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# Note

## X-ray structure of methyl 1,6-di-*O*-(4-bromobenzoyl)-3,4-di-*O*-(4-methoxycinnamoyl)-β-D-fructofuranoside

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Tetrachromophoric derivatives of methyl α- and β-fructofuranosides functionalized with 4-bromobenzoate and 4-methoxycinnamate chromophores were prepared in connection with a study involving the structure determination of fructose-containing oligosaccharides by circular dichroism (CD) spectroscopy[1]. The CD spectra of these derivatives are directly related to the orientations of the chromophoric groups about the furanose ring, so that understanding of the conformations of these derivatives may help explain the origin of the observed CD spectra. $^1$H NMR spectroscopy provided the approximate averaged conformations of the furanose ring, but more precise conformational data available through X-ray crystallography was desired. We also wished to observe any conformational differences between the solid-state and solution structures that might indicate the degree of flexibility of the furanose ring. Crystals of the title compound **1** were obtained and subjected to X-ray analysis.

The relevant crystallographic data are given in Table I. Crystals were obtained as clusters of plates upon slow evaporation of a solution of **1** in ether; **1** crystallized with two independent molecules in the asymmetric unit. The structure was solved[2] by using SHELXS86 and refined by full-matrix least-squares. The four bromine atoms were initially identified, and the rest of the atoms were secured during two iterations of difference-Fourier computations in DIRDIF. All calculations were performed using the TEXSAN[3] crystallographic software package. The final atomic parameters are given in Table II and the selected torsional angles in Table III **. Molecules I and II of the unit cell are nearly identical (except for the

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** Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre. The coordinates may be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.


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TABLE I

Crystallographic data for **1**

| | | | |
|---|---|---|---|
| Formula | $C_{41}H_{34}O_{12}Br_2$ | Diffractometer | Rigaku AFC5S |
| $M$ (amu) | 878.52 | Monochromator | graphite |
| Crystal size (mm) | $0.23\times0.13\times0.03$ | $\lambda$(Cu $K\alpha$) (Å) | 1.54178 |
| $T$ (°C) | 23 | Abs coeff ($cm^{-1}$) | 31.95 |
| Triclinic | | Orienting reflectns, range (°) | 24, $19.13 \le 2\theta \le 28.14$ |
| Space group | $P1$ (No. 1) | Reflections measured | $+h, +k, \pm l$ |
| Cell parameters | | Max $2\theta$ (°) | 116 |
| $a$ (Å) | 9.960 (1) | No. unique reflections | 5409 |
| $b$ (Å) | 25.965 (2) | Data used, $F^2 \ge 3\sigma(F^2)$ | 3819 |
| $c$ (Å) | 7.5358 (5) | Parameters refined | 988 |
| $\alpha$ (°) | 94.889 (6) | $p$-factor | 0.03 |
| $\beta$ (°) | 90.464 (9) | $R$ [a], $R_w$ [b] | 0.038, 0.058 |
| $\gamma$ (°) | 93.835 (9) | esd of unit weight [c] | 2.12 |
| Volume (Å$^3$) | 1937.3 (3) | Convergence, largest shift/error | 0.15 |
| $Z$ | 2 | Largest positive peak (e/Å$^3$) | 0.35 |
| Density (calcd) (g $cm^{-3}$) | 1.506 | | |
| | | Largest negative peak (e/Å$^3$) | −0.26 |

[a] $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}$, $w = 4F_o^2/\sigma^2(F_o)^2$. [c] $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$.

different orientation of the $p$-methoxy group on the 4-cinnamate), and an ORTEP[4] drawing of one is shown in Fig. 1 with the numbering system used.

