0·245 (2) Å [for B(2)], all other distances being less than 0·08 Å. To minimize steric repulsion, the planes through the phenyl ring and the C(4)—CO_2 group are rotated by 76·99 (6) and 79·35 (5)° with respect to the plane *A*. In contrast, the N(12)—CO_2 group is tilted by only 9·90 (6)° with respect to the same plane, giving the strong intramolecular interaction O(28)···H(10) [2·30 (2) Å] and a good overlap between the π systems of indole and C(27)=O(28) groups. The crystal structure is mainly based on van der Waals interactions, and only a few weak H bonds are present, among which the strongest are: C(19)—H(19)···F(14) with C···F 3·304 (3) and H···F 2·59 (2) Å, and C(20)—H(20)···F(15) [C···F 3·494 (3), H···F 2·66 (2) Å].

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References

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Frenz, B. A. (1983). *Enraf-Nonius Structure Determination Package; SDP User's Guide*. Version of 6 January 1983. Enraf-Nonius, Delft, The Netherlands.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 149–150. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kliegel, W., Rettig, S. J. & Trotter, J. (1983). *Can. J. Chem.* **62**, 1363–1368.

Larson, R. C. (1967). *Acta Cryst.* **23**, 664–665.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Marchesini, A. A. (1989). Unpublished.

Nardelli, M. (1982). *PARST. A System of Computer Routines for Calculating Molecular Parameters from the Results of Crystal Structure Analysis*. Univ. of Parma, Italy.

Rettig, S. J. & Trotter, J. (1983). *Can. J. Chem.* **61**, 206–210.

Acta Cryst. (1990). C**46**, 1503–1507

Structure of α-Hydroximinopentyl 1-Thio-β-D-glucopyranoside

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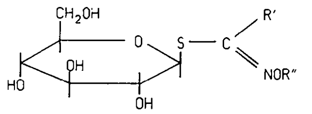
Abstract. 1-(β-D-Glucopyranosylthio)pentanone oxime, $C_{11}H_{21}NO_6S$, $M_r = 295·3$, orthorhombic, $P2_12_12_1$, $a = 9·032$ (2), $b = 11·081$ (3), $c = 14·453$ (2) Å, $V = 1446·5$ (6) Å^3, $Z = 4$, $D_x = 1·356$ Mg m^{-3}, $F(000) = 632$, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·233$ mm^{-1}. The final R was 0·038, wR 0·041 for 1849 observed reflections ($|F| > 2\sigma_F$). The pyranose ring is in the usual $^4C_1$ chair conformation, the O—C—S—C glycosidic torsion angle is −73·9 (3)°, and the C(1)—S—C(=NO)—C entity is planar. The C(1)—S bond length is 1·809 (3) Å and the S—C(sp^2) bond length is 1·764 (3) Å while the ring C(1)—O is 1·415 (3) and C(5)—O is 1·439 (3) Å. The molecules are held in three dimensions by hydrogen bonding in which all five O—H H atoms take part. Two of these H atoms form bifurcated hydrogen bonds, the weaker component being intramolecular; one of these is from the primary alcohol to the pyranose oxygen.

Introduction. Glucosinolates, (I), are found in brassica plants and render the residues poisonous after the oil has been extracted from oil seed rape, (Heaney & Fenwick, 1987). They may be detected and analyzed (Palmer, Yeung & Sang, 1987) by treatment with arylsulfatase followed by high performance liquid chromatography of the desulfoglucosinolate, (II).



(I) R″ = OSO_3H

(II) R″ = H

The title compound, (II), $R' = C_4H_9$, was synthesized (Parsons, 1986) from D-glucose and shown to be identical with one of the naturally occurring derivatives. It was of particular interest to determine whether the desulfo derivative had the same configuration about the S—C=N entity as the compound, extracted from the seeds of black mustard, known as Sinigrin, the hydrated potassium salt of myronic acid, (I), R' = allyl. The crystal structure of Sinigrin was determined by Marsh & Waser (1970) who were able to establish the absolute configuration despite

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extensive radiation damage. We were more fortunate, the crystals diffract very well.

