International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed., p. 276. Birmingham: Kynoch Press.
POKORNY, M., ZISSIS, E., FLETCHER, H. G. JR & PRAVDIĆ, N. (1975). *Carbohydr. Res.* **43**, 345–354.
POPOVIĆ, S. (1974). *J. Appl. Cryst.* **7**, 291–292.
RUŽIĆ-TOROŠ, Ž. & KOJIĆ-PRODIĆ, B. (1976). *Acta Cryst.* B**32**, 2333–2336.
STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
WILSON, A. J. C. (1942). *Nature (London)*. **150**, 151–152.

Acta Cryst. (1978). B**34**, 858–862

Stereochemistry of Unsaturated Amino Sugars. III. The Crystal and Molecular Structure of Peracetylated 1,2-Dideoxy-D-*arabino*-aldopyranose, $C_{16}H_{21}O_9N$

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3,4,6-Tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*arabino*-hex-1-enopyranose crystallizes in space group $P2_12_12$ with $a = 11{\cdot}805$, $b = 18{\cdot}586$, $c = 8{\cdot}3196$ Å, $Z = 4$. The structure was solved by *MULTAN* and refined with a full-matrix least-squares procedure to $R = 0{\cdot}045$. The sugar ring exhibits an alternate sofa conformation; four C atoms and the ring O atom are coplanar and only one C atom is below this plane. The substituents are attached to C(3) in quasi-equatorial, and to C(4) and C(5) in equatorial positions. Owing to the absence of free hydroxyl groups, hydrogen bonds of the type O—H···O are not possible. In the crystal lattice the molecules are joined by van der Waals interactions only.

Introduction

3,4,6-Tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*arabino*-hex-1-enopyranose was synthesized (Pravdić & Fletcher, 1967; Pravdić, Franjić-Mihalić & Danilov, 1975) as the first representative of a new class of unsaturated amino sugars. The crystal structures of three compounds from this series have already been solved (Kojić-Prodić, Rogić & Ružić-Toroš, 1976; Rogić, Ružić-Toroš, Kojić-Prodić & Pravdić, 1977). The main interest of the structural study of the above series is the sugar-ring conformation. The presence of the double bond in these ring systems suggests a half-chair conformation. Indeed, it was found to be highly predominant in this series. The present structure determination, as part of this study, shows the sugar ring to be in an unusual alternate sofa conformation.

Experimental

The space group was determined as $P2_12_12$ from Weissenberg photographs recorded with Cu $K\alpha$ radiation. Cell constants were obtained by the least-squares procedure using the θ values for 19 reflexions in the interval $50{\cdot}2° < 2\theta < 57{\cdot}6°$ (at 18 °C) with Cu $K\alpha$ radiation. Crystal data are given in Table 1. Integrated intensities for 2151 independent reflexions with $\theta < 75°$ were measured on an Enraf–Nonius CAD-4 diffractometer using Cu $K\alpha$ radiation. The data were corrected for background, Lorentz and polarization effects.

Structure determination and refinement

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971) using normalized structure amplitudes calculated by the *K*-curve method (Hauptman & Karle, 1953). The solution was based on 271 reflexions with $|E| \geq 1{\cdot}50$. The *E* map corresponding to the solution with the best figure of merit revealed the positions of all the non-hydrogen atoms. The H atoms were located from a difference Fourier map with the exception of H(8,2), H(10,3), H(12,3), and H(16,3). Their positions were calculated on stereo-

Table 1. *Crystallographic and physical data*

3,4,6-Tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*arabino*-hex-1-enopyranose, $C_{16}H_{21}O_9N$

FW	371·35	Z	4
Space group	$P2_12_12$	D_m	1·361 g cm^{-3}
a	11·805 (2) Å*	D_c	1·361
b	18·586 (1)	μ(Cu $K\alpha$)	9·75 cm^{-1}
c	8·3196 (7)	Crystal shape	Prismatic
U	1825·4 Å^3	Crystal dimensions	0·4 × 0·04 × 0·2 mm

* Numbers in parentheses here and throughout this paper are the estimated standard deviations in the least significant digit.

