Spek, A. L. (1995). *PLATON. Molecular Geometry Program.* October 1995 version. University of Utrecht, The Netherlands.

Stoe & Cie (1990). *DIF4. Diffractometer Control Program.* Version 7.09. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1995). *XRED. Data Reduction Program for Windows.* Stoe & Cie, Darmstadt, Germany.

Wang, A. H.-J. & Paul, I. C. (1977). *Acta Cryst.* B33, 2977–2979.

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The Major Isoxazoline Cycloadduct from Reaction of a Xylopyranosylnitrile Oxide with a Hex-5-enopyranoside

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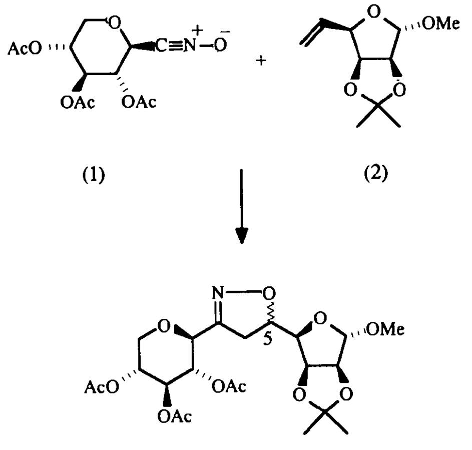
Abstract

The present structure determination of (5*R*)-5-(2,3-*O*-isopropylidene-1-*O*-methyl-α-D-*lyxo*-tetrafuranos-4-yl)-3-(2,3,4-tri-*O*-acetyl-β-D-xylopyranos-2-yl)-4,5-dihydroisoxazole, $C_{22}H_{31}NO_{12}$, at 150 K, taken with the known absolute configurations of the starting alkene and the nitrile oxide precursor, establishes the configuration (*R*) of the new stereogenic centre C(5) in the title compound, the major cycloadduct. The five-membered 4,5-dihydroisoxazole ring adopts a mainly envelope conformation folded between O(5) and O(6), whereas the furanoside and dioxolane rings lie between twist and envelope. The xylopyranosyl ring adopts a near ideal chair conformation.

Comment

As part of a programme aimed at developing a synthetic route to carbon-linked disaccharides (*C*-disaccharides) (Levy & Tang, 1995) based on nitrile oxide/isoxazoline chemistry (Kanemasa & Tsuge, 1990, and references therein), we have investigated the reaction of D-xylose-derived nitrile oxide, (1), with D-mannose-derived alkene, (2) (see Scheme). Two diastereomeric 4,5-dihydroisoxazole cycloadducts, (3) and (4), were formed in the ratio 82:18 in a combined yield of 67%. The major product provided crystals suitable for X-ray crystallography. Taken with the known absolute configurations of the starting alkene (Bock & Petersen, 1977) and the nitrile oxide precursor (Förtsch, Kogelberg & Köll, 1987), the present structure determination firmly establishes that this compound has structure (3) in which the new stereogenic centre C(5) has the *R*-configuration, and that the minor isomer has the 5*S* structure (4).



(3) 5*R*
(4) 5*S*

The Cremer–Pople puckering parameters (Cremer & Pople, 1975; Gould, Taylor & Thorpe, 1995) for the four rings are given in Table 2. The five-membered dihydroisoxazole ring adopts a mainly envelope conformation (E_5, corresponding to an ideal value of φ = 324°) with the fold between O(5) and C(6); the torsion angle for the O(5)—N(7)═C(7)—C(6) unit is 0.8 (5)° with C(5) lying 0.19 Å out of the best plane through these atoms. For the furanoside ring, φ = 6.6° indicating that it is intermediate between envelope (φ = 0°) and twist (φ = 18°). Likewise, the conformation of the dioxolane lies between twist (φ = 18°), and envelope (φ = 36°). The θ value for the pyranoid ring (3.4°) indicates that it is very close to the ideal chair $^4C_1$ with θ = 0°. No anomalies are found in the bond lengths and angles. The crystal structure consists of layers of molecules of (3); there appear to be no significant interactions between the layers, and only rather weak intermolecular C—H···O interactions [minimum and maximum C···O distances 3.261 (6) and 3.467 (6) Å, respectively] within the layers.

