by the C atom [C(5)] that is bound to the ester group. The orientation of the ester group with respect to the benzene ring would be expected to be anti- or synperiplanar because only these two conformations would allow resonance of the carbonyl group with the benzene π system. It is found that the ester group is out of plane by 103 (1)° and thus is not stabilized by resonance. This is confirmed by the bond lengths of the carbonyl C to O [C(8)—O(2)] and to the ring C [C(8)—C(5)], which are 1·19 (1) and 1·50 (1) Å, respectively. Both bond lengths are typical for a C—O double bond and a C—C single bond. The out-of-plane orientation of the ester group with respect to the benzene ring must be due to steric hindrance by the two bulky groups, the pyrrolidine ring and the Cl atom, which are *ortho* to the ester group.

A relatively short bond length of a 1·34 Å is shown by the C(8)—O(1) single bond. In 3-hydroxy-5-phenylisoxazole the C—O single bond showed the same distance (Marongiu, Biagini & Carmas, 1969). C(9) and C(10) have unusually large thermal parameters, and slight positional disorder may explain the unusually short C(9)—C(10) distance of 1·447 (8) Å.

The Nicolet R3/m X-ray diffractometer and crystallographic computing system at Washington State

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X-ray Structure of a (D-*galacto*-Pentaacetoxypentyl)pyrazoline

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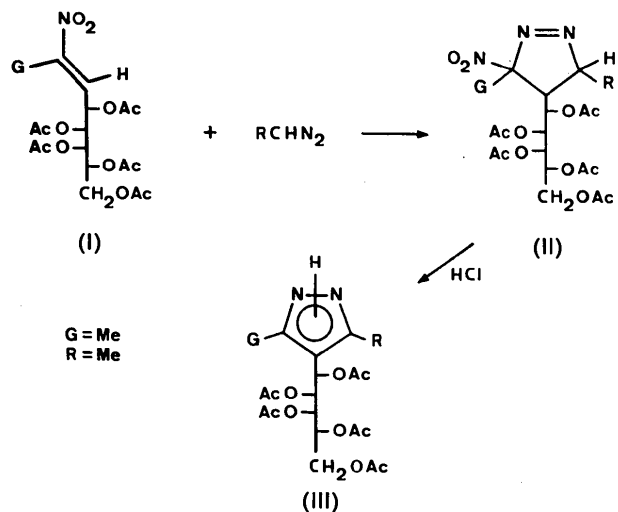
Abstract. 1-(3,5-Dimethyl-3-nitro-1-pyrazolin-4-yl)-penta-*O*-acetyl-D-*galacto*-pentitol, $C_{20}H_{29}N_3O_{12}$, M_r = 503·5, orthorhombic, $P2_12_12_1$, a = 14·471 (9), b = 14·518 (3), c = 12·028 (2) Å, V = 2527·0 (1·7) Å^3, Z = 4, D_x = 1·323 Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ = 0·10 mm^{-1}, $F(000)$ = 1064, room temperature, final wR = 0·035 for 1836 observed reflexions. Bond distances and angles are all within the expected ranges. The pyrazoline ring exhibits approximate mirror symmetry and a puckering amplitude of 0·244 (6) Å. Torsion angles of the acetoxy groups with the sugar chain range from 33 to 72°. Crystal cohesion is mainly due to van der Waals interactions but there are two intermolecular hydrogen bonds linking molecules related by screw axes along [100] and [001].

Introduction. The structure determination of 1-(3,5-dimethyl-3-nitro-1-pyrazolin-4-yl)-penta-*O*-acetyl-D-*galacto*-pentitol was undertaken as part of a continuing research project on C-nucleosides and precursors. The title compound was prepared as an intermediate product in the synthesis of (penta-acetoxypentyl)pyrazoles (III) with the sugar nitroolefins (I) as dipolarophiles. Initially, the cycloadditions gave the pyrazolines (II), which were aromatized to the pyrazoles (Mancera, Rodriguez, Roffe & Galbis, 1988). The stereochemistry was

$C_{20}H_{29}N_3O_{12}$

tentatively assigned on the basis of chemical and spectroscopic data and an X-ray study of the title compound was suggested to confirm the proposed configuration.