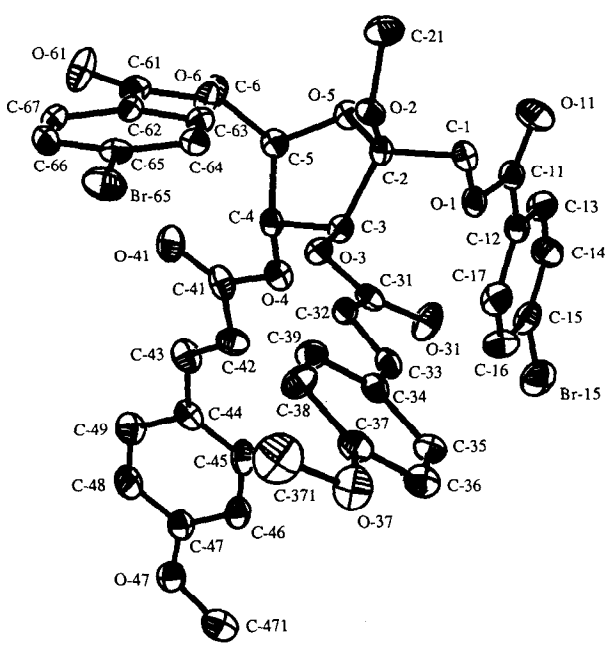


Fig. 1. ORTEP drawing of **1** (molecule I) showing atom numbering.

