

## The Crystal and Molecular Structure of Phenyl $\alpha$ -Maltoside

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The crystal structure of phenyl  $\alpha$ -maltoside, a substrate of  $\alpha$ -amylase, was determined with the vector space search method and partial structure tangent formula technique. The unit cell is monoclinic with space group  $P2_1$  and contains two independent molecules  $A$  and  $B$  in an asymmetric unit. Cell dimensions are  $a = 13.597(4)$ ,  $b = 14.457(2)$ ,  $c = 9.812(1)$  Å, and  $\beta = 93.88(2)^\circ$ . The final  $R$  index with all hydrogen atoms included is 0.044. The conformational angles  $\varphi$ ,  $\psi$ , which are defined by the rotation angles around the bonds to the bridged oxygen, are  $-11^\circ$ ,  $161^\circ$  and  $-13^\circ$ ,  $159^\circ$  respectively for  $A$  and  $B$  molecules. As observed in all other previously determined structures containing an  $\alpha$ -1,4 linkage, there are intramolecular hydrogen bonds between O(2) and O(3'), though the directions of hydrogen bonds from O(3') and O(2) are opposite to those of the other maltosides. The crystal structure of 6'-iodo phenyl  $\alpha$ -maltoside, which is an inhibitor for  $\alpha$ -amylase, was also determined and showed a quite different conformation from that of all the other maltosides, having no intramolecular hydrogen bond ( $\varphi = -52^\circ$ ,  $\psi = 146^\circ$ ).

### Introduction

The structural chemistry of the amylose group ( $\alpha$ -1,4-D-glucan) has been studied by the X-ray diffraction method for several compounds, cyclohexaamylose (Hybl, Rundle & Williams, 1965; McMullan, Saenger, Fayos & Mootz, 1973; Manor & Saenger, 1973),  $\beta$ -maltose (Quigley, Sarko & Marchessault, 1970), and methyl  $\beta$ -maltoside (Chu & Jeffrey, 1967) which commonly have the  $\alpha$ -1,4-D-glucoside linkage. The polymer structure of amylose itself was also studied in two different crystalline forms (Zobel, French & Hinkle, 1967; Blackwell, Sarko & Marchessault, 1969). In comparison with the  $\beta$ -1,4-D-glucoside linkage of cellulose, a fair degree of flexibility is expected for the  $\alpha$ -1,4-D-glucoside linkage of amylose. More structure determinations of  $\alpha$ -1,4 linked D-glucoside compounds may be needed to establish detailed structural characteristics of amylose.

Phenyl  $\alpha$ -maltoside (PM), a model compound of amylose, has an  $\alpha$ -1,4 linked glucoside bond, and is hydrolysed to maltose and phenol by taka-amylase A (TAA) produced by *Aspergillus oryzae*. This TAA activity on PM is called 'maltosidase activity' and has been used to investigate 'amylase activity' which is the reaction activity of this enzyme to the natural substrate amylose.

The detailed investigation of 'amylase activity' has been carried out by Arita, Isemura, Ikenaka & Matsushima (1970), who synthesized many analogues of amylose and derivatives of phenyl  $\alpha$ -maltoside, and studied their substrate activities. They reported that 6'-iodo phenyl  $\alpha$ -maltoside (IPM) acts as an inhibitor on TAA. This compound has also been studied in the present work.

It is the purpose of this investigation to determine the stereochemistry of the  $\alpha$ -1,4 linked D-glucopyranosides and to offer structural information about the enzyme-substrate interaction.

### Experimental

Crystal data and details of intensity measurement are given in Table 1.

Table 1. *Crystal data*

	PM	IPM
Space group	$P2_1$	$P2_1$
$a$	13.597 (4) Å	14.04 Å
$b$	14.457 (2)	6.02
$c$	9.812 (1)	12.66
$\beta$	93.88 (2) $^\circ$	103.7 $^\circ$
$Z$	4	2
$D_x$	1.40 g cm $^{-3}$	1.66 g cm $^{-3}$
$D_m$	1.40	1.66
Intensity measurement		
Diffractometer	Rigaku automatic 4-circle	Rigaku automatic 4-circle
X-ray	Ni-filtered Cu $K\alpha$	Zr-filtered Mo $K\alpha$
Scan method	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$
Scan range	$\Delta\omega =$ 0.75 + 0.15 tan $\theta$	$\Delta\omega =$ 1.25 + 0.35 tan $\theta$
Background	15 s at both ends of scan	10 s at both ends of scan
$2\theta_{\max}$	130 $^\circ$	50.57 $^\circ$
Total reflexions	3430	2072
Corrections	LP	LP and absorption correction by Furnas method

### Structure analysis

In the structure analysis of PM, the vector space search method, assuming the  $C1$  conformation for the pyranose ring, and the tangent formula technique were

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successfully applied. Search of vector space using the vectors involved in one pyranose ring gave the coordinates of the two rings. The phase angle for each reflexion based on these two pyranose rings was refined with the partial structure tangent formula technique (Karle, 1968). The  $E$  map revealed all the non-hydrogen atoms.

