Methyl α-L-sorboside monohydrate

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Methyl α-L-sorboside monohydrate, C7H14O6·H2O, was prepared from the rare sugar α-L-sorbose, C6H12O6, and crystallized. It was confirmed that methyl α-L-sorboside formed α-pyranose with a C5 conformation and crystallized with one water molecule of crystallization. In the crystal, molecules are linked by O—H⋯O hydrogen bonds, forming a three-dimensional network. The unit-cell volume of the title compound, methyl α-L-sorboside monohydrate, is 481.13 (2) Å³ (Z = 2), which is about 108.16 Å³ (29.0%) greater than that of half the amount of the chemical α-L-sorbose [745.94 (2) Å³ (Z = 4)].

Structure description

The rare sugar α-L-sorbose was the first α-form hexose found in nature (Itoh et al., 1995; Khan et al., 1992; Nordenson et al., 1979). Methyl α-L-sorboside (Fig. 1) is an α-pyranose form in which the OH group located on the C-2 position in α-L-sorbose is converted into a methoxy group OCH3. The molecular weight of methyl α-L-sorboside, C7H14O6·H2O, is 212.20. On the other hand, that of α-L-sorbose, C6H12O6, is 180. The increase in molecular weight from sorbose to sorboside is thus about 18%. In this study, we aimed to produce a single crystal of methyl α-L-sorboside that contains sorbose molecules and water molecules in the ratio of 1 to 1 in the unit cell. The crystal system of ethyl α-L-sorboside (Nagayama et al., 2020), which we reported previously, is orthorhombic, while that of methyl α-L-sorboside is triclinic. The space group of ethyl α-L-sorboside is P212121 (Z = 4), while that of methyl α-L-sorboside is P1 (Z = 2). Furthermore, concerning the crystal solvent, ethyl α-L-sorboside contains no solvent molecules in the crystal, whereas crystals of methyl α-L-sorboside contain water molecules as crystallization water. Thus, methyl α-L-sorboside is only one molecule shorter in the alkyl-carbon chain length than ethyl
l-sorbose, but the crystal system, space group, and crystal solvent are significantly different.

It was confirmed that methyl l-sorbose formed an α-pyranose with a $^6$C$_3$ conformation and a water molecule of crystallization. Comparing these two independent methyl l-sorbose molecules, we found that the positions of the carbon and oxygen atoms are roughly the same. On the other hand, the positions of the hydrogen atoms determined from the X-ray diffraction measurement results are different, resulting in different orientations of the hydroxy groups.

Hydrogen bonds (Fig. 2, Table 1) occur between the hydroxy groups of the methyl l-sorbose molecules or through the water molecules of crystallization, and the overall network extends parallel to the $ab$ plane. However, the hydrogen-bond network is weak in the $c$-axis direction because the hydrophobic methoxy group does not take part in any hydrogen bonds. Therefore, the three-dimensional hydrogen-bonding network has become a pseudo two-dimensional network.

### Table 1

Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | $H$···$A$ | $D$···$A$ | $D$—H···$A$ |
|-------------|--------|----------|----------|-------------|
| O4—H4A···O3 | 0.85   | 1.94     | 2.729(7) | 154         |
| O11—H11···O21$^1$ | 1.00(8) | 1.87(8) | 2.799(4) | 154(6)      |
| O13—H13···O24 | 0.82   | 1.83     | 2.643(4) | 169         |
| O14—H14···O11$^{ii}$ | 0.82   | 1.94     | 2.719(4) | 159         |
| O15—H15···O13$^{iii}$ | 0.82   | 2.12     | 2.898(4) | 158         |
| O21—H21···O25$^{iv}$ | 0.82   | 2.10     | 2.874(4) | 157         |
| O23—H23···O14$^{v}$ | 0.82   | 1.84     | 2.653(4) | 169         |
| O24—H24···O4 | 0.82   | 1.83     | 2.650(5) | 176         |
| O25—H25···O23$^{iii}$ | 0.82   | 1.97     | 2.709(5) | 150         |

Symmetry codes: (i) $x+1, y-1, z$; (ii) $x, y+1, z$; (iii) $x+1, y, z$; (iv) $x-1, y+1, z$; (v) $x-1, y, z$.