Table 1. *Atomic coordinates and thermal parameters*
$(\text{Å}^2 \times 10^3)$

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.\cos(\mathbf{a}_i,\mathbf{a}_j).$$

	x	y	z	U_{eq}
O11	0·7034 (4)	0·0799 (5)	0·4340 (4)	110 (3)
O12	0·5870 (3)	0·1282 (4)	0·3367 (6)	125 (3)
O41	0·9479 (2)	0·1552 (2)	0·1666 (3)	38 (1)
O42	0·9541 (3)	0·0878 (3)	−0·0011 (4)	82 (3)
O51	0·8581 (2)	0·2748 (2)	0·3043 (3)	39 (1)
O52	0·7195 (3)	0·2937 (3)	0·3777 (3)	74 (2)
O61	0·8288 (2)	0·2989 (2)	0·0060 (3)	37 (1)
O62	0·9735 (3)	0·3119 (4)	−0·0542 (4)	83 (2)
O71	0·7276 (2)	0·4241 (2)	0·1464 (3)	39 (1)
O72	0·7322 (3)	0·5085 (3)	0·3032 (3)	73 (2)
O81	0·8549 (3)	0·5805 (3)	0·0970 (3)	47 (2)
O82	0·9849 (3)	0·6179 (3)	0·0056 (4)	82 (2)
N1	0·7776 (4)	−0·0815 (4)	0·2382 (5)	66 (2)
N2	0·7030 (4)	−0·0435 (3)	0·2555 (5)	64 (2)
N11	0·6620 (4)	0·0931 (4)	0·3463 (6)	73 (3)
C1	0·7095 (4)	0·0593 (4)	0·2396 (5)	47 (2)
C2	0·8148 (4)	0·0800 (4)	0·2445 (5)	36 (2)
C3	0·8531 (4)	−0·0162 (4)	0·2128 (5)	44 (2)
C4	0·8475 (4)	0·1554 (4)	0·1645 (5)	34 (2)
C5	0·8187 (4)	0·2526 (4)	0·1966 (5)	29 (2)
C6	0·8580 (4)	0·3246 (4)	0·1175 (5)	30 (2)
C7	0·8269 (4)	0·4219 (4)	0·1416 (5)	33 (2)
C8	0·8622 (5)	0·4879 (4)	0·0534 (5)	46 (2)
C11	0·6584 (5)	0·0830 (6)	0·1366 (9)	89 (4)
C31	0·9366 (6)	−0·0456 (5)	0·2806 (9)	83 (4)
C41	0·9916 (4)	0·1219 (5)	0·0751 (6)	55 (3)
C42	1·0941 (5)	0·1365 (7)	0·0878 (7)	76 (4)
C51	0·8013 (5)	0·2944 (5)	0·3887 (7)	48 (3)
C52	0·8500 (6)	0·3177 (7)	0·4900 (7)	88 (4)
C61	0·8955 (5)	0·2946 (4)	−0·0732 (5)	51 (3)
C62	0·8558 (6)	0·2671 (6)	−0·1820 (6)	72 (3)
C71	0·6886 (4)	0·4695 (4)	0·2347 (5)	45 (2)
C72	0·5857 (5)	0·4601 (6)	0·2330 (7)	73 (3)
C81	0·9215 (5)	0·6404 (4)	0·0632 (6)	52 (3)
C82	0·9036 (6)	0·7351 (5)	0·1006 (6)	65 (3)

Experimental. Single crystals in the form of colourless needles elongated along [001] prepared in the Organic and Pharmaceutical Chemistry Department of the University of Sevilla. Cell parameters were refined by least-squares calculations from 25 reflexions with $5 < \theta < 20°$ on an Enraf–Nonius CAD-4 diffractometer. Intensity data from a crystal of dimensions $0·20 \times 0·15 \times 0·30$ mm were collected up to $\sin\theta/\lambda = 0·60 \text{ Å}^{-1}$ with an $\omega–2\theta$ scan using graphite-monochromated Mo $K\alpha$ radiation. Two reflexions ($41\bar{3}$, $34\bar{3}$) monitored periodically during data collection showed that the crystal was stable to X-rays. Index ranges of unique data were $0 \le h \le 17$, $0 \le k \le 17$, $0 \le l \le 14$. 2476 reflexions were collected of which 1836 unique reflexions were considered observed $[I > 2\sigma(I)]$. The structure was solved by direct methods using MULTAN80 (Main et al., 1980). All the H atoms were located from a difference Fourier map. Full-matrix least-squares refinement with non-H atoms refined anisotropically and H atoms isotropically converged at $R = 0·048$ and $wR = 0·035$, S (goodness of fit) = 1·38. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$. Maximum shift/e.s.d. ratio for non-H atoms = 0·02. Residual electron densities in the final difference Fourier map were within 0·20 and $-0·25$ e Å^{-3}. The atomic scattering factors were from *International Tables for X-ray Crystallography* (1974). Crystallographic programs of the XRAY76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) were used throughout.

