

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 $0.17 \text{ e } \text{Å}^{-3}$, 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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Structure of a Key Intermediate in the Asymmetric Synthesis of (+)-KDO

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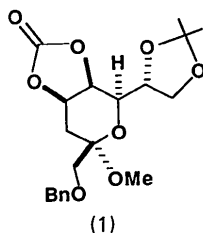
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Abstract. Methyl 3-deoxy-7,8-*O*-(1-methylethylidene)-1-*O*-(phenylmethyl)- α -*D*-manno-2-octalopyranoside cyclic carbonate, (1), C₂₀H₂₆O₈, $M_r = 394.42$, orthorhombic, $P2_12_12_1$, $a = 10.667$ (3), $b = 10.7972$ (14), $c = 16.509$ (5) Å, $V = 1901.4$ (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

while the fused five-membered ring is in the half-chair conformation. The isopropylidene moiety is in the envelope conformation.

Experimental. (1) was prepared as an intermediate in the total synthesis of (+)-KDO (3-deoxy-D-manno-2-octalosoic acid). Full details of the synthesis and spectral properties are reported elsewhere (Martin & Zinke, 1989). Crystals of (1) were obtained by slow evaporation from 4:1 hexane:ethyl acetate. The data



crystal was a colorless rod, cut from a larger crystal, and had dimensions $0.17 \times 0.18 \times 0.43$ mm. The data were collected at room temperature on a Nicolet R3 diffractometer and using a graphite monochromator. The lattice parameters were obtained from the least-squares refinement of 30 reflections with $24.9 < 2\theta < 28.8^\circ$. Data were collected using the ω -scan technique (4992 reflections, 2478 unique, $R_{\text{int}} = 0.0204$ from averaging hkl and $h, -k, -l$ reflections), with a 2θ range from 4.0 – 55° , with a 1° ω scan at a constant $10^\circ \text{ min}^{-1}$ ($h = 0 \rightarrow 13, k = -14 \rightarrow 14, l = -21 \rightarrow 21$). Four reflections ($23\bar{2}, \bar{1}60, \bar{2}25, 053$) were remeasured every 196 reflections to monitor instrument and crystal stability. The data were corrected for Lp effects and decay (maximum correction on I was 2.4%). Data reduction and decay correction were performed using the Nicolet XRD *SHELXTL-Plus* software package (Sheldrick, 1987). Reflections having $F_o < 4[\sigma(F_o)]$ were considered unobserved (230 reflections). The structure was solved by direct methods (Sheldrick, 1987) and refined by full-matrix least squares (Sheldrick, 1976). In all, 357 parameters were refined. The non-H atoms were refined with anisotropic thermal parameters. All the H-atom positions were obtained from a ΔF map and refined with isotropic thermal parameters. The function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/[\sigma(F_o)]^2$ and $\sigma(F_o) = \{0.5kI^{-1/2}[\sigma(I)]^2 + (0.02I)^2\}^{1/2}$. 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 Lp 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 $R = 0.0355$ for 2248 reflections, with $wR = 0.0438$ ($R_{\text{all}} = 0.0394, wR_{\text{all}} =$

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

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
O1	-0.1008 (1)	0.4388 (1)	0.35746 (9)	0.0258 (4)
C2	-0.0501 (2)	0.5240 (2)	0.4150 (1)	0.0261 (5)
C3	0.0558 (2)	0.4624 (2)	0.4606 (1)	0.0284 (6)
O4	0.16755 (1)	0.4581 (1)	0.4122 (1)	0.0336 (5)
C5	0.1868 (2)	0.3426 (2)	0.3854 (1)	0.0334 (6)
O6	0.2700 (2)	0.3143 (2)	0.3408 (1)	0.0473 (6)
O7	0.1023 (2)	0.2643 (1)	0.41454 (9)	0.0344 (5)
C8	0.0290 (2)	0.3255 (2)	0.4766 (1)	0.0283 (6)
C9	-0.1080 (2)	0.2914 (2)	0.4691 (1)	0.0292 (6)
C10	-0.1721 (2)	0.3429 (2)	0.3940 (1)	0.0256 (5)
O11	-0.2875 (1)	0.3879 (1)	0.42260 (9)	0.0315 (4)
C12	-0.3733 (2)	0.4313 (3)	0.3631 (2)	0.0431 (8)
C13	-0.1864 (2)	0.2494 (2)	0.3257 (1)	0.0286 (6)
O14	-0.2732 (2)	0.1593 (2)	0.35010 (8)	0.0325 (4)
C15	-0.3061 (2)	0.0762 (2)	0.2867 (1)	0.0322 (6)
C16	-0.4197 (2)	0.0073 (2)	0.3121 (1)	0.0294 (6)
C17	-0.4155 (2)	-0.1194 (2)	0.3250 (2)	0.0341 (7)
C18	-0.5205 (2)	-0.1821 (2)	0.3523 (2)	0.0380 (7)
C19	-0.6313 (2)	-0.1191 (2)	0.3663 (2)	0.0374 (7)
C20	-0.6360 (2)	0.0071 (2)	0.3524 (2)	0.0352 (7)
C21	-0.5319 (2)	0.0695 (2)	0.3256 (1)	0.0329 (6)
C22	-0.0135 (2)	0.6366 (2)	0.3657 (2)	0.0318 (6)
O23	0.0255 (2)	0.7342 (1)	0.4170 (1)	0.0452 (6)
C24	-0.0470 (2)	0.8421 (2)	0.3984 (2)	0.0359 (7)
O25	-0.1013 (2)	0.8192 (2)	0.3224 (1)	0.0384 (5)
C26	-0.1230 (3)	0.6897 (2)	0.3186 (2)	0.0402 (8)
C27	-0.1454 (3)	0.8627 (3)	0.4621 (2)	0.055 (1)
C28	0.0391 (3)	0.9511 (2)	0.3892 (2)	0.051 (1)

