Carbohydrate Research, 91 (1981) 97–100
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

Note

The X-ray crystal structure of 2,5-anhydro-1-chloro-1-deoxy-L-ribitol 3,4-cyclic sulfite*

HARRY P. C. HOGENKAMP**, ROBERT R. RYAN, AND ALLEN C. LARSON
Department of Biochemistry, The University of Minnesota, Minneapolis, MN 55455 (U.S.A.), and the Los Alamos Scientific Laboratory, The University of California, Los Alamos, New Mexico 87545 (U.S.A.)

(Received September 4th, 1980; accepted for publication, November 25th, 1980)

Organic compounds bearing *cis*-vicinal hydroxyl groups react with thionyl chloride to give cyclic sulfites. As the sulfite group is pyramidal, the cyclic sulfites of asymmetrically substituted diols should be mixtures of geometrical isomers[1]. Indeed, treatment of methyl β-D-ribofuranoside with thionyl chloride in hexamethylphosphoric triamide gives two diastereoisomeric methyl 5-chloro-5-deoxy-β-D-ribofuranoside 2,3-cyclic sulfites, which are readily discerned by ^{1}H- and ^{13}C-n.m.r. spectroscopy[2]. From their analysis of the ^{1}H-n.m.r. spectra of the two isomers of propylene sulfite, Pritchard and Lauterbur[1] concluded that hydrogen atoms *trans* to the double-bonded oxygen atom resonate upfield from those *cis* to that oxygen atom. Based on this analysis, Wang and Hogenkamp[2] determined the structure of the cyclic sulfites of several sugars, and concluded that the preponderant isomers have the *exo* configuration. When allowed to react with thionyl chloride in hexamethylphosphoric triamide, one of these sugars, 1,4-anhydro-DL-ribitol, gives only a single, crystalline diastereoisomer[2], and, in order to provide the unambiguous structure of the cyclic sulfites, we have determined the crystal structure of this diastereoisomer.

Pertinent information concerning the cell, crystal morphology, and intensity measurements is given in Table I. Two standard reflections measured after every 50 reflections varied by less than 5% over the period of the data-collection process. Correction curves for this decrease were estimated by least-squares refinement of the polynomial to the standards, and applied to the data. The variance for $\overline{F}^2$ (denotes the average of F^2 over equivalent reflections) was computed from $\sigma^2(\overline{F}^2) = \sigma_c^2(F^2) + \sigma_N^2 \cdot (\overline{F}^2)^2$, where σ_c^2 is the variance due to counting statistics, and σ_N is taken to be 0.015.

---

*An alternative name is 1,4-anhydro-5-chloro-5-deoxy-D-ribitol 2,3-cyclic sulfite.
**To whom enquiries should be addressed.

0008-6215/81/0000–0000/S 02.50,

TABLE I

CRYSTAL DATA FOR 2,5-ANHYDRO-1-CHLORO-1-DEOXY-L-RIBITOL 3,4-CYCLIC SULFITE

Formula	$C_5H_7ClO_4S$
Space group	$P2_12_12_1$
a (pm)	781.7 (3)
b (pm)	914.4 (4)
c (nm)	1.0766 (5)
z	4
Data collected	$2\theta \leqslant 45$
No. of unique reflections	1021
No. of observed ($I \geqslant 2\sigma(I)$)	1016
Scattering factors	neutral-atom scattering factors, with appropriate, anomalous scattering-terms[3].
Absorption correction	none
Unweighted *R* value	3.6%

Diffractometer: Picker FACS-1, P.G. Lenhert's Disk Operating System[4], Wang encoders, graphite monochromator, 3.5° take-off angle (1.5° + dispersion), continuous scans, 20-s symmetric background counts, MoKα radiation (λ 70.930 pm).

