respectively], are significantly less than the ideal value of 120°. Similar values of this angle have been reported for 2,2′-dichlorobiphenyl [116·2 (2)°; Rømming, Seip & Øymo, 1974], 4,4′-dichlorobiphenyl [116·9 (4) and 118·2 (5)°; Brock, Kuo & Levy, 1978] and biphenyl (118·9°; Trotter, 1961). The phenyl rings are planar to within 0·013 Å.

The C(4)′—Cl(4)′ bond distance, 1·741 (4) Å, is nearly the same as those found in 2,2′-dichlorobiphenyl [1·741 (3) Å] and 4,4′-dichlorobiphenyl [1·733 (5) and 1·754 (5) Å], but the C(2)—Cl(2) bond distance, 1·781 (4) Å, is greater.

The dihedral angle between the two phenyl rings is 49·6 (1)°. In 2,2′-dichlorobiphenyl (Rømming, Seip & Øymo, 1974) this angle is larger due to double *ortho* substitution (66·8°) and in 4,4′-dichlorobiphenyl (Brock, Kuo & Levy, 1978) these angles are smaller 38·7 and 42·1°) due to the absence of *ortho* substitution.

The crystallization method developed for PCB 35 (van der Sluis, Moes, Behm, Smykalla, Beurskens & Lenstra, 1990) has proven its usefulness for obtaining single crystals of PCB 8 as well. It is anticipated that the method will be generally applicable to other PCB's, thereby offering possibilities for determining their molecular structures by X-ray diffraction. The molecular geometry data provided by these analyses might prove useful in determining structure–activity relationships for toxicological studies of PCB's (*cf.* McKinney, Gottschalk & Pedersen, 1983).

References

Beurskens, P. T., Beurskens, G., Strumpel, M. & Nordman, C. E. (1986). *Patterson and Pattersons*, edited by J. P. Glusker, B. K. Patterson & M. Rossi, pp. 356–367. Oxford: Clarendon Press.

Beurskens, P. T., Bosman, W. P., Doesburg, H. M., van den Hark, Th. E. M., Prick, P. A. J., Noordik, J. H., Beurskens, G., Gould, R. O. & Parthasarathi, V. (1983). *Conformation in Biology*, edited by R. Srinivasan & R. H. Sarma, pp. 389–406. New York: Adenine Press.

Beurskens, G., Noordik, J. H. & Beurskens, P. T. (1980). *Cryst. Struct. Commun.* **9**, 23–28.

Brock, C. P., Kuo, M. S. & Levy, H. A. (1978). *Acta Cryst.* B**34**, 981-985.

Grant, D. F. & Gabe, E. J. (1978). *J. Appl. Cryst.* **11**, 114–120.

Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* A**30**, 580–584.

McKinney, J. D., Gottschalk, K. E. & Pedersen, L. (1983). *J. Mol. Struct.* **104**, 445–450.

Moes, G. W. H. & Lenstra, A. T. H. (1986). *Toxicol. Environ. Chem.* **12**, 255–266.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Rømming, C., Seip, H. M. & Øymo, I. M. A. (1974). *Acta Chem. Scand. Ser. A*, **28**, 507–514.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Sluis, P. van der, Moes, G. W. H., Behm, H., Smykalla, C., Beurskens, P. T. & Lenstra, A. T. H. (1990). *Toxicol. Environ. Chem.* **28**, 121–127.

Spek, A. L. (1982). *The EUCLID Package*. In *Computational Crystallography*, edited by D. Sayre, p. 528. Oxford: Clarendon Press.

Trotter, J. (1961). *Acta Cryst.* **14**, 1135–1140.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Wolff, M. S., Thornton, J., Fischbein, A., Lilis, R. & Selikoff, I. J. (1982). *Toxicol. Appl. Pharmacol.* **62**, 294.

