Carbohydrate Research, 123 (1983) 1–11
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CRYSTAL STRUCTURE OF MEROSINIGRIN, AN (*ap*,*ap*)-MONOTHIOACETAL; STRUCTURAL PROPERTIES OF THE THIOGLYCOSIDIC LINKAGE

LEIF NØRSKOV-LAURITSEN, FLEMMING S. JØRGENSEN,
Department of General and Organic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen (Denmark)

AND JERZY W. JAROSZEWSKI*
Department of Chemistry BC, Royal Danish School of Pharmacy, DK-2100 Copenhagen (Denmark)
(Received February 3rd, 1983, accepted for publication, May 19th, 1983)

ABSTRACT

The crystal structure of merosinigrin [(1′*S*,2′*S*)-1,2-*S*,*O*-(1-cyano-2-methyl-1,2-ethanediyl)-1-thio-β-D-glucopyranose], the long-known rearrangement product of allylglucosinolate, was determined by X-ray diffraction at 90 K, thereby revealing the geometry of an (*ap*,*ap*)-monothioacetal group. The crystals of merosinigrin, $C_{10}H_{15}NO_5S$, are triclinic, P1, with cell dimensions a = 5.349(2), b = 6.664(3), c = 9.266(4) Å, α = 85.91(3), β = 76.35(3), γ = 70.83(3)°, Z = 1. The structure was solved by direct methods and refined to R = 0.035 for 1789 independent reflections. For thioglycosides and other monothioacetals, the lengths of the central C-S and C-O bonds depend on the torsion angles about these bonds, consistent with a simple electron-delocalisation model. The central S-C-O valence angle in monothioacetals also depends in a regular way on the torsion angles. Energy optimisation of methoxy(methylthio)methane, a thioglycoside model, by semiempirical molecular orbital calculations (MNDO) reproduced trends observed in the experimental data.

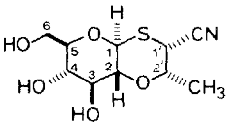
INTRODUCTION

Merosinigrin[1,2] (**1**) is formed by rearrangement of allylglucosinolate (**2**), the thioglucoside of black mustard seeds[3] (*Brassica nigra* Koch), upon treatment with methoxide. Although merosinigrin was first prepared[1] in 1914, its structure was proposed[2] only recently on the basis of spectroscopic evidence. We now report the structure of **1** as determined by single-crystal X-ray diffractometry, which permits,

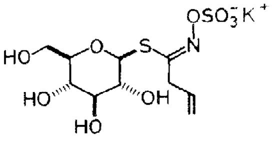
---

*To whom correspondence should be addressed.

for the first time, a comparison of the geometry of an (*ap,ap*)-monothioacetal group, determined experimentally, with other monothioacetal geometries available from the literature.



1



2

RESULTS

Merosinigrin (**1**) was obtained by a modification of the original[1] procedure, and its identity was confirmed on the basis of analytical and spectroscopic data for **1**[2] and its triacetate[1]. Suitable crystals were obtained from hot ethyl acetate. Weissenberg and precession photographs, showing no evidence of systematic absences, indicated triclinic symmetry and provided preliminary cell dimensions. A pyramidal crystal (length 0.35 mm, base 0.21 × 0.14 mm), mounted on a glass needle, was used for determination of final cell dimensions and data collection at ~90 K (constant to within 1°) on a Picker FACS-I diffractometer equipped with a graphite monochromator (MoKα radiation) and a modified Nonius cryogenic device (nitrogen stream). The data were measured using a normal ω–2θ scan mode (2°/min in 2θ) and an asymmetric scan (from $2\theta_0 - 1.1 - 0.231\tan\theta$ to $2\theta_0 + 1.6 + 0.462\tan\theta$), with a static background counting-time of 20 s on each side of the reflection. Owing to a failure of the temperature control, only 1809 out of 1955 possible reflections ($\theta < 30°$) were measured, 1704 having $I > 2\sigma(I)$. According to 5 intensity standards, there was no crystal decay, but some periodic fluctuations (±5%) due to instrumental instability were observed; no attempt was made to correct for these fluctuations. The data were corrected for Lorentz and polarisation effects, but absorption ($\mu = 2.77$ cm^{-1}) was ignored.

The structure was solved by using MULTAN-77[4]. Successive refinements and difference syntheses (XRAY-76[5]) progressed slowly until the last non-hydrogen atoms were included; hydrogens could then be located in a difference map. Positional and anisotropic temperature factors for the heavy atoms were refined, whereas only the positions of hydrogens were varied, their thermal parameters being fixed at 0.02 Å^2. The atomic scattering factors used were those of Cromer and Mann[6] for carbon, oxygen, and sulfur, and of Stewart and co-workers[7] for hydrogen. In the final least-squares cycles, "unobserved" reflections having $|F_c| > |F_O|$ were included to yield a total of 1789 data *versus* 196 variables. The final factors were $R = 0.035$ and $R_w = [\Sigma w(|F_O| - |F_c|)^2/\Sigma w F_O^2]^{1/2} = 0.043$, with weights $w = [3\sigma(F_O)^2 + 0.01|F_O| + 0.002|F_O|^2]^{-1}$, the maximum parameter shift being 0.08σ.