Experimental. The colourless crystals are elongated parallel to the *a* axis. Two crystals were used; *A* was 0·6 × 0·5 × 0·4 mm, *B*, for which complete results are given here, was 0·8 × 0·7 × 0·6 mm. The unit-cell dimensions were obtained from 25 carefully centred reflections having $19 < 2\theta < 32°$. A Guinier powder photograph was taken (with Cu $K\alpha_1$ radiation) and indexed, showing that the sample crystals were characteristic of the whole.

Observations were collected on a Nicolet *R*3*m* diffractometer over the range $3 < 2\theta < 55°$ for two octants, $h = 0$ to 12, $k = 0$ to 15, $l = 0$ to 19 and $h = 0$ to 12, $k = -15$ to -1, $l = -19$ to -1 by $\theta/2\theta$ scans at variable speed from 4 to 29° min^{-1} depending upon the intensity of a 2 s prescan, the scan width being from 0·6° below $K\alpha_1$ to 0·6° above $K\alpha_2$; backgrounds were measured at each side for half the scan time. Three check reflections (208, 431 and 342) were measured every 97 reflections and no deterioration of the crystal was found. Measurements were processed using profile analysis; Lorentz and polarization, but no absorption corrections were applied. 3873 reflections measured, 1925 unique ($R_{\text{int}} = 0·026$), 1849 observed ($|F| > 2\sigma_F$).

The structure solved by the direct methods in *SHELXTL-Plus* (Sheldrick, 1987). Two cycles of isotropic refinement of the non-H atoms with $|F| \geq 2\sigma_F$ gave $R = 0·12$ and the difference map showed ambiguous peaks which might be H atoms and others certainly attributable to anisotropic vibration. Four cycles allowing anisotropic displacement parameters for the non-H atoms reduced *R* to 0·065 and the first 21 peaks in the difference map were clearly H atoms. In the next four cycles their coordinates were also allowed to refine as were two common isotropic vibration parameters, one for H atoms on carbon and the other for H atoms on oxygen so there were 237 parameters. With a weighting scheme $w = 1/(\sigma^2{}_F + 0·001149F_o{}^2)$, the final *R* value was 0·038, $wR = 0·041$ for the 1849 observations used and 0·041 for all 1924 reflections. The most significant shift in any parameter for a non-H atom was 0·1 and for the H atoms, 0·5 of the corresponding standard deviation. The largest peak and trough were ±0·2 e Å^{-3} in the final difference map. Scattering factors in *SHELXTL-Plus*. Final coordinates are in Table 1.* The computer programs were Nicolet *R*3*m*/V crystallographic system on a MicroVAX II under VMS 4.5 (Sheldrick, 1987).