TABLE II

Positional parameter for **1** with estimated standard deviations in parentheses

| Atom | Molecule I | | | Molecule II | | |
|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | *x* | *y* | *z* |
| Br-15 | 1.9790 | 0.9379 | 0.2179 | 1.2870 (3) | 0.0224 (1) | 1.0874 (4) |
| C-1 | 1.598 (1) | 0.7058 (6) | 0.727 (2) | 1.019 (1) | 0.2500 (6) | 0.519 (2) |
| O-1 | 1.6575 (9) | 0.7456 (4) | 0.628 (1) | 1.0604 (9) | 0.2124 (4) | 0.628 (1) |
| C-11 | 1.724 (1) | 0.7860 (6) | 0.716 (2) | 1.117 (2) | 0.1714 (6) | 0.553 (2) |
| O-11 | 1.732 (1) | 0.7918 (4) | 0.875 (2) | 1.133 (2) | 0.1651 (5) | 0.396 (2) |
| C-12 | 1.784 (1) | 0.8216 (6) | 0.593 (2) | 1.160 (1) | 0.1369 (6) | 0.685 (2) |
| C-13 | 1.838 (2) | 0.8696 (6) | 0.662 (2) | 1.216 (2) | 0.0916 (7) | 0.627 (2) |
| C-14 | 1.895 (2) | 0.9040 (7) | 0.551 (3) | 1.251 (2) | 0.0574 (6) | 0.745 (3) |
| C-15 | 1.895 (2) | 0.8918 (7) | 0.371 (3) | 1.235 (2) | 0.0678 (7) | 0.924 (2) |
| C-16 | 1.840 (2) | 0.8459 (7) | 0.296 (2) | 1.176 (2) | 0.1126 (7) | 0.987 (2) |
| C-17 | 1.786 (2) | 0.8115 (6) | 0.409 (2) | 1.139 (2) | 0.1464 (6) | 0.864 (2) |
| C-2 | 1.451 (1) | 0.6970 (5) | 0.676 (2) | 0.875 (1) | 0.2616 (5) | 0.561 (2) |
| O-2 | 1.3965 (9) | 0.6533 (3) | 0.754 (1) | 0.8400 (9) | 0.3052 (3) | 0.479 (1) |
| C-21 | 1.376 (2) | 0.6604 (6) | 0.940 (2) | 0.826 (2) | 0.2974 (6) | 0.292 (2) |
| C-3 | 1.424 (1) | 0.6877 (4) | 0.471 (2) | 0.848 (1) | 0.2712 (4) | 0.764 (2) |
| O-3 | 1.3841 (9) | 0.6343 (3) | 0.415 (1) | 0.8260 (9) | 0.3242 (3) | 0.817 (1) |
| C-31 | 1.483 (2) | 0.6047 (5) | 0.359 (2) | 0.934 (2) | 0.3554 (5) | 0.868 (2) |
| O-31 | 1.596 (1) | 0.6211 (4) | 0.345 (2) | 1.044 (1) | 0.3381 (4) | 0.884 (2) |
| C-32 | 1.432 (1) | 0.5499 (5) | 0.326 (2) | 0.905 (1) | 0.4096 (5) | 0.904 (2) |
| C-33 | 1.514 (1) | 0.5152 (5) | 0.257 (2) | 1.000 (1) | 0.4440 (5) | 0.970 (2) |
| C-34 | 1.484 (1) | 0.4589 (5) | 0.216 (2) | 0.992 (1) | 0.5002 (5) | 1.012 (2) |
| C-35 | 1.586 (1) | 0.4298 (5) | 0.142 (2) | 1.102 (1) | 0.5289 (5) | 1.091 (2) |
| C-36 | 1.567 (2) | 0.3779 (5) | 0.094 (2) | 1.103 (1) | 0.5802 (5) | 1.136 (2) |
| C-37 | 1.444 (2) | 0.3528 (6) | 0.128 (2) | 0.9897 (2) | 0.6067 (6) | 1.105 (2) |
| O-37 | 1.439 (1) | 0.3006 (4) | 0.072 (2) | 1.001 (1) | 0.6584 (4) | 1.156 (2) |
| C-371 | 1.313 (2) | 0.2710 (6) | 0.094 (3) | 0.889 (2) | 0.6879 (7) | 1.134 (3) |
| C-38 | 1.342 (1) | 0.3796 (5) | 0.206 (2) | 0.877 (1) | 0.5799 (5) | 1.024 (2) |
| C-39 | 1.364 (1) | 0.4318 (5) | 0.249 (2) | 0.881 (1) | 0.5272 (5) | 0.978 (2) |
| C-4 | 1.314 (1) | 0.7221 (5) | 0.426 (2) | 0.725 (1) | 0.2360 (5) | 0.799 (2) |
| O-4 | 1.3666 (10) | 0.7564 (4) | 0.302 (1) | 0.767 (1) | 0.2024 (4) | 0.926 (1) |
| C-41 | 1.278 (2) | 0.7862 (6) | 0.230 (2) | 0.665 (2) | 0.1722 (6) | 0.995 (2) |
| O-41 | 1.165 (1) | 0.7876 (4) | 0.282 (2) | 0.550 (1) | 0.1729 (4) | 0.951 (2) |
| C-42 | 1.341 (2) | 0.8153 (6) | 0.088 (2) | 0.721 (2) | 0.1417 (6) | 1.135 (2) |
| C-43 | 1.273 (2) | 0.8477 (6) | 0.004 (2) | 0.644 (2) | 0.1135 (6) | 1.232 (2) |
| C-44 | 1.320 (2) | 0.8735 (5) | −0.152 (2) | 0.678 (2) | 0.0851 (6) | 1.381 (2) |
| C-45 | 1.448 (2) | 0.8734 (6) | −0.215 (2) | 0.812 (3) | 0.0789 (7) | 1.419 (3) |
| C-46 | 1.480 (2) | 0.8948 (6) | −0.371 (2) | 0.846 (2) | 0.0556 (8) | 1.570 (3) |
| C-47 | 1.386 (2) | 0.9174 (6) | −0.466 (2) | 0.749 (2) | 0.0375 (7) | 1.679 (3) |
| O-47 | 1.407 (1) | 0.9396 (4) | −0.623 (2) | 0.793 (2) | 0.0144 (6) | 1.823 (2) |
| C-471 | 1.532 (2) | 0.9332 (7) | −0.706 (2) | 0.699 (3) | −0.0035 (10) | 1.936 (3) |
| C-48 | 1.259 (2) | 0.9186 (7) | −0.401 (2) | 0.617 (3) | 0.0421 (8) | 1.639 (3) |
| C-49 | 1.224 (2) | 0.8971 (6) | −0.248 (2) | 0.5816 (2) | 0.0656 (7) | 1.492 (3) |
| C-5 | 1.280 (1) | 0.7519 (5) | 0.605 (2) | 0.682 (1) | 0.2086 (5) | 0.620 (2) |
| O-5 | 1.3876 (9) | 0.7421 (3) | 0.727 (1) | 0.7930 (9) | 0.2166 (3) | 0.506 (1) |
| C-6 | 1.142 (2) | 0.7375 (6) | 0.674 (2) | 0.549 (2) | 0.2226 (6) | 0.545 (2) |
| O-6 | 1.1253 (9) | 0.6814 (4) | 0.658 (1) | 0.553 (1) | 0.2790 (4) | 0.566 (2) |

