

Table 4. *Hydrogen-bonding scheme*

Standard deviations: 0.1 Å and 0.8°.

For each hydrogen bond, the first O atom listed is the donor atom.

O(2)···O(4)	2.98 Å	O(4)···O(2)···O(3 ⁱⁱⁱ)	120.3°
O(3)···O(2)	2.74	O(2)···O(3)···O(4 ⁱⁱⁱ)	110.1
O(4)···O(3 ⁱⁱ)	2.92	O(2)···O(4)···O(2 ⁱⁱ)	86.3
		O(3 ⁱ)···O(4)···O(3 ⁱ)	98.7
		O(2)···O(4)···O(3 ⁱ)	95.2
		O(2)···O(4)···O(3 ⁱⁱ)	149.3

Symmetry code: (i) $-\frac{1}{2} - x, \frac{1}{2} + y, -z$; (ii) $\frac{1}{2} + x, \frac{1}{2} + y, z$; (iii) $-\frac{1}{2} - x, -\frac{1}{2} + y, -z$; (iv) $-x, y, -z$.

reflections, no intensity variation. Direct phase determination revealed all non-H atoms and an O atom belonging to a water molecule. All O atoms and the four non-ring C atoms were assigned anisotropic thermal parameters while the ring C atoms were refined isotropically. The H atoms attached to C atoms were generated geometrically (C—H = 0.96 Å; the methyl groups were handled as rigid groups), assigned fixed isotropic thermal factors and allowed to ride on their respective parent C atoms. The H atoms attached to O atoms were located from a difference Fourier map; their positional parameters were not refined and they were given a fixed isotropic thermal parameter of 0.06 Å².

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Structure of (\pm)-7(S)-16-Deformyl-21-oxogeissoschizine–Oxindole

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Abstract. Methyl (3*S**,7*S**,8*a*'*S**)-2',3',6',7',8*a*'-hexahydro-6'(*E*)-ethylidene-2,5'-dioxospiro[3*H*-indole-3,1'(*S*'*H*)-indolizine]-7'-yl acetate, C₂₀H₂₂N₂O₄, *M_r* = 354.50, monoclinic, *P*2₁/*c*, *a* = 10.5052 (7), *b* = 16.442 (2), *c* = 10.3415 (8) Å, β = 95.358 (6)°, *V* = 1778.4 (3) Å³, *Z* = 4, *D_x* = 1.32 g cm⁻³ (198 K), μ = 0.8677 cm⁻¹, Mo *K* α radiation, λ = 0.7107 Å, *F*(000) = 752, *T* = 198 K, *R* = 0.0351 for 2635 reflections with *F_o* \geq 4[σ (*F_o*)]. The indole NH group is hydrogen bonded to a carbonyl oxygen, O8 (related by $-x, 1-y, 1-z$), with relevant parameters: N1···O8 2.857 (2) Å, H1···O8 1.94 (2) Å, N1—H1···O8 170 (2)°. The rings of the indolizine moiety are quasi-*trans* fused with ring junction torsion angles for C3—C8*a*—N4'—C3' of -12.08 (15)° and C8'—C8*a*—N4'—C5' of 43.9 (2)°.

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All computations were performed on a Data General Corporation Nova 3/12 minicomputer with the *SHELXTL* program package (Sheldrick, 1982). Analytical expressions of neutral-atom scattering factors were employed (Cromer, 1974). Blocked-cascade least-squares refinement on *F* (Schilling, 1970) yielded the *R* indices and other parameters listed in Table 1.* Final atomic parameters are given in Table 2; Table 3 gives bond lengths and angles. Fig. 1 shows a molecule with the atom numbering, while Fig. 2 shows the hydrogen-bonding scheme (see also Table 4).

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53567 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 KUMAR DAS, V. G., CHEN, W., YAP, C. K. & MAK, T. C. W. (1986). *J. Organomet. Chem.* **229**, 41–49.
 SCHILLING, J. W. (1970). In *Crystallographic Computing*, edited by F. R. AHMED, pp. 201–204. Copenhagen: Munksgaard.
 SHELDRICK, G. M. (1982). In *Computational Crystallography*, edited by D. SAYRE, pp. 506–514. Oxford Univ. Press.