A difference Fourier synthesis gave the locations of all the hydrogen atoms. The structure was refined by block-diagonal least-squares calculations, in which non-hydrogen atoms are assumed to have anisotropic temperature factors of the form  $\exp \{ -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl) \}$ . The hydrogen atoms were

Table 2. Atomic ( $\times 10^3$ ) and thermal ( $\times 10^4$ ) parameters with their *e.s.d.*'s in parentheses (*PM*)

Thermal parameters are in the form  $\exp \{ -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl) \}$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
O(1A)	971 (2)	283 (2)	764 (2)	34 (1)	21 (1)	51 (2)	-3 (2)	16 (3)	-15 (3)
O(2A)	1093 (3)	266 (3)	1000 (2)	73 (2)	37 (1)	58 (3)	51 (3)	1 (4)	2 (4)
O(3A)	978 (3)	365 (4)	1175 (2)	100 (3)	60 (2)	48 (3)	85 (4)	25 (4)	11 (4)
O(4A)	827 (2)	487 (3)	1043 (2)	30 (1)	33 (1)	69 (3)	-5 (2)	25 (3)	-19 (3)
O(5A)	991 (2)	444 (2)	769 (2)	46 (1)	20 (1)	59 (2)	9 (2)	37 (3)	5 (3)
O(6A)	945 (4)	633 (3)	807 (3)	104 (3)	27 (1)	123 (4)	1 (3)	99 (6)	-5 (4)
O(1'A)	912 (2)	10 (2)	594 (2)	42 (1)	28 (1)	49 (2)	-20 (2)	6 (3)	-8 (3)
O(2'A)	1109 (2)	-12 (2)	649 (2)	40 (1)	20 (1)	81 (3)	11 (2)	7 (3)	-2 (3)
O(3'A)	1136 (2)	151 (2)	800 (2)	34 (1)	29 (1)	66 (3)	1 (2)	-13 (3)	-16 (3)
O(5'A)	940 (2)	139 (2)	456 (2)	45 (1)	23 (1)	41 (2)	0 (2)	0 (3)	-1 (3)
O(6'A)	789 (2)	276 (3)	408 (2)	39 (1)	42 (1)	80 (3)	6 (3)	-8 (3)	26 (4)
C(1A)	1032 (3)	357 (4)	810 (3)	34 (2)	22 (1)	56 (4)	3 (3)	3 (4)	-13 (4)
C(2A)	1050 (4)	354 (4)	964 (3)	40 (2)	28 (2)	55 (4)	15 (3)	-1 (5)	-11 (5)
C(3A)	955 (4)	372 (4)	1032 (3)	52 (2)	28 (2)	46 (3)	5 (4)	14 (5)	-2 (5)
C(4A)	918 (3)	467 (4)	987 (3)	32 (2)	28 (2)	46 (3)	3 (3)	11 (4)	-16 (4)
C(5A)	902 (3)	468 (4)	831 (3)	38 (2)	27 (2)	48 (3)	6 (3)	10 (4)	-1 (4)
C(6A)	872 (4)	563 (5)	776 (4)	54 (3)	35 (2)	87 (5)	36 (4)	21 (6)	15 (6)
C(1'A)	978 (3)	55 (4)	511 (3)	38 (2)	24 (1)	49 (3)	-4 (3)	15 (4)	-4 (4)
C(2'A)	1072 (3)	73 (4)	601 (3)	33 (2)	25 (2)	50 (3)	2 (3)	17 (4)	1 (4)
C(3'A)	1047 (3)	137 (4)	718 (3)	32 (2)	21 (1)	50 (3)	3 (2)	-4 (4)	-5 (4)
C(4'A)	1005 (3)	227 (3)	656 (3)	32 (2)	19 (1)	47 (3)	-5 (3)	5 (4)	-2 (4)
C(5'A)	914 (3)	206 (4)	558 (3)	37 (2)	22 (1)	46 (3)	0 (3)	3 (4)	-1 (4)
C(6'A)	883 (4)	293 (4)	480 (4)	42 (2)	25 (2)	72 (4)	4 (3)	-11 (5)	11 (5)
C(11A)	842 (3)	-47 (4)	531 (3)	33 (2)	27 (2)	64 (4)	-13 (3)	0 (4)	-10 (5)
C(12A)	825 (4)	-130 (4)	597 (4)	51 (2)	33 (2)	78 (4)	-27 (4)	-8 (5)	11 (6)
C(13A)	753 (5)	-190 (5)	541 (5)	73 (3)	39 (2)	104 (5)	-46 (5)	-3 (7)	12 (6)
C(14A)	701 (5)	-167 (6)	420 (5)	71 (3)	59 (3)	105 (6)	-64 (6)	-15 (7)	5 (7)
C(15A)	718 (5)	-85 (6)	356 (5)	69 (3)	60 (3)	83 (5)	-42 (5)	-43 (7)	16 (7)
C(16A)	789 (4)	-24 (5)	409 (4)	49 (2)	39 (2)	80 (5)	-17 (4)	-15 (5)	4 (6)
O(1B)	489 (2)	214 (2)	745 (2)	32 (1)	27 (1)	45 (2)	12 (2)	-3 (3)	-12 (3)
O(2B)	646 (3)	251 (3)	588 (3)	46 (1)	50 (2)	77 (3)	-30 (3)	24 (4)	-13 (4)