Table 2. *Final atomic parameters* (× 10^4) *for the non-hydrogen atoms*

	x	y	z
C(1)	2374 (3)	−23 (2)	906 (4)
C(2)	2421 (3)	481 (2)	2021 (5)
C(3)	2655 (3)	315 (2)	3765 (4)
C(4)	2784 (3)	−489 (2)	4032 (4)
C(5)	3274 (3)	−864 (2)	2573 (5)
C(6)	3360 (3)	−1670 (2)	2752 (5)
C(7)	1227 (3)	1532 (2)	1287 (5)
C(8)	222 (3)	1078 (2)	1622 (6)
C(9)	3351 (3)	1591 (2)	1326 (5)
C(10)	3379 (4)	2355 (3)	725 (8)
C(11)	1872 (4)	825 (2)	6183 (5)
C(12)	759 (5)	1041 (3)	6939 (7)
C(13)	3170 (4)	−832 (2)	6756 (5)
C(14)	4102 (5)	−997 (3)	7901 (6)
C(15)	2164 (4)	−2416 (2)	4364 (6)
C(16)	972 (4)	−2631 (2)	4615 (9)
N	2298 (2)	1231 (2)	1542 (4)
O(0)	2553 (2)	−732 (1)	1194 (3)
O(1)	1127 (2)	2136 (2)	789 (5)
O(2)	4200 (2)	1268 (2)	1630 (5)
O(3)	1690 (2)	582 (1)	4679 (3)
O(4)	2773 (3)	850 (2)	6817 (4)
O(5)	3579 (2)	−627 (1)	5305 (3)
O(6)	2194 (3)	−868 (2)	7041 (4)
O(7)	2253 (2)	−1957 (1)	3137 (4)
O(8)	2953 (3)	−2610 (2)	5169 (5)

Table 3. *Positional* (× 10^3) *and isotropic thermal parameters* (× 10^2 Å^2) *for the hydrogen atoms*

	x	y	z	U
H(1)	218	6	−35	3·9
H(3)	348	56	407	3·4
H(4)	192	−63	436	3·3
H(5)	406	−64	239	3·9
H(6,1)	394	−178	347	4·9
H(6,2)	363	−186	169	4·9
H(8,1)	30	71	223	5·8
H(8,2)	−38	133	227	5·8
H(8,3)	−10	96	45	5·8
H(10,1)	433	251	60	7·6
H(10,2)	302	259	160	7·6
H(10,3)	294	236	−41	7·6
H(12,1)	8	128	617	6·7
H(12,2)	44	62	796	6·7
H(12,3)	106	149	768	6·7
H(14,1)	401	−160	823	7·2
H(14,2)	485	−95	730	7·2
H(14,3)	424	−68	856	7·2
H(16,1)	86	−286	566	7·3
H(16,2)	59	−231	435	7·3
H(16,3)	90	−305	374	7·3

chemical grounds. Refinement was by full-matrix least squares minimizing $\Sigma w||F_o| - |F_c||^2$ with $w = 1/\sigma_F^2$, where σ_F is as defined by Stout & Jensen (1968, equation *H*.14). The instability correction was 0·06 rather than 0·01. A scale factor, heavy-atom coordinates and anisotropic thermal parameters (235 variables in all) were refined. The H atoms were included in structure factor calculations only. For H atoms the isotropic thermal parameters are those of the bonded atoms.

The final R factors were: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0{\cdot}045$, and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2} = 0{\cdot}063$.*

Scattering factors given by *International Tables for X-ray Crystallography* (1974) and (for H) by Stewart, Davidson & Simpson (1965) were used.

All calculations were carried out at the Medical Foundation of Buffalo, Buffalo, USA, with local modifications of Nonius programs.

Positional parameters are listed in Tables 2 and 3.

Description and discussion of the structure

The structural formula and intramolecular distances are given in Fig. 1. The conformation of the sugar ring and the molecular packing are illustrated in Fig. 2.

Bond angles are listed in Table 4, and displacements of the atoms from the least-squares plane through the sugar ring in Table 5. Torsion angles defining the configuration and conformation are given in Table 6.