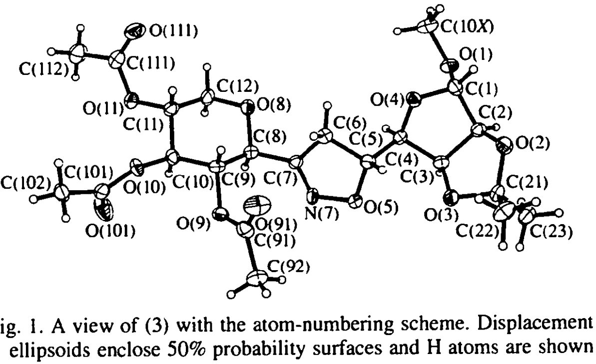


Fig. 1. A view of (3) with the atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces and H atoms are shown as spheres of arbitrary radius.

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Experimental

The title compound was obtained by cycloaddition to methyl-5,6-dideoxy-2,3-*O*-isopropylidene-1-*O*-methyl-α-D-*lyxo*-hex-5-enofuranoside, (2), of 2,3,4-tri-*O*-acetyl-β-D-xylopyranosylformonitrile oxide, (1), which was generated by dehydration of the corresponding pyranosylnitromethane as previously reported (Paton & Penman, 1994). Crystals were grown by recrystallization from methanol.

Crystal data

$C_{22}H_{31}NO_{12}$
$M_r = 501.48$
Orthorhombic
$P2_12_12_1$
$a = 8.518\,(2)$ Å
$b = 16.514\,(3)$ Å
$c = 17.250\,(3)$ Å
$V = 2426.5\,(8)$ Å^3
$Z = 4$
$D_x = 1.373$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 40 reflections
$\theta = 20$–$22°$
$\mu = 0.959$ mm^{-1}
$T = 150.0\,(2)$ K
Needle
0.62 × 0.08 × 0.08 mm
Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems variable-temperature device (Cosier & Glazer, 1986)
ω–θ scans with on-line profile learning (Clegg, 1981)
Absorption correction: none
3897 measured reflections