O(3B)	554 (3)	205 (3)	327 (2)	54 (2)	67 (2)	59 (3)	-34 (3)	28 (4)	16 (4)
O(4B)	364 (3)	106 (4)	342 (2)	48 (1)	70 (2)	65 (3)	-10 (3)	-18 (4)	5 (5)
O(5B)	489 (2)	60 (3)	676 (2)	48 (1)	25 (1)	58 (2)	1 (2)	-6 (3)	4 (3)
O(6B)	303 (2)	-45 (3)	676 (3)	39 (1)	42 (1)	87 (3)	-12 (3)	6 (3)	8 (4)
O(1'B)	434 (2)	453 (2)	975 (2)	39 (1)	25 (1)	74 (3)	11 (2)	29 (3)	6 (3)
O(2'B)	634 (2)	451 (3)	1047 (2)	34 (1)	28 (1)	87 (3)	-11 (2)	14 (3)	-24 (3)
O(3'B)	672 (2)	311 (3)	858 (3)	33 (1)	43 (1)	88 (3)	-5 (2)	19 (3)	-36 (4)
O(5'B)	420 (2)	306 (2)	1074 (2)	38 (1)	24 (1)	59 (2)	-11 (2)	21 (3)	-12 (3)
O(6'B)	413 (3)	117 (3)	1073 (2)	61 (2)	28 (1)	67 (3)	-6 (3)	-2 (4)	5 (3)
C(1B)	547 (3)	141 (4)	697 (3)	34 (2)	26 (2)	56 (4)	8 (3)	0 (4)	-4 (4)
C(2B)	590 (4)	169 (4)	563 (4)	34 (2)	35 (2)	67 (4)	0 (3)	5 (5)	-9 (5)
C(3B)	508 (4)	183 (4)	450 (3)	40 (2)	38 (2)	54 (4)	4 (4)	20 (5)	4 (5)
C(4B)	448 (4)	93 (4)	435 (4)	41 (2)	41 (2)	60 (4)	-5 (4)	6 (5)	-18 (5)
C(5B)	410 (4)	67 (4)	571 (4)	36 (2)	34 (2)	62 (4)	-7 (4)	4 (5)	-7 (5)
C(6B)	362 (4)	-28 (4)	564 (4)	52 (2)	36 (2)	78 (4)	-22 (4)	18 (6)	-15 (5)
C(1'B)	474 (4)	389 (4)	1074 (4)	35 (2)	27 (2)	65 (4)	0 (3)	17 (5)	-6 (5)
C(2'B)	577 (3)	367 (4)	1033 (3)	35 (2)	22 (1)	61 (4)	-8 (3)	4 (4)	-13 (4)
C(3'B)	573 (4)	329 (4)	888 (4)	32 (2)	27 (2)	71 (4)	-2 (3)	19 (5)	-16 (5)
C(4'B)	510 (3)	242 (3)	885 (3)	34 (2)	21 (1)	48 (3)	1 (3)	-1 (4)	-3 (4)
C(5'B)	410 (3)	259 (4)	944 (3)	36 (2)	25 (2)	51 (3)	-3 (5)	3 (4)	-6 (4)
C(6'B)	355 (4)	170 (4)	974 (4)	40 (2)	31 (2)	64 (4)	-12 (3)	3 (5)	4 (5)
C(11B)	349 (3)	502 (4)	1002 (4)	30 (2)	25 (2)	75 (4)	-9 (3)	9 (5)	-20 (5)
C(12B)	292 (4)	484 (4)	1108 (4)	37 (2)	32 (2)	78 (4)	-7 (4)	22 (5)	-8 (5)
C(13B)	209 (4)	539 (5)	1124 (4)	47 (2)	40 (2)	99 (5)	-7 (4)	34 (6)	-17 (6)
C(14B)	185 (4)	611 (5)	1035 (5)	41 (2)	39 (2)	132 (6)	11 (4)	18 (6)	-8 (7)
C(15B)	243 (4)	628 (5)	927 (5)	48 (2)	33 (2)	119 (6)	17 (4)	0 (6)	1 (6)
C(16B)	326 (4)	574 (4)	910 (4)	44 (2)	29 (2)	81 (4)	-3 (4)	9 (5)	3 (5)

assumed to be isotropic. The final  $R$  index was 0.044. The positional and thermal parameters are listed in Tables 2 and 3.

In the IPM determination, the Patterson function was analysed using the minimum function based on the iodine-iodine vector, and the locations of all the non-hydrogen atoms were found, in spite of the pseudo mirror symmetry perpendicular to the  $b$  axis. The positional and thermal parameters of non-hydrogen atoms were refined by block-diagonal least-squares calculations, reducing  $R$  to 0.178. Anisotropic temperature factors were assigned only to the iodine atoms. The positions of the hydrogen atoms could not be determined. The final parameters are listed in Table 4.\*

### Crystal structure

The crystal structures of PM and IPM are shown in Figs. 1 and 2 respectively, indicating the hydrogen-bonding schemes.