In the preparation of the unsaturated amino sugar reported in this paper, D compounds were used as the

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33070 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

starting materials, *i.e.* *N*-acetyl-D-mannosamine (Pravdić & Fletcher, 1967) and *N*-acetyl-D-glucosamine (Pravdić, Franjić-Mihalić & Danilov, 1975). There is no reason to expect a conversion from the D to the L enantiomer. During the structure determination of the title compound the D enantiomer was chosen, and the configuration and the conformation were defined in accordance with its torsion angles (Table 6).

The sugar ring in the crystal structure of the D-*arabino* compound exhibits an alternate sofa conformation: C(1), C(2), C(3), C(4), O(0) are coplanar, only C(5) is 0·699 Å below this plane (Table 5, Fig. 2). The substituents are attached to C(3) in quasi-equatorial, and to C(4) and C(5) in equatorial positions. A half-chair conformation is predominant for unsaturated sugars with six-membered rings. In the crystal structure of 1,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-2,3-dideoxy-α-D-*threo*-hex-2-enopyranose (Kojić-Prodić, Rogić & Ružić-Toroš, 1976) and its *erythro* isomer (Rogić, 1975) the ${}^{O}H_5$ conformation was observed. But 3,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*xylo*-hex-1-enopyranose and the D-*ribo* compound (Rogić, Ružić-Toroš, Kojić-Prodić & Pravdić, 1977)

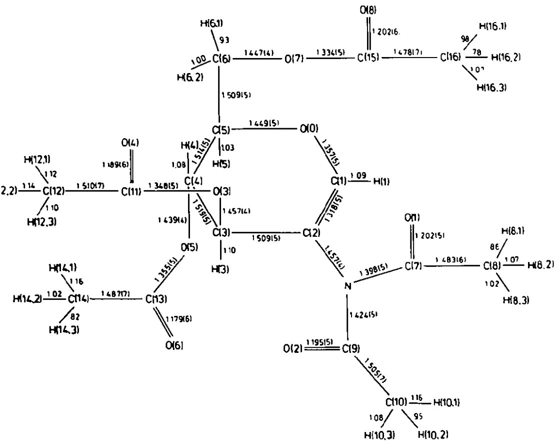

Fig. 1. The structural formula and intramolecular distances (Å).

Table 4. *Bond angles* (°)

Pyranose ring	
O(0)–C(1)–C(2)	124·0 (3)
C(1)–C(2)–C(3)	122·7 (3)
C(2)–C(3)–C(4)	111·1 (3)
C(3)–C(4)–C(5)	112·0 (3)
C(4)–C(5)–O(0)	109·4 (2)
C(5)–O(0)–C(1)	113·3 (2)
O(0)–C(1)–H(1)	110·2
C(2)–C(1)–H(1)	125·8
C(1)–C(2)–N	118·8 (3)
N–C(2)–C(3)	118·4 (2)
C(2)–C(3)–H(3)	107·4
H(3)–C(3)–O(3)	115·6
C(2)–C(3)–O(3)	106·8 (2)
H(3)–C(3)–C(4)	106·3
O(3)–C(3)–C(4)	109·7 (2)
H(4)–C(4)–O(5)	112·4
H(4)–C(4)–C(3)	100·3
C(3)–C(4)–O(5)	110·4 (2)
C(5)–C(4)–H(4)	116·8
O(5)–C(4)–C(5)	105·0 (2)
C(4)–C(5)–H(5)	106·1
C(4)–C(5)–C(6)	113·8 (3)
C(6)–C(5)–O(0)	106·6 (2)
C(6)–C(5)–H(5)	110·5
H(5)–C(5)–O(0)	110·5

O(3) acetyl group	
C(3)–O(3)–C(11)	118·3 (2)
O(3)–C(11)–O(4)	124·6 (3)
O(3)–C(11)–C(12)	109·7 (3)
O(4)–C(11)–C(12)	125·7 (3)

N acetyl groups	
C(2)–N–C(7)	121·0 (2)
N–C(7)–C(8)	117·8 (3)
O(1)–C(7)–C(8)	121·1 (3)
C(7)–N–C(9)	125·6 (3)
C(2)–N–C(9)	113·4 (2)
N–C(9)–C(10)	120·3 (3)
N–C(9)–O(2)	117·9 (3)
O(2)–C(9)–C(10)	121·7 (3)

