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Note

Crystal and molecular structure of ethyl 6,7,8-tri-*O*-acetyl-5,9-anhydro-2,3,4-trideoxy-2-diphenylmethyleneamino-4-nitro-D-*threo*-D-*altro*-nononate

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In an attempt to prepare the *C*-glycosyl amino acid analogue of *O*-(β-D-xylopyranosyl)serine, the mixture of the two epimeric addition products of β-D-xylopyranosylnitromethane (1,5-anhydro-6-deoxy-6-nitro-L-*gluco*-hexitol) to one equivalent of formaldehyde was acetylated and treated under basic conditions with *N*-diphenylmethyleneglycine ethyl ester. This reaction, which should proceed via a Michael-type addition to an intermediate nitro-olefin, yielded a mixture of four diastereomers, from which a major isomer (**1**), after partial fractionation by chromatography, could be crystallised in an overall yield of 9% [1]. Because ambiguities in the configurational assignments of isomers by ^{1}H- and ^{13}C-NMR spectroscopy, compound **1** was subjected to X-ray analysis at 300 K.

The relevant crystallographic data of **1** are given in Table I. The structure was solved by direct methods in the usual way with the help of the programs SHELXS90 [2] and SHELX76 [3]; **1** crystallized with two independent molecules in the asymmetric unit.

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TABLE I

Crystallographic data for **1** [a]

Formula	$C_{30}H_{34}O_{11}N_2$	Density (calcd) ($g \cdot cm^{-3}$)	1.195
Mol wt	598.60	λ(Cu-K_α) (pm)	154.051
Mp (degrees)	150	μ (cm^{-1})	7.3
Crystal size (mm)	$0.4 \times 0.3 \times 0.2$	2θ range (degrees)	4.5–153
Space group	$P2_1$	Reflections measured	7355
Cell parameters (pm, degrees)		Symmetry independent reflections	6463
a	845.4(1)	Symmetry independent reflections with $F_o > 3\sigma(F_o)$	5973
b	4383.3(3)		
c	989.5(1)	Number of refined parameters	775
β	114.82(1)	Final residual factors	
Volume (pm^3)	$3328.0(6) \times 10^6$	R	0.065
Z	4	R_w	0.062
$F(000)$	1264	Diffractometer	Enraf-Nonius CAD4

[a] Standard deviations in parentheses.

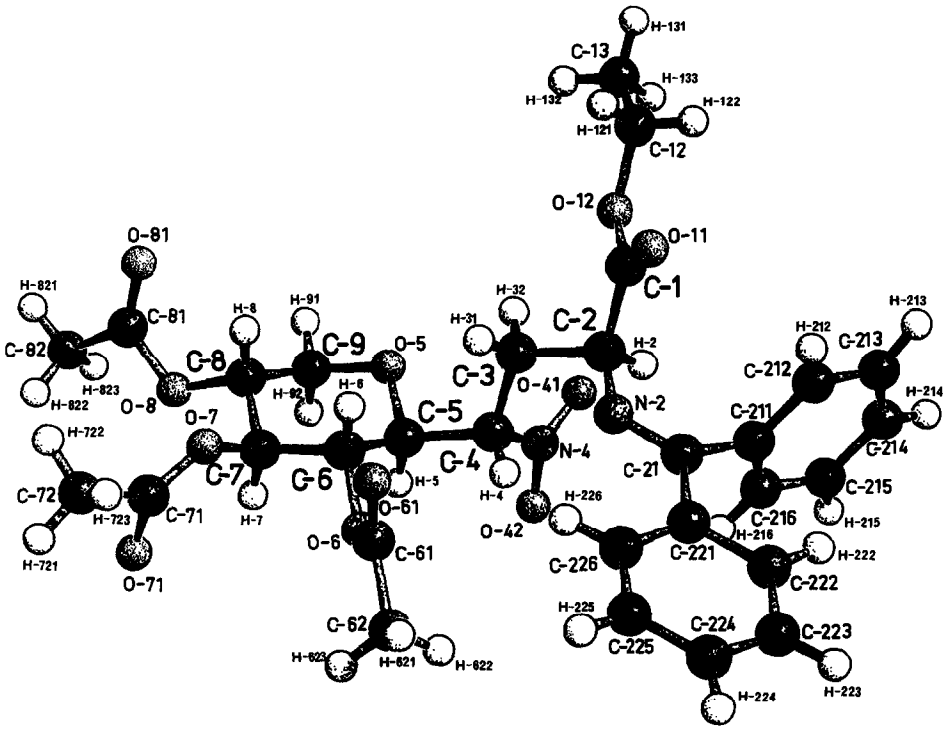

Fig. 1. SCHAKAL88[4] plot of **1** (molecule I) showing atom numbering.

