C(5) and C(6) are suggestive of unfavorable steric interactions between the Cl atoms and between Cl(5) and O(6). The Cl···Cl distance is within the range of values observed for the S···S distances in thianthrenes.

Although the H-bonded dimers lie around a center of symmetry in both forms, the relative orientation of these dimers is different. This difference in orientation arises from what appear to be C—H(C3)···*X*-type H bonds, where *X* is O(6) in form (I) and Cl(5) in form (II). In form (II), the molecules with short C—H···Cl contacts are nearly parallel with each other, having a dihedral angle of 18·02 (4)° between the ring planes. While in form (I), molecules with short C—H···O contacts are nearly perpendicular to each other, having a dihedral angle of 86·50 (5)° between the ring planes. Such an orientation minimizes Cl···Cl contacts between dimers separated by a translation in **b** (Fig. 2). In form (I), the H(C3)···O(6) and the C(3)···O(6) contacts are 2·25 (2) and 3·076 (2) Å, respectively, while the C—H···O angle is 176 (2)°. In form (II), the H(C3)···Cl(5) and C(3)···Cl(5) contacts are 2·74 (2) and 3·534 (1) Å, respectively, while the C—H···Cl angle is 142 (1)°. The H(C3)···*X* contacts are significantly less than the sum of the van der Waals radii (2·95 Å for Cl···O and 2·7 Å for O···H, Bondi, 1964). The fact that in both forms short H(C3)···*X* contacts are observed is suggestive that these interactions are attractive. It has been observed that molecules with C—H groups adjacent to N atoms frequently have short C—H···*X* contacts where *X* is O, N or Cl (Taylor & Kennard, 1982). The C—H···*X*-type H bonding results in the formation of infinite layers of interconnected dimers parallel to the *bc* plane in form (I) and lying at an angle of 38·07 (1)° to the *ab* plane in form (II).

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Structure and Stereochemistry of (±)-Demethoxycarbonyl-3α- and -3β-nauclechine

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Abstract. Demethoxycarbonyl-3α-nauclechine (1*a*) as an ethyl acetate solvate, $C_{19}H_{19}N_3O.0{\cdot}5C_4H_8O_2$, $M_r = 349{\cdot}4$, monoclinic, $P2_1/c$, $a = 11{\cdot}255$ (1), $b = 11{\cdot}515$ (2), $c = 13{\cdot}657$ (4) Å, $\beta = 91{\cdot}29$ (2)°, $U = 1769$ Å^3, $D_x = 1{\cdot}31$ Mg m^{-3}, $Z = 4$, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}0801$ mm^{-1}, $F(000) = 744$, $T = 298$ K, $R = 0{\cdot}072$ ($wR = 0{\cdot}091$) for 1369 reflections with $I > 2{\cdot}5\sigma(I)$. Demethoxycarbonyl-3β-nauclechine (2*a*) as a monohydrate, $C_{19}H_{19}N_3O.H_2O$, $M_r = 323{\cdot}4$, monoclinic, $P2_1/c$, $a = 8{\cdot}253$ (4), $b = 18{\cdot}449$ (6), c

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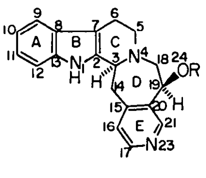
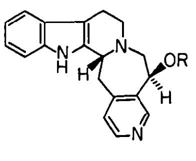
= 11·053 (6) Å, β = 102·32 (4)°, U = 1644 Å^3, D_x = 1·31 Mg m^{-3}, Z = 4, λ(Mo $K\bar{\alpha}$) = 0·71069 Å, μ = 0·0807 mm^{-1}, F(000) = 688, T = 298 K, R = 0·062 (wR = 0·049) for 1055 reflections with $I > 2{\cdot}5\sigma(I)$. In (1*a*) the hydroxyl substituent is pseudoaxial: in (2*a*) it is pseudoequatorial. In both isomers the two substituted 2,3,6,7-tetrahydroazepine seven-membered rings have slightly distorted C_s chair conformations. The coupling constants observed in the ^{1}H NMR spectra of the acetates of (1*a*) and (2*a*) indicate that the C_s chair conformation is also preferred in solution.