O(5) acetyl group	
C(4)–O(5)–C(13)	118·3 (2)
O(5)–C(13)–O(6)	122·9 (3)
O(5)–C(13)–C(14)	111·4 (3)
O(6)–C(13)–C(14)	125·6 (3)

C(6)–O(7) acetyl group	
C(5)–C(6)–O(7)	109·1 (3)
C(5)–C(6)–H(6,1)	109·4
C(5)–C(6)–H(6,2)	106·2
H(6,1)–C(6)–H(6,2)	105·1
H(6,1)–C(6)–O(7)	116·0
H(6,2)–C(6)–O(7)	110·6
C(6)–O(7)–C(15)	118·5 (2)
O(7)–C(15)–O(8)	123·8 (3)
O(7)–C(15)–C(16)	110·9 (3)
O(8)–C(15)–C(16)	125·3 (3)

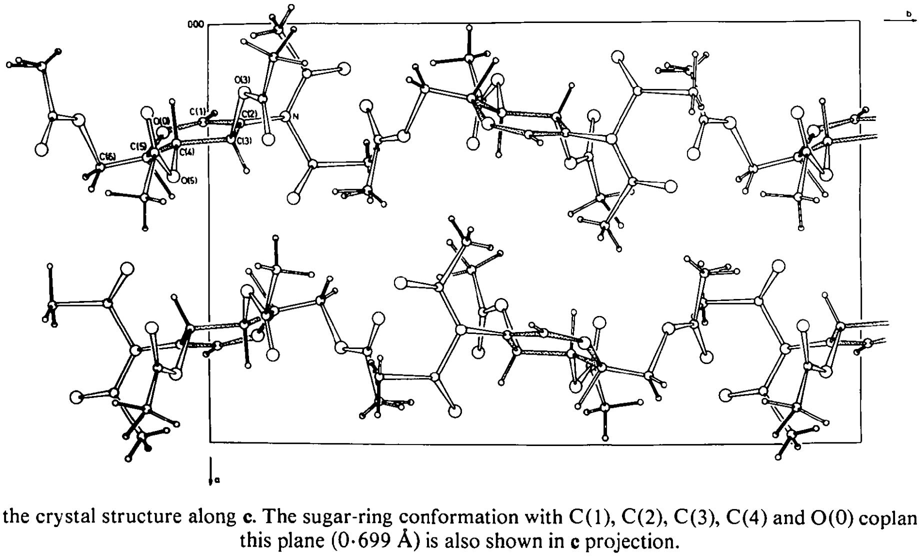

Fig. 2. A view of the crystal structure along **c**. The sugar-ring conformation with C(1), C(2), C(3), C(4) and O(0) coplanar and C(5) below this plane (0·699 Å) is also shown in **c** projection.

Table 5. *Deviations of atoms from the least-squares planes through the sugar ring*

Atoms included in the calculation of the least-squares plane are denoted by an asterisk.

Plane I		Plane II	
C(1)*	−0·005 Å	C(1)*	0·006 Å
C(2)*	0·009	C(2)*	−0·006
C(3)*	−0·008	C(3)*	0·003
C(4)*	0·004	C(4)	0·071
C(5)	−0·699	C(5)	−0·614
O(0)*	−0·065	O(0)*	−0·003

Table 6. *Torsion angles* (°)