Table 1. *Atomic coordinates* (×10^4, ×10^3 *for* H *atoms) and thermal parameters* (Å^2 × 10^4, Å^2 × 10^3 *for* H *atoms*)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	$U_{\text{eq}}/U_{\text{iso}}$
C(1)	3030 (3)	7046 (2)	4708 (2)	246 (6)
C(2)	3123 (3)	6962 (2)	3659 (2)	238 (6)
C(3)	3647 (3)	8171 (2)	3265 (2)	253 (7)
C(4)	2763 (3)	9228 (2)	3651 (2)	273 (7)
C(5)	2702 (3)	9151 (2)	4705 (2)	269 (7)
C(6)	1737 (3)	10101 (3)	5145 (2)	360 (8)
O(7)	2081 (2)	8005 (2)	4967 (1)	286 (5)
O(8)	4125 (2)	6042 (2)	3415 (1)	326 (6)
O(9)	3515 (3)	8072 (2)	2289 (1)	442 (7)
O(10)	3326 (3)	10344 (2)	3340 (2)	380 (6)
O(11)	1800 (3)	10017 (2)	6128 (2)	489 (8)
S(12)	2240 (1)	5636 (1)	5101 (1)	304 (2)
C(13)	2548 (3)	5665 (3)	6306 (2)	285 (7)
C(14)	3321 (4)	6691 (3)	6782 (2)	371 (9)
C(15)	3711 (4)	6453 (3)	7793 (2)	411 (9)
C(16)	4573 (4)	7476 (3)	8217 (2)	410 (9)
C(17)	5082 (5)	7214 (4)	9194 (3)	553 (12)
N(18)	2094 (3)	4777 (2)	6781 (2)	330 (6)
O(19)	1354 (3)	3913 (2)	6230 (1)	384 (6)
H(2)	216 (5)	681 (3)	338 (3)	47 (3)
H(1)	403 (5)	721 (3)	500 (3)	47 (3)
H(3)	472 (4)	833 (3)	346 (3)	47 (3)
H(4)	169 (4)	912 (4)	341 (3)	47 (3)
H(5)	372 (4)	922 (3)	494 (3)	47 (3)
H(6*A*)	213 (4)	1091 (4)	499 (3)	47 (3)
H(6*B*)	72 (5)	1003 (3)	496 (3)	47 (3)
H(8)	375 (5)	575 (4)	302 (3)	53 (5)
H(9)	351 (5)	876 (4)	209 (3)	53 (5)
H(10)	437 (5)	1050 (4)	349 (3)	53 (5)
H(11)	123 (5)	957 (4)	626 (3)	53 (5)
H(14*A*)	437 (4)	685 (4)	645 (3)	47 (3)
H(14*B*)	272 (4)	745 (4)	672 (3)	47 (3)
H(15*A*)	436 (4)	565 (4)	782 (3)	47 (3)
H(15*B*)	302 (5)	631 (4)	810 (3)	47 (3)
H(16*A*)	400 (5)	820 (4)	815 (3)	47 (3)
H(16*B*)	530 (4)	769 (4)	783 (3)	47 (3)
H(17*A*)	574 (5)	656 (4)	916 (3)	47 (3)
H(17*B*)	570 (5)	783 (4)	946 (3)	47 (3)
H(17*C*)	422 (5)	720 (4)	958 (3)	47 (3)
H(19)	136 (5)	330 (4)	649 (3)	53 (5)

Discussion. Fig. 1 shows the designations of the atoms. Bond lengths and angles are in Table 2. Attempts to apply corrections for libration showed that the whole molecule cannot be treated as a rigid body. If the hydroxy O atoms are allowed to 'ride' on the corresponding C atoms the C—O bond lengths would be increased by 0·01 Å, *i.e.* range from 1·418 to 1·439 (3) Å. A similar treatment increases the short C(15)—C(16) bond length, 1·505 (5) Å by only 0·001 Å. Comparison of the coordinates at the same stage of refinement with those obtained from observations collected with the smaller crystal, *A*, at $R = 0·037$, shows that the average Δ/σ is 1·5 in line with the results of a survey (Taylor & Kennard, 1986) of more than one hundred crystal structures. The most significant difference between our two sets of coordinates was in *x*/*a* for S(12), Δ/σ 5·4, leading to bond lengths C(1)—S(12) 1·801 (3) Å and S(12)—C(13) 1·763 (3) Å for crystal *A*.

The bond lengths in Table 2 do not differ significantly from those found on averaging many struc-

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* Lists of structure amplitudes, anisotropic thermal parameters and equations of planes through various groups of atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52825 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

tures (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987) but there is no exact comparison for the S—C bonds. C(1)—S(12), 1·809 (3) Å, is the same as in $(CH_3)_2S$ (Iijima, Tsuchiya & Kimura, 1977) while the C—S—C angle is larger *cf.* 99° in dimethyl sulfide. However, Allen *et al.* (1987) show that for S to an sp^3 carbon atom $>$CH—S, the average is 1·819 (11) Å, for S to an sp^2 carbon atom C=C—S, the average is 1·751 (17) Å. Some π bonding is indicated in S(12)—C(13) because the atoms C(1)—S(12)—C(13)—C(14)-N(18)—O(19) are coplanar to within 0·012 (3) Å. Our C—H bond lengths range from 0·78 to 1·07 (4) Å and the O—H bond lengths from 0·74 to 0·98 (5) Å (see Table 2).

