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O^2,O^3:O^4,O^5-Bis(phenylboranediyl)-β-D-fructopyranose acetone solvate

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Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.003 Å
Disorder in solvent or counterion
R factor = 0.037
wR factor = 0.084
Data-to-parameter ratio = 10.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

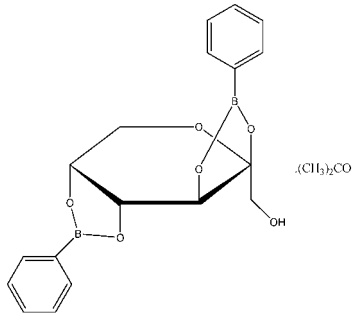
The title compound, $C_{18}H_{18}B_2O_6\cdot C_3H_6O$, formed by reaction between phenylboronic acid and D-fructose, is shown to be β-D-fructopyranose 2,3; 4,5-bis(phenylboronate) and is analogous to D-fructoboronates previously prepared and characterized by NMR.

Comment

For a number of years, we (Duggan, 2004) and others (Smith & Gardiner, 1999; Smith, 1996) have been investigating the arylboronate esters formed between D-fructose and arylboronic acids. Our main interest has been in the arylboronic acid-promoted selective transport of D-fructose through lipophilic membranes, with the ultimate aim of developing a low-energy alternative to the current industrial methods for the production of high-fructose syrup. Boronic acids have also received much attention as potential components of online D-glucose sensors (James & Shinkai, 2002). In the latter application, D-fructose commonly causes interference with D-glucose monitoring because of its high affinity for boronic acids. Many diboronic acids, designed to be selective for either D-glucose or D-fructose, have been synthesized. The selectivity of these compounds has often relied on relatively subtle structural differences in their scaffolds, in order to orient the boronic acid functional groups such that binding of one of these monosaccharides is favoured. Such investigations have used information available for the solution structures of D-glucose and D-fructose boronates, determined using NMR methods (Wood & Siddiqui, 1974; Norrild & Eggert, 1995, 1996) as well as molecular-modelling studies. However, the most accurate structural description of a diboronate ester of D-fructose, *i.e.* an X-ray crystal structure, has, until now, been missing from the literature, despite the fact that the information provided by such a structure could significantly assist the development of selective sugar transporters and sensors.

Wood & Siddiqui (1974) first described a crystalline diphenylboronate of D-fructose, which was formed in pyridine and crystallized from light petroleum–benzene, then recrystallized from toluene. Two moles of pyridine per mole of fructodiboronate were found to be present in the crystalline material, and attempts to remove the pyridine were unsuccessful. An X-ray crystal structure of this product has not been reported, but it seems likely that the pyridine N atom is associated with the Lewis acidic B atoms in this compound. This would be likely to cause the boronate centres to adopt a tetrahedral configuration and would be more relevant to the D-fructose boronates formed in higher-pH solutions. Of particular interest to membrane transport and carbohydrate sensing are the D-fructose boronates formed under physiolo-

gical conditions, and thus our aim was to prepare a crystalline boronate in a non-basic medium. We thus obtained the title compound, (I), and present its crystal structure here.



(I)

Compound (I) was formed at room temperature from a 2:1 mixture of phenylboronic acid and D-fructose in methanol and, after evaporation of the methanol, was crystallized by slow evaporation from an acetone–hexane mix. The X-ray crystal structure of (I) (Fig. 1) confirmed that the compound was a diboronate of β-D-fructopyranose, with five-membered cyclic boronates having been formed from the 2,3- and 4,5-diols. This is the same structure as that determined by Wood & Siddiqui (1974) and is analogous to the di-*p*-vinylphenylboronate described by Wulff & Schauhoff (1991) and the only di-*p*-tolylboronate identified by Norrild & Eggert (1996) in solutions of D-fructose and *p*-tolylboronic acid in $(CD_3)_2SO$. Consistent with the finding here, Norrild & Eggert found that, at boronic acid:D-fructose ratios of 2:1 or higher, the β-D-fructopyranose 2,3:4,5-bis(*p*-tolylboronate) was also a major component in non-aqueous solution.