Introduction. Demethoxycarbonylnauclechine is an alkaloid of assigned structure but of undetermined configuration at its two chiral centres [C(3) and C(19)] (Hotellier, Delaveau, Besselièvre & Pousset, 1976). For convenience we arbitrarily represent the configuration at C(19) as that of the related dihydrocadambines (Hamilton, Saunders & McLean, 1983; Brown & Chapple, 1976) and define the diastereoisomeric possibilities as 3α (1*a*) and 3*β* (2*a*). Our synthesis of demethoxycarbonylnauclechine provided both diastereoisomers in crystalline racemic form (Shariff & McLean, 1983); one isomer (labelled HC) predominated when hydrogen chloride was used for the final cyclization, and the other (labelled FA) predominated when formic acid was used. Although the isomers could be clearly distinguished by ^{1}H NMR spectroscopy, their relative configurations could not be assigned on this basis because the conformation of their seven-membered rings was uncertain; conformational analysis of flexible seven-membered rings continues to receive attention (Toromanoff, 1980; DeClercq, 1981; Esteban, Galiano, Diez & Bermejo, 1982; Ménard & St-Jacques, 1983) but remains a much more complex problem than that of six-membered rings. Furthermore, in the molecules of interest, the presence of the annulated pyridine ring and an N atom susceptible to inversion adds to the complexity; for ^{1}H NMR purposes, the two three-spin systems are effectively isolated, and the configurational relationship between C(3) and C(19) can be deduced from coupling constants only if the conformation of the seven-membered ring can be assigned with confidence. Under these circumstances we turned to X-ray crystal structure analysis.



(1*a*) R = H
(1*b*) R = Ac



(2*a*) R = H
(2*b*) R = Ac

Table 1. *Experimental details*

	HC isomer (1*a*)	FA isomer (2*a*)
Crystal size [faces: distances (mm)]	{1,0,0}: 0·025 {0,1,0}: 0·175 {0,1,1}: 0·300	{1,0,0}: 0·100 $(0,1,\bar{1})$: 0·081 $(0,\bar{1},1)$: 0·081 $(0,\bar{1},\bar{2})$: 0·056 (0,2,1): 0·056
Reflections for cell determination [No./θ range (°)]	25 $4{\cdot}6 < \theta < 11{\cdot}7$	20 $2{\cdot}9 < \theta < 12{\cdot}6$
Data-collection mode	ω:2θ	ω:2θ
Scan range (°)	0·80 + 0·35tanθ	0·90 + 0·35tanθ
Prescan speed (° min^{-1})*	6·7	20
Max. time in final scan (s)	120	100
Max 2θ (°)	50	50
Standard reflections [No./interval(s)]	3/10000	3/12000
No. of data collected	3603	3344
No. of unique data	3107	2884
No. of data in final refinement	1369 [$I > 2{\cdot}5\sigma(I)$]	1055 [$I > 2{\cdot}5\sigma(I)$]
Final R(wR)	0·072 (0·091)	0·062 (0·049)
S	1·54	1·56
Max. Δ/σ	0·05	0·06
Factor used in weighting scheme†	0·080	0·010
Max. $\Delta\rho$ (e Å^{-3})	0·47	0·28

* Acceptance ratio for prescan [$\sigma(I)/I$] = 0·04; otherwise scan rates chosen to give a ratio $\sigma(I)/I$ = 0·04 within the maximum scan times quoted.
† $w = 4F^2[\sigma^2(I) + (pF^2)^2]^{-1}$.