As shown in Fig. 1, where the torsion angles are displayed, the sugar is in the usual ${}^4C_1$ conformation with all substituents equatorial. The normal to the plane through the six atoms of the pyranose ring is at 44·7 (2)° to the normal to the plane through C(1)—S(12)—C(13)—C(14)-N(18)—O(19). Hence the non-H atoms C(1)···C(14), N(18) and O(19) are essentially the same as in Sinigrin (Marsh & Waser, 1970); our dimensions are more accurate because the crystal was stable in the X-ray beam. In both structures the configuration at C(2) and C(13) results in a close contact between the H atom on C(1) and one on C(14), 2·16 (4) Å in the present work. Because the hydrogen bonding and packing are quite different, the orientations of the hydroxy groups are not the same as those in Sinigrin. The other major difference is that the *R′* allyl group in Sinigrin is not approximately coplanar with the other atoms around C(13) whereas the atoms of the *n*-butyl chain C(14)···C(17), which are in an all-*trans* conformation, are coplanar to within 0·03 Å and the normal to this plane is at 12·4 (2)° to that of C(1)—S(12)—C(13)—C(14)-N(18)—O(19).

Table 2. *Bond lengths* (Å) *and angles* (°)

C(1)—C(2)	1·521 (3)	C(1)—H(1)	1·01 (4)
C(1)—O(7)	1·415 (3)	C(1)—S(12)	1·809 (3)
C(2)—H(2)	0·97 (4)	C(2)—C(3)	1·531 (4)
C(2)—O(8)	1·408 (3)	C(3)—H(3)	1·02 (4)
C(3)—C(4)	1·523 (4)	C(3)—O(9)	1·420 (3)
C(4)—H(4)	1·02 (4)	C(4)—C(5)	1·527 (4)
C(4)—O(10)	1·411 (3)	C(5)—H(5)	0·98 (4)
C(5)—C(6)	1·507 (4)	C(5)—O(7)	1·439 (3)
C(6)—H(6*A*)	0·99 (4)	C(6)—H(6*B*)	0·97 (4)
C(6)—O(11)	1·425 (4)	O(8)—H(8)	0·74 (5)
O(9)—H(9)	0·82 (5)	O(10)—H(10)	0·98 (4)
O(11)—H(11)	0·74 (5)	S(12)—C(13)	1·764 (3)
C(13)—C(14)	1·502 (4)	C(13)—N(18)	1·268 (4)
C(14)—H(14*A*)	1·07 (4)	C(14)—H(14*B*)	1·01 (4)
C(14)—C(15)	1·525 (4)	C(15)—H(15*A*)	1·06 (4)
C(15)—H(15*B*)	0·78 (3)	C(15)—C(16)	1·505 (5)
C(16)—H(16*A*)	0·97 (4)	C(16)—H(16*B*)	0·90 (4)
C(16)—C(17)	1·514 (5)	C(17)—H(17*A*)	0·93 (4)
C(17)—H(17*B*)	0·96 (4)	C(17)—H(17*C*)	0·95 (4)
N(18)—O(19)	1·414 (3)	O(19)—H(19)	0·78 (4)