### Table 2

Experimental details.

| Crystal data | Chemical formula | $C_7H_{14}O_6$·$H_2O$ |
|--------------|------------------|------------------------|
| Crystal system, space group | Triclinic, $P1$ | $C_7H_{14}O_6·H_2O$ |
| Temperature (K) | 296 | $a = 6.7320$ (5), 7.7574 (5), 10.6128 (8) |
| $\alpha, \beta, \gamma$ ($^\circ$) | $67.596$ (5), 65.476 (5) | $82.458$ (6), 72.596 (5), 65.476 (5) |
| $\beta$, $\gamma$, $\delta$ ($^\circ$) | $111.162$ (6) | $111.162$ (6) |
| $V$ ($\AA^3$) | 481.13 (6) | 481.13 (6) |
| $Z$ | 2 | 2 |
| Radiation type | Cu $K\alpha$ | Cu $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 1.15 | 1.15 |
| Crystal size (mm) | $0.1 \times 0.1 \times 0.1$ | $0.1 \times 0.1 \times 0.1$ |

Data collection

| Rigaku R-Axis Rapid | Rigaku R-Axis Rapid |
|---------------------|---------------------|
| $T_{min}, T_{max}$ | 0.098, 1.000 |
| No. of measured, independent and observed $|F| > 2\sigma(F)$ | 5541, 2880, 2751 |
| $R_{int}$ (sin $\theta/\lambda$)$_{max}$ ($\AA^{-1}$) | 0.045 | 0.045 |
| 0.602 | 0.602 |

Refinement

| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.048, 0.125, 1.13 |
| No. of reflections | 2880 |
| No. of parameters | 272 |
| No. of restraints | 3 |
| $H$-atom treatment | H atoms treated by a mixture of independent and constrained refinement |

### Synthesis and crystallization

Methyl l-sorbose, α-sorbusyranoside form, was prepared by Fischer glycosidation from l-sorbose and methanol (Taguchi et al., 2016).
The Fisher method produces isomers such as α-, β-, and furanose. Therefore, chromatographic separation using an ion-exchange resin was performed. The reaction mixture was evaporated under vacuum at 40°C to remove the solvent and dissolved in water. Then the mixture was applied to a column of ion-exchange resins (Dowex 50W-X2, Ca²⁺ form) and was eluted with deionized water. After separation, each fraction was analysed by HPLC, and fractions containing the α-pyranoside type were collected and concentrated to syrup. Small single crystals were obtained by placing the syrup in a Petri dish and keeping it at 4°C. It is obvious that the synthesized methyl α-L-sorbose is still in the L-form after dehydrative condensation, because L-sorbose is used as the starting material. The absolute structure was also confirmed by the Flack parameter (Flack, 1983).

Refinement
Crystal data, data collection and structure refinement details are summarized in Table 2.

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full crystallographic data

Methyl \(\alpha\)-l-sorboside monohydrate

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Crystal data

\[\text{C}_7\text{H}_{14}\text{O}_6\cdot\text{H}_2\text{O}\]

Mr = 212.20

Triclinic, \(P\bar{1}\)

\(a = 6.7320 (5)\) Å

\(b = 7.7574 (5)\) Å

\(c = 10.6128 (8)\) Å

\(\alpha = 82.458 (6)°\)

\(\beta = 72.596 (5)°\)

\(\gamma = 65.476 (5)°\)

\(V = 481.13 (6)\) Å³

Z = 2

\(F(000) = 228\)

\(D_\text{x} = 1.465\) Mg m\(^{-3}\)