Experimental. Both synthetic isomers were obtained in small amounts: FA isomer [m.p. 492–493 K (decomp.)] as small yellow irregular prisms and rhombs; HC isomer (m.p. 491–494 K) as thin white plates. As a precaution crystals of both isomers sealed in Lindemann capillaries. Nevertheless the crystal of the HC isomer gradually turned yellow during data collection. Precession photographs to check crystal quality. D_m not determined. Enraf–Nonius diffractometer, graphite monochromator. Other experimental details in Table 1. No correction for absorption or extinction. Lorentz and polarization corrections to all data collected. Equivalent data then averaged and systematically absent and zero $F_{\rm obs}$ data excluded. Of the unique data in Table 1 only 1055 (37%) and 1369 (44%) for the FA and HC isomers respectively were considered observed [$I > 2{\cdot}5\sigma(I)$]. This has slightly limited the resolution of the final structures. Both structures solved using direct methods. For the FA isomer one additional peak in initial E map and subsequent difference Fourier map refined as water of crystallization. Similarly the E map and subsequent Fourier maps for the HC isomer contained several additional diffuse peaks around a centre of symmetry in the lattice. Peak heights indicated that these positions were only partially occupied, which, with the requirement of centrosymmetry, made it difficult to define accurately the solvent molecule. Since the crystals were finally recrystallized from ethyl acetate, it was assumed that these peaks represent half a disordered molecule of this solvent. Introduction of several peak positions as half-occupancy C atoms lowered the crystallographic residual by *ca* 10%, although all attempts to resolve the disorder into individual orientations have failed. H atoms (with the exception of those in the solvent molecule of the HC isomer) located in difference Fourier maps or in calculated positions were constrained in the final cycles. Least-squares refinement minimizing $w||F_o| - |F_c||^2$ then converged to the final agreement indices in Table 1. Calculations on a PDP 11/23 computer using programs in the *Enraf–Nonius Structure Determination Package* (1981).

Table 2. *Positional parameters, thermal parameters and their estimated standard deviations*

For anisotropically refined atoms $B_{eq} = \frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