Experimental. (1) was synthesized by an oxidative rearrangement of 16-deformyl-21-oxogeissoschizine. Treatment of 16-deformyl-21-oxogeissoschizine with *tert*-butylhypochlorite and triethylamine was followed by stirring at ambient temperature in acidic methanol in the presence of AgClO₄. Full details of the synthetic procedure will appear elsewhere (Martin, Benage, Hunter, Geraci & Mortimore,

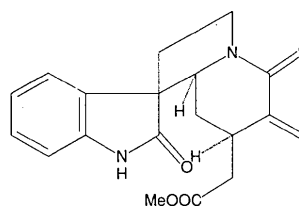


Table 1. Fractional coordinates and equivalent isotropic thermal parameters (\AA^2) for the non-H atoms of (1)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
N1	0.026292 (12)	0.55818 (8)	0.35046 (13)	0.0261 (4)
C2	0.10500 (13)	0.49300 (9)	0.34729 (14)	0.0218 (4)
C3	0.17681 (13)	0.49863 (8)	0.22599 (14)	0.0204 (4)
C3a	0.13566 (14)	0.58097 (9)	0.17219 (14)	0.0209 (4)
C4	0.16929 (15)	0.62445 (9)	0.06619 (15)	0.0259 (5)
C5	0.1061 (2)	0.69723 (10)	0.0345 (2)	0.0306 (5)
C6	0.01128 (15)	0.72558 (10)	0.1070 (2)	0.0330 (5)
C7	-0.02182 (15)	0.68342 (10)	0.2161 (2)	0.0303 (5)
C7a	0.04231 (14)	0.61168 (9)	0.24641 (14)	0.0236 (4)
O8	0.11537 (10)	0.43737 (6)	0.42739 (10)	0.0284 (3)
C2'	0.13597 (15)	0.42803 (9)	0.13148 (15)	0.0246 (5)
C3'	0.24558 (14)	0.42101 (10)	0.04599 (15)	0.0244 (5)
N4'	0.35576 (11)	0.44460 (7)	0.13485 (11)	0.0208 (4)
C5'	0.47802 (14)	0.43086 (8)	0.11288 (14)	0.0199 (4)
C6'	0.57285 (13)	0.45197 (8)	0.22501 (14)	0.0201 (4)
C7'	0.54738 (13)	0.52330 (8)	0.31360 (14)	0.0194 (4)
C8'	0.40877 (14)	0.55340 (9)	0.28924 (15)	0.0209 (4)
C8a'	0.32087 (13)	0.48212 (9)	0.25560 (13)	0.0192 (4)
O9'	0.50791 (10)	0.39906 (6)	0.01185 (10)	0.0268 (3)
C10'	0.67155 (14)	0.40119 (9)	0.2470 (2)	0.0271 (5)
C11'	0.7722 (2)	0.40352 (13)	0.3591 (2)	0.0425 (6)
C12'	0.64314 (15)	0.59217 (9)	0.29504 (15)	0.0227 (5)
C13'	0.64956 (14)	0.66149 (9)	0.39004 (14)	0.0235 (4)
O14'	0.71330 (12)	0.72152 (7)	0.37851 (12)	0.0417 (4)
O15'	0.57954 (10)	0.64991 (6)	0.48985 (10)	0.0274 (3)
C16'	0.5874 (2)	0.71394 (11)	0.5867 (2)	0.0390 (6)

For anisotropic atoms, the *U* value is U_{eq} , calculated as $U_{eq} = 1/3 \sum_i \sum_j U_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$ where A_{ij} is the dot product of the *i*th and *j*th direct-space unit-cell vectors.

1990). Crystals were obtained by slow evaporation from a methanol solution. The data crystal was a colorless prism of approximate dimensions $0.16 \times 0.30 \times 0.60$ mm. The data were collected at 198 K on a Nicolet P3 diffractometer using a graphite monochromator and equipped with a Nicolet LT-2 low-temperature device. Lattice parameters were obtained from the least-squares refinement of 25 reflections with $18.1 < 2\theta < 23.7^\circ$. The data were collected using the ω scan technique with a 2θ range from 4.0 – 50.0° , with a $1.2^\circ \omega$ scan at 5 – 10°min^{-1} ($h = 0 \rightarrow 12$, $k = -19 \rightarrow 19$, $l = -12 \rightarrow 12$). 6831 reflections were collected of which 3156 were unique ($R_{int} = 0.0112$). Four reflections ($2\bar{5}4$, $5\bar{5}1$, $14\bar{5}$, $4\bar{2}2$) were remeasured every 196 reflections to monitor instrument and crystal stability. A smoothed curve of the intensities of these check reflections was used to scale the data. The scaling factor ranged from 0.9950–1.006. The data were also corrected for Lp effects but not absorption. The data reduction and decay correction were applied using the Nicolet XRD SHELXTL-Plus software package (Sheldrick, 1987). Reflections having $F_o < 4[\sigma(F_o)]$ were considered unobserved (521 reflections). The structure was solved by direct methods (Sheldrick, 1987) and refined by full-matrix least-squares (Sheldrick, 1987). In all, 323 parameters were refined. The non-H atoms were refined with anisotropic thermal parameters. H-atom positions were obtained from a ΔF