In pyranose ring	
O(0)–C(1)–C(2)–C(3)	−1·5 (6)
C(1)–C(2)–C(3)–C(4)	−1·8 (5)
C(2)–C(3)–C(4)–C(5)	31·1 (4)
C(3)–C(4)–C(5)–O(0)	−57·8 (4)
C(4)–C(5)–O(0)–C(1)	54·9 (4)
C(5)–O(0)–C(1)–C(2)	−26·3 (5)
On pyranose ring	
O(0)–C(1)–C(2)–N	175·4 (3)
C(1)–C(2)–C(3)–H(3)	114·0
C(2)–C(3)–C(4)–H(4)	−93·6
C(2)–C(3)–C(4)–O(5)	147·7 (3)
C(3)–C(4)–C(5)–H(5)	61·3
C(3)–C(4)–C(5)–C(6)	−177·0 (3)
C(5)–O(0)–C(1)–H(1)	154·5
C(1)–C(2)–C(3)–O(3)	−121·4 (4)
H(5)–C(5)–O(0)–C(1)	−61·4
C(6)–C(5)–O(0)–C(1)	178·5 (3)
H(4)–C(4)–C(5)–O(0)	57·0
O(5)–C(4)–C(5)–O(0)	−177·7 (2)
O(1)–C(1)–C(2)–N	−20·9 (2)
H(1)–C(1)–C(2)–N	−5·5
N–C(2)–C(3)–H(3)	−62·9
N–C(2)–C(3)–O(3)	61·7 (4)
H(3)–C(3)–C(4)–H(4)	149·9
H(3)–C(3)–C(4)–O(5)	31·2
O(3)–C(3)–C(4)–H(4)	24·3
O(3)–C(3)–C(4)–O(5)	−94·5 (3)
H(4)–C(4)–C(5)–H(5)	176·1
H(4)–C(4)–C(5)–C(6)	−62·1
O(5)–C(4)–C(5)–H(5)	−58·5
O(5)–C(4)–C(5)–C(6)	63·2 (4)
Acetyl groups	
C(2)–N–C(7)–O(1)	−175·0 (4)
C(2)–N–C(7)–C(8)	3·9 (6)
C(2)–N–C(9)–O(2)	−3·8 (5)
C(2)–N–C(9)–C(10)	175·9 (4)
C(8)–C(7)–N–C(9)	−178·2 (4)
O(1)–C(7)–N–C(9)	2·8 (6)
C(7)–N–C(9)–O(2)	178·2 (4)
C(7)–N–C(9)–C(10)	−2·0 (6)
C(3)–O(3)–C(11)–O(4)	1·4 (5)
C(3)–O(3)–C(11)–C(12)	−177·3 (3)
C(4)–O(5)–C(13)–O(6)	−3·8 (5)
C(4)–O(5)–C(13)–C(14)	176·4 (3)
C(5)–C(6)–O(7)–C(15)	−131·4 (3)
C(6)–O(7)–C(15)–O(8)	−0·4 (6)
C(6)–O(7)–C(15)–C(16)	178·0 (3)
H(3)–C(3)–O(3)–C(11)	−28·9
H(4)–C(4)–O(5)–C(13)	−6·6
H(5)–C(5)–C(6)–O(7)	175·1
H(5)–C(5)–C(6)–H(6,1)	47·2
H(5)–C(5)–C(6)–H(6,2)	−65·7
Others	
C(1)–C(2)–N–C(7)	81·7 (5)
C(1)–C(2)–N–C(9)	−96·4 (4)
C(2)–C(3)–O(3)–C(11)	−148·2 (3)
C(3)–C(4)–O(5)–C(13)	104·5 (4)
C(3)–C(2)–N–C(7)	−101·3 (4)
C(3)–C(2)–N–C(9)	80·6 (4)
C(4)–C(3)–O(3)–C(11)	91·2 (3)
C(4)–C(5)–C(6)–O(7)	55·9 (4)
C(4)–C(5)–C(6)–H(6,1)	−72·0
C(4)–C(5)–C(6)–H(6,2)	175·1
O(0)–C(5)–C(6)–O(7)	−64·8 (4)
O(0)–C(5)–C(6)–H(6,1)	167·3
O(0)–C(5)–C(6)–H(6,2)	54·4
H(6,1)–C(6)–O(7)–C(15)	−7·3
H(6,2)–C(6)–O(7)–C(15)	112·2
O(0)–C(5)–C(6)–H(6,1)	167·3
O(0)–C(5)–C(6)–H(6,2)	54·4