TABLE I

FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC THERMAL PARAMETERS[a]

Atom	x	y	z	U_{iso} ($Å^2$)
C-1	0.5597(6)	0.5962(4)	0.5276(3)	0.0133(7)
C-2	0.6887(6)	0.3651(4)	0.5690(3)	0.0124(7)
C-3	0.4769(5)	0.2920(4)	0.6783(3)	0.0113(7)
C-4	0.3491(6)	0.4447(4)	0.8112(3)	0.0132(7)
C-5	0.2494(6)	0.6748(4)	0.7593(3)	0.0128(7)
C-6	0.1502(6)	0.8307(4)	0.8878(3)	0.0152(8)
C-1′	0.9086(6)	0.4852(4)	0.2639(3)	0.0157(8)
C-2′	1.0046(6)	0.2671(4)	0.3359(3)	0.0159(8)
C-1′1	0.6853(6)	0.5025(4)	0.1902(3)	0.0167(8)
C-2′1	1.1151(7)	0.0881(4)	0.2224(3)	0.0217(9)
S	0.8	0.7	0.4	0.0184(2)
O-2	0.7840(4)	0.2287(3)	0.4428(2)	0.0158(6)
O-3	0.5971(4)	0.0850(3)	0.7322(2)	0.0148(6)
O-4	0.1232(5)	0.4044(3)	0.9067(2)	0.0217(7)
O-5	0.4676(4)	0.7271(3)	0.6569(2)	0.0139(6)
O-6	0.0386(5)	1.0432(3)	0.8432(2)	0.0176(6)
N	0.5048(6)	0.5191(4)	0.1410(3)	
H-1	0.403(8)	0.609(6)	0.483(4)	
H-2	0.862(8)	0.357(6)	0.612(4)	
H-3	0.336(8)	0.292(6)	0.629(4)	
H-4	0.497(8)	0.426(6)	0.864(4)	
H-5	0.102(8)	0.690(6)	0.708(4)	
H-6A	0.302(8)	0.831(6)	0.930(4)	
H-6B	0.016(8)	0.786(5)	0.966(4)	
H-1′	1.041(8)	0.507(5)	0.193(4)	
H-2′	1.158(8)	0.264(6)	0.391(4)	
H-2′1A	1.242(8)	0.111(5)	0.142(4)	
H-2′1B	0.979(8)	0.077(5)	0.175(4)	
H-2′1C	1.201(8)	−0.045(6)	0.266(4)	
H-O–3	0.549(8)	0.004(6)	0.710(4)	
H-O–4	0.120(8)	0.293(6)	0.890(4)	
H-O–6	−0.086(8)	1.054(6)	0.806(4)	

[a]Space group P1, a = 5.349(2), b = 6.664(3), c = 9.266(4) Å, α = 85.91(3)°, β = 76.35(3)°, γ = 70.83(3)°, Z = 1, D_{calc} = 1.431 g/cm^3. U_{iso} = 1/3 trace of diagonalised U-matrix; for hydrogen atoms, U_{iso} = 0.02 $Å^2$. Estimated standard deviations are given in parentheses.

Pertinent crystal data and selected molecular parameters are collected in Tables I and II, and an ORTEP[8] drawing of the merosinigrin molecule is shown in Fig. 1*. The triclinic crystals can be regarded as composed of sheets parallel to the *ab* plane, the packing within the sheets being apparently dominated by hydrogen bonds: O-6–H · · · O-3 1.92 Å, O-4–H · · · O-6 1.95 Å, and O-3–H · · · O-5 2.15

---

*The table of anisotropic thermal parameters of non-hydrogen atoms and a list of structure factors are deposited with, and may be obtained from, Elsevier Scientific Publishing Company, BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/264/ *Carbohydr. Res.*, 123 (1983) 1–11.