Acta Cryst. (1990). C**46**, 2171–2174

Conformation of the Xyl-β-(1→2)-Man Glycosidic Linkage. Structure of 3,4,6-Tri-*O*-acetyl-1-*O*-methyl-2-*O*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-β-D-mannopyranose

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Abstract. $C_{24}H_{34}O_{16}$, $M_r = 578{\cdot}52$, monoclinic, $P2_1$, $a = 5{\cdot}580$ (2), $b = 18{\cdot}959$ (4), $c = 13{\cdot}415$ (3) Å, $\beta = 92{\cdot}71$ (1)°, $V = 1417{\cdot}6$ (7) Å^3, $Z = 2$, $D_x = 1{\cdot}355$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 1{\cdot}1$ cm^{-1}, $F(000) = 612$, $T = 295$ K, $R = 0{\cdot}070$ for 507 unique observed diffractometer data [$I \geq 3\sigma(I)$]. Only very small crystals could be obtained, but the resulting moderate quality of the diffraction data did not prevent the determination of the important conformational features of the title compound. Both glycopyranosyl moieties have the normal $^4C_1$ conformation. For the title compound, values of the β-(1→2) glycosidic linkage angles ψ and φ are found to agree well with those observed in four related compounds as determined by NMR experiments.

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Introduction. Xylose-containing N-linked carbohydrate chains occur in glycoproteins of plant (*e.g.* D'Andrea, Bouwstra, Kamerling & Vliegenthart, 1988) and animal origin (*e.g.* van Kuik, Sijbesma, Kamerling, Vliegenthart & Wood, 1987). They contain the β-D-Xyl-(1→2)-Man linkage. Recently a series of tri- and tetrasaccharides including β-D-Xyl-(1→2)-[α-D-Man-(1→3)]-β-D-Man-OMe (1), β-D-Xyl-(1→2)-[α-D-Man-(1→6)]-β-D-Man-OMe (2) and β-D-Xyl-(1→2)-[α-D-Man-(1→3)]-[α-D-Man-(1→6)]-β-D-Man-OMe (3), which are the building blocks of these carbohydrate chains, have been synthesized (Kerékgyártó, Kamerling, Bouwstra, Vliegenthart & Lipták, 1989) and characterized by NMR spectroscopy (Bouwstra, Kerékgyártó, Kamerling & Vliegenthart, 1989). Conformational data for (1)–(3) were obtained by rotating-frame nuclear Overhauser enhancement spectroscopy in combination with hard-sphere *exo*-anomeric (HSEA) calculations (Leeflang, Bouwstra, Kerékgyártó, Kamerling & Vliegenthart, 1990).

Also for the carbohydrate chain of the proteolytic enzyme bromelain from pineapple stem {α-D-Man-(1→6)-[β-D-Xyl-(1→2)]-β-D-Man-(1→4)-β-D-GlcNAc-(1→4)-[α-L-Fuc-(1→3)]-β-D-GlcNAc-(1→N)-Asn~, (4)} a conformational model has been deduced from NMR data using homo- and heteronuclear correlation spectroscopy, two-dimensional homonuclear Hartmann–Hahn and two-dimensional nuclear Overhauser enhancement experiments and HSEA calculations (Bouwstra, Spoelstra, De Waard, Leeflang, Kamerling & Vliegenthart, 1989). It was established that the conformations around the glycosidic linkages are more or less conserved in all four carbohydrates.

The present study was undertaken to find out whether this conformation could also be observed in the solid state. Fully acetylated β-D-Xyl-(1→2)-β-D-Man-OMe (5) was chosen as a model compound, because the least crystallization problems could be expected from this small hydroxyl-free saccharide. The absence of free hydroxyl groups prevents strong hydrogen-bonded crystal packing which could impose certain conformations. In addition, the proposed conformation around the Xyl-β-(1→2)-Man glycosidic linkage in the liquid can easily accommodate the introduction of the relatively bulky acetyl groups without a conformational change, therefore making comparison possible.

Experimental. A transparent crystal 0·06 × 0·06 × 0·8 mm was obtained by vapor diffusion of water into an ethanol solution. Despite numerous attempts no larger crystal could be obtained, owing to the very limited amount of material available.