For IPM the possible hydrogen bonds are shown in Fig. 2, and were assigned by considering the O...O lengths and C-O...O angles. Two hydrogen-bond sequences are found in this crystal structure, both of which are intermolecular. One sequence is ...O(3')...O(2')...O(2)...O(3')..., which extends roughly parallel to the  $b$  axis, the other is O(4)...O(6)...O(3)...O(5).

\* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31172 (26 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. Atomic and thermal parameters with their *e.s.d.*'s in parentheses (IPM)

	$x$	$y$	$z$	$B$
O(1)	0.65 (1)	0.53 (2)	0.85 (1)	1.8 (2)
O(2)	0.71 (1)	0.75 (3)	1.03 (1)	2.7 (2)
O(3)	0.87 (1)	1.02 (2)	0.99 (1)	3.2 (3)
O(4)	0.93 (1)	0.87 (2)	0.80 (1)	4.6 (4)
O(5)	0.81 (1)	0.39 (1)	0.87 (1)	2.6 (3)
O(6)	1.00 (1)	0.30 (2)	0.84 (1)	3.4 (3)
O(1')	0.34 (1)	0.33 (1)	0.74 (1)	2.2 (3)
O(2')	0.40 (1)	-0.02 (2)	0.87 (1)	3.0 (3)
O(3')	0.59 (1)	0.15 (2)	0.97 (1)	3.0 (3)
O(5')	0.46 (1)	0.27 (3)	0.64 (1)	2.1 (2)
I	0.666 (1)	0.250 (4)	0.560 (1)	*
C(1)	0.74 (2)	0.47 (2)	0.92 (2)	1.2 (4)
C(2)	0.78 (2)	0.68 (2)	0.99 (1)	0.7 (3)
C(3)	0.82 (2)	0.84 (2)	0.93 (2)	2.9 (5)
C(4)	0.90 (2)	0.71 (4)	0.87 (2)	4.1 (5)
C(5)	0.85 (2)	0.53 (3)	0.81 (2)	2.6 (5)
C(6)	0.92 (2)	0.41 (2)	0.76 (2)	2.5 (5)
C(1')	0.40 (2)	0.16 (2)	0.71 (2)	1.5 (4)
C(2')	0.46 (2)	0.07 (2)	0.81 (2)	1.4 (4)
C(3')	0.53 (2)	0.24 (4)	0.88 (2)	2.1 (4)
C(4')	0.59 (2)	0.33 (2)	0.80 (2)	2.2 (4)
C(5')	0.52 (2)	0.41 (2)	0.69 (2)	1.1 (4)
C(6')	0.58 (2)	0.52 (3)	0.61 (2)	3.0 (5)
C(11)	0.26 (2)	0.41 (3)	0.67 (2)	3.5 (5)
C(12)	0.23 (2)	0.32 (2)	0.56 (2)	2.8 (5)
C(13)	0.15 (2)	0.41 (3)	0.50 (2)	4.1 (6)
C(14)	0.09 (2)	0.59 (3)	0.53 (2)	5.1 (7)
C(15)	0.13 (2)	0.68 (3)	0.63 (2)	5.3 (7)
C(16)	0.21 (2)	0.57 (3)	0.70 (2)	3.9 (6)

\* The thermal parameter of the iodine atom is in the form:

$$\exp \{ -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl) \}$$

$\beta_{11}$	$\beta_{22}$	$\beta_{33}$
0.00475 (7)	0.0413 (6)	0.00533 (9)
$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
-0.0100 (9)	0.0031 (1)	-0.0175 (9)

Table 3. Positional parameters of hydrogen atoms (PM)