\(\lambda = 1.54187\) Å

Cell parameters from 5608 reflections

\(\theta = 4.4–68.4°\)

\(\mu = 1.15\) mm\(^{-1}\)

\(T = 296\) K

Block, clear light colourless

0.1 × 0.1 × 0.1 mm

Data collection

Rigaku R-AXIS RAPID diffractometer

\(\omega\) scans

Absorption correction: multi-scan

(ABSCOR; Rigaku, 1995)

\(T_{\text{min}} = 0.698, T_{\text{max}} = 1.000\)

5541 measured reflections

2880 independent reflections

2751 reflections with \(I > 2\sigma(I)\)

\(R_{\text{int}} = 0.045\)

\(\theta_{\text{max}} = 68.2°, \theta_{\text{min}} = 4.4°\)

\(h = -8\rightarrow8\)

\(k = -9\rightarrow9\)

\(l = -12\rightarrow12\)

Refinement

Refinement on \(F^2\)

Least-squares matrix: full

\(R[F^2 > 2\sigma(F^2)] = 0.048\)

\(wR(F^2) = 0.125\)

\(S = 1.13\)

2880 reflections

272 parameters

3 restraints

Primary atom site location: iterative

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

\(w = 1/\left[\sigma^2(F_c^2) + (0.0704P)^2 + 0.106P\right]\)

where \(P = (F_c^2 + 2F_s^2)/3\)

\((\Delta\sigma/\sigma)_{\text{max}} < 0.001\)

\(\Delta\rho_{\text{max}} = 0.26\) e Å\(^{-3}\)

\(\Delta\rho_{\text{min}} = -0.44\) e Å\(^{-3}\)

Absolute structure: Flack \(x\) determined using

1053 quotients [(\(I^+\)−\(I^−\))/(\(I^+\)+\(I^−\))] (Parsons et al., 2013)