Data were collected on a CAD-4F diffractometer for a crystal mounted on a glass fiber. The cell parameters were calculated by least squares from the setting angles of 25 reflections with $4 \le \theta \le 11°$. 2634 reflections were scanned (h 0→6, k 0→18, l −15→15; $\theta \le 25°$; $\omega/2\theta$-scan mode; $\Delta\omega = 0{\cdot}50° + 0{\cdot}35°\tan\theta$; Zr-filtered Mo $K\alpha$ radiation). The final scan speed was adjusted to obtain $\sigma(I)/I = 0{\cdot}02$ and a scan time limit of 60 s. Two reference reflections ($\bar{3}4\bar{2}$, 342) showed negligible decay during the 61 h of X-ray exposure time. The data were corrected for Lp but not for absorption, resulting in the unique set of 2385 reflections ($R_{int} = 0{\cdot}069$) of which 507 were used in the structure determination [$I > 3\sigma(I)$]. $\sigma^2(I) = \sigma^2_{cs}(I) + (pI)^2$ (McCandlish, Stout & Andrews, 1975) with $p = 0{\cdot}086$.

All non-hydrogen atoms were found by direct methods followed by peak optimization (*SHELXS*86; Sheldrick, 1986). The structure was refined on F by full-matrix least-squares procedures using isotropic thermal parameters for all non-hydrogen atoms (*SHELX*76; Sheldrick, 1976). Anisotropic thermal parameters could not be used due to an insufficient number of data as a result of

Table 1. *Final coordinates and isotropic thermal parameters and their e.s.d.'s in parentheses*

	x	y	z	U_{iso} (Å²)
O(1)	0·726 (4)	0·345 (2)	0·150 (1)	0·038 (7)
O(2)	0·764 (4)	0·290 (2)	−0·043 (2)	0·037 (7)
O(3)	0·340 (4)	0·327 (2)	−0·175 (2)	0·034 (7)
O(4)	0·302 (4)	0·481 (2)	−0·166 (2)	0·042 (8)
O(5)	0·480 (4)	0·431 (2)	0·087 (2)	0·037 (7)
O(21)	0·566 (5)	0·188 (2)	−0·016 (2)	0·08 (1)
O(31)	0·630 (5)	0·317 (2)	−0·287 (2)	0·066 (9)
O(41)	−0·053 (6)	0·516 (2)	−0·129 (2)	0·09 (1)
O(101)	1·123 (4)	0·258 (2)	0·161 (2)	0·043 (7)
O(103)	0·710 (4)	0·463 (2)	0·282 (1)	0·021 (6)
O(104)	0·773 (4)	0·403 (2)	0·466 (2)	0·040 (7)
O(105)	0·929 (4)	0·258 (2)	0·307 (2)	0·037 (7)
O(106)	0·876 (5)	0·189 (2)	0·489 (2)	0·042 (7)
O(131)	0·960 (6)	0·521 (2)	0·183 (2)	0·059 (8)
O(141)	0·369 (6)	0·400 (2)	0·471 (2)	0·08 (1)
O(161)	0·547 (6)	0·132 (2)	0·525 (2)	0·10 (1)
C(1)	0·666 (6)	0·3837	0·062 (2)	0·015 (9)
C(2)	0·562 (9)	0·334 (2)	−0·021 (3)	0·06 (1)
C(3)	0·492 (6)	0·375 (2)	−0·111 (2)	0·024 (9)
C(4)	0·328 (6)	0·434 (2)	−0·084 (2)	0·03 (1)
C(5)	0·419 (8)	0·477 (2)	0·007 (3)	0·05 (1)
C(21)	0·746 (8)	0·222 (3)	−0·049 (3)	0·05 (1)
C(22)	0·974 (7)	0·185 (3)	−0·070 (3)	0·06 (1)
C(31)	0·430 (7)	0·309 (2)	−0·261 (2)	0·03 (1)
C(32)	0·239 (6)	0·268 (2)	−0·323 (2)	0·04 (1)
C(41)	0·109 (8)	0·529 (3)	−0·183 (3)	0·05 (1)
C(42)	0·139 (8)	0·573 (2)	−0·261 (3)	0·08 (2)
C(101)	1·074 (7)	0·298 (2)	0·243 (3)	0·05 (1)
C(102)	0·942 (6)	0·365 (2)	0·205 (2)	0·012 (8)
C(103)	0·879 (7)	0·406 (3)	0·293 (2)	0·04 (1)
C(104)	0·754 (6)	0·363 (2)	0·376 (2)	0·018 (9)
C(105)	0·883 (7)	0·294 (2)	0·396 (2)	0·04 (1)
C(106)	0·739 (7)	0·251 (3)	0·461 (2)	0·05 (1)
C(111)	1·316 (7)	0·209 (2)	0·190 (3)	0·07 (1)
C(131)	0·764 (7)	0·516 (2)	0·219 (2)	0·03 (1)
C(132)	0·587 (6)	0·574 (2)	0·215 (3)	0·05 (1)
C(141)	0·558 (7)	0·419 (2)	0·509 (3)	0·03 (1)
C(142)	0·607 (7)	0·466 (2)	0·592 (3)	0·06 (1)
C(161)	0·762 (7)	0·132 (2)	0·528 (3)	0·04 (1)
C(162)	0·933 (7)	0·079 (3)	0·561 (3)	0·07 (1)

