Carbohydrate Research, 241 (1993) 273–277
Elsevier Science Publishers B.V., Amsterdam

Note

Crystal and molecular structure of 2,3,4-tri-*O*-acetyl-1,5-anhydro-6,7-dideoxy-7-*S*-methyl-6-nitro-7-thio-L-*glycero*-L-*gluco*-heptitol

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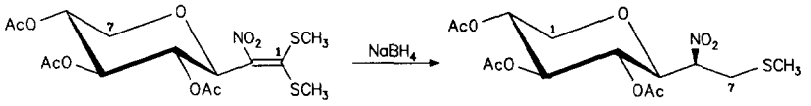
(Received March 18th, 1992; accepted August 31st, 1992)

The base-catalyzed addition of nitromethane to aldoses (Fischer–Sowden reaction) yields a mixture of epimeric nitroalditols[1] which can easily be dehydrated to anhydronitroalditols ("glycosylnitromethanes")[2]. The latter can be used for carbon-chain extensions, e.g., the reaction of *O*-protected glycosylnitromethanes with carbon disulfide in the presence of an alkylating agent, like methyl iodide, under the influence of sodium hydride[3]. By subjecting D-xylose to this four-step strategy, 4,5,6-tri-*O*-acetyl-3,7-anhydro-2-deoxy-2-nitro-D-*gulo*-hept-1-enose dimethyl dithioacetal (**1**) is accessible in about 25% yield[4].

The 2-nitro-ketene dimethyl dithioacetal **1** should be of interest for further reactions. In investigating the behaviour of **1** towards sodium borohydride, a reduction product was isolated as a single crystalline compound in 23% yield[4]. Because of ambiguities in configurational assignments by other methods, this compound was subjected to X-ray analysis at 295 K and shown to be 2,3,4-tri-*O*-acetyl-1,5-anhydro-6,7-dideoxy-7-*S*-methyl-6-nitro-7-thio-L-*glycero*-L-*gluco*-heptitol (**2**).



1 2

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TABLE I

Crystallographic data for 2,3,4-tri-*O*-acetyl-1,5-anhydro-6,7-dideoxy-7-*S*-methyl-6-nitro-7-thio-L-*glycero*-L-*gluco*-heptitol (**2**) [a]

Formula	$C_{14}H_{21}NO_9S$
Mol wt	379.38
Mp (degrees)	107–108
Crystal size (mm)	$0.4\times0.3\times0.2$
Space group	$P2_1$
Cell parameters (pm, degrees)	
a	641.7(1)
b	1284.2(2)
c	1132.6(2)
β	94.73(1)
Volume (pm^3)	$930.2(3)\times10^6$
Z	2
F(000)	400
Density D_x ($g\cdot cm^{-3}$)	1.354
λ (Mo$K\alpha$) (pm)	70.9261
μ (cm^{-1})	2.1
2 θ range (degrees)	4.5–55.0
Symmetry independent reflections	2089
Observed reflections with $F_o > 3\ \sigma\ (F_o)$	1774
Number of refined parameters	309
Ratio of parameters to valued reflections	5.7
Final residual parameters	
R	0.050
R_w	0.029
Diffractometer	Syntex $P2_1$

[a] Standard deviations in parentheses.

The relevant crystallographic data for **2** are given in Table I. The structure was solved by direct methods in the usual way with the help of the program SHELXS90[5], and refined with SHELX76[6].

All atoms (hydrogens introduced at theoretical positions) were refined. The final co-ordinates of C, N, O, and S are listed in Table II *. A SCHAKAL88 plot[7] of **2** is shown in Fig. 1, which gives the numbering scheme of the atoms.

The six-membered ring adopts a chair conformation [puckering parameters[8]: Q = 57.4 pm, $\theta = 176.4°$, $\phi = 180.0°$] with C-6 equatorial and the nitro group *gauche* to the ring oxygen and *trans* to C-4. This orientation leaves C-7 in *gauche* positions to both O-1 and C-4. This is not the conformation usually found for *C*-β-D-glycopyranosylalkanes[9], whereas the arrangement of the nitro group coincides with many examples in simple glycosylnitromethanes, as observed not only in the crystalline state but also in solution[10]. Recently, the structure of 4,8-anhydro-

* Lists of observed and calculated structure amplitudes, fractional co-ordinates for all atoms, anisotropic and isotropic thermal parameters, tables of bond distances and angles, and further information have been deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, Netherlands. Reference should be made to No. BBA/DD/525/*Carbohydr. Res.*, 241 (1993) 273–277.

TABLE II

Fractional positional parameters of C, N, O, and S atoms ($\times 10^4$) [a] and the temperature factors U_{eq} [b] ($\times 10^3$) for **2**