	$x$	$y$	$z$	Bonded to		$x$	$y$	$z$	Bonded to
H(1A)	1.10	0.35	0.76	C(1A)	H(1B)	0.61	0.12	0.77	C(1B)
H(2A)	1.10	0.41	0.99	C(2A)	H(2B)	0.64	0.11	0.53	C(2B)
H(3A)	0.90	0.33	1.00	C(3A)	H(3B)	0.46	0.24	0.48	C(3B)
H(4A)	0.97	0.52	1.02	C(4A)	H(4B)	0.50	0.04	0.40	C(4B)
H(5A)	0.84	0.42	0.81	C(5A)	H(5B)	0.35	0.11	0.60	C(5B)
H(6A)	0.99	0.01	0.43	C(1'A)	H(6B)	0.47	0.42	1.17	C(1'B)
H(7A)	1.13	0.11	0.54	C(2'A)	H(7B)	0.61	0.32	1.11	C(2'B)
H(8A)	1.00	0.11	0.78	C(3'A)	H(8B)	0.54	0.38	0.82	C(3'B)
H(9A)	1.06	0.26	0.61	C(4'A)	H(9B)	0.54	0.19	0.94	C(4'B)
H(10A)	0.86	0.18	0.62	C(5'A)	H(10B)	0.37	0.30	0.87	C(5'B)
H(11A)	0.85	0.56	0.67	C(6A)	H(11B)	0.31	-0.03	0.47	C(6B)
H(12A)	0.81	0.58	0.82	C(6A)	H(12B)	0.41	-0.08	0.56	C(6B)
H(13A)	0.88	0.35	0.56	C(6'A)	H(13B)	0.29	0.19	1.01	C(6'B)
H(14A)	0.93	0.31	0.41	C(6'A)	H(14B)	0.34	0.13	0.88	C(6'B)
H(15A)	0.87	-0.15	0.68	C(12A)	H(15B)	0.31	0.43	1.17	C(12B)
H(16A)	0.74	-0.25	0.59	C(13A)	H(16B)	0.17	0.53	1.21	C(13B)
H(17A)	0.64	-0.22	0.37	C(14A)	H(17B)	0.12	0.65	1.06	C(14B)
H(18A)	0.68	-0.07	0.27	C(15A)	H(18B)	0.23	0.68	0.85	C(15B)
H(19A)	0.80	0.04	0.36	C(16A)	H(19B)	0.37	0.59	0.83	C(16B)
H(20A)	1.08	0.25	1.07	O(2A)	H(20B)	0.69	0.26	0.53	O(2B)
H(21A)	0.93	0.41	1.23	O(3A)	H(21B)	0.51	0.20	0.26	O(3B)
H(22A)	0.84	0.54	1.10	O(4A)	H(22B)	0.38	0.11	0.25	O(4B)
H(23A)	0.99	0.63	0.74	O(6A)	H(23B)	0.33	-0.03	0.76	O(6B)
H(24A)	1.17	-0.01	0.68	O(2'A)	H(24B)	0.71	0.44	1.03	O(2'B)
H(25A)	1.12	0.19	0.87	O(3'A)	H(25B)	0.68	0.29	0.77	O(3'B)
H(26A)	0.75	0.24	0.40	O(6'A)	H(26B)	0.41	0.06	1.04	O(6'B)

The crystal structure of PM is characterized by the two different kinds of molecular chains linked through the hydrogen-bonding schemes. The crystallographically independent molecules *A* and *B* form their own molecular chains along the *b* axis. There are three O(2)···O(6), O(3)···O(2'), O(4)···O(3') hydrogen bonds binding the *A* molecular chain, while two O(2')···O(6), O(2')···O(6') hydrogen bonds bind the *B* molecular chain. All but one [O(3*B*)] of the 14 crystallographically independent hydroxyl oxygens are in the hydrogen-bonding system; however, the hydrogen-acceptor capacities of the ring oxygens and bridged oxygens are not utilized in this structure. The hydrogen-bond distances of PM are listed in Table 5.

Table 5. *Hydrogen-bond distances (PM)(Å)*

Symmetry code			
(a)	<i>x</i> ,	<i>y</i> ,	<i>z</i>
(b)	<i>x</i> ,	<i>y</i> ,	$-1.0+z$
(c)	$1.0-x$ ,	$0.5+y$ ,	$1.0-z$
(d)	$1.0-x$ ,	$0.5+y$ ,	$2.0-z$
(e)	$2.0-x$ ,	$0.5+y$ ,	$2.0-z$
(f)	$1.0+x$ ,	<i>y</i> ,	<i>z</i>

O(2 <i>A</i> ) <i>a</i> –O(3' <i>A</i> ) <i>a</i>	2.664	O(2' <i>B</i> ) <i>a</i> –O(6 <i>B</i> ) <i>d</i>	2.783
O(2 <i>B</i> ) <i>a</i> –O(3' <i>B</i> ) <i>a</i>	2.785	O(2' <i>B</i> ) <i>a</i> –O(6' <i>B</i> ) <i>d</i>	2.746
O(4 <i>A</i> ) <i>a</i> –O(2' <i>B</i> ) <i>a</i>	2.683	O(4 <i>A</i> ) <i>a</i> –O(3' <i>A</i> ) <i>e</i>	2.845
O(6' <i>A</i> ) <i>a</i> –O(2 <i>B</i> ) <i>a</i>	2.734	O(3 <i>A</i> ) <i>a</i> –O(2' <i>A</i> ) <i>e</i>	2.783
O(4 <i>B</i> ) <i>a</i> –O(6' <i>B</i> ) <i>b</i>	2.773	O(6 <i>A</i> ) <i>a</i> –O(2 <i>A</i> ) <i>e</i>	2.769
O(6' <i>A</i> ) <i>a</i> –O(6 <i>B</i> ) <i>c</i>	2.968	O(2' <i>A</i> ) <i>a</i> –O(6 <i>B</i> ) <i>f</i>	2.679

### Molecular structure

All glucose residues are in the C1 chair conformation. Bond lengths and bond angles in the structure of PM are shown in Fig. 3. The mean C–C and C–O bond lengths in the structure of PM are 1.525 and 1.425 Å, respectively, and are in agreement with lengths of other  $\alpha$ -pyranosyl systems. Asymmetry of the ring C–O bonds is observed in this molecule as in other  $\alpha$ -pyranosyl systems; the bond lengths of the *A* and *B* molecules are C(1)–O(5) 1.421, 1.417 Å; C(1')–C(5') 1.421, 1.397 Å; C(5)–O(5) 1.438, 1.437 Å; C(5')–O(5') 1.447, 1.446 Å.