TABLE II

SELECTED MOLECULAR PARAMETERS OF THE MEROSINIGRIN MOLECULE[a]

C-1–O-5	1.423(3)	S–C-1′	1.828(3)
C-1–C-2	1.529(3)	C-1′–C-2′	1.534(4)
C-2–C-3	1.516(4)	C-2′–O-2	1.432(4)
C-3–C-4	1.531(3)	C-2–O-2	1.421(3)
C-4–C-5	1.531(3)	C-1′–C-1′1	1.479(5)
C-5–C-6	1.515(4)	C-1′1–N	1.133(5)
C-5–O-5	1.443(4)	C-2′–C-2′1	1.517(4)
C-1–S	1.811(3)		
O-5–C-1–C-2	109.7(2)	C-4–C-5–O-5	110.3(2)
C-1–C-2–C-3	109.1(2)	C-5–O-5–C-1	110.5(2)
C-2–C-3–C-4	110.0(2)	O-5–C-1–S	105.9(2)
C-3–C-4–C-5	110.8(2)	C-1–S–C-1′	95.0(1)
O-5–C-1–C-2–C-3	61.3(3)	O-5–C-1–S–C-1′	172.9(2)
C-1–C-2–C-3–C-4	54.0(3)	S–C-1–C-2–C-3	178.7(2)
C-2–C-3–C-4–C-5	51.5(3)	C-1–S–C-1′–C-2′	−54.3(2)
C-3–C-4–C-5–O-5	−54.8(3)	S–C-1′–C-2′–O-2	64.5(3)
C-4–C-5–O-5–C-1	62.2(3)	C-1′–C-2′–O-2–C-2	−67.1(3)
C-5–O-5–C-1–C-2	−65.6(3)	C-2′–O-2–C-2–C-1	66.0(3)
O-5–C-1–C-2–O-2	−179.9(2)	O-2–C-2–C-1–S	−62.5(3)
C-5–O-5–C-1–S	172.9(2)		

[a] Bond lengths in Å, angles in degrees. Estimated standard deviations are given in parentheses.

Å; the geometry of the glucopyranose ring is, however, not appreciably distorted by the hydrogen bonding[9–11]. The absolute configuration of the molecule follows from the D configuration[12] of the glucose moiety[13], but was also determined by the procedure described by Rogers[14]; the ratio between the R values for the wrong and correct configurations was 1.015.

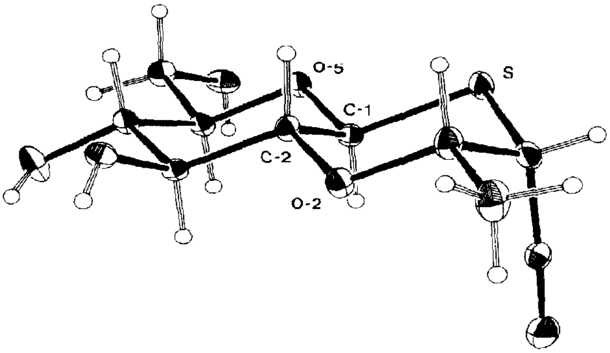


Fig. 1. ORTEP drawing of the merosinigrin molecule. Thermal ellipsoids have been scaled to enclose regions of 50% probability; hydrogens are represented by spheres with radii of 0.07 Å.

(*ap*,*ap*) (*ap*,*sc*) (*sc*,*ap*) (*sc*,*sc*)

Fig. 2. Geometries of the monothioacetal group exemplified by conformers of methoxy(methylthio)methane.

TABLE III

CALCULATED (MNDO) ENERGIES, DIPOLE MOMENTS, AND GEOMETRIES OF METHOXY(METHYLTHIO)METHANE CONFORMERS

Conformer[a]	*Relative energy (kcal/mol)*	*Dipole moment (D)*	*Torsion angles (degrees)*		*Bond angles (degrees)*			*Bond lengths (Å)*			
			C-S-C-O	*S-C-O-C*	*C-S-C*	*S-C-O*	*C-O-C*	*C-SC*	*S-CO*	*SC-O*	*CO-C*
(*ap*,*ap*)	4.1	2.9	180[b]	180[b]	105.7	106.0	119.7	1.732	1.759	1.390	1.399
(*ap*,*sc*)	2.3	2.3	180[b]	78	106.6	110.6	121.5	1.731	1.770	1.384	1.401
(*sc*,*ap*)	1.7	2.2	61	180[b]	109.6	110.5	120.0	1.733	1.750	1 392	1.398
(*sc*,*sc*)	0.0[c]	0.8	69	78	109.2	114.4	121.4	1.732	1.761	1.386	1.400

[a]See Fig. 2. [b]Fixed values. [c]$\Delta H_f^0 = -56.4$ kcal/mol.

The molecular structures of four conformers of methoxy(methylthio)methane (Fig. 2), the simplest monothioacetal, were optimised by the MNDO method[15]. All of the molecular parameters were optimised, except for the antiperiplanar (*ap*) torsion-angles which were fixed at 180°. The results are collected in Table III.