Absolute structure parameter: 0.10 (17)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
Refinement. H atoms were positioned geometrically (C—H = 0.98, 0.97 or 0.96 Å, and O—H = 0.82 Å) and refined using as riding with $U_{	ext{iso}}(H) = 1.2U_{eq}(\text{C(H)) or C(H,H) groups, or } U_{\text{iso}}(H) = 1.5U_{eq}(\text{C(H,H,H) or O), allowing for free rotation of the OH groups and crystallization water molecules (O3(H3A,H3B) and O4(H4A,H4B)).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|   | $x$    | $y$    | $z$    | $U_{\text{iso}}*/U_{eq}$ |
|---|--------|--------|--------|--------------------------|
| O3 | 0.3171 (6) | −0.0810 (5) | 0.6471 (5) | 0.0640 (11) |
| H3A | 0.382215 | −0.200873 | 0.640005 | 0.096* |
| H3B | 0.176598 | −0.058481 | 0.675652 | 0.096* |
| O4 | 0.3946 (9) | 0.0979 (7) | 0.4096 (5) | 0.0750 (13) |
| H4A | 0.330101 | 0.051068 | 0.478141 | 0.113* |
| H4B | 0.327723 | 0.101353 | 0.352282 | 0.113* |
| O11 | 0.8495 (5) | −0.0155 (4) | 0.6286 (3) | 0.0423 (7) |
| H11 | 0.842 (12) | 0.045 (11) | 0.540 (8) | 0.06 (2)* |
| O12 | 0.4941 (5) | 0.3476 (4) | 0.8818 (3) | 0.0373 (7) |
| H13 | 0.4864 (4) | 0.5035 (4) | 0.6457 (3) | 0.0361 (6) |
| O14 | 0.8089 (5) | 0.6575 (4) | 0.6023 (3) | 0.0394 (7) |
| H14 | 0.841401 | 0.738990 | 0.622566 | 0.059* |
| O15 | 1.0305 (5) | 0.5731 (5) | 0.8089 (4) | 0.0514 (9) |
| H15 | 1.166424 | 0.550381 | 0.782309 | 0.077* |
| O16 | 0.8842 (5) | 0.1669 (4) | 0.8198 (3) | 0.0382 (7) |
| C11 | 0.6562 (7) | 0.0918 (6) | 0.7280 (5) | 0.0398 (10) |
| H11A | 0.627277 | 0.008418 | 0.801180 | 0.048* |
| H11B | 0.525403 | 0.144048 | 0.692746 | 0.048* |
| C12 | 0.6836 (6) | 0.2508 (5) | 0.7784 (4) | 0.0287 (8) |
| C13 | 0.7011 (6) | 0.4015 (5) | 0.6724 (4) | 0.0285 (8) |
| H13A | 0.812148 | 0.338344 | 0.591341 | 0.034* |
| C14 | 0.7743 (6) | 0.5397 (5) | 0.7129 (4) | 0.0279 (8) |
| H14A | 0.652616 | 0.617405 | 0.785360 | 0.033* |
| C15 | 0.9857 (7) | 0.4371 (6) | 0.7581 (5) | 0.0360 (9) |
| H15A | 1.113508 | 0.370500 | 0.683889 | 0.043* |
| C16 | 0.9460 (8) | 0.2978 (7) | 0.8656 (5) | 0.0433 (10) |
| H16A | 1.082904 | 0.228958 | 0.894020 | 0.052* |
| H16B | 0.826033 | 0.365798 | 0.940980 | 0.052* |
| C17 | 0.4524 (9) | 0.2445 (8) | 1.0017 (5) | 0.0505 (12) |
| H17A | 0.432290 | 0.135576 | 0.983637 | 0.076* |
| H17B | 0.317821 | 0.324424 | 1.063570 | 0.076* |
| H17C | 0.579122 | 0.204193 | 1.038288 | 0.076* |
| O21 | −0.0310 (5) | 1.0841 (4) | 0.3619 (3) | 0.0416 (7) |
| H21 | −0.088305 | 1.198374 | 0.348118 | 0.062* |
| O22 | 0.2120 (5) | 0.7111 (4) | 0.1172 (3) | 0.0358 (6) |
| O23 | 0.0693 (5) | 0.5868 (5) | 0.3561 (3) | 0.0382 (7) |
| H23 | −0.000861 | 0.594835 | 0.434404 | 0.057* |
| O24 | 0.4907 (6) | 0.3936 (4) | 0.4191 (3) | 0.0407 (7) |
| H24 | 0.461466 | 0.303180 | 0.412308 | 0.061* |
| O25 | 0.8573 (5) | 0.4521 (5) | 0.2383 (4) | 0.0505 (9) |
### Atomic displacement parameters (Å²)

