

Francesco Punzo,^{a*} David J. Watkin,^b Sarah F. Jenkinson,^c Filipa P. da Cruz^c and George W. J. Fleet^c

^aDipartimento di Scienze Chimiche, Facoltà di Farmacia, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy, ^bDepartment of Chemical Crystallography, Chemical Research Laboratory, Mansfield Road, Oxford OX1 3TA, England, and ^cDepartment of Organic Chemistry, Chemical Research Laboratory, Mansfield Road, Oxford OX1 3TA, England

* Visiting Scientist at the Department of Chemical Crystallography, Chemical Research Laboratory, Mansfield Road, Oxford OX1 3TA, England.

Correspondence e-mail: fpunzo@unict.it

Key indicators

Single-crystal X-ray study

$T = 250$ K

Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å

R factor = 0.047

wR factor = 0.129

Data-to-parameter ratio = 11.3

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

2-C-Azidomethyl-2-deoxy-3,4-O-isopropylidene-D-ribo-1,5-lactone

X-ray crystallographic analysis firmly establishes the *ribo* stereochemistry and the unusual boat conformation of the title branched carbon chain lactone, $\text{C}_9\text{H}_{13}\text{N}_3\text{O}_4$, arising from an unexpected rearrangement in the nucleophilic substitution of a trifluoromethanesulfonate. There are two molecules in the asymmetric unit.

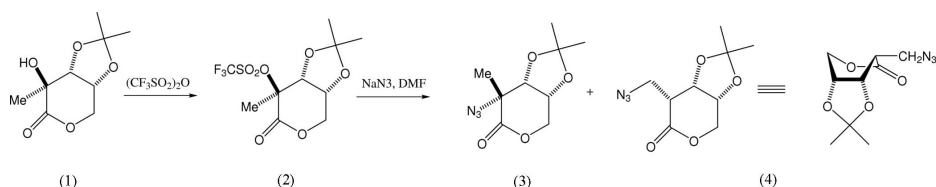
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Comment

The Kiliani reaction of ketoses with cyanide (Hotchkiss *et al.*, 2004; Soengas *et al.*, 2005) provides access to a novel class of carbohydrate scaffold which contains a branched carbon chain. Such sugar building blocks have hitherto been rare and difficult to prepare in large quantities (Bols, 1996; Lichtenhaler & Peters, 2004). However, naturally occurring ketoses restrict the branched carbon chain to a hydroxymethyl group. A further class of branched carbohydrates is available from the Kiliani ascension on 1-deoxyketoses, themselves prepared by addition of organometallic reagents to sugar lactones. Thus, reaction of cyanide with a protected 1-deoxy-D-ribose allowed the isolation of the isopropylidene derivative of arabinono-1,5-lactone, (1) (Hotchkiss *et al.*, 2006), shown to crystallize in a boat conformation (Punzo, Watkin, Jenkinson & Fleet, 2005).



The value of protected sugar lactones such as (1) depends on being able to modify the tertiary alcohol functionality to other groups. Thus, the esterification of the free alcohol (1) with triflic anhydride in pyridine afforded the trifluoromethanesulfonate, (2), which on further reaction with sodium azide in dimethylformamide gave the *ribo*-azide, (3), as the major product in good yield, even though the overall reaction is a nucleophilic displacement at a very hindered position. It was possible that neighbouring group participation by an O atom might have been involved in the reaction but the X-ray crystal structure (Punzo, Watkin, Jenkinson, Cruz & Fleet, 2005) showed that the reaction proceeded with inversion of configuration to give the ribonolactone (3) in a boat conformation, with the C2-methyl group in a hindered flag-pole position. A small quantity of a second crystalline azide, the title compound, (4), was also isolated.

X-ray crystal-structure analysis of (4) firmly establishes that the relative configuration of the azidomethyl branch at C2 is in

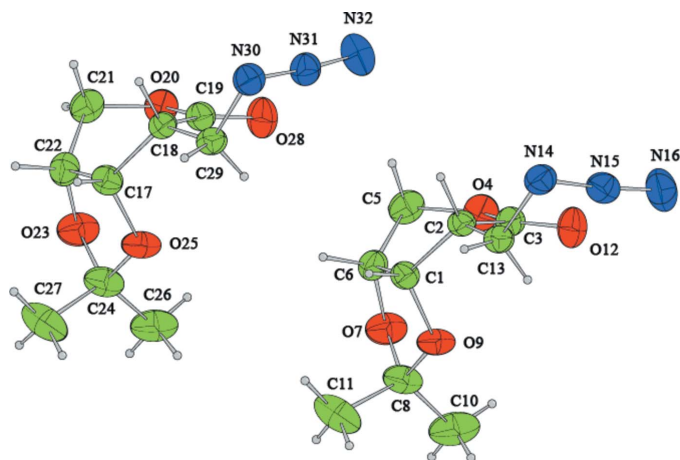


Figure 1
The asymmetric unit of (4), containing two molecules, with displacement ellipsoids drawn at the 50% probability level. H-atom radii are arbitrary.