DISCUSSION

Owing to the presence of the rigid *trans*-decalin framework, the monothioacetal group in merosinigrin is forced to adopt the (*ap*,*ap*) geometry (C-S-C-O and S-C-O-C torsion-angles close to 180°; *cf.* Figs. 1 and 2). In conformationally mobile monothioacetals, on the other hand, the C-S-C-O and S-C-O-C fragments preferentially adopt the *gauche* (synclinal, *sc*) geometry (torsion-angles ~60°), as shown by X-ray data[13,16–28] and by solution studies[29–32]. This preference is known in many 1,3-diheteroatomic systems and, as the anomeric and exo-anomeric effects, is of special importance in the chemistry and biochemistry of carbohydrates[33,34].

The anomeric effect can be generally expressed as a sum of electron delocalisation and electrostatic effects[34–42]. The former effect is often stated as a back-donation of non-bonding heteroatom electrons into a periplanar, antibonding orbital of the adjacent polar bond (n → σ^* interaction), which can only occur along a *gauche*-oriented bond[35]. The donation of electrons causes contraction of the *gauche* bond and elongation of the accepting bond. An early recognised[43] manifestation of this phenomenon is shortening of equatorial, as compared to axial, glycosidic bonds in pyranosides[44–46]. The geometrical consequences of the anomeric effect have been extensively studied in acetals and α-haloethers, relatively less attention being paid to sulfur-containing compounds[34,47].

The relative energies of conformers of methoxy(methylthio)methane (Fig. 2), calculated by the MNDO method, are shown in Table III. The relative stability of the conformers is analogous to that for dimethoxymethane[37–41,48], for which, according to the MNDO method, the (*sc*,*sc*) conformation is preferred to the (*ap*,*sc*) and (*ap*,*ap*) conformations by 1.9 and 4.4 kcal/mol, respectively*. The corresponding figures[49] for bis(methylthio)methane are 1.2 and 2.6 kcal/mol*. Thus, the replacement of oxygen in acetals with sulfur results, in general, in a decrease of the *gauche* preference (a decrease of the anomeric effect)[29–31,34,47,50–52], but it is noteworthy that, according to the MNDO calculations, there is a larger energy gap (2.3 kcal/mol) between (*ap*,*sc*) and (*sc*,*sc*) conformations of methoxy(methylthio)methane (Table III) than between (*ap*,*sc*) and (*sc*,*sc*) conformations of dimethoxymethane§. Similar results were recently obtained by *ab initio* calculations with mercaptomethanol at the STO-3G level[47].

Although the MNDO calculations underestimated seriously the carbon–sulfur bond lengths[56], the data (Table III) show the excepted coupling of bond lengths with torsion angles. The (*ap*,*ap*) monothioacetal geometry will be regarded as "normal" in the sense that it is unaltered by the n → σ^* back-donation effects brought in when a *gauche* component is present. Using the (*ap*,*ap*) methoxy(methylthio)methane geometry as a reference, it is to be expected that the $n_O \rightarrow \sigma^*_{CS}$ interaction in the (*ap*,*sc*) and the $n_S \rightarrow \sigma^*_{CO}$ interaction in the (*sc*,*ap*) monothioacetals (*cf.* Fig. 2) will lead to longer S-CO bonds and shorter SC-O bonds in the former case, and shorter S-CO bonds and longer SC-O bonds in the latter case. This is indeed the result of the MNDO calculations (Table III), the changes in the S-CO bond lengths being more pronounced than the changes in the SC-O bond lengths. The lengthening of the SC-O bond in the (*sc*,*ap*) conformation is especially small. In the (*sc*,*sc*) conformation, there are two possible n → σ^* interactions whose effects on bond lengths are in opposition, and the effect of the $n_O \rightarrow \sigma^*_{CS}$ interaction appears to be slightly dominant (Table III)§. The values of the central S-C-O angle also exhibit regular changes, increasing steadily by ~4° for each *gauche* component, as also observed in *ab initio* results for dimethoxymethane[37,48]. The effect of conformation on the outer bond lengths and angles is marginal, as it is in acetals[48].

In order to compare the above results with experimental data, the available structural data for various monothioacetals[13,16–28] have been collected in Table

---

*Fully relaxed geometries[49], except for the antiperiplanar torsion-angles which were held at 180°

§Compare the relative abilities of sulfur and oxygen to stabilise adjacent positive charges during hydrolysis of monothioacetals[53,54], and the effect of sulfur *versus* oxygen on bond lengths of adjacent C-Cl bonds in *trans*-diaxial 2,3-dichloro-1,4-thioxane[55].