TABLE II

Fractional positional parameters of C, N, and O atoms ($\times 10^4$) [a] for **1**

Atom	Molecule I			Molecule II		
	x	*y*	*z*	*x*	*y*	*z*
O-5	7228(4)	3621	378(3)	948(4)	1635(1)	7664(3)
O-6	6544(4)	4328(1)	−1709(3)	2434(4)	917(1)	9633(3)
O-7	6288(5)	4514(1)	1080(4)	−558(5)	744(1)	7000(4)
O-8	8636(4)	4158(1)	3486(4)	−768(4)	1115(1)	4491(3)
O-11	532(5)	3294(1)	−5186(5)	−271(6)	1930(1)	13174(5)
O-12	2258(4)	3028(1)	−3215(4)	−365(5)	2218(1)	11347(4)
O-41	7298(6)	3164(1)	2270(5)	3714(6)	2090(1)	10341(5)
O-42	8990(6)	3522(1)	−2248(5)	5338(6)	1734(1)	10210(6)
O-61	3787(7)	4481(2)	−2529(7)	754(8)	808(1)	10774(6)
O-71	8085(9)	4866(1)	897(9)	913(8)	435(1)	6178(8)
O-81	7033(6)	3977(1)	4600(4)	−3472(5)	1296(1)	3425(4)
N-2	3207(5)	3647(1)	−5117(4)	2430(5)	1585(1)	13154(4)
N-4	7634(7)	3429(1)	−2255(5)	3999(6)	1828(1)	10276(5)
C-1	1942(7)	3245(1)	−4230(5)	265(6)	1992(1)	12311(5)
C-2	3614(6)	3398(1)	−4063(5)	1801(6)	1840(1)	12130(5)
C-3	4603(6)	3516(1)	−2474(5)	1232(6)	1725(1)	10517(5)
C-4	6353(6)	3666(1)	−2229(5)	2704(6)	1587(1)	10230(5)
C-5	7238(6)	3830(1)	−721(5)	2085(6)	1427(1)	8724(5)
C-6	6366(6)	4121(1)	−629(5)	1194(6)	1131(1)	8635(5)
C-7	7311(6)	4261(1)	922(5)	519(6)	994(1)	7083(5)
C-8	7481(6)	4029(1)	2080(5)	−523(6)	1233(1)	5949(5)
C-9	8259(7)	3741(1)	1850(5)	450(7)	1525(1)	6190(5)
C-12	810(8)	2844(2)	−3249(7)	−1758(7)	2393(1)	11412(7)
C-13	1383(10)	2646(3)	−2037(9)	−2278(11)	2623(2)	10241(9)
C-21	3301(6)	3604(1)	−6362(5)	3718(6)	1627(1)	14419(5)
C-61	5159(9)	4493(2)	−2632(7)	2071(10)	772(1)	10670(7)
C-62	5574(10)	4679(2)	−3635(8)	3482(12)	572(2)	11598(8)
C-71	6838(11)	4799(2)	1112(9)	−297(10)	482(2)	6550(8)
C-72	5707(13)	5017(2)	1491(9)	−1541(13)	244(1)	6447(10)
C-81	8285(8)	4105(2)	4663(6)	−2298(8)	1174(1)	3323(5)
C-82	9724(10)	4226(2)	6073(7)	−2160(9)	1083(2)	1916(6)
C-211	3805(7)	3309(1)	−6814(5)	4645(6)	1927(1)	14925(5)
C-212	2572(7)	3078(1)	−7466(6)	4038(8)	2135(1)	15617(6)
C-213	3079(10)	2812(2)	−7921(7)	4919(10)	2419(1)	16075(7)
C-214	4775(11)	2770(2)	−7706(7)	6420(10)	2469(1)	15877(8)
C-215	5950(8)	2984(2)	−7060(7)	7012(8)	2256(2)	15231(7)
C-216	5509(7)	3258(1)	−6625(6)	6122(8)	1988(1)	14735(6)
C-221	2865(6)	3860(1)	−7434(5)	4326(6)	1357(1)	15423(5)
C-222	2676(7)	3809(1)	−8884(6)	5605(7)	1394(1)	16897(5)
C-223	2207(8)	4037(2)	−9868(7)	6196(9)	1153(2)	17836(7)
C-224	1958(9)	4319(2)	−9545(9)	5494(11)	867(2)	17373(9)
C-225	2188(9)	4381(2)	−8075(9)	4254(10)	830(1)	15946(9)
C-226	2646(7)	4147(1)	−7016(6)	3705(7)	1072(1)	14995(6)

[a] Standard deviations in parentheses.

