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# Crystal Structure and Molecular Conformation of 1-*O*-Acetyl-2,3,5-*O*-benzoyl-*β*-D-ribofuranose

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**Synopsis.** The crystal structure of a derivative of *β*-D-ribofuranose has been determined by X-ray diffraction method in order to characterize the molecular conformation. The phase angle $P$ and the degree of puckering $\tau_m$ of the sugar ring are −7.6 and 34.3° respectively. The ring shows C(3′)-*endo*-C(2′)-*exo* puckering (${}^{3}_{2}T$) as found in sucrose and 1,2,3,5-tetra-*O*-acetyl-*β*-D-ribofuranose. The furanoid carbons C(1′), C(2′), and C(3′) adopt the *cis* conformation with the carbonyl oxygens of their corresponding side chains. This conformation is favored by intramolecular C–H···O=C interactions. All carbonyl oxygens also participate in intermolecular C–H···O=C interactions in the crystal.

The title compound (**1**) is a pentose sugar whose anomeric hydroxyl group has been replaced by an acetoxyl group and the other three hydroxyl groups by benzoyloxyl groups. It can be synthesized from 2,3,5-tri-*O*-benzoyl-D-ribofuranose and a mixture of pyridine and acetic anhydride at low temperature.[1] Nucleosides obtained from RNA, DNA and the adenosines have a sugar component which is either a D-ribose or a 2-deoxyribose.[2] A major difference between these compounds and **1** lies in the nature of substituents of the sugar ring. In the present work, an attempt is made to compare the conformation of (**1**) to an acetylated analogue, 1,2,3,5-tetra-*O*-acetyl-*β*-D-ribofuranose (**2**)[3] and sucrose (**3**)[4] with particular emphasis on the furanoid sugar ring and the corresponding side chains.

It will be of interest in view of the molecular design to find out what conformational orientation this heavily substituted ribofuranose (**1**) adopts compared to its less bulky substituted analogues.

## Experimental

Crystals of **1** (Aldrich 15901-8) were obtained by slow evaporation from a diethyl ether–pentane solution (1 : 1 in volume). A colorless crystal of dimensions 0.20×0.40×0.10 mm cut from a larger crystal was mounted on a glass fiber. Diffraction measurements were made on a Rigaku AFC-5R diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda$=0.71073 Å, 50 kV, 200 mA). Cell constants were determined from a least-squares refinement using 25 reflections in the $2\theta$ range of 23 to 25°.

The crystal data: $C_{28}H_{24}O_9$, $M_r$=504.49, monoclinic, $P2_1$, $a$=11.125(4), $b$=8.467(7), $c$=13.989(3) Å, $\beta$=103.12(2)°, $V$=1283(1) Å$^3$, $Z$=2, $D_x$=1.306 Mg m$^{-3}$, $\mu$(Mo $K\alpha$)=0.92 cm$^{-1}$, $F$(000)=528.

The intensity data were collected using the $\omega$–$2\theta$ scan method to a maximum $2\theta$ of 50° [scan width (0.70+0.10 tan $\theta$)° in $\omega$, scan speed 6° min$^{-1}$ in $\omega$]. Of 2489 reflections (ranging $h$=0 to 13, $k$=0 to 10, $l$=−16 to 16) 2308 were unique ($R_{\text{int}}$=0.022). The fluctuations of the intensities of three standard reflections, which were measured after every 97 reflections, were within 1%. The intensity data were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by direct method (MITHRIL[5]). The non-H atoms were refined anisotropically by block-diagonal least-squares method. Most of the H atoms were found in a difference Fourier map, but the positional parameters of two H atoms of the methyl group were calculated by assuming an usual geometry. All the H atoms were refined isotropically. The final cycle of least-squares was based on 1799 reflections larger than $\sigma(F_o)$ and 431 variable parameters. $\Sigma w(|F_o|-|F_c|)^2$ was minimized with $w=1.0/(\sigma(F_o)^2+0.0103|F_o|)$. Final $R$=0.084, $wR$=0.054, and $S$=1.172. $(\Delta/\sigma)_{\max}$ was 0.5. The maximum and minimum $\Delta\rho$ in the final difference Fourier map were 0.24 and −0.20 e Å$^{-3}$.

