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Note

Crystal structure of the cyclohexaamylose-*p*-iodophenol complex

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Cyclohexaamylose (**1**) forms a number of complexes with a variety of "guest" molecules[1] Structures of several crystalline complexes have been investigated by the X-ray method[2–7] The structure analysis of the **1**–*p*-iodoaniline (**2**) complex[8] has shown that the iodophenyl group is included in the cavity, and that the amino group protrudes from the O-2, O-3 side of the **1** ring We now report the crystal structure of the **1** complex with *p*-iodophenol (**3**) which is isomorphous with that of the **2** complex Therefore, we discuss the structure of the **3** complex mainly in comparison with the **2** complex

The geometry of the complex is nearly the same as that of the **2** complex Each D-glucose residue has the $^4C_1$ conformation and is α-D-(1→4)-linked. No significant difference of bond distances, angles, and conformation angles in **1** was observed between the two complexes In both **2** and **3** complexes, the iodophenyl group is included in the cavity, but the amino or hydroxyl group protrudes from the cavity This indicates that the interior of the cavity is relatively hydrophobic, and that it binds the hydrophobic portion of the "guest" molecule. The cavity is tapered at the O-6 side Therefore, the benzene ring, which is bulkier than the iodine atom, is located near the O-2, O-3 side in the cavity There is a neck near C-5 and O-5 in the cavity The diagonal C-5H–HC-5 distances at the neck are 6–7 Å The I–C bond penetrates through the neck, and the iodine atom is located at the O-6 side A location of the benzene ring or iodine atom at the neck seems unfavorable because of the bad fit of the iodophenyl group in the cavity A similar effect has been observed for the iodine complex[4].

The hydrogen-bonding schemes are shown in Figs. 1 and 2 In spite of the different "guest" molecules, the hydrogen-bonding schemes are nearly the same in the two complexes The O–O contacts at less than 3 0 Å were considered as hydrogen bonds, although a complete explanation of the hydrogen-bonding scheme is not possible since the hydrogen atoms bonded to an oxygen atom were not located. Twenty two O–O distances of less than 3 0 Å were observed in the **3** complex, whereas 21 O–O and O–N contacts were observed in the **2** complex The phenolic hydroxyl group is hydrogen-bonded to G5O-6 and G2O-2 at distances of 2 69 and 2 55 Å,

respectively. On the other hand, the amino group in the **2** complex also forms hydrogen bonds with those atoms at distances of 2 67 and 2 66 Å

The positions of the water molecules are similar in the two complexes WO-1 forms hydrogen bonds with three hydroxyl groups and WO-3′, WO-3, and WO-3′ are hydrogen-bonded to G5O-2 and G2O-6 The distance of G4O-6–WO-3′ is 2 38 Å,

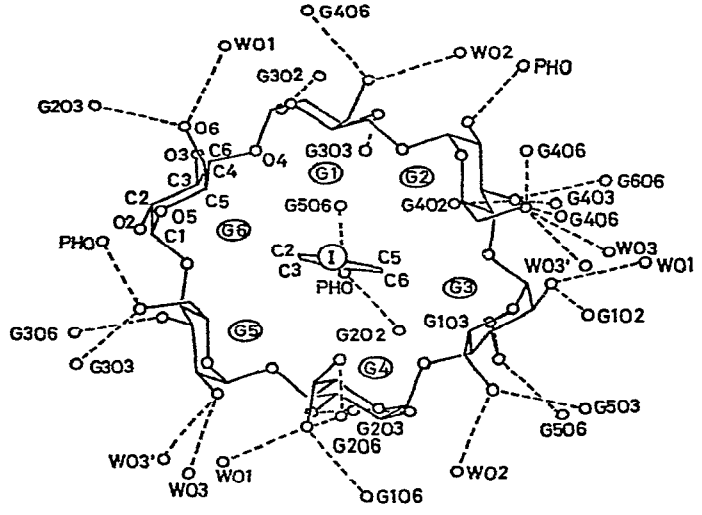

Fig 1 A schematic drawing of hydrogen bonds Dashed lines indicate O–O contacts at less than 3 0 Å