|   | $U^{11}$       | $U^{22}$       | $U^{33}$       | $U^{12}$       | $U^{13}$       | $U^{23}$       |
|---|----------------|----------------|----------------|----------------|----------------|----------------|
| O3| 0.0457 (19)    | 0.048 (2)      | 0.090 (3)      | −0.0091 (17)   | −0.0201 (19)   | −0.004 (2)     |
| O4| 0.098 (3)      | 0.062 (3)      | 0.098 (3)      | −0.054 (3)     | −0.047 (3)     | 0.016 (3)      |
| O11| 0.0536 (18)   | 0.0270 (15)    | 0.0462 (17)    | −0.0171 (13)   | −0.0100 (14)   | −0.0037 (13)   |
| O12| 0.0428 (15)   | 0.0325 (15)    | 0.0320 (14)    | −0.0159 (12)   | −0.0030 (12)   | 0.0017 (12)    |
| O13| 0.0333 (14)   | 0.0382 (16)    | 0.0424 (15)    | −0.0142 (12)   | −0.0193 (12)   | 0.0026 (12)    |
| O14| 0.0534 (18)   | 0.0294 (15)    | 0.0389 (15)    | −0.0254 (14)   | −0.0056 (13)   | 0.0026 (12)    |
| O15| 0.0384 (15)   | 0.0462 (19)    | 0.082 (2)      | −0.0216 (14)   | −0.0207 (16)   | −0.0160 (17)   |
| O16| 0.0411 (15)   | 0.0254 (14)    | 0.0507 (17)    | −0.0103 (12)   | −0.0219 (13)   | 0.0033 (12)    |
| C11| 0.043 (2)     | 0.030 (2)      | 0.050 (2)      | −0.0201 (18)   | −0.0071 (19)   | −0.0055 (19)   |
| C12| 0.0268 (17)   | 0.0219 (17)    | 0.0372 (19)    | −0.0091 (14)   | −0.0091 (15)   | −0.0007 (15)   |
| C13| 0.0302 (18)   | 0.0288 (19)    | 0.0299 (17)    | −0.0135 (16)   | −0.0102 (14)   | −0.0007 (15)   |
| C14| 0.0286 (17)   | 0.0256 (18)    | 0.0302 (18)    | −0.0129 (15)   | −0.0048 (15)   | −0.0033 (15)   |
| C15| 0.0282 (17)   | 0.031 (2)      | 0.051 (2)      | −0.0111 (16)   | −0.0104 (17)   | −0.0108 (18)   |
| C16| 0.049 (2)     | 0.040 (2)      | 0.054 (3)      | −0.020 (2)     | −0.031 (2)     | 0.003 (2)      |
| C17| 0.063 (3)     | 0.053 (3)      | 0.039 (2)      | −0.031 (2)     | −0.009 (2)     | 0.005 (2)      |
| O21| 0.0458 (16)   | 0.0250 (14)    | 0.0488 (18)    | −0.0019 (13)   | −0.0207 (13)   | −0.0058 (13)   |
| O22| 0.0518 (16)   | 0.0281 (14)    | 0.0327 (14)    | −0.0150 (13)   | −0.0201 (12)   | 0.0003 (11)    |
| O23| 0.0395 (15)   | 0.0497 (17)    | 0.0363 (14)    | −0.0298 (14)   | −0.0083 (12)   | 0.0002 (13)    |
| O24| 0.0595 (18)   | 0.0286 (15)    | 0.0457 (16)    | −0.0187 (14)   | −0.0329 (14)   | 0.0089 (13)    |
| O25| 0.0264 (14)   | 0.0376 (17)    | 0.086 (2)      | −0.0052 (12)   | −0.0183 (15)   | −0.0139 (17)   |
| O26| 0.0357 (15)   | 0.0260 (14)    | 0.0492 (17)    | −0.0154 (12)   | −0.0142 (13)   | 0.0061 (12)    |
| C21| 0.035 (2)     | 0.029 (2)      | 0.052 (3)      | −0.0013 (17)   | −0.0217 (18)   | −0.0054 (18)   |
| C22| 0.0272 (18)   | 0.028 (2)      | 0.036 (2)      | −0.0089 (15)   | −0.0130 (16)   | −0.0019 (16)   |
| C23| 0.0271 (17)   | 0.0285 (19)    | 0.0293 (18)    | −0.0117 (15)   | −0.0100 (14)   | −0.0002 (15)   |
| C24| 0.0337 (18)   | 0.0232 (18)    | 0.0335 (19)    | −0.0082 (15)   | −0.0157 (15)   | −0.0015 (15)   |

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C25  0.0250 (17)  0.025 (2)  0.053 (2)  −0.0048 (15)  −0.0132 (17)  −0.0078 (17)
C26  0.030 (2)  0.040 (2)  0.055 (3)  −0.0174 (18)  −0.0025 (19)  0.001 (2)
C27  0.064 (3)  0.048 (3)  0.033 (2)  −0.018 (2)  −0.022 (2)  0.007 (2)