The conformations of the primary alcohol groups are listed in Table 6. Of the six independent primary alcohol groups, four groups take the *gauche-gauche* conformation and the remaining two the *gauche-trans* conformation, according to the convention of Sundaralingam (1968) and Quigley *et al.* (1970). For the iodine derivative the *gauche-gauche* conformation is observed.

### The conformation of maltoside

In order to study the structure of amylose the nature of the  $\alpha$ -1,4-glucoside bond must be clarified. The character of this bond is represented by the two rotation angles  $\varphi$  [C(4')–O(1)–C(1)–O(4)] and  $\psi$  [C(1)–O(1)–C(4')–O(1')] (Quigley *et al.*, 1970). Fig. 4 shows the state when the maltose backbone is straight ( $\varphi=0^\circ$ ,  $\psi=180^\circ$ ). All maltosides which have been determined

in the crystalline state resemble this 'backbone straight state' and the intramolecular hydrogen bonds between O(2) and O(3') stabilize this conformation.

The conformations at the phenyl  $\alpha$ -maltoside linkage of the two molecules *A* and *B* show a strong resemblance to each other (Fig. 4). Though they are similar to

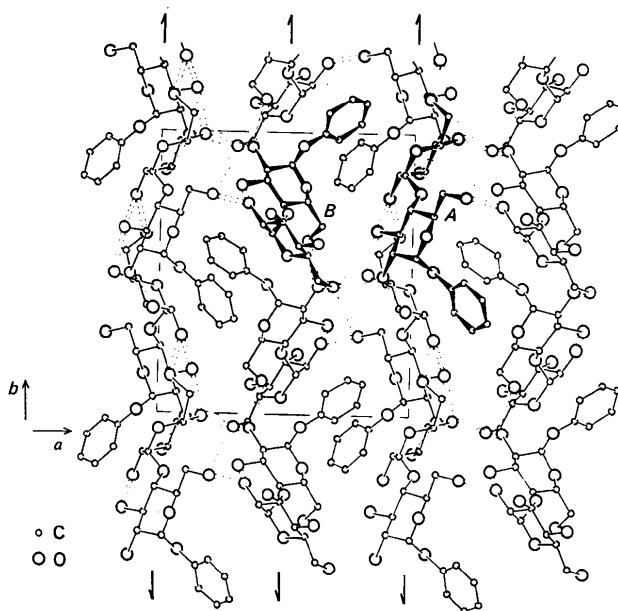


Fig. 1. The crystal structure of phenyl  $\alpha$ -maltoside viewed down the *c* axis. Hydrogen bonds are shown by broken lines.

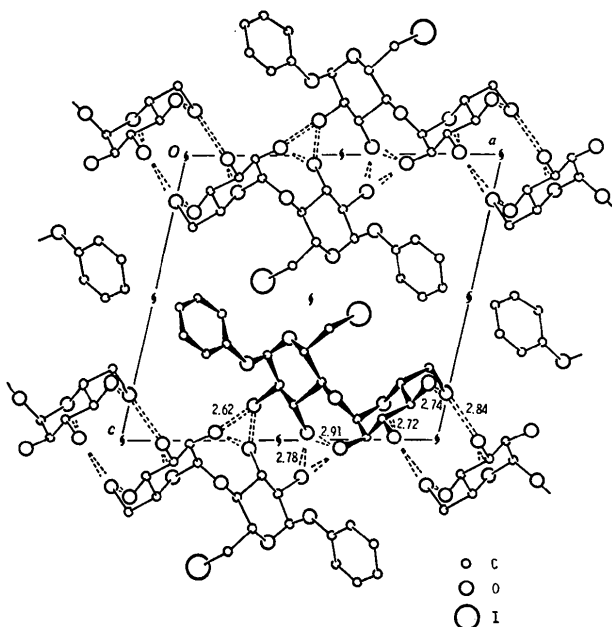


Fig. 2. The crystal structure of 6'-iodo phenyl  $\alpha$ -maltoside viewed down the *b* axis. Hydrogen bonds are shown by broken lines.

other  $\alpha$ -1,4 linked  $\alpha$ -pyranosyl systems, there do exist two significant differences between the conformations of PM and other compounds. One concerns the direction of the intramolecular hydrogen bonds. In the structure of methyl  $\beta$ -maltoside, O(2) acts as a hydrogen donor and O(3') as a hydrogen acceptor. In PM, O(3') is a hydrogen donor and O(2) a hydrogen acceptor.