TABLE IV

STRUCTURAL DATA FOR MONOTHIOACETALS IN THE CRYSTAL PHASE DETERMINED BY X-RAY DIFFRACTION

Compound	*Torsion angles (degrees)*		*S-C-O bond angle*[a] *(degrees)*	*Bond lengths*[b] *(Å)*	
	C-S-C-O	*S-C-O-C*		*S-CO*	*SC-O*
1 *(ap,ap)*	173	173	106	1.811(3)	1.423(3)
[c] *(ap,sc)*	−178	−69	109	1.83(2)	1.40(2)
[d]	75	180	108	1.796(3)	1.435(4)
[e]	66	−173	108	1.80(1)	1.44(1)
[f]	−89	173	109	1.809(6)	1.411(8)
[g]	−75	177	109	1.793(3)	1.421(4)
[h]	−99	171	109	1.806(1)	1.429(2)
[i]	−95	174	110	1.77(1)	1.43(2)
(mean sc,ap)[j]	83(13)	175(3)	109(1)	1.801(8)[k]	1.424(10)[k]
[l]	−68	−65	111	1.826(2)	1.425(2)
[m]	−53	−80	112	1.830(4)	1.436(4)
[n]	92	76	113	1.805(2)	1.423(2)
[o]	74	71	113	1.821(5)	1.405(6)
[p]	−68	−76	114	1.839(6)	1.424(8)
[r]	68	64	114	1.824(2)	1.433(2)
[s]	−56	−73	114	1.79(2)	1.44(2)
[t]	−57	−70	115	1.82(1)	1.41(2)
(mean sc,sc)[j]	67(13)	72(6)	113(1)	1.824(11)[k]	1.424(11)[k]

[a] Estimated standard deviations below 1°. [b] Estimated standard deviations in parentheses. [c] Methyl 5-thio-β-D-ribopyranoside, from ref. 16. [d] Methyl 1-thio-α-D-ribopyranoside, from ref. 17. [e] Methyl 1-thio-β-D-xylopyranoside, averaged data of two molecules present in the asymmetric unit, from ref. 18. [f] Potassium allylglucosinolate monohydrate, from ref. 19 (see also ref. 13). [g] 2-Pyridyl 1-thio-β-D-glucopyranoside monohydrate, from ref. 20. [h] Methyl 1-thio-β-D-galactopyranoside, from ref. 21. [i] 1-Oxa-3,5,7,9-tetrathiacyclodecane, from ref. 22. [j] Unweighted average values with standard deviations in parentheses. [k] Omitting less-accurate data (compounds *e*, *i*, and *s*). [l] 1-Methoxy-3-(4-methoxyphenyl)-5-phenyl-2-thiabicyclo[4.4.0]dec-3-ene, from ref. 23. [m] 4′,6′-Dihydrospiro{3*H*-2-benzothiopyran-3,2′(3′*H*)-[2]benzothiopyrano[4,3-*b*]pyran}-4(1*H*)-one, from ref. 24 [n] 7,11b-Dihydro-2-methoxy-11b-(1-methylethyl)-3,4-diphenyl-2*H*,6*H*-[1,3]thiazino[2,3-*a*]isoquinoline, from ref. 25. [o] Methyl 5-thio-α-D-ribopyranoside, from ref. 16. [p] [(2-Pyridylthio)methoxy]methanol *N*-oxide, from ref. 26. [r] Heptyl 1-thio-α-D-mannopyranoside, from ref. 27. [t] Ethyl 2,3:4,5-di-*O*-(1-methylethylidene)-1-thio-β-D-glucoseptanoside, from ref. 28.

IV. Only pyranosides and other monothioacetals considered unconstrained are included, furanosides and monothioacetals in which both heteroatoms are placed in the same small or medium-size ring being excluded. In Table IV, only data for the S-C-O fragment of the monothioacetal systems are included. The remaining parameters, *i.e.*, C-S-C and C-O-C bond angles and lengths of terminal bonds, are omitted because they are expected to be affected primarily by the nature of terminal substituents rather than by the conformational changes (*cf.* Table III).

The monothioacetals collected in Table IV fall distinctly into four classes corresponding to the four conformers of methoxy(methylthio)methane shown in Fig. 2. Using the bond lengths of the S-C-O system in merosinigrin (**1**) as a reference, the data demonstrate trends towards shortening of the *gauche* bonds in the (*sc,ap*) and (*ap,sc*) systems, and towards lengthening of the antiperiplanar bond in the (*ap,sc*) system. As anticipated by the calculations, there is no difference in SC-O bond lengths between the (*ap,ap*) and (*ap,sc*) systems. The most conspicuous effect is the difference in S-CO bond length between the (*sc,ap*) and (*sc,sc*) arrangements, which corresponds to the difference in lengths of the thioglycosidic bonds between axial and equatorial 1-thiopyranosides. The corresponding difference in pyranosides, which is likewise very pronounced, also amounts[44–46] on average to 0.02 Å. When comparing bond lengths in Table IV, it should be borne in mind not only that they are subject to ordinary experimental uncertainty, but also that the compounds represent widely different chemical classes, in which the same type of monothioacetal bond, affected by the same kind of orbital interactions, may contract or elongate to a slightly different degree; *cf.* the effect of conformation on bond lengths for exocyclic *versus* endocyclic acetal bonds, and bond-length variations within the same type of anomeric bond in pyranosides[44–46,57].