appear in the $^{O}H_5$ conformation. Thus, in the D-*arabino* isomer, a $^{4}H_5$ conformation which would place all the substituents in the most favourable orientation was also expected. However, the crystal structure determination reveals a quite unusual type of conformation: five contiguous atoms are planar, the sixth atom is below this plane (Table 5, plane I). This conformation can be described as an alternate sofa conformation (Fig. 2). Such a form can also be compared with the envelope found in five-membered rings. If one considers the geometry of the six-membered ring this form with five coplanar atoms and one atom below this plane could be regarded as a transition state from chair to boat conformation. Analysing the displacements of the atoms from the least-squares planes I and II (Table 5) we can provide two explanations for the sugar-ring conformation. Plane I gives support to an alternate sofa conformation. In calculating plane II an attempt was made to show the $^{4}H_5$ conformation. In this case a highly distorted $^{4}H_5$ conformation with C(4) and C(5) atom displacements of 0·071 and −0·614 Å, respectively, should be accepted. Although the O(0) displacement (−0·065 Å, Table 5, plane I) is of the same order of magnitude as the C(4) displacement (0·071 Å, plane II), an alternate sofa conformation is preferred. The NMR spectral data ($J_{4,5}$ coupling constant of 6·0 Hz) for the D-*arabino* compound (Pravdić & Fletcher, 1967) are in accordance with the proposed conformation. Available data on an alternate sofa conformation in the series of unsaturated aldopyranoses are very limited. Therefore the appearance of this conformation cannot be explained at this time.

Sundaralingam (1968) has defined the conformation about C(5)–C(6) in pyranosides by the angle φ_{OO} = O(5)–C(5)–C(6)–O(6). In the present structure this angle is described by the sequence O(0)–C(5)–C(6)–O(7) and its value of −64·8 (4)° is in the range −60° ± 30° common for pyranoside derivatives.

The mean value of the C–C length in the ring is 1·514 (5) Å. In the acetyl groups the mean C–C length is 1·488 (7) Å. There are two categories of C to O bonds: the C–O bonds range from 1·439 (4) to 1·457 (4) Å and the O–C=O bonds from 1·334 (5) to 1·355 (5) Å. Endocyclic C(1)–O(0) at 1·357 (5) Å and C(5)–O(0) at 1·449 (5) Å are asymmetric. The asymmetry of the endocyclic C–O bonds is observed in some pyranose derivatives (Sundaralingam, 1968) but in 1,2-unsaturated aldopyranose it is still more pronounced owing to the influence of the C–C double bond. The presence of the C(1)=C(2) bond excludes the appearance of the anomeric effect and its influence on the asymmetry of the C–O endocyclic bonds. The carbonyl bonds are in the range 1·179 (6) to 1·202 (6) Å.

The mean value of the endocyclic valence angles of the C atom in sp^3 hybridization is 110·8 (3)°. The valence angle of the ring O is 113·3 (2)°. In the crystal structures of the D-*xylo* and D-*ribo* isomers (Rogić, Ružić-Toroš, Kojić-Prodić & Pravdić, 1977) this angle is 116·1 (3) and 115·4 (6)° respectively. The reason for such differences among these 1,2-unsaturated aldopyranoses is not obvious. The C(sp^3) valence angles exterior to the pyranose ring are in a wider range [105·0 (2) to 113·8 (3)°] than the interior angles.

All hydroxyl groups are acetylated and O–H···O hydrogen bonds are not possible. The intermolecular distances do not give any evidence of C–H···O contacts. In the crystal structure, molecules are connected by van der Waals forces only.

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References

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

HAUPTMAN, H. & KARLE, J. (1953). *Solution of the Phase Problem.* I. *The Centrosymmetric Crystal.* ACA Monograph No. 3. Pittsburgh: Polycrystal Book Service.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

KOJIĆ-PRODIĆ, B., ROGIĆ, V. & RUŽIĆ-TOROŠ, Ž. (1976). *Acta Cryst.* B**32**, 1833–1838.

PRAVDIĆ, N. & FLETCHER, H. G. JR (1967). *J. Org. Chem.* **32**, 1806–1810, 1811–1814.

PRAVDIĆ, N., FRANJIĆ-MIHALIĆ, I. & DANILOV, B. (1975). *Carbohydr. Res.* **45**, 302–306.

ROGIĆ, V. (1975). PhD Thesis, Faculty of Science, Univ. of Zagreb.

ROGIĆ, V., RUŽIĆ-TOROŠ, Ž., KOJIĆ-PRODIĆ, B. & PRAVDIĆ, N. (1977). *Acta Cryst.* B**33**, 3737–3743.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination.* New York: Macmillan.

SUNDARALINGAM, M. (1968). *Biopolymers*, **6**, 189–213.