TABLE III

Selected torsion angles (°) in **1** [a] (molecules I and II)

Angles in the carbon chain	I	II	*Angles between vicinal oxygens*	I	II
C-1–C-2–C-3–C-4	178.3(4)	176.8(4)	O-5–C-5–C-6–O-6	176.0(3)	174.9(4)
C-2–C-3–C-4–C-5	171.2(4)	170.4(4)	O-6–C-6–C-7–O-7	73.7(5)	70.9(5)
C-3–C-4–C-5–C-6	−72.6(5)	−73.2(5)	O-7–C-7–C-8–O-8	−70.9(5)	−74.0(5)
C-4–C-5–C-6–C-7	178.4(4)	176.6(4)	O-8–C-8–C-9–O-5	−173.9(4)	−172.2(4)
C-5–C-6–C-7–C-8	−52.3(6)	−50.5(6)			
C-6–C-7–C-8–C-9	51.9(6)	49.5(6)			
Angles around the amino and nitro group	I	II	*Angles between vicinal hydrogens*	I	II
O-12–C-1–C-2–N-2	−175.9(4)	−177.4(4)	H-2–C-2–C-3–H-31	176.0(4)	179.1(4)
C-1–C-2–N-2–C-21	−97.1(5)	−95.3(5)	H-2–C-2–C-3–H-32	−60.8(6)	−61.5(6)
N-2–C-2–C-3–C-4	−61.2(5)	−62.5(5)	H-31–C-3–C-4–H-4	−66.0(5)	−67.1(5)
N-4–C-4–C-5–O-5	−72.7(5)	−74.2(5)	H-32–C-3–C-4–H-4	173.1(4)	171.1(4)
N-4–C-4–C-5–C-6	165.9(4)	163.8(4)	H-4–C-4–C-5–H-5	−72.6(6)	−77.0(5)
N-4–C-4–C-3–C-2	−69.9(5)	−68.7(5)	H-5–C-5–C-6–H-6	176.9(4)	177.3(4)
C-3–C-4–C-5–O-5	48.8(5)	48.8(5)	H-6–C-6–C-7–H-7	−168.2(4)	−169.2(4)
			H-7–C-7–C-8–H-8	170.3(5)	166.4(4)
			H-8–C-8–C-9–H-91	−55.1(6)	−56.8(6)
			H-8–C-8–C-9–H-92	−176.3(4)	−175.9(4)

[a] Standard deviations in parentheses.

All atoms (hydrogens included in theoretical positions) were refined. The final co-ordinates of C, N, and O are listed in Table II *. Selected torsion angles are given in Table III, and a perspective view (SCHAKAL88 [4] plot) of one of the independent molecules, which are only slightly different, is presented in Fig. 1, which clearly shows that the structure is as given in the title. By reactions already described [1], **1** can be transformed into the above-mentioned *C*-xylosyl amino acid with the correct "L" configuration of the amino acid part.

The six-membered ring in both independent molecules adopts a chair conformation [puckering parameters [5] in molecule I, Q = 57.9(5) pm, $\theta = 5.5(5)°$, $\phi = 17(6)°$; in molecule II, Q = 55.6(5) pm, $\theta = 5.1(5)°$, $\phi = 8(6)$] with C-4 equatorial and the nitro group *gauche* to the ring oxygen and *trans* to C-6. This orientation leaves C-3 in *gauche* positions to both O-5 and C-6, which is not the conformation usually observed [6] in "alkyl β-C-glycosides", whereas the arrangement of the nitro grop compares with that in many simple glycosylnitromethanes in the solid state as well as in solution [7]. Recently, the structure of 4,8-anhydro-3-deoxy-3-nitro-D-*lyxo*-D-*gluco*-nonitol was published [8]. In that case, opposite orientations of the nitro group and the alkyl carbon chain with respect to the pyranoid ring were observed.

* Lists of observed and calculated structure amplitudes, fractional co-ordinates of 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, The Netherlands. Reference should be made to No. BBA/DD/504/ *Carbohydr. Res.*, 232 (1992) 321–325.

Therefore, we conclude that both topologies compete, and it remains to be demonstrated which is the more favoured.

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