One equivalent of acetone is incorporated into the crystal structure of (I). The acetone shows no significant intermolecular association with the diboronate, but there is a strong hydrogen bond between it and the remaining free hydroxyl group [H···O7 = 1.98 Å, O6···O7 = 2.808 (2) Å and O6—H···O7 = 168°]. Accordingly, the B centres show very little deviation from planarity.

Experimental

Phenylboronic acid (2.00 g, 16.4 mmol), D-fructose (1.49 g, 8.2 mmol) and methanol (100 ml) were combined and stirred for 2 h. The methanol was then removed and the residue crystallized by slow evaporation of an acetone–hexane solution.

Crystal data

$C_{18}H_{18}B_2O_6\cdot C_3H_6O$
M_r = 410.02
Orthorhombic, $P2_12_12_1$
a = 7.8840 (1) Å
b = 10.5648 (1) Å
c = 24.6438 (4) Å
V = 2052.65 (5) Å^3
Z = 4
D_x = 1.327 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 21 398 reflections
θ = 3.2–28.3°
μ = 0.10 mm^{-1}
T = 123 (2) K
Prism, colourless
0.22 × 0.20 × 0.19 mm

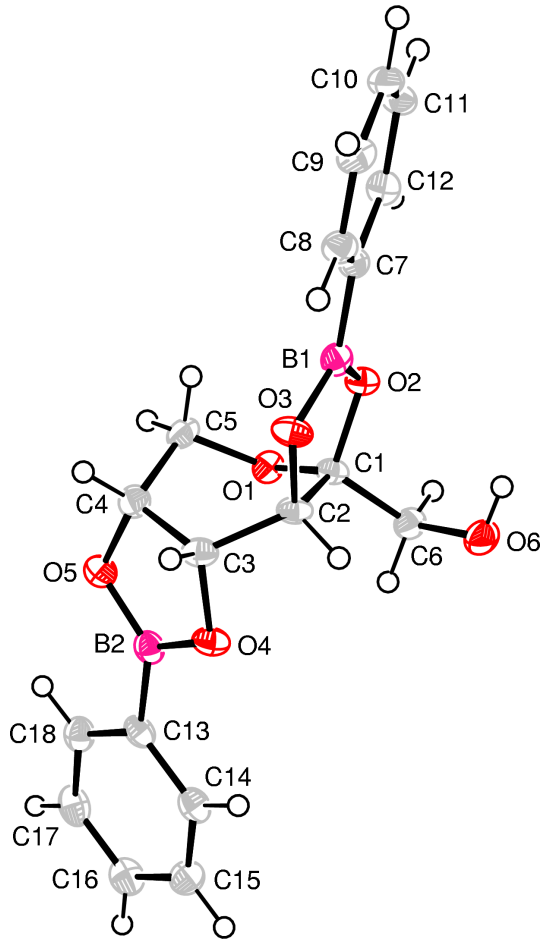


Figure 1
A view of the structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The acetone solvent molecule has been omitted for clarity.

Data collection

Nonius KappaCCD area-detector diffractometer
CCD rotation images, thick-slice φ and ω scans
21 398 measured reflections
2871 independent reflections
2221 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
θ_{max} = 28.3°
$h = -10 \rightarrow 10$
$k = -14 \rightarrow 14$
$l = -32 \rightarrow 32$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.084
S = 1.04
2871 reflections
273 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.1032P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

All H atoms were constrained in the riding model approximation, with C—H = 1.00, 0.95, 0.99 and 0.98 Å for $CH_{methine}$, $CH_{aromatic}$, CH_2 and CH_3, respectively, and O—H = 0.84 Å, and with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C,O) for the remaining H atoms. The H atoms on C20 (solvent molecule) were included in two orientations, each of equal occupancy. In the absence of significant

anomalous dispersion effects, Friedel pairs were merged and the absolute configuration assigned by reference to D-fructose.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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