	x	y	z	B_{eq} or B_{iso}(Å^2)
(*a*) HC isomer (1*a*)				
O(24)	0·1427 (4)	0·3602 (3)	0·8964 (3)	4·5 (1)
N(1)	0·1804 (4)	−0·1116 (4)	1·0062 (3)	3·3 (1)
N(4)	0·2975 (4)	0·1780 (4)	0·9326 (3)	3·1 (1)
N(23)	0·0182 (5)	0·2351 (5)	0·5937 (4)	4·8 (1)
C(2)	0·2451 (5)	−0·0109 (5)	0·9951 (4)	2·9 (1)
C(3)	0·2383 (5)	0·0669 (5)	0·9059 (4)	3·1 (1)
C(5)	0·4125 (5)	0·1592 (5)	0·9835 (5)	4·1 (1)
C(6)	0·3957 (6)	0·1081 (5)	1·0848 (5)	4·1 (1)
C(7)	0·3142 (5)	0·0062 (5)	1·0757 (4)	3·1 (1)
C(8)	0·2947 (5)	−0·0875 (5)	1·1417 (4)	3·4 (1)
C(9)	0·3412 (6)	−0·1182 (6)	1·2343 (5)	4·5 (2)
C(10)	0·2988 (6)	−0·2183 (6)	1·2770 (5)	5·1 (2)
C(11)	0·2132 (7)	−0·2881 (6)	1·2306 (5)	5·1 (2)
C(12)	0·1668 (6)	−0·2591 (6)	1·1398 (5)	4·2 (1)
C(13)	0·2091 (5)	−0·1590 (5)	1·0958 (4)	3·4 (1)
C(14)	0·1092 (5)	0·0831 (5)	0·8750 (4)	3·2 (1)
C(15)	0·0839 (5)	0·1353 (5)	0·7747 (4)	3·0 (1)
C(16)	0·0136 (5)	0·0771 (5)	0·7075 (4)	3·7 (1)
C(17)	−0·0174 (6)	0·1298 (6)	0·6194 (5)	4·6 (2)
C(18)	0·3160 (5)	0·2529 (6)	0·8469 (5)	4·0 (1)
C(19)	0·2038 (6)	0·3143 (5)	0·8142 (4)	3·8 (1)
C(20)	0·1243 (5)	0·2445 (5)	0·7484 (4)	3·1 (1)
C(21)	0·0889 (6)	0·2878 (5)	0·6576 (5)	4·2 (2)
C(1*S*)	0·500	0·000	0·500	8·2 (7)*
C(2*S*)	0·686 (2)	0·011 (2)	0·451 (2)	12·2 (7)*
C(3*S*)	0·569 (2)	−0·011 (2)	0·455 (1)	8·8 (5)*
C(4*S*)	0·631 (2)	0·049 (2)	0·468 (2)	9·7 (6)*
C(5*S*)	0·680 (1)	−0·040 (1)	0·398 (1)	6·4 (4)*
C(6*S*)	0·536 (2)	−0·092 (2)	0·400 (1)	9·1 (5)*
C(7*S*)	0·508 (2)	0·011 (2)	0·543 (1)	9·3 (5)*
(*b*) FA isomer (2*a*)				
O(1*S*)	0·4945 (5)	0·1392 (2)	0·1424 (3)	5·1 (1)
O(24)	0·6823 (5)	0·2713 (2)	−0·1671 (3)	4·4 (1)
N(1)	0·7585 (5)	−0·0829 (2)	0·0534 (3)	3·1 (1)
N(4)	0·7985 (5)	0·1182 (2)	0·0488 (3)	3·0 (1)
N(23)	0·6676 (6)	0·1440 (2)	−0·4639 (4)	4·2 (1)
C(2)	0·7965 (6)	−0·0103 (3)	0·0817 (4)	2·9 (1)
C(3)	0·7914 (6)	0·0468 (3)	−0·0161 (4)	2·8 (1)
C(5)	0·9362 (7)	0·1196 (3)	0·1593 (5)	3·9 (1)
C(6)	0·9028 (8)	0·0696 (3)	0·2591 (5)	4·4 (2)
C(7)	0·8469 (6)	−0·0020 (3)	0·2047 (4)	3·0 (1)
C(8)	0·8383 (7)	−0·0706 (3)	0·2602 (4)	3·5 (1)
C(9)	0·8731 (8)	−0·0950 (3)	0·3831 (5)	5·2 (2)
C(10)	0·8485 (8)	−0·1666 (4)	0·4031 (5)	6·3 (2)
C(11)	0·7927 (7)	−0·2143 (3)	0·3090 (5)	5·7 (2)
C(12)	0·7608 (7)	−0·1928 (3)	0·1869 (5)	4·4 (2)
C(13)	0·7830 (6)	−0·1205 (3)	0·1652 (5)	3·4 (1)
C(14)	0·6400 (6)	0·0400 (3)	−0·1192 (4)	3·1 (1)
C(15)	0·6526 (7)	0·0770 (3)	−0·2395 (5)	3·2 (1)
C(16)	0·6513 (7)	0·0371 (3)	−0·3462 (5)	3·7 (1)
C(17)	0·6587 (7)	0·0726 (3)	−0·4543 (5)	4·1 (2)
C(18)	0·8273 (7)	0·1782 (3)	−0·0350 (5)	3·5 (1)
C(19)	0·6739 (7)	0·1978 (3)	−0·1327 (4)	3·3 (1)
C(20)	0·6640 (7)	0·1517 (3)	−0·2472 (4)	3·1 (1)
C(21)	0·6707 (7)	0·1810 (3)	−0·3610 (5)	4·1 (2)

* Isotropically refined atoms.

Table 5. *Selected torsion angles* (°)