the small crystal size. All H atoms were introduced at expected positions (C—H = 0·98 Å) and refined in the riding mode on their carrier atoms with an isotropic thermal parameter common to all H atoms [U = 0·09 (2) Å^2]. Final convergence was reached at R = 0·070 [wR = 0·072, $w = 1{\cdot}0/\sigma^2(F)$; S = 2·19; $(\Delta/\sigma)_{max}$ = 0·07; number of refined parameters = 161]. No residual density was outside the range −0·30 and +0·32 e Å^{-3}. Scattering factors were from Cromer & Mann (1968), anomalous-dispersion corrections from Cromer & Liberman (1970). The final atomic coordinates and isotropic temperature factors are listed in Table 1.* The program package *EUCLID* (Spek, 1982) was used for geometrical calculations and illustrations. All calculations were carried out on a MicroVAX II.

Discussion. A perspective view of the molecule with adopted labeling is depicted in Fig. 1. This labeling is also used for the other compounds discussed. Lack of data and low accuracy of the observed data, both caused by the small size of the crystal, result in high standard deviations of atomic parameters.

Both glycopyranosyl residues have the normal $^4C_1$ conformation. The conformation of the acetyl groups connected directly to the sugar rings is such that the C=O bond of the acetyl group is roughly parallel to the nearest C—H bond of the sugar moiety. This is a common observation for acetylated sugars [*e.g.* in 1,2,4,6-tetra-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-α-D-galactopyranose (Foces-Foces, Cano & Garcia-Blanco, 1980) and 1,2,4,6-tetra-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-glucopyranose (Perez, Vergelati & Tran, 1985)].

The calculated density is 1·355 g cm^{-3}, which is close to the normal range for acetylated oligosaccharides [*e.g.* 1·283 g cm^{-3} in 1,2,4,6-tetra-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyransoyl)-α-D-galactopyranose (Foces-Foces, Cano & Garcia-Blanco, 1980), 1·310 g cm^{-3} in 1,2,3,6-tetra-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-ga-lactopyranose (Foces-Foces, Cano & Garcia-Blanco, 1981) and 1·296 g cm^{-3} in 1,2,4,6-tetra-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-glucopyranose (Perez, Vergelati & Tran, 1985)]. These densities are significantly lower than in saccharides with free hydroxyl groups [*e.g.* 1·570 g cm^{-3} in *O*-α-D-galactopyranosyl-(1–4)-D-galactopyranose (Svensson, Albertsson, Svensson, Magnusson & Dahmen, 1986) and 1·577 g cm^{-3} in *O*-β-D-mannopyranosyl-(1–4)-α-D-mannopyranose (Sheldrick, Mackie & Akrigg, 1984)]. This points to a looser packing. It may be expected that such a loose packing modifies the conformation of the glycosidic linkage to a lesser extent than a tight hydrogen-bonded packing, when compared with a conformation in solution.