As predicted by the MNDO calculations on methoxy(methylthio)methane (Table III), the S-C-O valence-angles of monothioacetals collected in Table IV show regular variations according to the number of *gauche* components in the C-S-C-O-C system. However, since the X-ray data show that in 1,2-*O*-(1,2-ethanediyl)-β-D-glucopyranose[10,11], a counterpart of **1**, the O-C-O angle is significantly larger than in acyclic (*ap,ap*) acetals[58], there may be a ring effect on the S-C-O angle in merosinigrin as well.

Thus, it is concluded that there is a coupling between bond lengths, bond angles, and torsion angles in monothioacetals similar to that observed in acetals. Most of the trends anticipated by the MNDO calculations can be observed in experimental data from the crystal phase. Finally, it should be noted that a survey of X-ray data[59–67] for dithioacetals shows that, despite the weakened anomeric effect, the (*ap,ap*) dithioacetal geometry[59] is quite exceptional. Furthermore, in the currently available data, there appears to be no systematic coupling between CS-C bond lengths and C-S-C-S torsion angles similar to that discussed above. The S-C-S angle in dithioacetals, however, clearly depends[59–67] on conformation in a manner similar to that for acetals and monothioacetals, emphasising that the two effects (on bonds and on angle) are different in origin.

EXPERIMENTAL

*Synthesis of merosinigrin [(1'S,2'S)-1,2-S,O-(1-cyano-2-methyl-1,2-ethanediyl)-1-thio-β-*D*-glucopyranose* (**1**)]. — Potassium allylglucosinolate monohydrate (sinigrin monohydrate, obtained from Aldrich, 1 g) was treated briefly with 1 equiv. of sodium methoxide in boiling methanol[1], the solution was neutralised with Amberlite IR-120 (H^+) resin, and merosinigrin (90 mg, 14%) was isolated by column chromatography on silica gel (0.063–0.2 mm) with ethyl acetate methanol (10:1), m.p. 195–197° (corr., from ethyl acetate); $[\alpha]_{D}^{22}$ +160° (*c*

0.2, water); lit.[1] m.p. 192° (uncorr.), $[\alpha]_D^{20}$ +149.2° (*c* 5.4, water); ν_{max}^{KBr} 3490 (s), 3350 (s), and 2245 (m) cm^{-1}. ^{1}H-N.m.r. (270 MHz, CD_3OD): δ 1.39 (CH_3), 3.3–3.5 (H-2,3,4,5), 3.66 (H-6A), 3.86 (H-6B), 3.95 (H-2′), 4.08 (H-1′), and 4.59 (H-1); $J_{1,2}$ 8.8, $J_{5,6A}$ 4.9, $J_{5,6B}$ 1.8, $J_{6A,6B}$ 12.3, $J_{1',2'}$ 2.1, and J_{2',CH_3} 6.3 Hz.

Merosinigrin triacetate, obtained in practically quantitative yield by conventional treatment of **1** with acetic anhydride–pyridine, had m.p. 179–180° (corr., from ether–pentane); lit.[1] m.p. 177° (uncorr.); ν_{max}^{KBr} 2235 (m), 1755 (s), and 1745 (s) cm^{-1}. ^{1}H-N.m.r. (270 MHz, $CDCl_3$): δ 1.41 (CH_3), 2.04, 2.06, 2.09 (3 AcO), 3.57 (H-1′), 3.64 (H-2), 3.85 (H-5), 3.93 (H-2′), 4.12 (H-6A), 4.24 (H-6B), 4.71 (H-1), 5.08 (H-4, distinguished from H-3 by selective decoupling of H-5), and 5.20 (H-3); $J_{1,2}$ 9.0, $J_{2,3}$ 9.2, $J_{3,4}$ 9.5, $J_{4,5}$ 9.9, $J_{5,6A}$ 2.2, $J_{5,6B}$ 5.0, $J_{6A,6B}$ 12.4, $J_{1',2'}$ 2.1, and J_{2',CH_3} 6.4 Hz.

ACKNOWLEDGMENTS

We thank Dr. M. G. Ettlinger (University of Copenhagen) for suggesting this crystal structure determination, Professor P. H. Laur and Dr. I. K. Nielsen (Technical University, Aachen) for gifts of sinigrin and crude merosinigrin, Dr. K. Schaumburg (University of Copenhagen) for the high-field proton spectra, and the Danish Natural Science Research Council for financial support (to F.S.J.).