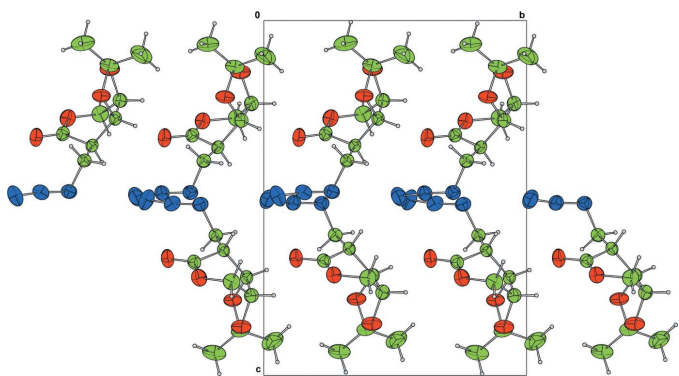


Figure 2
A packing diagram of (4), viewed down the *a* axis.

a bowsprit conformation. The absolute configuration of (4) was determined by the use of D-erythronolactone as the starting material for the synthesis. Azides (3) and (4) are likely to be useful building blocks for the synthesis of novel branched prolines and pipercolic acids, respectively.

In Fig. 2, a pseudo-translational operator of the form $(0.48 + x, 0.48 + y, +z)$ is clearly detectable.

Experimental

The title lactone, (4) {m.p. 365–367 K; $[\alpha]_{\text{D}}^{23}$ -168.2% (*c* 1.0 in MeCN)}, was crystallized by dissolving it in ethyl acetate, adding cyclohexane and allowing slow competitive evaporation of the two solvents until clear colourless crystals formed. The multi-scan technique was used to correct for changes in the illuminated volume.

Crystal data

$\text{C}_9\text{H}_{13}\text{N}_5\text{O}_4$	$D_x = 1.366 \text{ Mg m}^{-3}$
$M_r = 227.22$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 2605 reflections
$a = 6.6145(2) \text{ \AA}$	$\theta = 5\text{--}30^\circ$
$b = 11.1194(4) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$c = 15.0252(8) \text{ \AA}$	$T = 250 \text{ K}$
$\beta = 91.6306(13)^\circ$	Plate, colourless
$V = 1104.65(8) \text{ \AA}^3$	$0.30 \times 0.20 \times 0.10 \text{ mm}$
$Z = 4$	

Data collection

Bruker Nonius KappaCCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (DENZO/SCALEPACK; Otwinowski & Minor, 1997)
 $T_{\text{min}} = 0.98$, $T_{\text{max}} = 0.99$
 5623 measured reflections

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.129$
 $S = 1.08$
 3275 reflections
 290 parameters
 H-atom parameters constrained
 $w = [1 - (F_o - F_c)^2/36\sigma^2(F)]^2 / [38.7T_0(x) + 61.9T_1(x) + 38.9T_2(x)]$ where T_i are

3275 independent reflections
 1944 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$
 $\theta_{\text{max}} = 29.9^\circ$
 $h = -9 \rightarrow 9$
 $k = -15 \rightarrow 15$
 $l = -21 \rightarrow 21$

Chebyshev polynomials and $x = F_c/F_{\text{max}}$ (Prince, 1982; Watkin, 1994)
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.54 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.52 \text{ e \AA}^{-3}$
 Extinction correction: Larson (1970), eq. 22
 Extinction coefficient: $1.0(2) \times 10^2$

Table 1

Selected geometric parameters (\AA , $^\circ$).

C5–C6	1.497 (6)	C21–C22	1.498 (6)
C2–C1–C6	111.9 (3)	C18–C17–O25	107.6 (3)
C2–C1–O9	107.8 (3)	C22–C17–O25	104.5 (3)
O9–C8–C11	111.4 (4)	O20–C21–C22	110.4 (3)
C18–C17–C22	112.1 (3)		

In the absence of significant anomalous dispersion effects, Friedel pairs were merged before refinement. H atoms were seen in difference Fourier maps. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry [C–H in the range 0.93–0.98 \AA and $U_{\text{iso}}(\text{H})$ in the range 1.2–1.5 times U_{eq} of the parent atom], after which their positions were refined with riding constraints.

Data collection: COLLECT (Nonius, 2001); cell refinement: DENZO/SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO/SCALEPACK; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: CRYSTALS (Betteridge *et al.*, 2003); molecular graphics: CAMERON (Watkin *et al.*, 1996); software used to prepare material for publication: CRYSTALS.

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