Discussion. The final positional and equivalent isotropic thermal parameters for the non-H atoms are
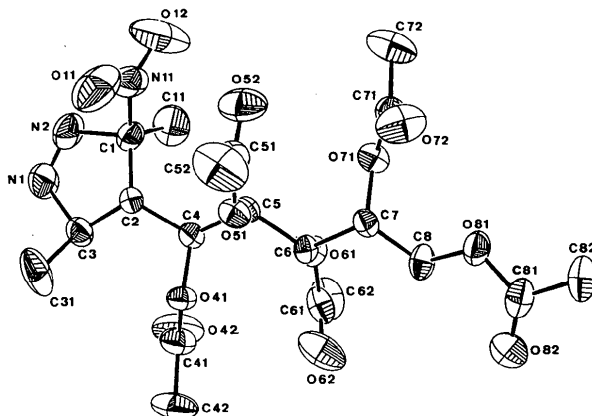

Fig. 1. An *ORTEP* view of the molecule with atom labelling.

given in Table 1.* An *ORTEP* (Johnson, 1965) plot of the molecule with atomic labelling is displayed in Fig. 1. Bond lengths and angles involving non-H atoms are listed in Table 2 and the values are all within the expected ranges.

The puckering of the pyrazoline ring can be described (Cremer & Pople, 1975) by a puckering

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51944 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances (Å) and angles (°) involving non-H atoms*

O62—C61	1·179 (9)	C62—C61	1·484 (10)
C61—O61	1·358 (8)	O82—C81	1·195 (9)
C31—C3	1·519 (11)	C82—C81	1·470 (10)
C4—O41	1·453 (6)	C4—C5	1·521 (8)
C4—C2	1·532 (8)	O51—C51	1·337 (7)
O51—C5	1·452 (6)	O71—C7	1·440 (6)
O71—C71	1·371 (7)	C6—O61	1·454 (7)
C6—C7	1·511 (8)	C6—C5	1·524 (8)
C7—C8	1·517 (8)	O41—C41	1·359 (8)
C51—O52	1·191 (8)	C51—C52	1·448 (11)
C8—O81	1·447 (7)	O81—C81	1·361 (8)
C3—C2	1·550 (8)	C3—N1	1·478 (8)
C42—C41	1·507 (10)	C2—C1	1·553 (8)
C41—O42	1·174 (8)	N1—N2	1·230 (7)
O72—C71	1·182 (7)	C72—C71	1·495 (9)
C1—N2	1·507 (7)	C1—N11	1·536 (10)
C1—C11	1·484 (12)	N11—O11	1·229 (9)
N11—O12	1·204 (8)		