The atomic scattering factors were taken from International Tables for X-Ray Crystallography.[6] Calculations were performed by using the TEXSAN[7] at the X-Ray Laboratory of Okayama University, and by using HBLS-V and DAPH[8] and MOLCON[9] at the Okayama University Computer Center.

## Results and Discussion

Final atomic parameters are listed in Table 1.[10] The ORTEP drawing of the molecule[11] and numbering of atoms are shown in Fig. 1. The projection of the crystal structure is shown in Fig. 2.

In the crystal the acetate and benzoate groups are maximally extended from the central furanoid ring. The crystal structure is stabilized by C–H···O=C interactions[12,13] as well as normal van der Waals interactions.

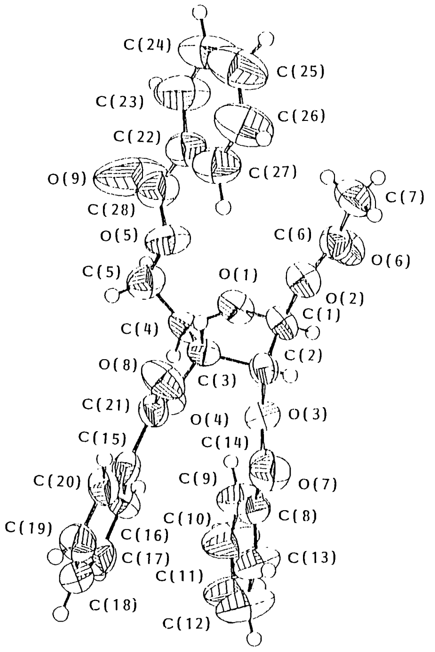

Fig. 1. The thermal ellipsoids with atomic numbering. Ellipsoids of 50% probability are drawn for the non-H atoms; the H atoms are represented as spheres equivalent to $B$=1.0 Å$^2$.

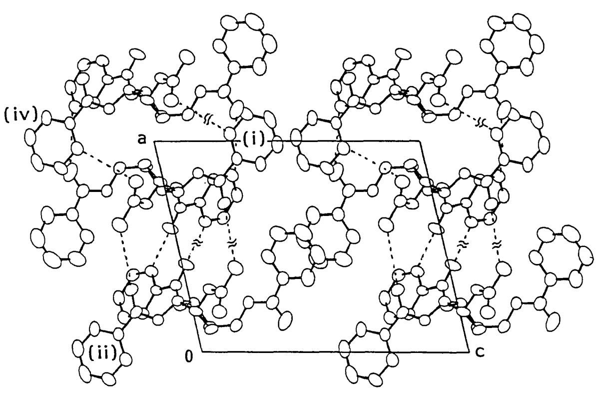

Fig. 2. The crystal structure viewed along the b axis. The H atoms are omitted for the sake of clarity. The C and O atoms involved in the intermolecular C–H···O=C interactions are connected by dotted lines. The symmetry codes are given in Table 2.

Table 1. Final Atomic Parameters with Their esd's in Parentheses $B_{eq}=4/3(\sum\beta_{ii}/a_i^{*2})$