REFERENCES

1 W. Schneider and F. Wrede, *Ber.*, 47 (1914) 2225–2229.
2 M. Benn, *Can. J. Chem.*, 58 (1980) 1892–1893.
3 *Cf.* P. O. Larsen, in P. K. Stumpf and E. E. Conn (Eds.), *The Biochemistry of Plant Products, A Comprehensive Treatise, Vol. 7: Secondary Plant Products*, Academic Press, New York, 1981, pp. 501–525.
4 P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, *MULTAN-77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data*, Universities of York (Great Britain) and Louvain (Belgium), 1978.
5 J. M. Stewart, *The XRAY System*, Tech. Rep. TR-446, Computer Science Center, University of Maryland, U.S.A., 1976.
6 D. T. Cromer and J. B Mann, *Acta Crystallogr., Sect. A*, 24 (1968) 321–324.
7 R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42 (1965) 3175–3187.
8 C. K. Johnson, *ORTEP*, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, U.S.A., 1965.
9 B. Sheldrick and D. Akrigg, *Acta Crystallogr., Sect. B*, 36 (1980) 1615–1621.
10 R. Norrestam, K. Bock, and H. Thøgersen, *Acta Crystallogr., Sect. B*, 37 (1981) 1689–1693.
11 C.-D. Zheng, J.-Z. Qin, Y.-X. Gu, and Q.-T. Zheng, *Wu Li Hsueh Pao*, 30 (1981) 242–248.
12 M. G. Ettlinger and A. J. Lundeen, *J. Am. Chem. Soc* , 78 (1956) 4172–4173.
13 R. E. Marsh and J. Waser, *Acta Crystallogr , Sect. B*, 26 (1970) 1030–1037.
14 D. Rogers, *Acta Crystallogr., Sect. A*, 37 (1981) 734–741.
15 *QCPE* No. 353. *Cf.* M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 99 (1977) 4899–4907, 4907–4917; M. J. S. Dewar, M. L. McKee, and H. S. Rzepa, *ibid.*, 100 (1978) 3607; M. J. S. Dewar and G. P. Ford, *ibid.*, 101 (1979) 5558–5561.
16 R. L. Girling and G. A. Jeffrey, *Acta Crystallogr., Sect. B*, 29 (1973) 1102–1111.
17 R. L. Girling and G. A. Jeffrey, *Acta Crystallogr., Sect. B*, 29 (1973) 1006–1011.
18 A. McL. Mathieson and B. J. Poppleton, *Acta Crystallogr.*, 21 (1966) 72–79.
19 W. H. Watson and Z. Taira, *Cryst. Struct. Commun.*, 6 (1977) 441–446.