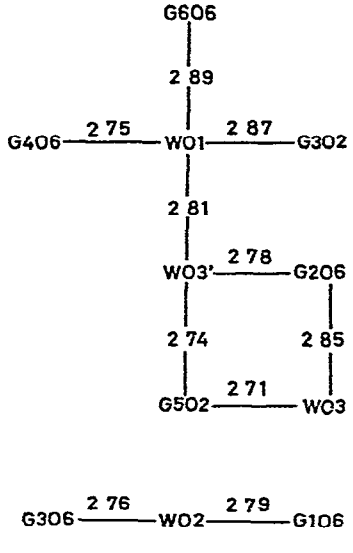

Fig 2 A hydrogen-bonding scheme involving water molecules

which is short as compared with the other O–O contacts, in the **2** complex, a distance of 2 22 Å was observed. This indicates that WO-3′ is disordered and does not coexist with G4O-6. WO-3 and WO-3′ may coexist with G4O-6 and G4O-6′, respectively. WO-1, WO-3, and WO-3′ form an hydrogen-bonding network with the hydroxyl groups of **1**, but WO-2 is isolated from the other water molecules and hydrogen-bonded to G3O-6 and G1O-6.

EXPERIMENTAL

Crystals of the **3** complex, which are colorless, thick plates, were prepared by cooling slowly a hot, aqueous solution of **1** saturated with *p*-iodophenol The space group was determined by the inspection of oscillation and Weissenberg photographs The density was measured by the flotation method with a mixture of tetrabromoethane and carbon tetrachloride The unit-cell parameters and intensity data were measured with a Rigaku AFC four-circle diffractometer on a specimen of 0 3×0 5×0 5 mm, with a graphite monochromatized MoKα radiation ($\lambda = 0\ 70926$ Å) and in the ω-scanning mode The number of independent reflections obtained up to 50° in 2θ was 4979. No corrections were made for absorption and extinction Crystal data are shown in Table I

TABLE I

CRYSTAL DATA

Molecular formula	$(C_6H_{10}O_5)_6 \cdot C_6H_5IO\ 3H_2O$
Molecular weight	1246 9
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Cell dimensions	*a* 13 477(1) Å
	b 15 373(1)
	c 24 573(3)
Cell volume	5091 1 Å^3
Z	4
Density	D_o 1 616 g cm^{-3}
	D_c 1 627

The crystal structure of the **3** complex was deduced on the basis of the isomorphous structure of **2** complex[8]. The atomic parameters of **1** and *p*-iodophenol were refined by the block-diagonal, least-squares method Water molecules were found on a difference-Fourier map In these refinements, G4O-6 and WO-3 were found to be disordered The occupancies were estimated on the electron-density map, but were not refined since the least-squares procedure did not incorporate routinely the refinement of the occupancy. The occupancies of G4O-6, G4O-6′ WO-3, and WO-3′ are 0 5 Using 3428 reflections with $F_o \geqq 3\sigma(F)$, the final block-diagonal, least-squares refinement with anisotropic-thermal factors reduced the *R*-value to 0 061 The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1\ 0$ for all

TABLE II

ATOMIC COORDINATES AND THERMAL FACTORS ($\times 10^4$)[a]