Table 2. Bond lengths (\AA) and angles ($^\circ$) for the non-H atoms of (1)

1	2	3	1–2	1–2–3
C2	N1	C7a	1.352 (2)	111.27 (13)
C7a	N1		1.411 (2)	
C3	C2	O8	1.526 (2)	125.34 (13)
C3	C2	N1		108.64 (12)
O8	C2	N1	1.232 (2)	126.02 (14)
C3a	C3	C8a'	1.511 (2)	118.24 (12)
C3a	C3	C2'		112.67 (12)
C3a	C3	C2		102.16 (11)
C8a'	C3	C2'	1.540 (2)	101.66 (11)
C8a'	C3	C2		112.21 (11)
C2'	C3	C2	1.552 (2)	110.09 (12)
C4	C3a	C7a	1.382 (2)	119.61 (14)
C4	C3a	C3		132.05 (14)
C7a	C3a	C3	1.395 (2)	108.26 (13)
C5	C4	C3a	1.393 (2)	118.65 (15)
C6	C5	C4	1.382 (2)	120.9 (2)
C7	C6	C5	1.395 (2)	121.2 (2)
C7a	C7	C6	1.380 (2)	117.1 (2)
N1	C7a	C3a		109.30 (13)
N1	C7a	C7		128.18 (14)
C3a	C7a	C7		122.52 (14)
C6'	C5'	N4'	1.497 (2)	114.03 (12)
N4'	C5'	O9'	1.344 (2)	122.46 (13)
O9'	C5'	C6'	1.235 (2)	123.37 (13)
C7'	C6'	C10'	1.527 (2)	123.74 (13)
C7'	C6'	C5'		120.10 (11)
C10'	C6'	C5'	1.334 (2)	115.92 (13)
C8'	C7'	C12'	1.536 (2)	111.30 (11)
C8'	C7'	C6'		111.44 (11)
C12'	C7'	C6'	1.539 (2)	109.70 (12)
C8a'	C8'	C7'	1.512 (2)	109.70 (12)
N4'	C8a'	C3	1.470 (2)	102.91 (10)
N4'	C8a'	C8'		108.99 (12)
C3	C8a'	C8'		118.47 (12)
C3'	C2'	C3	1.520 (2)	104.07 (12)
N4'	C3'	C2'	1.461 (2)	102.27 (12)
C5'	N4'	C8a'		122.16 (11)
C5'	N4'	C3'		124.21 (12)
C8a'	N4'	C3'		113.58 (11)
C11'	C10'	C6'	1.495 (3)	126.7 (2)
C13'	C12'	C7'	1.502 (2)	117.83 (13)
O14'	C13'	O15'	1.205 (2)	122.99 (14)
O14'	C13'	C12'		123.25 (14)
O15'	C13'	C12'	1.336 (2)	113.76 (13)
C16'	O15'	C13'	1.450 (2)	115.48 (13)

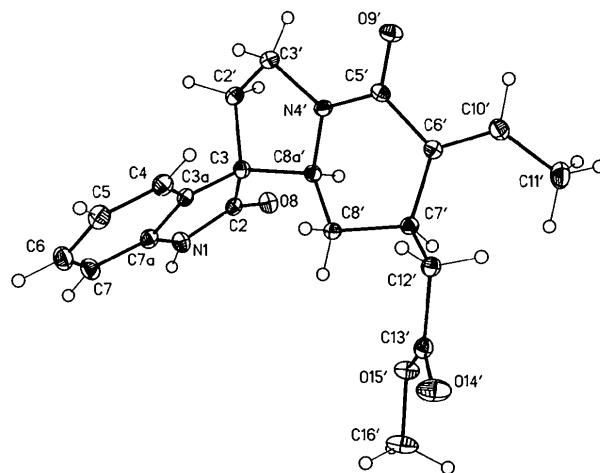


Fig. 1. View of (1) showing the atom-labeling scheme. The non-H atoms are scaled to the 30% probability level while the H atoms are drawn to an arbitrary size.