C(2)—C(1)—H(1)	112 (2)	C(2)—C(1)—O(7)	110·1 (2)
H(1)—C(1)—O(7)	107 (2)	C(2)—C(1)—S(12)	106·4 (2)
H(1)—C(1)—S(12)	112 (2)	O(7)—C(1)—S(12)	109·0 (2)
C(1)—C(2)—H(2)	112 (2)	C(1)—C(2)—C(3)	109·5 (2)
H(2)—C(2)—C(3)	106 (2)	C(1)—C(2)—O(8)	109·2 (2)
H(2)—C(2)—O(8)	110 (2)	C(3)—C(2)—O(8)	110·0 (2)
C(2)—C(3)—H(3)	110 (2)	C(2)—C(3)—C(4)	112·0 (2)
H(3)—C(3)—C(4)	105 (2)	C(2)—C(3)—O(9)	106·0 (2)
H(3)—C(3)—O(9)	112 (2)	C(4)—C(3)—O(9)	112·3 (2)
C(3)—C(4)—H(4)	108 (2)	C(3)—C(4)—C(5)	110·0 (2)
H(4)—C(4)—C(5)	104 (2)	C(3)—C(4)—O(10)	111·6 (2)
H(4)—C(4)—O(10)	111 (2)	C(5)—C(4)—O(10)	112·3 (2)
C(4)—C(5)—H(5)	108 (2)	C(4)—C(5)—C(6)	113·8 (2)
H(5)—C(5)—C(6)	110 (2)	C(4)—C(5)—O(7)	109·0 (2)
H(5)—C(5)—O(7)	110 (2)	C(6)—C(5)—O(7)	106·3 (2)
C(5)—C(6)—H(6*A*)	109 (2)	C(5)—C(6)—H(6*B*)	112 (2)
H(6*A*)—C(6)—H(6*B*)	111 (3)	C(5)—C(6)—O(11)	110·6 (2)
H(6*A*)—C(6)—O(11)	106 (2)	H(6*B*)—C(6)—O(11)	108 (2)
C(1)—O(7)—C(5)	110·9 (2)	C(2)—O(8)—H(8)	102 (3)
C(3)—O(9)—H(9)	106 (3)	C(4)—O(10)—H(10)	115 (2)
C(6)—O(11)—H(11)	105 (4)	C(1)—S(12)—C(13)	103·5 (1)
S(12)—C(13)—C(14)	122·6 (2)	S(12)—C(13)—N(18)	118·0 (2)
C(14)—C(13)—N(18)	119·3 (2)	C(13)—C(14)—H(14*A*)	109 (2)
C(13)—C(14)—H(14*B*)	110 (2)	H(14*A*)—C(14)—H(14*B*)	108 (3)
C(13)—C(14)—C(15)	114·5 (3)	H(14*A*)—C(14)—C(15)	105 (2)
H(14*B*)—C(14)—C(15)	111 (2)	C(14)—C(15)—H(15*A*)	108 (2)
C(14)—C(15)—H(15*B*)	113 (3)	H(15*A*)—C(15)—H(15*B*)	105 (4)
C(14)—C(15)—C(16)	112·3 (3)	H(15*A*)—C(15)—C(16)	109 (2)
H(15*B*)—C(15)—C(16)	110 (3)	C(15)—C(16)—H(16*A*)	108 (2)
C(15)—C(16)—H(16*B*)	109 (3)	H(16*A*)—C(16)—H(16*B*)	96 (4)
C(15)—C(16)—C(17)	113·1 (3)	H(16*A*)—C(16)—C(17)	115 (2)
H(16*B*)—C(16)—C(17)	114 (3)	C(16)—C(17)—H(17*A*)	107 (3)
C(16)—C(17)—H(17*B*)	114 (2)	H(17*A*)—C(17)—H(17*B*)	102 (4)
C(16)—C(17)—H(17*C*)	107 (3)	H(17*A*)—C(17)—H(17*C*)	122 (4)
H(17*B*)—C(17)—H(17*C*)	105 (3)	C(13)—N(18)—O(19)	111·9 (2)
N(18)—O(19)—H(19)	108 (3)		

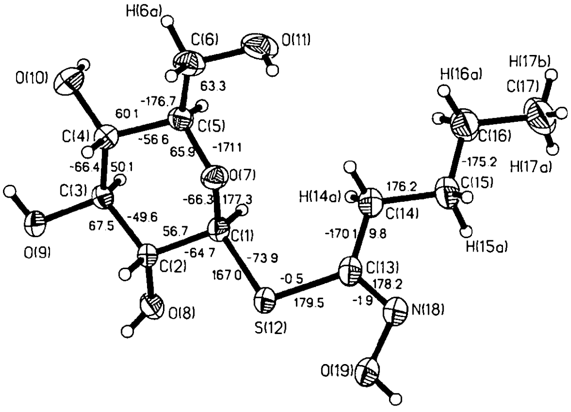

Fig. 1. One molecule showing thermal ellipsoids at the 50% confidence level, designations of the non-H atoms, and torsion angles excluding H atoms, e.s.d.'s 0·2–0·3°.