Geometric parameters (Å, °)

| Bond          | Length (Å) | | Length (Å) | Angle (°) |
|---------------|------------|-----------------------------|-----------|
| O3—H3A       | 0.8500     | C17—H17B                   | 0.9600    |
| O3—H3B       | 0.8500     | C17—H17C                   | 0.9600    |
| O4—H4A       | 0.8502     | O21—H21                    | 0.8200    |
| O4—H4B       | 0.8500     | O21—C21                    | 1.409 (5) |
| O11—H11      | 1.00 (8)   | O22—C22                    | 1.405 (5) |
| O11—C11      | 1.417 (5)  | O22—C27                    | 1.423 (5) |
| O12—C12      | 1.407 (5)  | O23—H23                    | 0.8200    |
| O12—C17      | 1.429 (5)  | O23—C23                    | 1.413 (5) |
| O13—H13      | 0.8200     | O24—H24                    | 0.8200    |
| O13—C13      | 1.425 (5)  | O24—C24                    | 1.429 (5) |
| O14—H14      | 0.8200     | O25—H25                    | 0.8200    |
| O14—C14      | 1.414 (4)  | O25—C25                    | 1.417 (5) |
| O15—H15      | 0.8200     | O26—C22                    | 1.413 (5) |
| O15—C15      | 1.416 (5)  | O26—C26                    | 1.420 (5) |
| O16—C12      | 1.411 (5)  | C21—H21A                   | 0.9700    |
| O16—C16      | 1.429 (6)  | C21—H21B                   | 0.9700    |
| C11—H11A     | 0.9700     | C21—C22                    | 1.519 (5) |
| C11—H11B     | 0.9700     | C22—C23                    | 1.528 (5) |
| C11—C12      | 1.505 (6)  | C23—H23A                   | 0.9800    |
| C12—C13      | 1.529 (5)  | C23—C24                    | 1.512 (5) |
| C13—H13A     | 0.9800     | C24—H24A                   | 0.9800    |
| C13—C14      | 1.505 (5)  | C24—C25                    | 1.493 (6) |
| C14—H14A     | 0.9800     | C25—H25A                   | 0.9800    |
| C14—C15      | 1.503 (5)  | C25—C26                    | 1.514 (6) |
| C15—H15A     | 0.9800     | C26—H26A                   | 0.9700    |
| C15—C16      | 1.508 (6)  | C26—H26B                   | 0.9700    |
| C16—H16A     | 0.9700     | C27—H27A                   | 0.9600    |
| C16—H16B     | 0.9700     | C27—H27B                   | 0.9600    |
| C17—H17A     | 0.9600     | C27—H27C                   | 0.9600    |
| H3A—O3—H3B   | 104.5      | H17B—C17—H17C              | 109.5     |
| H4A—O4—H4B   | 104.5      | C21—O21—H21               | 109.5     |
| C11—O11—H11  | 111 (4)    | C22—O22—C27               | 117.3 (3) |
| C12—O12—C17  | 117.3 (3)  | C23—O23—H23               | 109.5     |
| C13—O13—H13  | 109.5      | C24—O24—H24               | 109.5     |
| C14—O14—H14  | 109.5      | C25—O25—H25               | 109.5     |
| C15—O15—H15  | 109.5      | C22—O26—C26               | 114.6 (3) |