	HC (1*a*)	FA (2*a*)
C(6)–C(7)–C(2)–C(3)	−0·7 (9)	1·4 (8)
N(1)–C(2)–C(3)–N(4)	166·5 (5)	166·6 (4)
N(1)–C(2)–C(3)–C(14)	44·1 (7)	43·6 (6)
C(7)–C(2)–C(3)–N(4)	−13·5 (7)	−18·3 (6)
C(7)–C(2)–C(3)–C(14)	135·8 (6)	−141·3 (5)
C(2)–C(3)–N(4)–C(5)	46·7 (6)	49·8 (5)
C(2)–C(3)–N(4)–C(18)	169·5 (4)	169·0 (4)
C(14)–C(3)–N(4)–C(5)	166·9 (5)	172·7 (4)
C(14)–C(3)–N(4)–C(18)	−70·3 (6)	−68·1 (5)
C(3)–N(4)–C(5)–C(6)	−69·0 (6)	−69·0 (5)
C(18)–N(4)–C(5)–C(6)	166·1 (5)	170·1 (4)
N(4)–C(5)–C(6)–C(7)	49·8 (6)	47·7 (5)
C(5)–C(6)–C(7)–C(2)	−16·8 (8)	−15·2 (7)
C(5)–C(6)–C(7)–C(8)	161·7 (6)	162·9 (5)
C(3)–N(4)–C(18)–C(19)	77·8 (6)	75·7 (5)
C(5)–N(4)–C(18)–C(19)	−157·6 (5)	−163·1 (4)
N(4)–C(18)–C(19)–O(24)	44·2 (6)	152·5 (4)
N(4)–C(18)–C(19)–C(20)	−84·1 (6)	−88·4 (5)
O(24)–C(19)–C(20)–C(15)	−72·5 (7)	−179·3 (4)
O(24)–C(19)–C(20)–C(21)	107·8 (6)	2·7 (6)
C(18)–C(19)–C(20)–C(15)	55·0 (7)	60·7 (6)
C(18)–C(19)–C(20)–C(21)	−124·7 (6)	−117·4 (5)
C(19)–C(20)–C(15)–C(14)	5·0 (8)	3·5 (7)
C(20)–C(15)–C(14)–C(3)	−59·4 (7)	−66·1 (6)
C(16)–C(15)–C(14)–C(3)	123·9 (6)	114·6 (5)
C(15)–C(14)–C(3)–N(4)	74·3 (6)	80·4 (5)
C(15)–C(14)–C(3)–C(2)	−166·6 (5)	−160·1 (4)

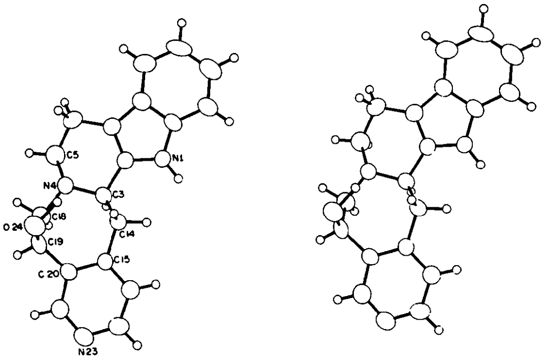


Fig. 1. Stereoscopic view (*ORTEP*, Johnson, 1965) of the HC isomer. Thermal ellipsoids are drawn at the 50% probability level. All H atoms are drawn with uniform isotropic thermal parameters.

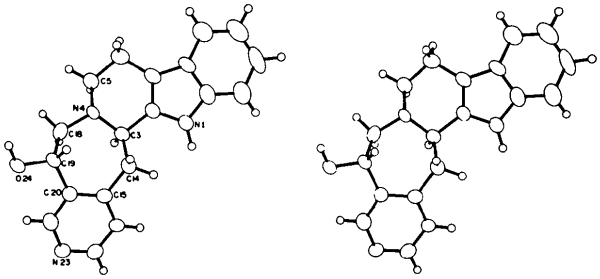


Fig. 2. Stereoscopic view (*ORTEP*) of the FA isomer (as for Fig. 1).

Discussion. The final atomic positional parameters and selected torsional angles for both isomers are given in Tables 2 and 5 respectively.*

The X-ray analyses establish the HC isomer as (±)-demethoxycarbonyl-3α-nauclechine (1*a*) with disordered ethyl acetate in the crystal and the FA isomer as (±)-demethoxycarbonyl-3*β*-nauclechine (2*a*) with water of crystallization. In both isomers the indole moiety is planar; maximum deviations from the plane are ±0·010 (7) Å in (1*a*) and ±0·017 (6) Å in (2*a*).

In both isomers ring *C* exists in a half-chair conformation with N(4) and C(5) above and below the C(3)—C(2)—C(7)—C(6) plane by 0·344 (4) [0·426 (4)] and 0·425 (6) Å [0·350 (6) Å] respectively for the (1*a*) [(2*a*)] isomers.† Alternatively, this ring may be described by the asymmetry parameters (Duax, Weeks & Rohrer, 1976) $\Delta C_2^{(2-7)}$ 3·2° [2·6°] and $\langle|\varphi^{\rm tors}|\rangle$ 32·8° [33·6°] for the (1*a*) [(2*a*)] isomers.