TABLE II (continued)

| Atom | Molecule I | | | Molecule II | | |
|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | *x* | *y* | *z* |
| C-61 | 1.000 (2) | 0.6613 (6) | 0.629 (2) | 0.437 (2) | 0.2996 (6) | 0.600 (2) |
| O-61 | 0.903 (1) | 0.6851 (5) | 0.629 (2) | 0.331 (1) | 0.2742 (5) | 0.604 (2) |
| C-62 | 0.997 (1) | 0.6040 (6) | 0.589 (2) | 0.453 (1) | 0.3562 (7) | 0.641 (2) |
| C-63 | 1.110 (1) | 0.5757 (6) | 0.618 (2) | 0.573 (1) | 0.3849 (6) | 0.609 (2) |
| C-64 | 1.103 (2) | 0.5223 (6) | 0.576 (2) | 0.587 (1) | 0.4374 (6) | 0.650 (2) |
| C-65 | 0.985 (2) | 0.4976 (6) | 0.507 (2) | 0.478 (2) | 0.4622 (6) | 0.726 (2) |
| Br-65 | 0.9762 (3) | 0.4248 (1) | 0.4474 (4) | 0.4954 (3) | 0.5353 (1) | 0.7832 (4) |
| C-66 | 0.875 (2) | 0.5244 (7) | 0.476 (2) | 0.360 (2) | 0.4351 (7) | 0.758 (2) |
| C-67 | 0.879 (1) | 0.5771 (7) | 0.518 (2) | 0.346 (1) | 0.3823 (7) | 0.714 (2) |

TABLE III

Selected torsional angles for **1** with estimated standard deviations in parentheses