Features of the structure, apart from the orientation of the hydroxy groups, for the atoms C(1)···C(13) are similar to the corresponding ones in pyridyl-1-thio-β-D-glucopyranoside monohydrate (Nordenson & Jeffrey, 1980) quoted with the same e.s.d.'s as in this work. In the pyridyl compound the atom corresponding to our C(13) is C(2) of the pyridyl ring. These features include C(5)—O(7) being 0·024 (4) Å longer than C(1)—O(7), the thioglycosidic torsion angle O(7)—C(1)—S(12)—C(13) of −73·9 (2)° and the C(1)—S(12)—C(13) angle of 103·5 (2)°. The first is usual in β-pyranosides, the second gives rise to the crowding between the H atoms H(1) and (H14*A*) and the third may be attributed to alleviation of this steric crowding; possibly the angle S(12)—C(13)—C(14) is 122·6 (2)° instead of 120° for the same reason.

Sterically unfavourable thioglucosidic and glucosidic torsion angles, −70 to −90°, have been found in many pyranosides even when the derivative is methyl or another sugar; it is one manifestation of the *exo*-anomeric effect (Jeffrey, Pople, Binkley & Vishveshwara, 1978) which usually also results in a shortening of the C(1)—O bond. There are fewer examples of thio-β-pyranosides and our own observations, *i.e.* a difference of 0·008 Å for the same bond length C(1)—S(12) measured on different crystals, provides a cautionary tale. Literature values include 1·806 (1) Å in methyl-1-thio-β-D-galactopyranoside (Atkinson, Ruble & Jeffrey, 1981) and 1·793 (3) Å in pyridyl-1-thio-β-D-glucopyranoside monohydrate (Nordenson & Jeffrey, 1980).

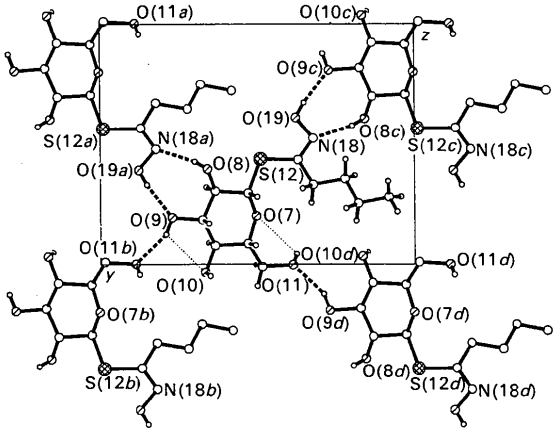

Fig. 2. Projection down the *a* (needle) axis of the crystal chemical unit (c.c.u.) with coordinates in Table 1 and those molecules forming sheets of hydrogen bonds in the *bc* plane *viz.* (*a*) $\frac{1}{2}-x$, $1-y$, $-\frac{1}{2}+z$, (*b*) $\frac{1}{2}-x$, $2-y$, $-\frac{1}{2}+z$, (*c*) $\frac{1}{2}-x$, $1-y$, $\frac{1}{2}+z$, (*d*) $\frac{1}{2}-x$, $2-y$, $\frac{1}{2}+z$. For clarity the H atoms on carbon are shown only on the c.c.u.. Broken lines show intermolecular hydrogen bonds, and the c.c.u. dotted lines show the intramolecular hydrogen bonds. Dimensions of the hydrogen bonds are in Table 3.

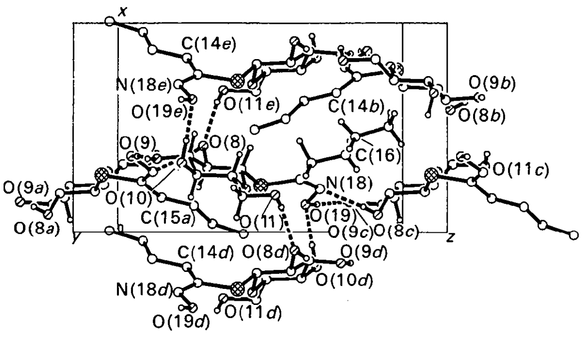

Fig. 3. Slightly offset projection down the *b* axis. All H atoms are shown on the c.c.u. only. Broken lines represent hydrogen bonds between the c.c.u. and the molecules at (*a*) $\frac{1}{2}-x$, $1-y$, $-\frac{1}{2}+z$, (*b*) $1-x$, $-\frac{1}{2}+y$, $1\frac{1}{2}-z$, (*c*) $\frac{1}{2}-x$, $1-y$, $\frac{1}{2}+z$, (*d*) $-\frac{1}{2}+x$, $1\frac{1}{2}-y$, $1-z$, (*e*) $\frac{1}{2}+x$, $1\frac{1}{2}-y$, $1-z$.

