (1975). *An. Asoc. Quim. Argent.* **63**, 259.

SHORT COMMUNICATION

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Single-crystal neutron diffraction of Cs₂KFe(CN)₆ at 4·2 K.

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Abstract

The structure of $Cs_2KFe(CN)_6$ at 4·2 K has been determined by a neutron diffraction study of single-crystal and powder samples. The unit cell is monoclinic, $P2_1/n$, with $a = 10.976$ (7), $b = 8.118$ (4), $c = 7.542$ (5) Å, $\beta = 90.71$ (1)°, $Z = 2$. Corresponding to $R = 7.95\%$ for 307 reflections, the mean distances are Fe–C 1·93 (1) and C–N 1·15 (1) Å. The low-temperature structure does not differ essentially from the room-temperature configuration determined by X-ray diffraction.

Introduction

The salts $Cs_2LiM(CN)_6$ (M = Cr, Mn, Fe, Co, Ir) crystallize at high temperatures in the cubic elpasolite structure ($Fm3m$). On cooling, a first phase transformation produces a tetragonal structure (phase II) while a second leads to a monoclinic phase (III) with space group $P2_1/n$ (Swanson & Lucas, 1978). Two analogous salts, $Cs_2NaFe(CN)_6$ and $Cs_2KFe(CN)_6$, crystallize in the same monoclinic space group at room temperature (Fletcher & Gibb, 1977). A study of the optical properties of $Cs_2NaFe(CN)_6$, however, presented evidence that the symmetry of the room-temperature structure may be lower than monoclinic (Ryan, Smyth & Swanson, 1979). Our neutron diffraction study at 4·2 K was undertaken to investigate the possibility of a phase change occurring below room temperature.

Experimental

Suitable crystals of $Cs_2KFe(CN)_6$ were grown by cooling a saturated aqueous solution from 308 to 298 K. A crystal 2·5 × 1·5 × 1 mm was oriented by precession photographs, sealed under He in a vanadium container, and placed on a two-axis spectrometer at the Saphir reactor in Würenlingen. The neutron wavelength was 1·050 ± 0·005 Å (graphite monochromator). Powder patterns of $Cs_2KFe(CN)_6$ and $Cs_2LiFe(CN)_6$ were recorded with a neutron wavelength of 2·346 ± 0·005 Å (graphite monochromator). The crystal was oriented with the reflections 202, 20$\bar{2}$, $\bar{2}$02, and $\bar{2}$0$\bar{2}$, *b* being perpendicular to the scattering plane. 307 unique reflections were measured with the θ–2θ scan technique by tilting the counter around the horizontal axis (111 *h0l*, 140 *h1l*, 56 *h2l*). 248 reflections had $I > \sigma(I)$. Typical peak half-widths were 0·3° (θ). No reflections disobeying the extinction rule *h0l*, $h + l \neq 2n$ were observed. Accurate lattice constants were determined from powder patterns (53 lines) recorded at 293 and 4·2 K, by profile analysis (Rietveld, 1969) based on the structural parameters given in Table 1. Structural calculations based on F^2 were performed with a local version of *ORFLS* (Busing, Martin & Levy, 1962). The following scattering lengths (in 10^{-11} mm) were taken from Koester (1977): C 0·665, N 0·936, K 0·371, Fe 0·954, Cs 0·542. Isotropic least-squares refinement with the results of Fletcher & Gibb (1977) as starting parameters gave a rather high R_w of 12·1%. Introduction of corrections for absorption and for primary and secondary extinction (Zachariasen, 1967) led to