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

1	2	3	1-2	1-2-3
C2	O1	C10	1.429 (3)	113.0 (2)
C10	O1		1.418 (2)	
C3	C2	C22	1.512 (3)	115.4 (2)
C3	C2	O1		109.3 (2)
C22	C2	O1	1.514 (3)	105.0 (2)
O4	C3	C8	1.436 (3)	102.7 (2)
O4	C3	C2		110.9 (2)
C8	C3	C2	1.529 (3)	111.8 (2)
C5	O4	C3	1.340 (3)	110.0 (2)
O6	C5	O7	1.192 (3)	124.5 (2)
O6	C5	O4		123.9 (2)
O7	C5	O4	1.327 (3)	111.6 (2)
C8	O7	C5	1.448 (3)	109.5 (2)
C9	C8	C3	1.512 (3)	113.7 (2)
C9	C8	O7		110.6 (2)
C3	C8	O7		102.6 (2)
C10	C9	C8	1.522 (3)	114.3 (2)
O11	C10	C13	1.405 (2)	113.0 (2)
O11	C10	O1		111.1 (2)
O11	C10	C9		104.2 (2)
C13	C10	O1	1.520 (3)	102.9 (2)
C13	C10	C9		113.9 (2)
O1	C10	C9		111.9 (2)
C12	O11	C10	1.423 (3)	116.5 (2)
O14	C13	C10	1.402 (3)	108.3 (2)
C15	O14	C13	1.423 (3)	112.9 (2)
C16	C15	O14	1.483 (3)	108.1 (2)
C17	C16	C21	1.385 (3)	118.7 (2)
C17	C16	C15		120.9 (2)
C21	C16	C15	1.390 (3)	120.4 (2)
C18	C17	C16	1.384 (4)	120.5 (2)
C19	C18	C17	1.383 (4)	120.3 (2)
C20	C19	C18	1.382 (4)	119.2 (2)
C21	C20	C19	1.373 (3)	120.5 (2)
C16	C21	C20		120.7 (2)
O23	C22	C26	1.414 (3)	104.6 (2)
O23	C22	C2		110.6 (2)
C26	C22	C2	1.516 (4)	112.4 (2)
C24	O23	C22	1.433 (3)	108.6 (2)
O25	C24	C27	1.404 (3)	111.3 (2)
O25	C24	C28		107.5 (2)
O25	C24	O23		105.7 (2)
C27	C24	C28	1.502 (4)	112.5 (2)
C27	C24	O23		110.3 (2)
C28	C24	O23	1.501 (4)	109.2 (2)
C26	O25	C24	1.418 (3)	106.3 (2)
C22	C26	O25		102.9 (2)

0.0446) and a goodness of fit = 1.611. The maximum $|\Delta/\sigma| < 0.1$ in the final refinement cycle and the min. and max. peaks in the final ΔF map were -0.24 and 0.15 e \AA^{-3} , respectively. Differentiation between enantiomorphs could not be made on the basis of the X-ray results ($wR = 0.0438$ for the enantiomorph). Scattering factors for the non-H atoms were taken from Cromer & Mann (1968), with anomalous-dispersion corrections from Cromer & Liberman (1970), while scattering factors for the H atoms are from Stewart, Davidson & Simpson (1965). The linear absorption coefficient was calculated from values found in *International Tables for X-ray Crystallography* (1974, Vol. IV, p. 55).^{*} Figures were generated using *SHELXTL-Plus* (Sheldrick, 1987). 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 programs from reference 11 of Gadol & Davis (1982).

Related literature. The total synthesis of KDO (Unger, 1981) and its crystal structure (Birnbbaum, Roy, Brisson & Jennings, 1987) have been reported. A synthetic procedure related to that used to prepare the title compound is described elsewhere (Martin, Campbell, Gluchowski & Chapman, 1988).

Funding for this project was supplied by the Robert A. Welch Foundation (F-652) and the National Institutes of Health (GM 31077) to SFM.

^{*} Lists of structure factors, anisotropic thermal parameters, bond distances and angles involving H atoms, torsion angles, H-atom parameters and a unit-cell packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53617 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

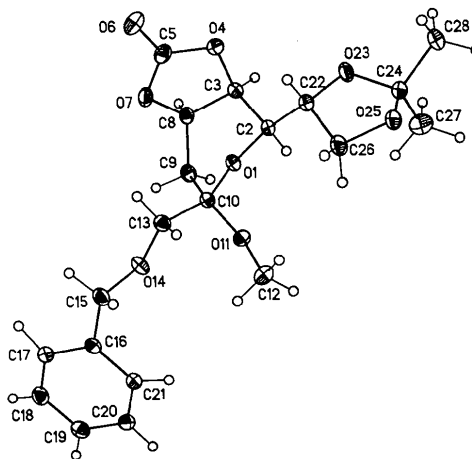


Fig. 1. View of (1) showing the atom-labeling scheme. The non-H atoms are scaled to the 30% probability level while the H atoms are drawn to an arbitrary size.

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