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}
G1C-1	1446 (9)	−518 (8)	6962 (5)	36 (8)	20 (5)	10(2)	−9(11)	−6 (6)	7 (7)
G1C-2	1200(11)	−1231 (8)	6560 (5)	60(10)	29 (6)	7(2)	−22(13)	−1 (6)	−2 (8)
G1C-3	1845(11)	−1133 (8)	6060 (5)	62(10)	17 (5)	12(2)	−4(12)	−7 (6)	−9 (8)
G1C-4	1706(10)	−263 (8)	5800 (5)	41 (8)	26 (6)	9(2)	2(12)	5 (6)	7 (7)
G1C-5	1922(10)	467 (7)	6230 (5)	55 (9)	15 (5)	12(2)	5(11)	6 (6)	10 (9)
G1C-6	1700(15)	1382 (9)	6021 (7)	113(16)	23 (7)	23(4)	27(18)	−1 (8)	−2(13)
G1O-2	1418 (8)	−2056 (6)	6831 (3)	78 (8)	36 (5)	8(2)	−59(10)	12 (4)	−15 (6)
G1O-3	1531 (8)	−1781 (6)	5661 (3)	73 (7)	23 (4)	9(2)	−13 (9)	0 (4)	−13 (6)
G1O-4	2411 (6)	−162 (5)	5381 (3)	29 (5)	26 (4)	9(1)	12 (8)	5 (4)	3 (5)
G1O-5	1286 (7)	310 (6)	6704 (4)	43 (6)	42 (5)	11(2)	29(10)	−4 (5)	6 (5)
G1O-6	714(10)	1446 (8)	5786 (5)	106(11)	49 (6)	25(3)	82(14)	19 (7)	18 (9)
G2C-1	2043(10)	106 (9)	4847 (5)	36 (8)	36 (7)	11(2)	16 (3)	13 (6)	−1 (7)
G2C-2	2287(10)	−639 (8)	4455 (5)	48 (9)	27 (6)	7(2)	−29(12)	0 (6)	4 (7)
G2C-3	3400(10)	−836 (9)	4453 (5)	46 (9)	25 (6)	11(2)	−3(13)	−2 (7)	−1 (7)
G2C-4	3924 (9)	26 (7)	4291 (5)	36 (8)	11 (4)	8(2)	4(10)	5 (5)	−5 (7)
G2C-5	3625 (9)	776 (7)	4681 (5)	31 (7)	14 (5)	15(2)	−7(11)	−7 (6)	11 (7)
G2C-6	4052(12)	1651 (9)	4496 (6)	68(12)	30 (6)	15(3)	−12(15)	10 (7)	15(10)
G2O-2	1745 (7)	−1403 (6)	4600 (3)	45 (6)	40 (5)	10(2)	−37 (9)	3 (5)	−8 (5)
G2O-3	3643 (7)	−1440 (5)	4049 (4)	65 (7)	18 (4)	16(2)	−11 (9)	−12 (4)	7 (6)
G2O-4	4938 (7)	−141 (5)	4355 (5)	31 (5)	25 (3)	6(1)	24 (9)	3 (3)	−2 (5)
G2O-5	2563 (6)	861 (6)	4682 (3)	39 (5)	22 (4)	12(2)	−8 (8)	4 (4)	8 (5)
G2O-6	3808 (9)	1791 (7)	3924 (5)	78 (9)	36 (5)	34(3)	17(12)	38 (7)	6 (9)
G3C-1	5595 (9)	75 (7)	3921 (4)	34 (8)	21 (5)	7(2)	10(10)	4 (5)	−6 (6)
G3C-2	6222 (9)	−740 (7)	3811 (5)	38 (7)	19 (5)	9(2)	11(10)	−1 (6)	1 (7)
G3C-3	6770 (9)	−957 (9)	4335 (5)	32 (7)	29 (6)	10(2)	22(13)	12 (7)	−4 (7)