Ring *D* in both isomers adopts a slightly distorted C_s chair conformation with its plane of symmetry passing through N(4) and bisecting the aromatic double bond [C(15)—C(20)]; in (1*a*) the hydroxyl substituent at C(19) is pseudoaxial (Fig. 1) and in (2*a*) the hydroxyl is pseudoequatorial (Fig. 2). This conformation is analogous to that assigned to benzocycloheptene and a number of its simple derivatives (Ménard & St-Jacques, 1983). The slight distortion from C_s symmetry can be seen in the C(14)—C(15)—C(20)—C(19) torsion angles of 5·0 (8)° in (1*a*) and 3·5 (7)° in (2*a*) (despite the annulated pyridine ring) and in the torsion angles about bonds C(3)—C(14) and C(14)—C(15) which differ by 6·1 and 6·7° between the two isomers.

This latter difference is presumably due to transannular interactions in (1*a*), which has the pseudoaxial hydroxyl substituent. The conformation of ring *D* can also be described using the puckering constants (Esteban *et al.*, 1982; Cano, Foces-Foces & García-Blanco, 1981) $\Delta = 4{\cdot}6$ [4·6], $A = 91{\cdot}0$ [94·0] and $B = 19{\cdot}0$ [24·6] for the (1*a*) [(2*a*)] isomers respectively (with $C = D = 0$). The root-mean-square deviations for the fits between the observed and calculated torsion angles are 3·35° [2·98°] for (1*a*) [(2*a*)] respectively and are reasonable when the presence of the heteroatom and two sp^2-hybridized C atoms in the ring are taken into account.

Equivalent bond lengths between the two isomers are virtually the same within experimental error and are normal. There are some small but significant differences in bond angles between the isomers with the maximum difference involving angles C(18)—C(19)—C(20) and O(24)—C(19)—C(20) which have both opened out by *ca* 4° in the pseudoaxial isomer (1*a*) to accommodate an intramolecular hydrogen bond from H(241) to N(4). In both isomers rings *C* and *D* are flattened with internal angles all slightly greater than expected values.

The effect of the change in configuration at C(19) on the molecular conformation can be seen by fitting the coordinates of one isomer to those of the other using the program *BMFIT* (Yuen & Nyburg, 1979). In the first fit, the non-hydrogen atoms of rings *A*, *B*, and *C* fit almost exactly ($\sum\Delta^2 = 0{\cdot}0084$ Å^2) and the maximum deviation between the C and N atoms of rings *D* and *E* is 0·967 Å for N(23). However, a fit applied over all C and N atoms in the five rings gives a goodness of fit $\sum\Delta^2$ of 0·4960 Å^2, with the maximum deviation between related positions of 0·288 Å for N(23).

In the crystal packing of (1*a*) there is a short intramolecular hydrogen bond N(4)···H(241) of length 1·93 Å and an N(1)—H(11)···N(23) hydrogen bond of length 2·26 Å. Other possible hydrogen-bonding interactions are weak (>2·6 Å). Contacts C···H involving the disordered solvent are >2·35 Å in length.

The crystal packing of the isomer (2*a*) consists of a layered arrangement of (2*a*) molecules alternating with water molecules in the **a** direction (Fig. 3, deposited). Each water molecule forms a hydrogen bond to N(4) and is involved in a hydrogen bond from H(11) [on N(1)] giving $[(2a).{\rm H_2O}]_2$ 'dimeric' arrangements about centres of symmetry. These are further linked together by the hydrogen bond from H(2*S*) to the pseudo-equatorial O of an adjacent 'dimer' and by the hydrogen bond from the hydroxyl proton to N(23) of another 'dimer'.

The strong preference of a benzocycloheptene for the C_s chair conformation (Ménard & St-Jacques, 1983) has important consequences for structural studies, and it is significant that the present work shows that N-containing analogs show the same preference even when substituted and incorporated into a larger molecular framework. Although the conformations established for crystalline (1*a*) and (2*a*) are not necessarily those of their acetates (1*b*) and (2*b*) in solution, the ^{1}H NMR spectra (Shariff & McLean, 1983) of (1*b*) and (2*b*) provide vicinal coupling constants compatible with the dihedral angles associated with the C_s chair conformation. In short, the assignments of relative configuration could have been made on the basis of ^{1}H NMR data if the C_s chair conformation could have been confidently predicted at the start.