Table 3. *Hydrogen-bond geometry* (Å, °)

Values in parentheses are for H atoms in positions idealized to give O—H bond lengths of 0·97 Å. E.s.d.'s are 0·045 Å in distances, 4° at 180° and 3° at 90° in the O—H···*X* angles.

		H···*X*	O—H···*X*
O(8)—H(8)···N(18)	$\frac{1}{2}-x, 1-y, -\frac{1}{2}+z$	2·04 (1·81)	168 (167)
O(9)—H(9)···O(10)		2·52 (2·46)	114 (110)
···O(11)	$\frac{1}{2}-x, 2-y, -\frac{1}{2}+z$	1·96 (1·83)	153 (151)
O(10)—H(10)···O(19)	$\frac{1}{2}+x, 1\frac{1}{2}-y, 1-z$	1·95 (1·96)	171 (171)
O(11)—H(11)···O(7)		2·66 (2·65)	94 (89)
···O(8)	$-\frac{1}{2}+x, 1\frac{1}{2}-y, 1-z$	2·08 (1·86)	156 (153)
O(19)—H(19)···O(9)	$\frac{1}{2}-x, 1-y, \frac{1}{2}+z$	1·91 (1·72)	172 (171)

Hydrogen bonding and packing. The molecules are held in the crystal by three-dimensional hydrogen bonding as shown in Figs. 2 and 3; the dimensions are given in Table 3 as found, and after adjusting the O—H bond lengths to the neutron diffraction value, 0·97 Å, as suggested by Jeffrey & Takagi (1978). All five hydroxy H atoms act as donors in intermolecular hydrogen bonds, three to give infinite sheets in the *bc* planes and two, H(10) and H(11), holding the sheets together along the *a* axis. In addition there are intramolecular hydrogen bonds, H(9) and H(11) forming bifurcated bonds as indicated by their relatively small O—H···*X* intermolecular bond angles. While the H(9)···O(10) bond is not uncommon and has been found in solution (Christofides & Davies, 1987) the H(11) bond to the pyranose ring oxygen is unusual but not unique. In pyridyl 1-thio-β-D-glucopyranoside monohydrate (Nordenson & Jeffrey, 1980) an intramolecular hydrogen bond between the primary alcohol and the ring O atom is the weaker component of a bifurcated hydrogen bond.

As shown in Fig. 3, there are channels along the *b* axis in which the hydrocarbon tails are situated. They are loosely packed, the nearest C···C contacts are at 4·89 Å, C(15)···C(16*b*) of Fig. 3 and the angle between the normal to C(13)—C(14)–C(16)—C(17) is 42·8 (3)° to that through the chain related by the screw axis, relation *b* of Fig. 3. This contrasts with Sinigrin (Marsh & Waser, 1970) in which the allyl groups are parallel and the C···C separations are 3·5 and 3·6 Å; the authors postulated that interaction between these groups accounted for the decomposition of the crystals in the X-ray beam. Our arrangement of *n*-butyl chains also contrasts with that of alkyl 'tails' in carbohydrate derivatives which form liquid crystals (Jeffrey, 1986); in such mesogenic compounds the tail contains more than six C atoms (Jeffrey & Bhattacherjee, 1983) and the characteristic packing, found in heptyl-1-thio-α-D-mannopyranoside (Carter, Ruble & Jeffrey, 1982), is that the alkyl chains are parallel with minimum C···C contacts 3·8 Å. Clearly in the present structure the packing is dominated by hydrogen bonding.

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References

ALLEN, F. H., KENNARD, O., WATSON, D. G., BRAMMER, L., ORPEN, A. G. & TAYLOR, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.

ATKINSON, A., RUBLE, J. R. & JEFFREY, G. A. (1981). *Acta Cryst.* **B37**, 1465–1467.

CARTER, D. C., RUBLE, J. R. & JEFFREY, G. A. (1982). *Carbohydr. Res.* **102**, 59–67.

CHRISTOFIDES, J. C. & DAVIES, D. B. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. 98–102.