| Atom | $x$ | $y$ | $z$ | $B_{eq}/\text{Å}^2$ |
|---|---|---|---|---|
| O(1) | 0.8909(3) | 0.5053(6) | −0.0555(3) | 5.6(2) |
| O(2) | 0.7018(3) | 0.6365(5) | −0.0842(3) | 5.2(2) |
| O(3) | 0.8473(3) | 0.4417(6) | 0.1377(3) | 4.9(2) |
| O(4) | 0.7817(3) | 0.1683(5) | 0.0440(3) | 4.6(2) |
| O(5) | 0.7643(3) | 0.3253(8) | −0.2191(3) | 7.2(3) |
| O(6) | 0.8073(4) | 0.8537(6) | −0.1015(3) | 6.7(3) |
| O(7) | 0.7043(3) | 0.3365(7) | 0.2108(7) | 6.7(3) |
| O(8) | 0.5861(3) | 0.0926(6) | −0.0149(3) | 6.3(3) |
| O(9) | 0.8519(5) | 0.327(2) | −0.3401(4) | 19.0(7) |
| C(1) | 0.8059(5) | 0.5796(7) | −0.0120(4) | 4.5(3) |
| C(2) | 0.7567(5) | 0.4542(8) | 0.0469(4) | 4.4(3) |
| C(3) | 0.7642(4) | 0.3076(8) | −0.0137(4) | 4.2(3) |
| C(4) | 0.8777(4) | 0.3349(9) | −0.0527(4) | 5.1(3) |
| C(5) | 0.8735(6) | 0.2665(7) | −0.1523(5) | 6.7(4) |
| C(6) | 0.7157(5) | 0.7785(9) | −0.1251(4) | 5.6(4) |
| C(7) | 0.6020(6) | 0.823(1) | −0.1992(5) | 7.7(5) |
| C(8) | 0.9152(5) | 0.344(1) | 0.2974(4) | 5.4(3) |
| C(9) | 1.0347(6) | 0.367(1) | 0.2921(5) | 7.7(5) |
| C(10) | 1.1294(6) | 0.337(2) | 0.3719(6) | 10.6(6) |
| C(11) | 1.1030(8) | 0.281(2) | 0.4560(5) | 12.4(7) |
| C(12) | 0.9840(8) | 0.248(2) | 0.4616(5) | 11.4(7) |
| C(13) | 0.8913(6) | 0.286(1) | 0.3820(4) | 8.1(5) |
| C(14) | 0.8105(5) | 0.3720(8) | 0.2127(4) | 5.0(3) |
| C(15) | 0.7080(4) | −0.0472(8) | 0.1192(4) | 4.1(2) |
| C(16) | 0.8186(5) | −0.0504(8) | 0.1901(4) | 4.8(3) |
| C(17) | 0.8369(5) | −0.1614(9) | 0.2638(4) | 5.6(3) |
| C(18) | 0.7444(6) | −0.2720(9) | 0.2659(4) | 6.0(4) |
| C(19) | 0.6350(6) | −0.2710(9) | 0.1948(3) | 5.8(4) |
| C(20) | 0.6178(5) | −0.1590(8) | 0.1217(4) | 4.9(3) |
| C(21) | 0.6832(5) | 0.0746(7) | 0.0414(4) | 4.4(3) |
| C(22) | 0.6513(6) | 0.423(1) | −0.3683(4) | 6.4(4) |
| C(23) | 0.6469(8) | 0.469(2) | −0.4636(6) | 11.4(7) |
| C(24) | 0.5379(9) | 0.533(2) | −0.5204(6) | 11.4(7) |
| C(25) | 0.4351(8) | 0.544(1) | −0.4839(7) | 10.4(6) |
| C(26) | 0.4405(7) | 0.503(1) | −0.3892(6) | 10.5(6) |
| C(27) | 0.5481(5) | 0.442(1) | −0.3316(5) | 7.7(5) |
| C(28) | 0.7639(6) | 0.352(1) | −0.3091(5) | 7.7(4) |

The geometries of the C–H···O=C interactions are listed in Table 2.

The selected torsion angles in the molecule are listed in Table 3 along with those of **2** and **3**. The angles can be conveniently categorized into three main groups $\tau$, $\psi$, and $\phi$, where $\tau$ defines endocyclic torsion angles in the furanoid ring, $\psi$ the exocyclic angles, and $\phi$ the torsion angles around the O–C bonds in the extended parts of the molecule.

The conformation of the furanose ring can be characterized by the phase angle P and the degree of pucker $\tau_m$ in addition to $\tau$.[14] The values of $P$ and $\tau_m$ are 34.3 and −7.6° for **1**, 37.4 and −4.9° for **2** and 35.2 and −5.5° for **3**, respectively. The $P$ values are close to each other, and denote the five-membered sugar rings to be C(3′)-*endo*-C(2′)-*exo* puckered $({}^{3}_{2}\mathrm{T})$.[14] The observed $\tau_m$ values are close to the calculated $\tau_m$ for some proposed RNA and DNA models,[14] for which the values range from 35 to 42°.