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* Lists of structure factor amplitudes and tables of anisotropic thermal parameters, bond lengths and bond angles (Tables 3 and 4), best molecular fits, hydrogen-bond/contact distances, Figs. 3 and 4 [stereoviews of the crystal packing for (1*a*) and (2*a*)] have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42437 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Atoms are identified by numbers derived from the numbering system commonly used for these alkaloids. For H atoms, H(*nm*) defines an H atom bonded to atom *n*; where two stereochemical orientations are possible, $m = 1$ defines the α and $m = 2$ the *β* H atom. When the atom is in a molecule of solvent of crystallization, the letter *S* is added to the identifying number.

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Structure of Methyl 3-*C*-(Acetoxymethyl)-1,4-di-*O*-acetyl-α-*erythro*-pentofuranoside

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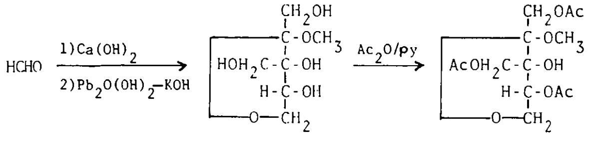
Abstract. $C_{13}H_{20}O_9$, $M_r = 320{\cdot}3$, orthorhombic, $Pbca$, $a = 21{\cdot}614\,(7)$, $b = 17{\cdot}239\,(5)$, $c = 8{\cdot}518\,(4)$ Å, $V = 3174$ Å^3, $Z = 8$, $D_x = 1{\cdot}34$ g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 9{\cdot}4$ cm^{-1}, $F(000) = 1360$, room temperature, $R = 0{\cdot}076$ for 1668 observed reflections. The five-membered ring is puckered at C(3), and its conformation is *endo*. The hydroxyl and methoxy groups occupy quasi-axial positions. There is an intermolecular hydrogen bond of 3·022 (6) Å between the hydroxyl group and one of the acetyl groups of a molecule related by the *c*-glide plane.

Introduction. The reaction of formaldehyde in the presence of base catalysts such as $Ca(OH)_2$, known as the formose reaction, gives a complex mixture of saccharides (Mizuno & Weiss, 1974). The reaction mechanism and the effect of reaction conditions on the selective formation of products have been studied extensively (Shigemasa, Nagae, Sakazawa, Nakashima & Matsuura, 1978; Shigemasa, Akagi, Waki & Nakashima, 1981). Addition of $Pb_2O(OH)_2$ and adjustment of the pH of the reaction mixture to 10·0 at the end of the induction period resulted in selective synthesis of 3-*C*-(hydroxymethyl)pentofuranose (1) (Shigemasa, Hamada, Hirabayashi, Waki, Nakashima, Harada, Takeda & Suzuki, 1981). The product was isolated as the triacetate (2) by silica-gel chromatography. Although the structures of (1) and (2) were examined by spectroscopic and chemical means, ambiguity concerning their configurations remained. The crystallographic analysis of (2) was carried out to establish the configuration of the molecule.



(1) (2)

Experimental. Colourless prisms of (2) (from benzene/cyclohexane solution), 0·1 × 0·15 × 0·3 mm. Rigaku diffractometer (Katsube, 1982), Ni-filtered Cu *Kα* radiation. Cell parameters determined by least squares from 2θ values measured for 18 reflections with $14{\cdot}9 < \theta < 15{\cdot}6°$. Integrated intensities recorded by θ–2θ scan, scan speed 4° min^{-1} (θ), scan range $1{\cdot}0° + 0{\cdot}2° \tan\theta$, 5 s stationary background counts. $2\theta_{\max} = 120°$ (h: 0→24, k: 0→19, l: 0→9). Two reference reflections monitored every 100 reflections showed no significant variation in intensity during data collection. 1960 independent reflections measured, 1668

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