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Acta Cryst. (1999). **C55**, 1533–1534

2-(2,3:5,6-Di-*O*-isopropylidene- β -D-mannofuranosyl)-*N,N*-(pentamethylene)ethane-thioamide†

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(Received 19 January 1999; accepted 7 May 1999)

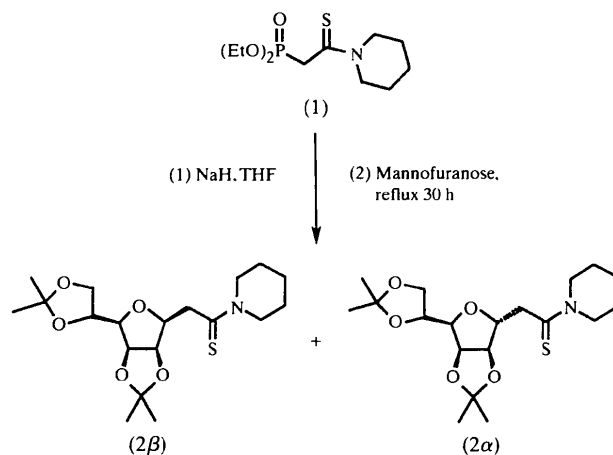
Abstract

The title compound, C₁₉H₃₁NO₅S, was prepared using a Wittig–Horner olefination followed by an intramolecular Michael addition. Two diastereoisomers were obtained in a 80:20 (β : α) ratio. The stereochemistry of the major anomer (β , thermodynamic) was based on NMR (¹³C and ¹H) spectra. The present X-ray structure determination confirms the configuration of this product.

Comment

C-Glycosides, *e.g.* shodomycin (Barret & Broughton, 1986), are known for their potential biological activity. Among the methods described by Postema (1992) to synthesize these compounds, one described the Wittig–Horner olefination of a sugar derivative followed by a Michael addition (Ohrei *et al.*, 1975). We used this strategy for the synthesis of some mannofuranosyl ethanethioamides starting from the readily available corresponding thiocarbamoyl methylphosphonates (Bulpin *et al.*, 1994) (see Scheme below). The reaction of metallated (Na) 2-(diethylphosphono)-*N,N*-(pentamethylene)ethanethioamide, (1), with a protected sugar (2,3:5,6-di-*O*-isopropylidene- α -D-mannofuranose)

† Alternative name: 2,3:5,6-di-*O*-isopropylidene-1-(piperidin-1-ylthiocarbonylmethyl)- β -D-mannofuranose.



allowed the preparation of the title compound, (2), which was later converted into the corresponding dithioester (Sandrinelli *et al.*, 1998). The configurational assignment of compound (2) (β or α) was deduced from NMR spectra (¹H and ¹³C) and by comparing the coupling constants of the two pure anomers. The X-ray structure determination reported herein confirms the configuration (β) and agrees with the assignment made previously by Mereyala *et al.* (1997). Two conformers of (2 β) are observed in this arrangement. As shown in Table 1, their geometrical features exhibit only very slight differences (values for the second conformer are reported using prime notation). One conformer is represented in Fig. 1 (*ORTEPII*; Johnson, 1976). All the substituents of the furanose ring (C7, O3, O2 and C2) are *cis*. The dimethyldioxolane and furanose rings adopt envelope conformations (Merino *et al.*, 1997), with O1, C9 and C12 at the flaps. The thioamide linkage is planar, as expected (Van Roey & Kerr, 1981); see Table 1 for details.

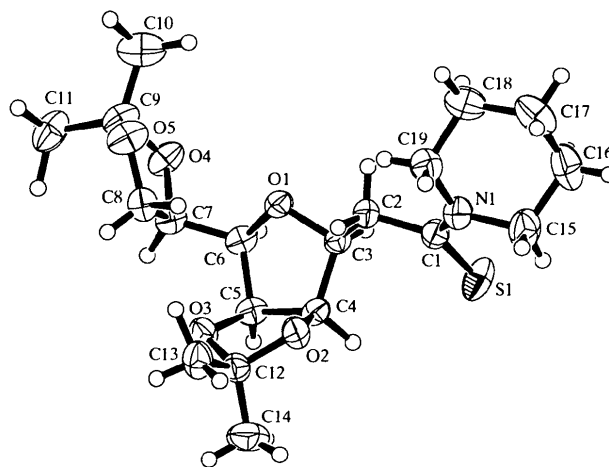


Fig. 1. An *ORTEPII* (Johnson, 1976) drawing of one of the two conformers shown with 45% probability displacement ellipsoids.