Another difference is the helical chirality. The conformational angles are marked in the  $\varphi$ - $\psi$  map (Fig. 5).  $\varphi$  and  $\psi$  of the proposed sixfold V and B amylose are also plotted. Both conformational angles in methyl  $\beta$ -maltoside and  $\beta$ -maltose are rather close to those of the right-handed sixfold helices. However phenyl  $\alpha$ -maltosides *A* and *B* are very close to the left-handed sixfold helices. The problem of the left- and right-

Table 6. *The conformation of the primary alcohol groups*

Ring	Dihedral angle between the planes O(5), C(5), C(6) and C(5), C(6), O(6)		Dihedral angle between the planes C(4), C(5), C(6) and C(5), C(6), O(6)		Conformation
PMA (unprimed)	60.1°		60.7°		<i>gauche-gauche</i>
PMA (primed)	71.5		169.9		<i>gauche-trans</i>
PMB (unprimed)	74.7		164.1		<i>gauche-trans</i>
PMB (primed)	60.9		61.0		<i>gauche-gauche</i>
PMI (unprimed)	53		65		<i>gauche-gauche</i>
PMI (primed)*	65		64		<i>gauche-gauche</i>

\* The hydroxyl group O(6') is substituted by the iodine atom.

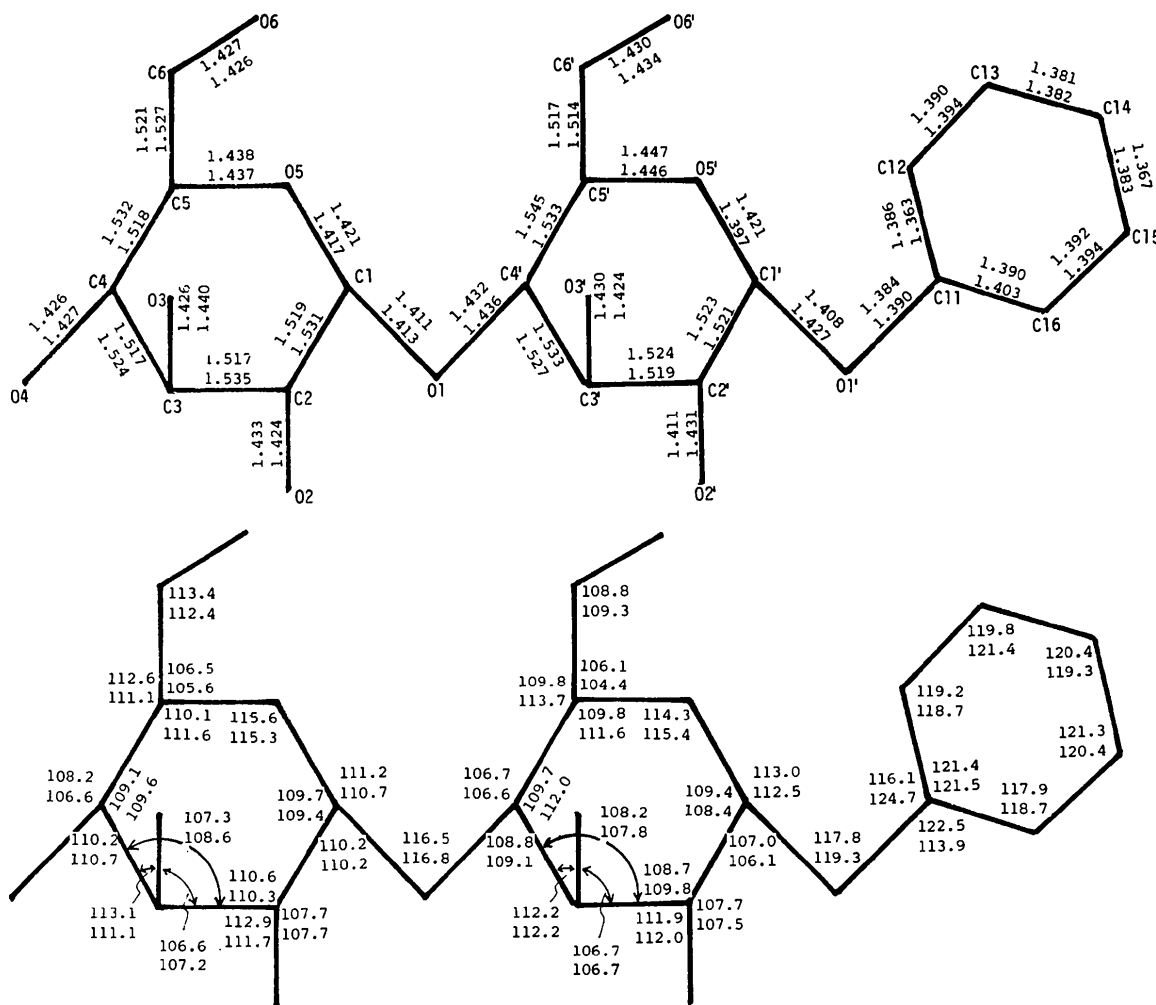


Fig. 3. Bond lengths and bond angles of the phenyl  $\alpha$ -maltoside *A* and *B* molecules.