The torsion angles $\psi_i$ indicate the preferred conformations in the glycosidic bonds to be either *trans* or *gauche* for **1** and **2**. These conformations are more favorable

Table 2. Geometries of C–H···O=C Interactions

| Donor (D) | Acceptor (A) | D···A $l$/Å | H···A $l$/Å | D–H···A $\phi$/° |
|---|---|---|---|---|
| (a) Intermolecular | | | | |
| C($20^{\text{ii}}$) | O($8^{\text{i}}$) | 3.20(1) | 2.53(7) | 122(5) |
| C($7^{\text{iii}}$) | O($7^{\text{i}}$) | 3.38(1) | 2.51(7) | 142(8) |
| C($17^{\text{iV}}$) | O($9^{\text{i}}$) | 3.39(2) | 2.55(7) | 153(6) |
| C($9^{\text{iv}}$) | O($6^{\text{i}}$) | 3.51(1) | 2.60(7) | 150(5) |
| C($5^{\text{v}}$) | O($6^{\text{i}}$) | 3.67(1) | 2.66(7) | 166(5) |
| (B) Intramolecular | | | | |
| C(28) | O(9) | 2.63(2) | 2.25(7) | 104(5) |
| C(6) | O(6) | 2.64(1) | 2.31(6) | 97(4) |
| C(21) | O(8) | 2.69(1) | 2.36(5) | 98(3) |
| C(14) | O(7) | 2.68(1) | 2.38(6) | 95(4) |

Symmetry codes: (i) $x$, $y$, $z$; (ii) $1-x$, $1/2+y$, $-z$; (iii) $1-x$, $-1/2+y$, $-z$; (iv) $2-x$, $1/2+y$, $-z$; (v) $x$, $1+y$, $z$.

Table 3. Selected Torsion Angles of **1** and The Related Compounds

| Compounds | **1**[a)] | **2**[b)] | **3**[c)] |
|---|---|---|---|
| | $\tau/°$ | $\tau/°$ | $\tau/°$ |
| $\tau_1$[C(4)–O(1)–C(1)–C(2)] | 15.7(7) | 15.6(3) | 14.6(1) |
| $\tau_2$[O(1)–C(1)–C(2)–C(3)] | −31.3(6) | −33.0(3) | −31.1(1) |
| $\tau_3$[C(1)–C(2)–C(3)–C(4)] | 34.5(7) | 37.3(1) | 35.0(1) |
| $\tau_4$[C(2)–C(3)–C(4)–O(1)] | −26.3(7) | −29.6(2) | −27.2(1) |
| $\tau_5$[C(3)–C(4)–O(1)–C(1)] | 6.8(7) | 9.1(3) | 8.1(1) |
| $\psi_1$[C(2)–C(1)–O(2)–C(6)] | 161(1) | −167.6(2) | |
| $\psi_2$[C(3)–C(2)–O(3)–C(14)] | −90(1) | −95.6(3) | |
| $\psi_3$[C(4)–C(3)–O(4)–C(21)] | −144(1) | −156.7(2) | |
| $\psi_4$[O(1)–C(4)–C(5)–O(5)] | −64(1) | −69.8(3) | |
| $\phi_1$[C(1)–O(2)–C(6)–O(6)] | −2(1) | 6.6(4) | |
| $\phi_2$[C(2)–O(3)–C(14)–O(7)] | −9(1) | 7.7(5) | |
| $\phi_3$[C(3)–O(4)–C(21)–O(8)] | 9(1) | 6.0(5) | |
| $\phi_4$[C(5)–O(5)–C(28)–O(9)] | 1(2) | 3.3(4) | |

a) 1-*O*-Acetyl-2,3,5-*O*-benzoyl-*β*-D-ribofuranose (**1**) (This work). b) 1,2,3,5-Tetra-*O*-acetyl-*β*-D-ribofuranose (**2**).[3] c) Sucrose (**3**).[4]

than the cis to avoid steric repulsion between the methyl or phenyl hydrogens and sugar-ring atoms. However, in C(3′)-*endo* $\beta$-pyrimidine nucleosides, $\psi$ values are generally small.[15]

The C–O–C=O groups of the acetate and benzoate moieties are observed to be *cis* planar in **1** and **2** as seen from $\phi$ values in Table 3. The preference for a planar *cis* conformation of the C–O–C=O groups in esters has long been noted.[16,17] This conformation is also observed in sucrose octaacetate (**4**).[18] This preference is irrespective of the space groups and thus the molecular packing: the space group being $P2_1$ for **1**, while $P2_12_12_1$ for **2** and **4**. This generally planar *cis* conformation is attributed to intramolecular C–H···O=C interactions.[16] As seen from Table 2, the carbonyl oxygens interact with adjacent H atoms to stabilize the *cis* conformation. It is noteworthy that the bulky benzoic ester moieties in the present compound (**1**) do maintain this planar conformation.

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