The conformation around the glycosidic bond is described by the bond angle τ = C(102)—O—C(1) and two torsion angles: ψ = H(102)—C(102)—O—C(1) and φ = H(1)—C(1)—O—C(102). For compounds (1)–(4) the angle τ was set at 117° for the deriviation of the torsion angles from the NMR data. The torsion angles could not be determined uniquely from the NMR data because only one distance restraint could be used. Therefore HSEA calculations were used to narrow down the ψ/φ combinations. Results are summarized in Table 2. Although no standard deviations are given we believe that 10–20° is a fair estimate. In addition, it should be kept in mind that the torsion angles derived from NMR data reflect a time average of a distribution of angles. Within this experimental error

* Lists of H-atom positions, bond angles and distances, torsion angles, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53083 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

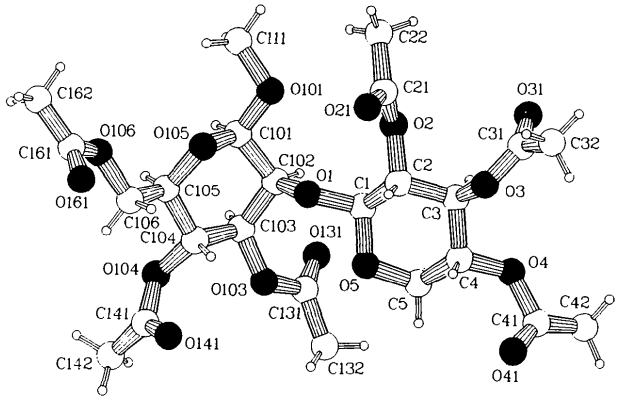

Fig. 1. *PLUTON* (Spek, 1982) drawing of the molecular structure with adopted labeling.

Table 2. *Conformation around the β-(1→2) glycosidic linkage (ψ and φ) and about the* C(5)—C(6) *bond in mannose (ω) for compounds* (1) *to* (6) *in* (°)

Compound indentification is given in the *Introduction*. ω-Conformer populations are given in parentheses with a % sign, otherwise standard deviations are given in parentheses.

	Link	τ	ψ	φ	ω
(1)	Xylβ-(1→2)-Man	117*	40	5	—
(2)	Xylβ-(1→2)-Man	117*	50	0	180(40%) − 60(60%)
(3)	Xylβ-(1→2)-Man	117*	40	5	180(40%) − 60(60%)
(4)	Xylβ-(1→2)-Man	117*	50	0	180(> 98%)
(5)	Xylβ-(1→2)-Man	117 (3)	20 (3)	−18 (5)	−55 (5)
(6)	Glcβ-(1→2)-Glc	113·6	41·7	−19·8	172·1

* Angle set at 117° by authors.

the conformations around the Xyl-β-(1→2)-Man glycosidic linkage in solution and the crystal are alike. X-ray evidence on the β-(1→2) glycosidic linkage is very scarce. The first reported crystal structure that contains such a linkage is sophorose [*O*-β-D-glucosyl-(1→2)-α-D-glucose (6); Ohanessian, Longchambon & Arene, 1978]. The ψ/φ values are quite comparable with those found in the xylose–mannose linkage. The conformations of (1)–(6) are compared in Fig. 2. The torsion angle ω found in the title compound corresponds to that of the predominant conformations in (2) and (3). No value for ω is determined for (1), while the discrepancy with (4) is not surprising since its oxygen is involved in a glycosidic linkage.

An intramolecular hydrogen bond, which influences the geometry of the glycosidic linkage, is not uncommon and is for instance found in α-lactose (Fries, Rao & Sundaralingam, 1971) and β-lactose (Chu & Jeffrey, 1968). For compounds (1)–(4) the quoted O—O distances are too large (> 3·1 Å) to allow a strong interaction. In compound (6) no intramolecular hydrogen-bond is found. For compound (5) hydrogen-bond formation is impossible due to the acetylation and methylation of the hydroxyl groups. The smallest observed O—O distance is 2·92 Å [O(103)—O(5)] making a hydrogen-bond interaction possible in the absence of acetylation.