G3C-4	7362(10)	−227 (7)	4555 (5)	41 (8)	18 (5)	8(2)	2(11)	7 (5)	−11 (7)
G3C-5	6751(10)	645 (8)	4582 (5)	44 (9)	31 (6)	7(2)	12(12)	−5 (6)	0 (7)
G3C-6	7366(11)	1437 (9)	4655 (6)	63(11)	27 (6)	16(3)	−23(14)	−7 (7)	−5(10)
G3O-2	5597 (6)	−1434 (5)	3631 (3)	40 (5)	19 (4)	9(1)	8 (7)	−9 (4)	−8 (5)
G3O-3	7450 (7)	−1692 (5)	4241 (3)	46 (6)	20 (4)	9(2)	11 (8)	−1 (4)	−7 (5)
G3O-4	7580 (6)	−483 (5)	5112 (3)	37 (5)	21 (4)	7(1)	−3 (8)	−4 (4)	−10 (5)
G3O-5	6238 (6)	765 (5)	4072 (3)	43 (5)	15 (4)	9(1)	3 (8)	6 (4)	2 (5)
G3O-6	8173 (8)	1501 (7)	4292 (4)	54 (7)	46 (5)	17(2)	−40(11)	10 (6)	−2 (6)
G4C-1	8548(10)	−362 (8)	5310 (5)	42 (8)	22 (6)	10(2)	1(12)	4 (6)	4 (7)
G4C-2	8871(10)	−1160 (8)	5625 (4)	49 (8)	27 (6)	5(2)	−2(11)	3 (5)	0 (7)
G4C-3	8250 (9)	−1255 (7)	6146 (5)	41 (8)	12 (4)	12(2)	−7(10)	−3 (6)	4 (8)
G4C-4	8323 (9)	−429 (7)	6491 (5)	28 (7)	15 (5)	12(2(	10(10)	−9 (6)	−3 (7)
G4C-5	7925(10)	326 (8)	6133 (5)	54 (9)	18 (5)	13(2)	1(12)	−13 (6)	11 (8)
G4C-6	8026(11)	1217 (8)	6423 (5)	62(10)	14 (5)	14(3)	−10(12)	−6 (6)	−5 (9)
G4O-2	8711 (7)	−1930 (6)	5288 (3)	58 (7)	31 (4)	9(2)	20 (9)	−17 (4)	−7 (6)
G4O-3	8703 (8)	−1972 (6)	6450 (4)	80 (8)	21 (4)	13(2)	32(10)	2 (4)	3 (6)
G4O-4	7663 (6)	−557 (5)	6928 (3)	34 (5)	23 (4)	5(1)	−8 (7)	1 (3)	2 (4)
G4O-5	8601 (7)	384 (6)	5656 (3)	46 (6)	31 (4)	8(1)	−26 (9)	−1 (4)	9 (5)
G4O-6	9042(15)	1450(10)	6510 (7)	73(15)	17 (8)	9(3)	−6(18)	−9 (8)	4(11)
G4O-6′	7460(15)	1846(11)	6109 (8)	66(14)	22 (7)	17(4)	10(18)	7 (9)	21(13)
G5C-1	8022(11)	−397 (7)	7485 (5)	59(10)	15 (5)	10(2)	1(12)	−4 (6)	3 (8)
G5C-2	7771(10)	−1213 (8)	7810 (5)	34 (8)	20 (5)	12(2)	7(11)	−5 (6)	−5 (8)
G5C-3	6635(10)	−1328 (8)	7844 (5)	44 (8)	21 (5)	9(2)	2(11)	−4 (6)	8 (7)
G5C-4	6141 (9)	−521 (8)	8020 (5)	33 (8)	22 (5)	7(2)	−13(11)	−7 (5)	5 (7)
G5C-5	6449 (9)	286 (9)	7687 (5)	32 (8)	30 (6)	10(2)	4(12)	5 (6)	4 (7)
G5C-6	6076(11)	1126 (8)	7905 (5)	56(10)	25 (6)	8(2)	14(12)	1 (6)	−6 (8)