HEANEY, R. K. & FENWICK, G. R. (1987). In *Natural Toxicants in Foods*, edited by D. H. WATSON, Ch. 3. New York: VCH Publishers.

IIJIMA, T. S., TSUCHIYA, S. & KIMURA, M. (1977). *Bull. Chem. Soc. Jpn*, **50**, 2564–2567.

JEFFREY, G. A. (1986). *Acc. Chem. Res.* **19**, 168–173.

JEFFREY, G. A. & BHATTACHERJEE, S. (1983). *Carbohydr. Res.* **115**, 53–58.

JEFFREY, G. A., POPLE, J. A., BINKLEY, J. S. & VISHVESHWARA, S. (1978). *J. Am. Chem. Soc.* **100**, 373–379.

JEFFREY, G. A. & TAKAGI, S. (1978). *Acc. Chem. Res.* **11**, 264–270.

MARSH, R. E. & WASER, J. (1970). *Acta Cryst.* **B26**, 1030–1037.

NORDENSON, S. & JEFFREY, G. A. (1980). *Acta Cryst.* **B36**, 1214–1216.

PALMER, M. V., YEUNG, S. P. & SANG, J. P. (1987). *J. Agric. Food Chem.* **35**, 262–265.

PARSONS, D. G. (1986). Personal communication.

SHELDRICK, G. M. (1987). *SHELXTL-Plus* for Nicolet *R3m/V*. *Crystallographic Systems for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Federal Republic of Germany.

TAYLOR, R. & KENNARD, O. (1986). *Acta Cryst.* **B42**, 112–120.

Acta Cryst. (1990). **C46**, 1507–1509

Structure of 5-Hydroxymethyl-7,7-dimethyl-6-oxabicyclo[3.2.1]octane-1-carboxylic Acid

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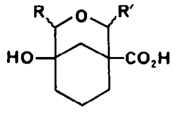
Abstract. $C_{11}H_{18}O_4$, $M_r = 214{\cdot}26$, monoclinic, $P2_1/c$, $a = 6{\cdot}832\,(1)$, $b = 14{\cdot}933\,(2)$, $c = 11{\cdot}315\,(1)$ Å, $\beta = 106{\cdot}74\,(1)°$, $V = 1105{\cdot}5\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}287$ g cm^{-3}, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}54184$ Å, $\mu = 7{\cdot}633$ cm^{-1}, $F(000) = 464$, room temperature, $R = 0{\cdot}069$ for 1359 unique observed reflections with $|F_o| > 3\sigma(|F_o|)$. The five-membered ring has a twist conformation with the twofold axis of symmetry bisecting the bond between the two out-of-plane atoms (C5—C6). The six-membered ring is in a distorted chair conformation flattened at C3. Each molecule is involved in four hydrogen bonds of the type O—H···O.

Introduction. Our interest in the asymmetric synthesis of medium-sized cyclic ethers with specific stereochemistry on the α,α'-dialkyl substituents (Alvarez, Manta, Martín, Rodríguez & Ruiz-Pérez, 1988) has led us to consider the synthesis of 2,4-dialkylated-1-hydroxy-2-oxabicyclo[3.3.1]nonane-5-carboxylic acids, such as (1), as suitable intermediates, which can afford substituted oxocane systems by decarboxylation and further Grob fragmentation. The success of the synthetic plan depends upon the cyclization of an epoxy alcohol such as (4) to give the required (5) or the 6-oxabicyclo[3.2.1]octane system (6). In this paper we report that the acid-catalyzed cyclization of (4) affords exclusively the crystalline heterocycle (6), whose structure is established by X-ray analysis.



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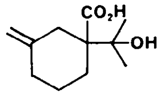

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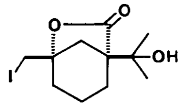

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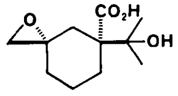

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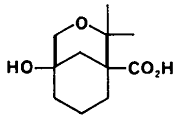

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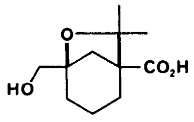

(6)

Experimental. The synthesis was initiated from the racemic β-hydroxy acid (2), available on a large scale by condensing the dilithium salt of 3-methylenecyclo-