3493 independent reflections
2713 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0359$
$\theta_{\rm max} = 59.99°$
$h = -9 \rightarrow 8$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 19$
3 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0569$
$wR(F^2) = 0.1226$
$S = 1.065$
3485 reflections
323 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 1.847P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.04$
$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.00035 (6)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = 0.2 (4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
C(1)	0.7293 (6)	0.0198 (3)	0.6515 (3)	0.0252 (12)
O(1)	0.8587 (4)	0.0308 (2)	0.6018 (2)	0.0272 (8)
C(10*X*)	0.9767 (6)	0.0823 (4)	0.6349 (3)	0.0344 (13)
C(2)	0.6128 (5)	−0.0340 (3)	0.6082 (3)	0.0219 (11)
O(2)	0.5201 (4)	−0.0774 (2)	0.6636 (2)	0.0290 (8)
O(3)	0.3463 (4)	0.0033 (2)	0.6009 (2)	0.0260 (8)
C(3)	0.4965 (5)	0.0256 (3)	0.5708 (3)	0.0215 (11)
C(4)	0.5487 (5)	0.1085 (3)	0.6000 (3)	0.0192 (11)
O(4)	0.6485 (4)	0.0932 (2)	0.6660 (2)	0.0221 (8)
O(5)	0.3082 (4)	0.1772 (2)	0.5658 (2)	0.0263 (8)
C(5)	0.4173 (6)	0.1627 (3)	0.6295 (3)	0.0217 (11)
C(6)	0.4728 (6)	0.2472 (3)	0.6540 (3)	0.0261 (12)
N(7)	0.3214 (5)	0.2588 (2)	0.5412 (2)	0.0243 (10)
C(7)	0.4095 (5)	0.2974 (3)	0.5890 (3)	0.0196 (11)
C(8)	0.4332 (5)	0.3855 (3)	0.5766 (3)	0.0229 (11)
O(8)	0.5930 (4)	0.4038 (2)	0.5955 (2)	0.0295 (9)
C(9)	0.3265 (6)	0.4378 (3)	0.6285 (3)	0.0227 (11)
O(9)	0.1658 (4)	0.4187 (2)	0.6092 (2)	0.0244 (8)
C(91)	0.0933 (6)	0.3641 (3)	0.6567 (3)	0.0254 (12)
O(91)	0.1453 (5)	0.3438 (2)	0.7182 (2)	0.0422 (10)
C(92)	−0.0534 (6)	0.3330 (3)	0.6212 (3)	0.0351 (13)
C(10)	0.3552 (5)	0.5259 (3)	0.6086 (3)	0.0205 (10)
O(10)	0.2645 (4)	0.5768 (2)	0.6598 (2)	0.0244 (8)
C(101)	0.1817 (6)	0.6392 (3)	0.6284 (3)	0.0279 (12)
O(101)	0.1625 (5)	0.6464 (2)	0.5598 (2)	0.0486 (11)
C(102)	0.1209 (6)	0.6939 (3)	0.6888 (3)	0.0281 (13)
C(11)	0.5280 (6)	0.5428 (3)	0.6245 (3)	0.0231 (12)
O(11)	0.5600 (4)	0.6253 (2)	0.6014 (2)	0.0273 (8)
C(111)	0.6844 (7)	0.6608 (3)	0.6385 (3)	0.0298 (13)
O(111)	0.7590 (4)	0.6255 (2)	0.6878 (2)	0.0403 (10)
C(112)	0.7137 (7)	0.7446 (3)	0.6104 (4)	0.0409 (15)
C(12)	0.6293 (6)	0.4864 (3)	0.5769 (3)	0.0314 (13)
C(21)	0.3617 (6)	−0.0751 (3)	0.6354 (3)	0.0270 (12)
C(22)	0.2519 (7)	−0.0814 (3)	0.7034 (3)	0.0375 (14)
C(23)	0.3356 (7)	−0.1399 (3)	0.5744 (3)	0.0352 (14)

Table 2. *Puckering parameters (Å, °) for (3)*

Ring*	Q	θ	φ
Isoxazoline			
O(5)—N(7)—C(7)—C(6)—C(5)	0.116	n/a	326.9
Furanoside			
O(4)—C(1)—C(2)—C(3)—C(4)	0.116	n/a	6.6
Dioxolane			
O(2)—C(21)—O(3)—C(3)—C(2)	0.321	n/a	23.3
Pyranoid			
O(8)—C(8)—C(9)—C(10)—C(11)—C(12)	0.625	3.4	100.1

* Numbered in order of calculation (Cremer & Pople, 1975).

H atoms were placed in idealized positions and allowed to ride on their parent atoms with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. Methyl groups were treated as rotating rigid groups with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$. The low value of $\theta_{\rm max}$ is a consequence of mechanical restrictions arising from the use of the low-temperature device.

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXTL/PC* (Sheldrick, 1995). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

We thank the EPSRC for provision of a four-circle diffractometer and DENI for the award of a studentship (WJF).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a packing diagram, have been deposited with the IUCr (Reference: BM1111). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A. & Polidori, G. (1994). *J. Appl. Cryst.* **27**, 435.
Bock, K. & Petersen, C. (1977). *Acta Chem. Scand.* **31B**, 248–250.
Clegg, W. (1981). *Acta Cryst.* **A37**, 22–28.

Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Förtsch, A., Kogelberg, H. & Köll, P. (1987). *Carbohydr. Res.* **164**, 391–402.
Gould, R. O., Taylor, P. & Thorpe, M. (1995). *PUCKER. A Program for the Calculation of Puckering Parameters.* University of Edinburgh, Scotland.
Kanemasa, S. & Tsuge, O. (1990). *Heterocycles*, **30**, 719–736.
Levy, D. E. & Tang, C. (1995). *The Chemistry of C-Glycosides*, pp. 237–277. Oxford: Elsevier.
Paton, R. M. & Penman, K. (1994). *Tetrahedron Lett.* **35**, 3163–3166.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, G. M. (1995). *SHELXTL/PC.* Version 5.04. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Stoe & Cie (1992*a*). *DIF4. Diffractometer Control Program.* Version 7.09. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1992*b*). *REDU4. Data Reduction Program.* Version 7.03. Stoe & Cie, Darmstadt, Germany.