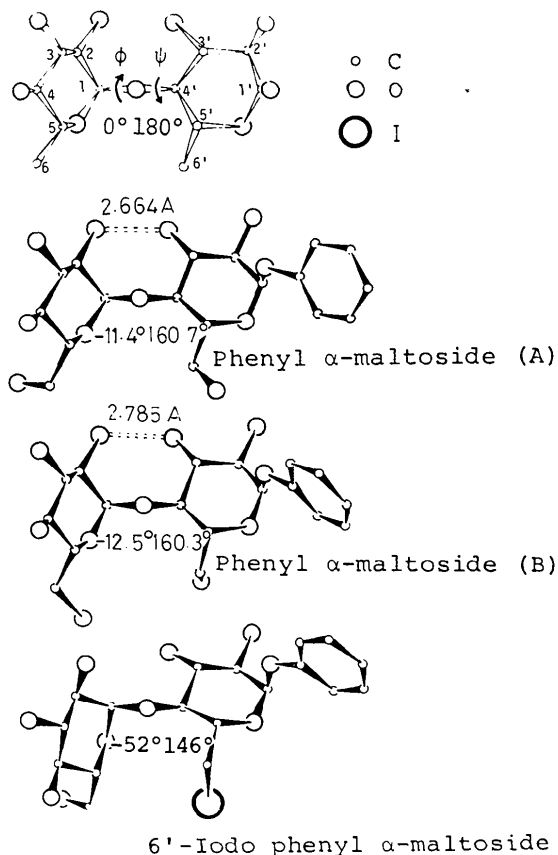


Fig. 4. Schematic representation of the maltoside conformational angles  $\phi$  and  $\psi$ . In the upper figure, the residues are in the 'backbone straight state',  $(\phi, \psi) = (0^\circ, 180^\circ)$ . All the maltosides having been determined in the crystalline state are in a similar configuration. Phenyl  $\alpha$ -maltoside (PM) *A* and *B* molecules also adopt a similar conformation. 6'-iodo phenyl  $\alpha$ -maltoside takes a quite different conformation having no intramolecular hydrogen bond.

handed chirality of amylose has not been determined. The results of the X-ray structure determination of PM support the existence of the sixfold left-handed helix in amylose. The lengths of the intramolecular hydrogen bonds 2.664 (PMA), 2.785 Å (PMB) are shorter than those of the other compounds: 2.852 (cyclohexaamylose), 2.825 (methyl  $\beta$ -maltoside), 2.79 Å ( $\beta$ -maltose).

The conformation of 6'-iodo phenyl  $\alpha$ -maltoside, which is an inhibitor of TAA, is quite different from that of  $\alpha$ -1,4 linked  $\alpha$ -pyranosyl systems. The steric effect of the iodine atom keeps O(2) and O(3') apart and there is no intramolecular hydrogen bond between them. The conformational angles  $\phi$  and  $\psi$  are  $-52^\circ$  and  $146^\circ$  respectively.

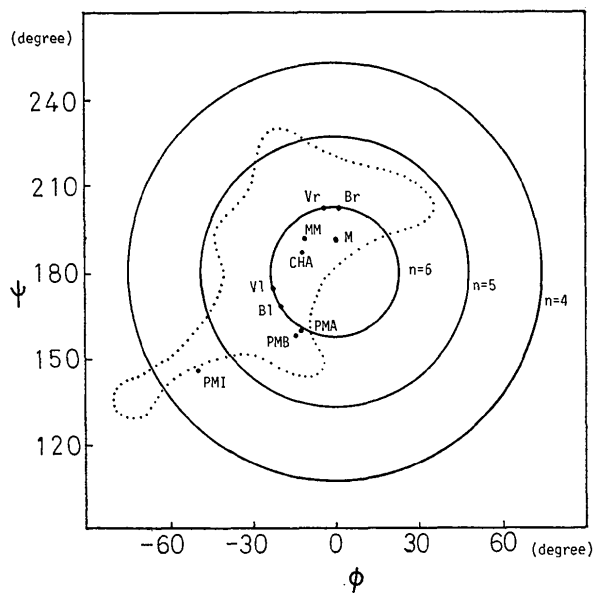


Fig. 5. Allowed conformational region (dotted line) for maltose with a bridge angle of  $117^\circ$ . The  $n$  contours are the number of residues per turn of helix. This figure is from Quigley *et al.* (1970) to which have been added our results. PMA and PMB, phenyl  $\alpha$ -maltoside *A* and *B* molecules (this work); PMI, 6'-iodo phenyl  $\alpha$ -maltoside (this work); M,  $\beta$ -maltose (Quigley *et al.*, 1970); MM, methyl  $\beta$ -maltoside (Chu & Jeffrey, 1967); CHA, cyclohexaamylose (Hybe *et al.*, 1965); V1 and Vr, left- and right-handed V amylose (Zobel *et al.*, 1967); B1 and Br, left- and right-handed B amylose (Blackwell *et al.*, 1969).

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