Atom	x	y	z	U_{eq}
S-7	4834(2)	10000 [c]	1888(1)	76(1)
O-1	3504(4)	6555(2)	1190(2)	50(1)
O-2	983(4)	4174(2)	2099(2)	57(1)
O-3	1105(4)	5479(2)	4214(2)	60(1)
O-4	4849(4)	6787(2)	4361(2)	58(1)
O-21	−2425(4)	4455(2)	1861(3)	112(2)
O-31	3006(6)	4307(3)	5292(2)	93(1)
O-41	2498(6)	7783(3)	5205(3)	105(2)
O-61	6661(6)	8122(3)	268(3)	110(1)
O-62	8902(6)	7621(3)	1671(4)	131(2)
N-6	7191(6)	7892(3)	1287(4)	70(1)
C-1	2824(5)	5489(3)	1145(3)	53(1)
C-2	1445(5)	5278(2)	2134(3)	46(1)
C-3	2577(5)	5528(3)	3328(3)	49(1)
C-4	3450(5)	6632(3)	3317(3)	47(1)
C-5	4741(5)	6783(3)	2262(3)	46(1)
C-6	5528(5)	7903(3)	2162(3)	47(1)
C-7	3860(6)	8683(3)	1768(4)	71(2)
C-21	−1000(6)	3874(3)	1899(3)	59(1)
C-22	−1169(7)	2719(3)	1754(4)	79(2)
C-31	1477(8)	4849(3)	5155(4)	68(2)
C-32	−205(8)	4942(4)	5967(4)	98(2)
C-41	4157(8)	7377(3)	5256(3)	69(2)
C-42	5829(9)	7410(3)	6257(4)	94(2)
C-71	2905(8)	10638(3)	913(4)	99(2)

[a] Standard deviations in parentheses. [b] $U_{eq} = 1/3\ \Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$. [c] This co-ordinate was fixed.

3-deoxy-3-nitro-D-*lyxo*-D-*gluco*-nonitol was published[11], in which opposite orientations of the nitro group and the alkyl chain with respect to the pyranoid ring were observed. Another closely related structure is that of ethyl 6,7,8-tri-*O*-acetyl-5,9-anhydro-2,3,4-trideoxy-2-diphenylmethyleneamino-4-nitro-D-*threo*-D-*altro*-nononate[12]. The overall topology of the latter compound, which has the same configuration at the carbon atom equivalent to C-6, is exactly that of **2**, whereas this configuration is inverted in the former compound. Therefore, we conclude that these conformations are a consequence of the configuration at the carbon atom which bears the nitro group, together with the configuration at C-4. If C-7 in **2** were to adopt the position usually occupied in *C*-β-D-glycopyranosylalkanes[9], the nitro group would occupy a 1,3 parallel position with respect to O-4, which obviously is unfavourable.

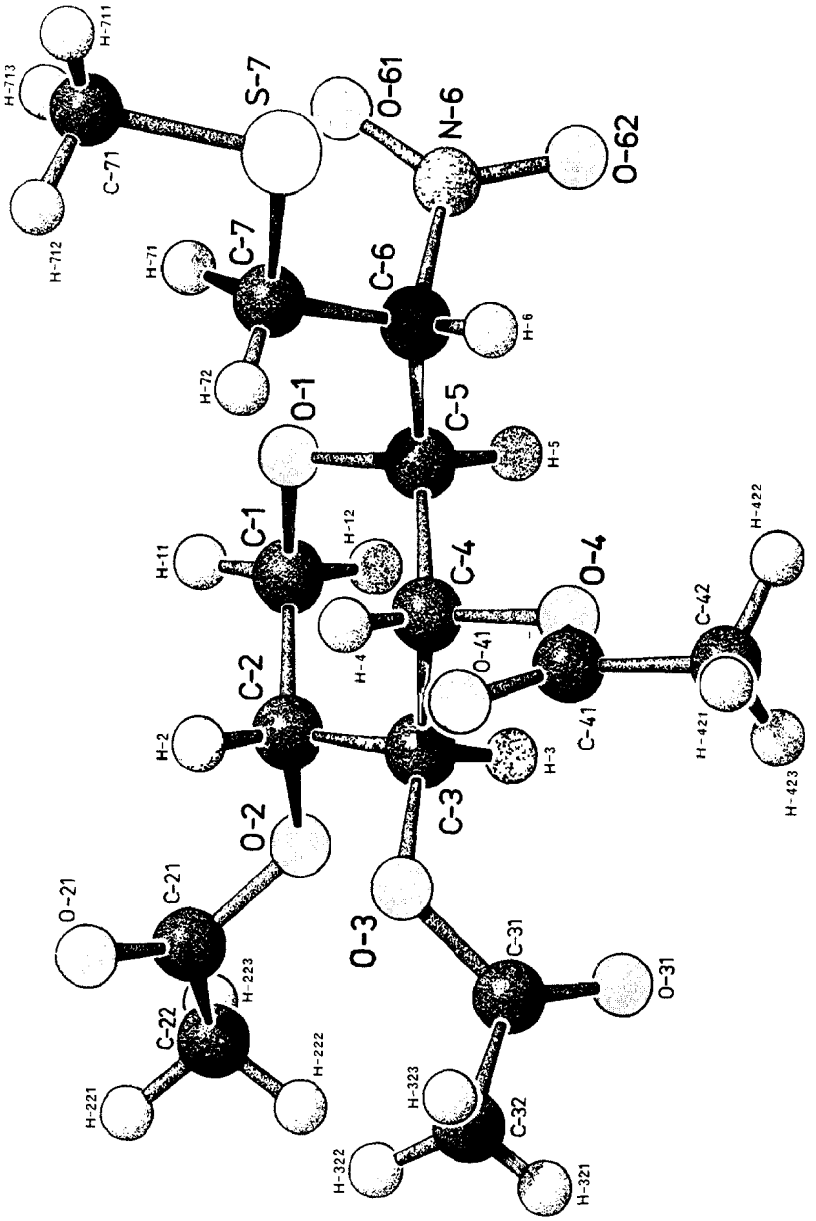

Fig. 1. SCHAKAL88 plot[7] of 2 showing atom numbering.

ACKNOWLEDGMENTS

The Deutsche Forschungsgemeinschaft (DFG) and the Fonds der Chemischen Industrie are thanked for financial support.

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