Experimental

Compound (1) (8.74 g, 1.1 equivalents) was added dropwise at 273 K and under nitrogen to a suspension of NaH (60% dispersion in mineral oil, 1.07 g, 1.2 equivalents, washed with pentane) in anhydrous tetrahydrofuran (THF). The mixture was stirred at room temperature for 2 h and 2,3:5,6-di-*O*-isopropylidene- α -D-mannofuranose (7.3 g, 1 equivalents, RN [14131-84-1]) diluted in anhydrous THF (25 ml) was added slowly. The solution was then heated at reflux for 30 h. After cooling, the mixture was quenched (HCl 5%) and extracted (Et₂O). The organic layers were dried over MgSO₄ and the solvents removed under reduced pressure. The residual oil was purified by chromatography (silica gel, AcOEt/petroleum ether 30/70). The yield reached 91% (73% anomer β /18% anomer α). The configurations of the anomers were assigned by ¹H and ¹³C NMR (AC Bruker, 250 MHz) and according to the coupling constants of the pure products: ³J_{H4-H3} = 3.4 Hz (β) and ³J_{H3-H4} = 0 Hz (α). All analyses (IR, mass spectra, elemental analysis) were in good agreement. Crystallization of β was achieved using ethyl acetate (m.p. = 391 K). Crystals suitable for X-ray analysis were obtained by slow evaporation from an ethanol solution.

Crystal data

C₁₉H₃₁NO₅S
M_r = 385.52
 Orthorhombic
 P2₁2₁2₁
a = 10.713 (3) Å
b = 13.569 (4) Å
c = 28.270 (9) Å
V = 4109 (2) Å³
Z = 8
D_x = 1.246 Mg m⁻³
D_m not measured

Mo K α radiation
 λ = 0.7107 Å
 Cell parameters from 25 reflections
 θ = 11.2–12.1°
 μ = 0.185 mm⁻¹
T = 293 K
 Orthorhombic prism
 0.42 × 0.41 × 0.40 mm
 Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω scans
 Absorption correction: none
 6626 measured reflections
 6626 independent reflections
 4681 reflections with *I* > $\sigma(I)$

θ_{\max} = 29.96°
h = 0 → 15
k = 0 → 19
l = 0 → 39
 2 standard reflections every 120 reflections
 intensity decay: 8.40%

Refinement

Refinement on *F*²
R = 0.043
 ωR = 0.042
S = 1.829
 4681 reflections
 470 parameters
 H atoms not refined
 $w = 1/[\sigma^2(F_o) + 0.00020|F_o|^2]$

$(\Delta/\sigma)_{\max}$ = 0.018
 $\Delta\rho_{\max}$ = 0.20 e Å⁻³
 $\Delta\rho_{\min}$ = -0.27 e Å⁻³
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

S1—C1	1.665 (2)	S1'—C1'	1.672 (2)
O1—C3	1.442 (2)	O1'—C3'	1.433 (2)
O1—C6	1.421 (2)	O1'—C6'	1.422 (2)

O2—C4	1.425 (2)	O2'—C4'	1.423 (2)
O2—C12	1.423 (3)	O2'—C12'	1.424 (2)
O3—C5	1.431 (2)	O3'—C5'	1.428 (2)
O3—C12	1.431 (3)	O3'—C12'	1.434 (2)
O4—C7	1.431 (2)	O4'—C7'	1.434 (2)
O4—C9	1.426 (2)	O4'—C9'	1.417 (2)
O5—C8	1.411 (3)	O5'—C8'	1.418 (3)
O5—C9	1.411 (3)	O5'—C9'	1.412 (3)
N1—C1	1.331 (3)	N1'—C1'	1.325 (2)
C1—C2	1.516 (3)	C1'—C2'	1.505 (3)
C3—O1—C6	106.9 (1)	C3'—O1'—C6'	107.4 (1)
C4—O2—C12	107.6 (1)	C4'—O2'—C12'	106.9 (1)
C5—O3—C12	107.0 (2)	C5'—O3'—C12'	107.8 (1)
C7—O4—C9	108.2 (2)	C7'—O4'—C9'	108.2 (2)
C8—O5—C9	108.3 (2)	C8'—O5'—C9'	107.8 (2)
S1—C1—N1	124.0 (2)	S1'—C1'—N1'	123.0 (1)
S1—C1—C2	120.3 (2)	S1'—C1'—C2'	120.5 (1)
N1—C1—C2	115.7 (2)	N1'—C1'—C2'	116.5 (2)
S1'—C1'—N1'—C15'	0.4 (3)	O4—C7—C8—O5	-2.3 (2)
S1—C1—N1—C15	-0.1 (3)	O4—C9—O5—C8	-32.0 (2)
O2'—C4'—C3'—C2'	33.7 (2)	O4'—C7'—C8'—O5'	-0.5 (2)
O2'—C4'—C5'—O3'	-8.5 (2)	O4'—C9'—O5'—C8'	-29.9 (2)
O2—C4—C3—C2	29.0 (2)	C2'—C1'—N1'—C15'	-179.6 (2)
O2—C4—C5—O3	-1.1 (2)	C2—C1—N1—C15	-180.0 (2)
O3'—C5'—C6'—C7'	-25.2 (2)	C3—C4—C5—C6	-2.0 (2)
O3'—C12'—O2'—C4'	-38.2 (2)	C3'—C4'—C5'—C6'	-6.8 (2)
O3—C5—C6—C7	-31.9 (2)	C4'—C3'—O1'—C6'	-39.0 (2)
O3—C12—O2—C4	-36.0 (2)	C4—C3—O1—C6	-38.1 (2)

The absolute configuration of the structure was fixed by the use as starting material of the D-form of 2,5:5,6-di-*O*-isopropylidene- α -D-mannofuranose. A decay correction was applied. H atoms were located by difference Fourier synthesis.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1037). Services for accessing these data are described at the back of the journal.

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