| | Mol. I | Mol. II | | Mol. I | Mol. II |
|---|---|---|---|---|---|
| (a) β-D-Fructofuranosyl ring | | | (b) Anomeric methoxyl group | | |
| C-2–C-3–C-4–C-5 | 7 (1) | 3 (2) | C-1–C-2–O-2–C-21 | 73 (2) | 70 (2) |
| C-2–O-5–C-5–C-4 | −21 (2) | −23 (2) | C-21–O-2–C-2–C-3 | −164 (1) | −166 (1) |
| C-3–C-2–O-5–C-5 | 25 (2) | 24 (2) | C-21–O-2–C-2–O-5 | −48 (2) | −51 (2) |
| C-3–C-4–C-5–O-5 | 7 (1) | 11 (2) | O-2–C-2–C-3–C-4 | 103 (1) | 105 (1) |
| C-4–C-3–C-2–O-5 | −19 (1) | −15 (1) | O-2–C-2–O-5–C-5 | −93 (1) | −94 (1) |
| (c) C-1 Benzoyl group | | | (d) C-6 Benzoyl group | | |
| C-1–O-1–C-11–O-11 | −5 (2) | −1 (3) | C-2–O-5–C-5–C-6 | 100 (1) | 103 (1) |
| O-1–C-1–C-2–O-2 | 171 (1) | 171 (1) | C-3–C-4–C-5–C-6 | −115 (1) | −115 (1) |
| C-1–C-2–C-3–O-3 | 108 (1) | 110 (2) | O-4–C-4–C-5–C-6 | 134 (1) | 133 (1) |
| C-1–C-2–C-3–C-4 | −137 (1) | −133 (1) | C-4–C-5–C-6–O-6 | 45 (2) | 47 (2) |
| C-1–C-2–O-5–C-5 | 145 (1) | 144 (1) | O-5–C-5–C-6–O-6 | −71 (2) | −74 (2) |
| C-11–O-1–C-1–C-2 | 127 (1) | 128 (1) | C-5–C-6–O-6–C-61 | −149 (1) | −148 (1) |
| O-11–C-11–C-12–C-13 | −10 (3) | −5 (3) | C-6–O-6–C-61–O-61 | −7 (3) | −3 (3) |
| | | | O-61–C-61–C-62–C-67 | 12 (3) | 9 (3) |
| (e) C-3 Cinnamoyl group | | | (f) C-4 Cinnamoyl group | | |
| C-2–C-3–O-3–C-31 | −97 (1) | −91 (1) | C-2–C-3–C-4–O-4 | 121 (1) | 120 (1) |
| C-3–O-3–C-31–O-31 | −3 (2) | −4 (2) | C-3–C-4–O-4–C-41 | 174 (1) | 172 (1) |
| O-3–C-3–C-2–O-5 | −135 (1) | −132 (1) | C-4–O-4–C-41–O-41 | 9 (2) | 2 (3) |
| O-3–C-3–C-4–O-4 | −121 (1) | −121 (1) | O-4–C-4–C-5–O-5 | −105 (1) | −101 (1) |
| O-3–C-3–C-4–C-5 | 125 (1) | 121 (1) | C-41–O-4–C-4–C-5 | −74 (2) | −74 (2) |
| O-31–C-31–C-32–C-33 | −8 (2) | −6 (2) | O-41–C-41–C-42–C-43 | 0 (3) | −3 (3) |
| C-32–C-33–C-34–C-39 | −3 (2) | −3 (2) | C-42–C-43–C-44–C-45 | −10 (3) | −11 (3) |
| C-371–O-37–C-37–C-38 | 1 (2) | 2 (2) | C-46–C-47–O-47–C-471 | 9 (3) | 180 (2) |

The anomeric methoxyl group is oriented quasiaxially to the plane of the ring (O-2–C-2–C-3–C-4 = 104°), and the C-21 methyl group is oriented *gauche* to O-5 (−50°) and *anti* to C-3 (−165°), in accord with the exoanomeric effect[5]. The furanose ring is found in the uncommon $E_o$ conformation with the average phase angle of pseudorotation ($P$) of 282° and the degree of pucker ($\tau_m$) of 24° (ref 6).

(In solution, the furanose ring adopts a $^4T_3$–$^4E$ ($P = 0$–$18°$) conformation, as evident in the $^1$H NMR coupling data.)[1,7] The molecules are tightly packed, with close interactions between the chromophores. The 1- and 6-benzoate groups are oriented on opposite sides of the ring and are both found in the *gg* conformation (*gauche* to the ring oxygen and carbon), possibly to decrease the molecular volume and too allow for efficient packing. The cinnamate groups are also oriented on opposite sides of the ring. There are close intermolecular contacts between the benzoate chromophores; the unusual conformation of the furanose ring and the small value for $\tau_m$, which indicates a flattening of the ring[8] may arise from these intermolecular forces.

The benzoate and cinnamate chromophores are nearly planar, allowing for good overlap between the $\pi$ systems. These acyl groups are oriented, as anticipated, with the carbonyl group *syn* to the ethereal C–O bond and *syn* to the adjacent carbinyl proton. The cinnamate chromophores are found in the *s-cis* conformation with the carbonyl groups *syn* to the alkenic groups. In this conformation rather than the *s-trans* conformation, the larger O=C–C($\alpha$) bond angle relative to the O–C–C($\alpha$) bond angle ($\sim$ 128 and 110°, respectively for **1**) can accommodate the greater steric bulk of the $\beta$-CH alkenic group[9].

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