TABLE II (*continued*)

	x	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}
G5O-2	8235 (7)	−1949 (5)	7576 (3)	54 (7)	21 (4)	11(2)	34 (9)	0 (5)	−2 (6)
G5O-3	6417 (7)	−2043 (6)	8215 (4)	55 (7)	26 (4)	14(2)	1 (9)	7 (4)	20 (6)
G5O-4	5106 (7)	−634 (5)	7936 (3)	32 (5)	26 (3)	7(1)	19 (8)	−5 (3)	1 (5)
G5O-5	7536 (6)	334 (5)	7686 (3)	34 (5)	18 (3)	9(1)	−9 (8)	−9 (4)	−10 (5)
G5O-6	6222 (7)	1174 (6)	8486 (4)	51 (6)	31 (4)	13(2)	27 (9)	−13 (4)	−8 (6)
G6C-1	4412(10)	−532 (8)	8361 (5)	43 (9)	21 (5)	9(2)	−6(11)	5 (6)	3 (7)
G6C-2	3722 (9)	−1314 (8)	8363 (5)	29 (8)	28 (6)	13(2)	2(12)	13 (6)	3 (7)
G6C-3	3248(10)	−1407 (7)	7807 (5)	47 (9)	13 (5)	10(2)	−25(11)	4 (6)	3 (7)
G6C-4	2707 (9)	−541 (7)	7681 (5)	28 (7)	15 (5)	11(2)	6(10)	2 (5)	0 (7)
G6C-5	3381 (9)	271 (7)	7734 (5)	36 (8)	10 (4)	11(2)	−5(10)	−7 (5)	1 (7)
G6C-6	2779(10)	1105 (7)	7722 (5)	42 (9)	17 (5)	17(3)	12(11)	2 (6)	2 (8)
G6O-2	4282 (8)	−2076 (6)	8499 (4)	59 (7)	22 (4)	20(2)	5 (9)	15 (5)	−4 (6)
G6O-3	2524 (8)	−2088 (6)	7835 (4)	62 (7)	23 (4)	17(2)	−30 (9)	−2 (5)	2 (6)
G6O-4	2462 (6)	−602 (5)	7113 (3)	24 (5)	28 (4)	8(1)	−8 (7)	−4 (4)	−3 (4)
G6O-5	3859 (6)	251 (5)	8274 (3)	32 (5)	24 (4)	8(1)	14 (8)	−6 (4)	−6 (5)
G6O-6	1844 (7)	1049 (6)	7975 (4)	50 (7)	27 (4)	20(2)	19 (9)	−7 (5)	5 (6)
I	4954 (1)	914 (1)	6205 (0)	80 (1)	24 (0)	20(0)	−5 (1)	−2 (1)	−4 (1)
PHC-1	5035(13)	−472 (7)	6133 (5)	54 (9)	27 (5)	13(2)	−6(16)	0 (6)	7(10)
PHC-2	4941(14)	−931 (9)	6610 (5)	91(12)	29 (5)	14(2)	−33(22)	−4 (7)	11(12)
PHC-3	5047(15)	−1846 (8)	6578 (5)	78(11)	30 (6)	12(2)	−19(20)	−3 (6)	10(11)
PHC-4	5266 (9)	−2220 (7)	6064 (5)	40 (9)	13 (4)	19(3)	6(10)	1 (6)	18 (8)
PHC-5	5355(13)	−1749(10)	5594 (6)	88(14)	37 (7)	12(3)	15(16)	8 (7)	33(10)
PHC-6	5262(12)	−830 (8)	5631 (5)	86(13)	25 (5)	10(2)	−1(15)	−5 (6)	1 (8)
PHO	5389 (7)	−3108 (6)	6053 (4)	59 (7)	25 (4)	18(2)	10 (9)	1 (5)	34 (6)
WO-1	5122(10)	−1129 (8)	2510 (4)	70 (9)	25 (7)	19(2)	−8(16)	10 (6)	−17 (8)
WO-2	4922(12)	−1530 (9)	9707 (5)	83(10)	102 (9)	30(3)	57(20)	34 (9)	8(11)
WO-3	130(19)	−1719(15)	7921 (8)	60(16)	69(13)	20(4)	7(28)	−13(13)	15(16)
WO-3′	−194(20)	−2474(17)	8204(10)	82(21)	73(15)	31(6)	40(32)	−28(16)	−11(20)

[a]The anisotropic thermal factors are of the form $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{23}kl+B_{31}lh)]$

reflections used The anomalous-dispersion terms were ignored The atomic-scattering factors were taken from the International Tables for X-Ray Crystallography[9] The atomic coordinates and thermal factors are listed in Table II The observed and calculated structure-factors are shown in Table III* The computation was carried out with our own programs on a HITAC 8450 computer in our laboratory

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*Table III is deposited with, and can be obtained from Elsevier Scientific Publishing Company, BBA Data Deposition, P O Box 1527, Amsterdam, The Netherlands Reference should be made to No BBA/DD/040/*Carbohydr Res*, 48 (1976) 265–270

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