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The First Crystal Structure Analysis of Cyclododeca-2,8-diyne-1,10-diols

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Abstract

Cyclododeca-2,8-diyne-1,10-diol, (6), $C_{12}H_{16}O_2$, and 1,10-dimethylcyclododeca-2,8-diyne-1,10-diol, (11), $C_{14}H_{20}O_2$, have been prepared and their structures determined. Both crystallize in centrosymmetric space groups and the molecules have approximate C_2 symmetry. For compound (6), the lengths of the triple bonds are 1.184 (3) ($C2\equiv C3$) and 1.189 (3) Å ($C8\equiv C9$). The bond angles at the triple bonds ($C1—C2\equiv C3$ and $C8\equiv C9—C10$) deviate by less than 6° from 180°. For compound (11), the lengths of the triple bonds are 1.190 (3) ($C2\equiv C3$) and 1.188 (3) Å ($C8\equiv C9$), and the bond angles at the triple bonds are close to 175.5°. In both compounds, the two 3-hexyne chains maintain a 'crossed' arrangement whereas the two alkylene chains are arranged in a manner similar to that described for unsubstituted cyclododecane.

Comment

Medium-sized ring compounds are of considerable interest because of their unique structure and transannular reactivity (Dunitz & Meyer, 1965; Johnson, 1986; Gleiter, Merger, Irngartinger & Nuber, 1993). The cyclododecadiynediols (6) and (11) (see schemes in *Experimental*) have been prepared for an investigation of reactions of the juxtaposed triple bonds with doubly functionalized reagents and in order to determine the influence of different substitution patterns at the propargylic centres on the structure of such ring compounds.

The expected C_2 symmetry of *rac*-(6) and *rac*-(11) is apparent from the structure analysis. For (6)

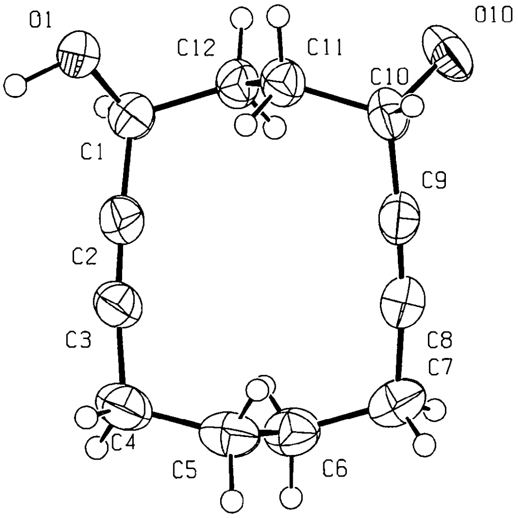

Fig. 1. Perspective view of (6). Displacement ellipsoids are shown at the 50% probability level.

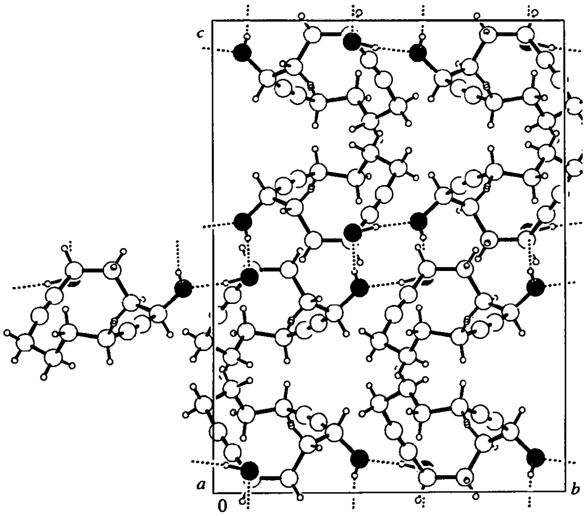

Fig. 2. Packing diagram for (6).