20 S. Nordenson and G. A. Jeffrey, *Acta Crystallogr., Sect. B*, 36 (1980) 1214–1216.
21 A. Atkinson, J. R. Ruble and G. A. Jeffrey, *Acta Crystallogr., Sect. B*, 37 (1981) 1465–1467.
22 G. Valle and G. Zanotti, *Cryst. Struct. Commun.*, 6 (1977) 651–654.
23 S. V. Soboleva, O. A. Dyachenko, L. O. Atovmyan, V. G. Kharchenko, and S. K. Klimenko, *Zh. Strukt. Khim.*, 19 (1978) 499–507; *J. Struct. Chem. USSR*, 19 (1978) 432–439.
24 Ø. H. Johansen, T. Ottersen and K. Undheim, *Acta Chem. Scand., Ser. B*, 33 (1979) 669–674.
25 H. Preut, T. Eicher, D. Krause and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 35 (1979) 1285–1287.
26 R. D. Haugwitz, B. Toeplitz and F. Z. Gougoutas, *Cryst. Struct. Commun.*, 9 (1980) 937–940.
27 D. C. Carter, J. R. Ruble, and G. A. Jeffrey, *Carbohydr. Res.*, 102 (1982) 59–67.
28 J. P. Beale, N. C. Stephenson and J. D. Stevens, *Acta Crystallogr., Sect. B*, 28 (1972) 3115–3121.
29 N. S. Zefirov and N. M. Shekhtman, *Usp. Khim.*, 40 (1971) 593–624; *Russ. Chem. Rev.*, 40 (1971) 315–329; Ref. 33, pp. 23–26.
30 N. A. Hughes, *Carbohydr. Res.*, 27 (1973) 97–105; J. B. Lambert and S. M. Wharry, *J. Org. Chem.*, 46 (1981) 3193–3196.
31 H. Matsuura, K. Kimura and H. Murata, *J. Mol. Struct.*, 64 (1980) 281–284.
32 P. Deslongchamps, D. D. Rowan, N. Pothier and J. K. Saunders, *Can. J. Chem.*, 59 (1981) 1122–1131.
33 A. J. Kirby, *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*, Springer-Verlag, Berlin, 1983.
34 S. Wolfe, M.-H. Whangbo, and D. J. Mitchell, *Carbohydr. Res.*, 69 (1979) 1–26.
35 C. Romers, C. Altona, H. R. Buys, and E. Havinga, *Top. Stereochem.*, 4 (1969) 39–97.
36 S. David, O. Eisenstein, W. J. Hehre, L. Salem, and R. Hoffmann, *J. Am. Chem. Soc.*, 95 (1973) 3806–3807.
37 D. G. Gorenstein and D. Kar, *J. Am. Chem. Soc.*, 99 (1977) 672–677.
38 D. G. Gorenstein, J. B. Findlay, B. A. Luxon and D. Kar, *J. Am. Chem. Soc.*, 99 (1977) 3473–3479.
39 I. Tvaroška and T. Bleha, *Tetrahedron Lett.*, (1975) 249–252.
40 I. Tvaroška and T. Bleha, *Can. J. Chem.*, 57 (1979) 424–435.
41 G. A. Jeffrey, J. A. Pople, J. S. Binkley, and S. Vishveshwara, *J. Am. Chem. Soc.*, 100 (1978) 373–379.
42 G. A. Jeffrey and J. H. Yates, *J. Am. Chem. Soc.*, 101 (1979) 820–825.
43 H. M. Berman, S. S. C. Chu, and G. A. Jeffrey, *Science*, 157 (1967) 1576–1577.
44 S. Arnott and W. E. Scott, *J. Chem. Soc., Perkin Trans. 2*, (1972) 324–335.
45 S. Perez and R. H. Marchessault, *Carbohydr. Res.*, 65 (1978) 114–120.
46 G. A. Jeffrey, *Am. Chem. Soc. Symp. Ser.*, 87 (1979) 50–62.
47 S. Vishveshwara and V. S. R. Rao, *Carbohydr. Res.*, 104 (1982) 21–32.
48 C. Van Alsenoy, L. Schäfer, J. N. Scarsdale, J. O. Williams and H. J. Geise, *J. Mol. Struct.*, 86 (1981) 111–117.
49 F. S. Jørgensen, unpublished results, 1982.
50 M. Ohsaku, N. Bingo, W. Sugikawa, and H. Murata, *Bull. Chem. Soc. Jpn.*, 52 (1979) 355–360.
51 O. Exner, V. Jehlicka, and J. Firl, *Collect. Czech. Chem. Commun.*, 37 (1972) 466–477; A. N. Vereshchagin and O. Exner, *ibid.*, 38 (1973) 690–696.
52 M. Mansson, *J. Chem. Thermodyn.*, 6 (1974) 1153–1159.
53 G. Modena, G. Scorrano and P. Venturello, *J. Chem. Soc., Perkin Trans. 2*, (1979) 1–6.
54 J. L. Jensen and W. P. Jencks, *J. Am. Chem. Soc.*, 101 (1979) 1476–1488.
55 N. de Wolf, C. Romers, and C. Altona, *Acta Crystallogr.*, 22 (1967) 715–719.
56 *Cf.* V. Barone, P. Cristinziano, F. Lelj and N. Russo, *J. Mol. Struct.*, 86 (1982) 239–253.
57 I. Tvaroška and T. Kožar, *Carbohydr. Res.*, 90 (1981) 173–185.
58 L. Nørskov-Lauritsen, S. Larsen, M. G. Ettlinger and J. W. Jaroszewski, *Acta Crystallogr., Sect. B*, 38 (1982) 3107–3110.
59 R. L. Girling and G. A. Jeffrey, *Acta Crystallogr., Sect. B*, 30 (1974) 327–333.
60 A. Ducruix and C. Pascard-Billy, *Acta Crystallogr., Sect. B*, 30 (1974) 1056–1063.
61 T. J. McLennan, W. T. Robinson, G. S. Bethell, and R. J. Ferrier, *Acta Crystallogr., Sect. B*, 33 (1977) 2888–2891.
62 A. Ducruix, D. Horton, C. Pascard, J. D. Wander, and T. Prange, *J. Chem. Res., Synop.*, (1978) 470–471.

63 J. F. McConnell, A. Schwartz, and J. D. Stevens, *Cryst. Struct. Commun.*, 8 (1979) 855–859.
64 J. Berthou, G. Jeminet, A. Laurent, B. Rérat, and C. Rérat, *C. R. Acad. Sci., Ser. C*, 271 (1970) 516–518.
65 J. Canonne, J.-C. Boivin, G. Nowogrocki, and D. Thomas, *Acta Crystallogr., Sect. B*, 33 (1977) 2550–2553.
66 J. Canonne, J.-C. Boivin, G. Nowogrocki, and D. Thomas, *Acta Crystallogr., Sect. B*, 34 (1978) 1283–1286.
67 J. Canonne, J.-C. Boivin, G. Nowogrocki, and D. Thomas, *Acta Crystallogr., Sect. B*, 34 (1978) 3233–3237.