| C12—O16—C16  | 114.6 (3)  | O21—C21—H21A              | 109.5     |
| O11—C11—H11A | 109.0      | O21—C21—H21B              | 109.5     |
| O11—C11—H11B | 109.0      | O21—C21—C22               | 110.9 (3) |
| O11—C11—C12  | 112.8 (3)  | H21A—C21—H21B             | 108.1     |
| H11A—C11—H11B| 107.8      | C22—C21—H21A              | 109.5     |
| Bond                  | Angle (°) | Bond                  | Angle (°) |
|----------------------|-----------|----------------------|-----------|
| C12—C11—H11A        | 109.0     | C22—C21—H21B        | 109.5     |
| C12—C11—H11B        | 109.0     | O22—C22—O26         | 112.4 (3) |
| O12—C12—O16         | 111.9 (3) | O22—C22—C21         | 111.3 (3) |
| O12—C12—C11         | 111.3 (3) | O22—C22—C23         | 104.6 (3) |
| O12—C12—C13         | 105.2 (3) | O26—C22—C21         | 106.0 (3) |
| O16—C12—C11         | 106.1 (3) | O26—C22—C23         | 110.0 (3) |
| O16—C12—C13         | 110.3 (3) | C21—C22—C23         | 112.7 (3) |
| C11—C12—C13         | 112.2 (3) | O23—C23—C22         | 109.2 (3) |
| O13—C13—C12         | 109.5 (3) | O23—C23—H23A        | 108.8     |
| O13—C13—H13A        | 108.7     | O23—C23—C24         | 109.6 (3) |
| O13—C13—C14         | 108.8 (3) | C22—C23—H23A        | 108.8     |
| C12—C13—H13A        | 108.7     | C24—C23—C22         | 111.5 (3) |
| C14—C13—C12         | 112.4 (3) | C24—C23—H23A        | 108.8     |
| C14—C13—H13A        | 108.7     | O24—C24—C23         | 109.4 (3) |
| O14—C14—C13         | 107.0 (3) | O24—C24—H24A        | 109.3     |
| O14—C14—H14A        | 109.1     | O24—C24—C25         | 109.4 (3) |
| O14—C14—C15         | 111.6 (3) | C23—C24—H24A        | 109.3     |
| C13—C14—H14A        | 109.1     | C25—C24—C23         | 110.1 (3) |
| C15—C14—C13         | 110.8 (3) | C25—C24—H24A        | 109.3     |
| C15—C14—H14A        | 109.1     | O25—C25—C24         | 108.6 (3) |
| O15—C15—C14         | 107.9 (3) | O25—C25—H25A        | 109.6     |
| O15—C15—H15A        | 110.1     | O25—C25—C26         | 110.9 (3) |
| O15—C15—C16         | 109.7 (4) | C24—C25—H25A        | 109.6     |
| C14—C15—H15A        | 110.1     | C24—C25—C26         | 108.5 (3) |
| C14—C15—C16         | 108.9 (3) | C26—C25—H25A        | 109.6     |
| C16—C15—H15A        | 110.1     | O26—C26—C25         | 111.7 (3) |
| O16—C16—C15         | 110.9 (4) | O26—C26—H26A        | 109.3     |
| O16—C16—H16A        | 109.5     | O26—C26—H26B        | 109.3     |
| O16—C16—H16B        | 109.5     | C25—C26—H26A        | 109.3     |
| C15—C16—H16A        | 109.5     | C25—C26—H26B        | 109.3     |
| C15—C16—H16B        | 109.5     | H26A—C26—H26B       | 108.0     |
| H16A—C16—H16B       | 108.1     | O22—C27—H27A        | 109.5     |