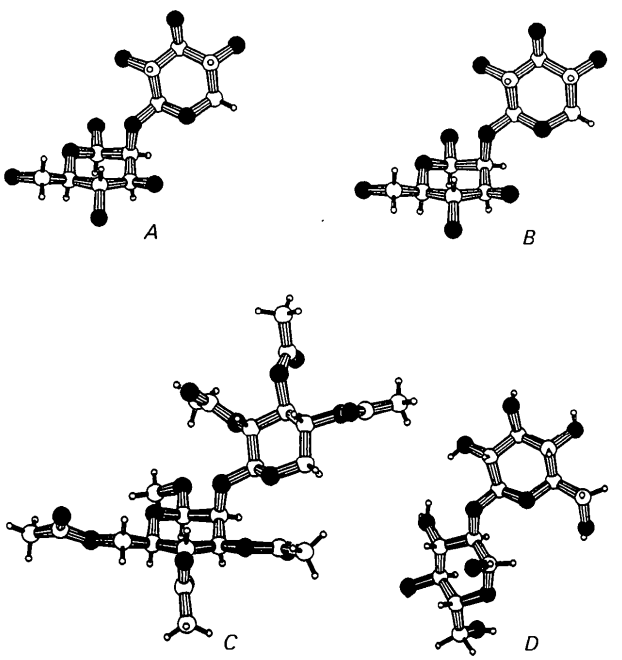

Fig. 2. Comparison of the conformation around the β-(1→2) glycosidic linkage. *A* is the conformation of (1) and (3), *B* is the conformation of (2) and (4) [ω in (4) is set at −60°], *C* is the conformation of the title compound, (5), and *D* is the conformation of (6). For (1)–(4) only the Xyl-β-(1→2)-Man part is shown.

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References

BOUWSTRA, J. B., KERÉKGYÁRTÓ, J., KAMERLING, J. P. & VLIEGENTHART, J. F. G. (1989). *Carbohydr. Res.* **186**, 39–49.

BOUWSTRA, J. B., SPOELSTRA, E. C., DE WAARD, P., LEEFLANG, B. R., KAMERLING, J. P. & VLIEGENTHART, J. F. G. (1989). *Carbohydr. Res.* **186**, 39–49.

CHU, S. S. C. & JEFFREY, G. A. (1968). *Acta Cryst.* B**24**, 830–838.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

D'ANDREA, G., BOUWSTRA, J. B., KAMERLING, J. P. & VLIEGENTHART, J. F. G. (1988). *Glycoconj. J.* **5**, 151–157.

FOCES-FOCES, C., CANO, F. H. & GARCIA-BLANCO, S. (1980). *Acta Cryst.* **36**, 377–384.

FOCES-FOCES, C., CANO, F. H. & GARCIA-BLANCO, S. (1981). *Acta Cryst.* **37**, 1270–1275.

FRIES, D. C., RAO, S. T. & SUNDARALINGAM, M. (1971). *Acta Cryst.* B**27**, 994–1001.

KERÉKGYÁRTÓ, J., KAMERLING. J. P., BOUWSTRA, J. B., VLIEGENTHART, J. F. G. & LIPTÁK, A. (1989). *Carbohydr. Res.* **186**, 51–62.

KUIK, J. A. VAN, SIJBESMA, R. P., KAMERLING, J. P., VLIEGENTHART, J. F. G. & WOOD, E. J. (1987). *Eur. J. Biochem.* **169**, 399–411.

LEEFLANG, B. R., BOUWSTRA, J. B., KERÉKGYÁRTÓ, J., KAMERLING, J. P. & VLIEGENTHART, J. F. G. (1990). *Carbohydr. Res.* In the press.

MCCANDLISH, L. E., STOUT, G. H. & ANDREWS, L. C. (1975). *Acta Cryst.* A**31**, 245–249.

OHANESSIAN, J., LONGCHAMBON, F. & ARENE, F. (1978). *Acta Cryst.* B**34**, 3666–3671.

PEREZ, S., VERGELATI, C. & TRAN, V. H. (1985). Acta Cryst. B**41**, 262–267.

SHELDRICK, B., MACKIE, W. & AKRIGG, D. (1984). *Carbohydr. Res.* **132**, 1–6.

SHELDRICK, G. M. (1976). *SHELX*76. Program for cyrstal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1986). *SHELXS*86. Program for the solution of crystal structures. Univ. of Göttingen, Federal Republic of Germany.

SPEK, A. L. (1982). *The EUCLID Package*. In *Computational Crystallography*, edited by D. SAYRE, p 528. Oxford: Clarendon Press.

SVENSSON, G., ALBERTSSON, J., SVENSSON, C., MAGNUSSON, G. & DAHMEN, J. (1986). *Carbohydr. Res.* **146**, 29–38.