map and refined with isotropic temperature factors. The function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/[\sigma(F_o)]^2$ and $\sigma(F_o) = (0.5kI^{-1/2}\{[\sigma(I)]^2 + (0.02I)^2\}^{1/2})$. The intensity, I , is given by $(I_{\text{peak}} - I_{\text{background}}) \times (\text{scan rate})$; where 0.02 is a factor to downweight intense reflections and to account for instrument instability and k is the correction due to L_p effects and decay. $\sigma(I)$ was estimated from counting statistics; $\sigma(I) = [(I_{\text{peak}} + I_{\text{background}})^{1/2} \times (\text{scan rate})]$. The final $R = 0.0351$ for 2635 reflections, with $wR = 0.0424$ ($R_{\text{all}} = 0.0437$, $wR_{\text{all}} = 0.0444$) and a goodness of fit = 1.516. The maximum $|\Delta/\sigma| = 0.1$ in the final refinement cycle and the minimum and maximum peaks in the final ΔF map were -0.25 and $0.17 \text{ e } \text{\AA}^{-3}$, respectively. The scattering factors for the non-H atoms were taken from Cromer & Mann (1968), with the anomalous-dispersion corrections taken from the work of Cromer & Liberman (1970). The scattering factors for the H atoms were obtained from Stewart, Davidson & Simpson (1965). Values used to calculate the linear absorption coefficient are from *International Tables for X-ray Crystallography* (1974, Vol. IV, p. 55). Figures were generated using *SHELXTL-Plus* (Sheldrick, 1987). The positional and thermal parameters for non-H atoms are listed in Table 1,* while the bond lengths and angles for the non-H atoms are listed in Table 2. The atom-labeling scheme is shown in Fig. 1. Other computer

* Lists of structure factors, anisotropic thermal parameters and a unit-cell packing diagram, bond distances and angles involving H atoms, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53599 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

programs used in this work are listed in reference 11 of Gadol & Davis (1982).

Related literature. The structure of (1) was determined during the course of developing a generalized approach to the syntheses of alkaloids of the indole family (Martin, Benage & Hunter, 1988) and to a new approach to oxindole alkaloids (Martin & Mortimore, 1990). The ultimate goal of these endeavors is the total syntheses of selected alkaloids of the *Strychnos* group. The crystal structure of the related (\pm)-21-oxoisopteropodine has been reported (Lynch, Mortimore, Martin & Davis, 1991).

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References

- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 GADOL, S. M. & DAVIS, R. E. (1982). *Organometallics*, **1**, 1607–1613.
 LYNCH, V. M., MORTIMORE, M., MARTIN, S. F. & DAVIS, B. E. (1991). *Acta Cryst.* **C47**, 234–236.
 MARTIN, S. F., BENAGE, B. & HUNTER, J. E. (1988). *J. Am. Chem. Soc.* **110**, 5925–5927.
 MARTIN, S. F., BENAGE, B., HUNTER, J. E., GERACI, L. S. & MORTIMORE, M. (1990). In preparation.
 MARTIN, S. F. & MORTIMORE, M. (1990). *Tetrahedron Lett.* pp. 4557–4560.
 SHELDRIK, G. M. (1987). *SHELXTL-Plus*. Release 3.4 for Nicolet R3m/V crystallographic system. Nicolet Instrument Corporation, Madison, Wisconsin.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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Structure of a Key Intermediate in the Asymmetric Synthesis of (+)-KDO

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Abstract. Methyl 3-deoxy-7,8-*O*-(1-methylethylidene)-1-*O*-(phenylmethyl)- α -*D*-manno-2-octalopyranoside cyclic carbonate, (1), C₂₀H₂₆O₈, $M_r = 394.42$, orthorhombic, $P2_12_12_1$, $a = 10.667$ (3), $b = 10.7972$ (14), $c = 16.509$ (5) Å, $V = 1901.4$ (8) Å³, $Z = 4$, $D_x = 1.38 \text{ g cm}^{-3}$, $\mu = 0.9960 \text{ cm}^{-1}$, $\lambda(\text{Mo K}\alpha) = 0.7107$ Å, $F(000) = 840$, $T = 298 \text{ K}$, $R = 0.0355$ for

2248 reflections, $F_o \geq 4[\sigma(F_o)]$. The X-ray structure was undertaken to confirm the stereochemistry of the substituents on the six-membered pyranose ring. The two rings are *cis*-fused with ring junction torsion angles of -18.7 (3)° for C2—C3—C8—C9 and -18.2 (2)° for O4—C3—C8—O7. The six-membered ring assumes a slightly distorted twist conformation