| O12—C17—H17A        | 109.5     | O22—C27—H27B        | 109.5     |
| O12—C17—H17B        | 109.5     | H27A—C27—H27B       | 109.5     |
| O12—C17—H17C        | 109.5     | H27A—C27—H27C       | 109.5     |
| H17A—C17—H17B       | 109.5     | H27B—C27—H27C       | 109.5     |
| H17A—C17—H17C       | 109.5     | H27B—C27—H27C       | 109.5     |
| O11—C11—C12—O12     | −176.7 (3) | O21—C21—C22—O22    | 179.4 (3) |
| O11—C11—C12—O16     | −54.8 (4)  | O21—C21—C22—O26    | −58.1 (4) |
| O11—C11—C12—C13     | 65.6 (4)   | O21—C21—C22—C23    | 62.3 (5)  |
| O12—C12—C13—O13     | −50.8 (4)  | O22—C22—C23—O23    | −52.9 (4) |
| O12—C12—C13—C14     | 70.2 (4)   | O22—C22—C23—C24    | 68.4 (4)  |
| O13—C13—C14—O14     | −65.1 (3)  | O23—C23—C24—O24    | −64.1 (4) |
| O13—C13—C14—C15     | 173.1 (3)  | O23—C23—C24—C25    | 175.6 (3) |
| O14—C14—C15—O15     | 67.4 (4)   | O24—C24—C25—O25    | 63.4 (4)  |
| O14—C14—C15—C16     | −173.6 (3) | O24—C24—C25—C26    | −176.0 (3) |
| O15—C15—C16—O16     | 175.8 (3)  | O25—C25—C26—O26    | 176.8 (3) |
|        |        |        |        |        |        |
|--------|--------|--------|--------|--------|--------|
| O16—C12—C13—O13 | −171.6 (3) | O26—C22—C23—O23 | −173.8 (3) |
| O16—C12—C13—C14 | −50.6 (4) | O26—C22—C23—C24 | −52.5 (4) |
| C11—C12—C13—O13 | 70.4 (4) | C21—C22—C23—O23 | 68.1 (4) |
| C11—C12—C13—C14 | −168.6 (3) | C21—C22—C23—C24 | −170.6 (3) |
| C12—O16—C16—C15 | −60.5 (5) | C22—O26—C26—C25 | −59.1 (5) |
| C12—C13—C14—O14 | 173.5 (3) | C22—C23—C24—O24 | 174.8 (3) |
| C12—C13—C14—C15 | 51.7 (4) | C22—C23—C24—C25 | 54.6 (4) |
| C13—C14—C15—O15 | −173.4 (3) | C23—C24—C25—O25 | −176.3 (3) |
| C13—C14—C15—C16 | −54.4 (4) | C23—C24—C25—C26 | −55.8 (4) |
| C14—C15—C16—O16 | 57.9 (5) | C24—C25—C26—O26 | 57.6 (5) |
| C16—O16—C12—O12 | −61.3 (4) | C26—O26—C22—O22 | −60.8 (4) |
| C16—O16—C12—C11 | 177.1 (4) | C26—O26—C22—C21 | 177.4 (4) |
| C16—O16—C12—C13 | 55.4 (4) | C26—O26—C22—C23 | 55.3 (4) |
| C17—O12—C12—O16 | −53.3 (5) | C27—O22—C22—O26 | −58.5 (4) |
| C17—O12—C12—C11 | 65.2 (5) | C27—O22—C22—C21 | 60.3 (5) |
| C17—O12—C12—C13 | −173.1 (4) | C27—O22—C22—C23 | −177.8 (3) |

**Hydrogen-bond geometry (Å, †)**

| D—H···A | D⋅⋅⋅A | D—H | H···A |
|---------|-------|------|-------|
| O4—H4..O3 | 2.729 (7) | 0.85 | 1.94 |
| O11—H11..O21i | 2.799 (4) | 1.00 (8) | 1.87 (8) |
| O13—H13..O24 | 2.643 (4) | 0.82 | 1.83 |
| O14—H14..O11ii | 2.719 (4) | 0.82 | 1.94 |
| O15—H15..O13iii | 2.898 (4) | 0.82 | 2.12 |
| O21—H21..O25iv | 2.874 (4) | 0.82 | 2.10 |
| O23—H23..O14v | 2.653 (4) | 0.82 | 1.84 |
| O24—H24..O4 | 2.650 (5) | 0.82 | 1.83 |
| O25—H25..O23iii | 2.709 (5) | 0.82 | 1.97 |

Symmetry codes: (i) x+1, y−1, z; (ii) x, y+1, z; (iii) x+1, y, z; (iv) x−1, y+1, z; (v) x−1, y, z.