TABLE II

FRACTIONAL COORDINATES OF 2,5-ANHYDRO-1-CHLORO-1-DEOXY-L-RIBITOL 3,4-CYCLIC SULFITE

Atom	*X*	*Y*	*Z*
S	0.5089(1)	0.3964(1)	0.3048(1)
O-6	0.6044(4)	0.2674(4)	0.3393(3)
O-4	0.3483(4)	0.4134(3)	0.3986(3)
O-3	0.3870(3)	0.3536(3)	0.1901(2)
O-2	0.0174(4)	0.4779(3)	0.2783(2)
C-5	0.0441(6)	0.3917(5)	0.3886(4)
C-4	0.2119(5)	0.3165(5)	0.3677(4)
C-3	0.2216(5)	0.2981(4)	0.2265(4)
C-2	0.0793(5)	0.3967(4)	0.1761(3)
C-1	−0.0602(6)	0.3058(4)	0.1175(4)
Cl	−0.2228(1)	0.4208(1)	0.0544(1)
H-3	0.214(5)	0.202(4)	0.200(3)
H-5	0.049(5)	0.322(4)	0.400(4)
H-4	0.224(5)	0.229(4)	0.400(4)
H-1	−0.120(5)	0.240(4)	0.185(3)
H-2	0.170(5)	0.461(4)	0.118(4)
H-5	0.023(5)	0.448(4)	0.474(4)
H-1	−0.013(5)	0.260(4)	0.038(4)

The structure was solved by direct methods (MULTAN), and hydrogen atoms were located by using Fourier techniques. Full matrix-refinements included anisotropic refinements on all atoms larger than hydrogen, converged to an *R* value of 3.6%. The positions of the hydrogen atoms were refined with isotropic, thermal parameters fixed at 3.0. No corrections were made for absorption or extinction.

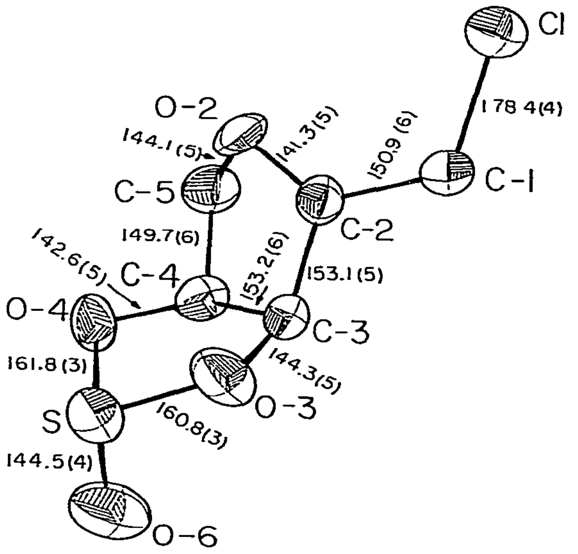

Fig. 1. Numbering of atoms, bond lengths (in pm), and ORTEP projection of 2,5-anhydro-1-chloro-1-deoxy-L-ribitol 3,4-cyclic sulfite.

Final parameters are listed in Table II, and an ORTEP projection of the molecule is presented in Fig. 1. The average C–H distance is 100.4 pm, which varies from 87.5 to 106.7 pm. The shortest intermolecular contacts are several O···H distances of ~195 pm.

The structure of 2,5-anhydro-1-chloro-1-deoxy-L-ribitol 3,4-cyclic sulfite presented in Fig. 1 shows that the hydrogen atoms on carbon atoms 3 and 4 are *cis* to the oxygen atom that is double-bonded to sulfur, and that one of the hydrogen atoms on C-5 and the hydrogen atom on C-2 are *trans* to this oxygen atom, exactly as concluded by Pritchard and Lauterbur[1] from their analysis of the ^{1}H-n.m.r. spectrum.

EXPERIMENTAL

The 2,5-anhydro-1-chloro-1-deoxy-DL-ribitol 3,4-cyclic sulfites were prepared as described[2]. Crystallization of the crude product from aqueous ethanol gave only a single diastereoisomer, which was recrystallized from aqueous ethanol. Details of the collection of the data are presented* in Table I.

ACKNOWLEDGMENTS

This work was supported by U.S. Public Health Research Grant GM-23773

---

*A complete atom list, with the temperature parameters included, can be obtained on request from Elsevier Scientific Publishing Company, BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/174 *Carbohydr. Res.*, 91 (1981) 97–100.

from the National Institutes of Health, and by the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy.

REFERENCES

1 T. G. Pritchard and P. C. Lauterbur, *J. Am. Chem. Soc.*, 83 (1961) 2105–2110.
2 Y. Wang and H. P. C. Hogenkamp, *Carbohydr. Res.*, 76 (1979) 131–140.
3 D. T. Cromer and J. T. Waber, in J. J. Ibers and W. A. Hamilton (Eds.), *International Tables for X-Ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, England, 1975, pp. 99–101.
4 P. G. Lenhert, *J. Appl. Crystallogr.*, 8 (1975) 568–570.