O62—C61—C62	126·8 (7)	C62—C61—O61	110·8 (6)
O62—C61—O61	122·3 (6)	C5—C4—C2	114·7 (5)
O41—C4—C2	107·3 (4)	O41—C4—C5	105·7 (4)
C51—O51—C5	118·9 (4)	C7—O71—C71	116·9 (4)
C7—C6—C5	114·2 (5)	O61—C6—C5	106·9 (4)
O61—C6—C7	109·3 (4)	C61—O61—C6	116·8 (4)
O71—C7—C6	109·0 (4)	C6—C7—C8	110·9 (5)
O71—C7—C8	110·5 (4)	C4—O41—C41	116·9 (4)
O51—C51—C52	112·9 (6)	O51—C51—O52	121·7 (6)
O52—C51—C52	125·4 (6)	O51—C5—C6	105·0 (4)
C4—C5—C6	112·0 (4)	C4—C5—O51	109·0 (4)
C7—C8—O81	108·0 (5)	C8—O81—C81	115·6 (5)
C31—C3—N1	107·3 (5)	C31—C3—C2	113·9 (5)
C2—C3—N1	105·3 (5)	C4—C2—C3	112·2 (5)
C3—C2—C1	99·6 (4)	C4—C2—C1	114·7 (5)
O41—C41—C42	109·0 (6)	C42—C41—O42	126·4 (6)
O41—C41—O42	124·6 (6)	C3—N1—N2	113·3 (5)
C2—C1—C11	118·3 (6)	C2—C1—N11	110·2 (5)
C2—C1—N2	104·4 (5)	N11—C1—C11	113·6 (6)
N2—C1—C11	107·7 (5)	N2—C1—N11	100·5 (5)
N1—N2—C1	111·6 (5)	O72—C71—C72	125·8 (6)
O71—C71—C72	110·8 (5)	O71—C71—O72	123·4 (5)
C82—C81—O81	112·4 (6)	O82—C81—O81	122·9 (6)
O82—C81—C82	124·6 (6)	C1—N11—O12	117·3 (7)
C1—N11—O11	116·7 (6)	O11—N11—O12	126·0 (7)

amplitude $q = 0·244$ (6) Å and a phase angle $\varphi = -149·9$ (14)° for the sequence C1—C2—C3—N1—N2. The asymmetry parameter (Nardelli, 1983*a*) $\Delta C_s(C2) = 0·021$ (3) indicates approximate mirror symmetry in the ring.

The five acetoxy groups are planar and their torsion angles with respect to the main chain are C2—C4—O41—C41 = 108·1 (5), C4—C5—O51—C51 = −119·0 (5), C5—C6—O61—C61 = −129·3 (5), C6—C7—O71—C71 = 132·8 (5) and C7—C8—O81—C81 = 146·7 (5)°. The Newman projections corresponding to C—C bonds of the chain are shown in Fig. 2 from which the configuration of the sugar can be deduced.

The crystal cohesion is mainly due to van der Waals interactions but two intermolecular contacts may be considered as hydrogen bonds. These interactions are: C72—H723···O42 $(x - \frac{1}{2}, -y + \frac{1}{2}, -z)$ linking molecules related by a screw axis parallel to [100], and C8—H81···O72 $(-x + \frac{3}{2}, -y + 1, z - \frac{1}{2})$ linking molecules related by a screw axis along [001]. Details of these contacts are: C72—H723 = 1·06 (5), C72···O42 = 3·448 (9), H723···O42 = 2·44 (6) Å, C72—H723···O42 = 159 (4)° and C8—H81 = 1·03 (5), C8···O72 = 3·306 (8), H81···O72 =
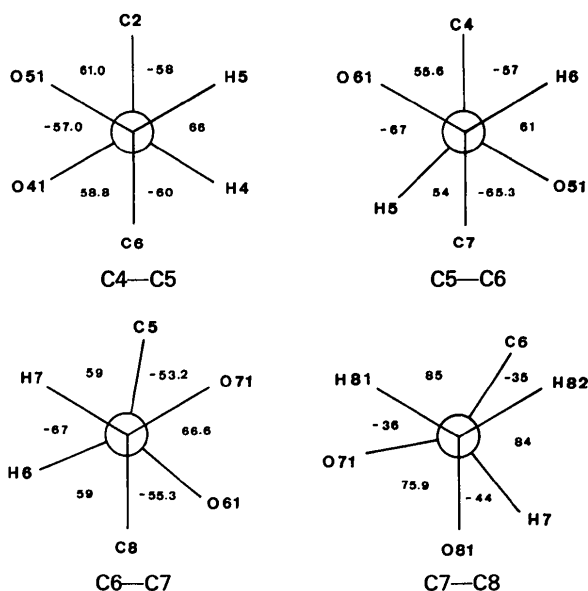

Fig. 2. Newman projections through the C—C bonds of the sugar chain. Standard deviations in torsion angles involving non-H atoms are in the range 0·5–0·8°.

2·35 (6) Å, C8—H81···O72 = 154 (4)°. No other contacts satisfy the criteria of Taylor & Kennard (1982) for hydrogen bonds. The molecular geometry and crystal packing were computed by *PARST* (Nardelli, 1983*b*).

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