

$$\begin{aligned} \langle 3p_y | y | 5s \rangle &= (4/135)(1/21)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta) \{H_0 - [(2\cos^2\theta - \sin^2\theta) + 3\sin^2\theta(\cos^2\phi - \sin^2\phi)] H_2\} \\ \langle 3d_{z^2} | y | 5s \rangle &= (4/1575)(\alpha/\beta)^{\frac{7}{2}}(1/\beta) \sin\theta \sin\phi \{3(4\cos^2\theta - \sin^2\theta) H_3 - 2H_1\} \\ \langle 3d_{xz} | y | 5s \rangle &= (8/45)(1/21)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta) \cos\theta \sin^2\theta \sin\phi \cos\phi H_3 \\ \langle 3d_{yz} | y | 5s \rangle &= (4/675)(3/7)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta) \cos\theta \{2H_1 + [(2\cos^2\theta - 3\sin^2\theta) - 5\sin^2\theta(\cos^2\phi - \sin^2\phi)] H_3\} \\ \langle 3d_{xy} | y | 5s \rangle &= (2/225)(1/21)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta) \sin\phi \cos\phi \{[5\sin\theta(4\cos^2\phi - 3) + (4\cos^2\theta - \sin^2\theta)] H_3 - 4H_1\} \\ \langle 3d_{x^2-y^2} | y | 5s \rangle &= (2/225)(1/21)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta) \sin\theta \sin\phi \{[5\sin\theta(3 - 4\sin^2\phi) + (4\cos^2\theta - \sin^2\theta)] H_3 - 4H_1\} \\ \langle 4s | y | 5s \rangle &= (4/945)(2/5)^{\frac{1}{2}}(\alpha/\beta)^{\frac{9}{2}}(1/\beta) \sin\theta \sin\phi I_1 \\ \langle 4p_x | y | 5s \rangle &= (4/315)(2/15)^{\frac{1}{2}}(\alpha/\beta)^{\frac{9}{2}}(1/\beta) \cos\theta \sin\theta \sin\phi I_2 \\ \langle 4p_y | y | 5s \rangle &= (4/315)(2/15)^{\frac{1}{2}}(\alpha/\beta)^{\frac{9}{2}}(1/\beta) \sin^2\theta \sin\phi \cos\phi I_2 \\ \langle 4p_z | y | 5s \rangle &= (2/945)(2/15)^{\frac{1}{2}}(\alpha/\beta)^{\frac{9}{2}}(1/\beta) \{I_0 - [(2\cos^2\theta - \sin^2\theta) + 3\sin^2\theta(\cos^2\phi - \sin^2\phi)] I_2\} \\ \langle 5s | y | 5s \rangle &= (8/14175)(\alpha/\beta)^{\frac{11}{2}}(1/\beta) \sin\theta \sin\phi J_1 \\ \langle 5p_x | y | 5s \rangle &= (8/14175)(3)^{\frac{1}{2}}(\alpha/\beta)^{\frac{11}{2}}(1/\beta) \cos\theta \sin\theta \cos\phi J_2 \\ \langle 5p_y | y | 5s \rangle &= (8/14175)(3)^{\frac{1}{2}}(\alpha/\beta)^{\frac{11}{2}}(1/\beta) \sin^2\theta \sin\phi \cos\phi J_2 \\ \langle 5p_z | y | 5s \rangle &= (4/14175)(1/3)^{\frac{1}{2}}(\alpha/\beta)^{\frac{11}{2}}(1/\beta) \{J_0 - [(2\cos^2\theta - \sin^2\theta) + 3\sin^2\theta(\cos^2\phi - \sin^2\phi)] J_2\} \end{aligned}$$

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## The Crystal and Molecular Structure of Phlorizin Dihydrate

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The crystal structure of phlorizin, a  $\beta$ -D-glucopyranoside of a flavonoid dihydrochalcone phloretin, has been determined by single crystal diffraction methods using diffractometer data obtained by the  $\omega$ -2 $\theta$  scan technique with Cu K $\alpha$  radiation from a crystal with space group symmetry P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> and unit cell parameters  $a=4.9094$  (2),  $b=19.109$  (1),  $c=23.275$  (4) Å. The structure was solved by direct methods and refined by full-matrix least-squares to a final R = 0.047 for the 1697 observed reflections. The dihydrochalcone moiety is flat and fully extended. The glucose ring has the <sup>4</sup>C<sub>1</sub> chair conformation and the conformation of the primary alcohol group is *gauche-gauche*. The crystal packing is dominated by an extensive hydrogen bonding pattern. There are one strong and two weak intramolecular hydrogen bonds in the phlorizin molecule.

## Introduction

Some of the flavonoid dihydrochalcones and their saccharide derivatives display an intensely sweet taste and have potential use for the nonnutritive sweeteners, while the cor-

responding flavanones are usually bitter compounds.<sup>1-3</sup> Little is known about the conformational characteristics of the flavonoid dihydrochalcones themselves and their modes of linkage to the saccharides. Phlorizin, 2- $\beta$ -D-glucopyranoside of phloretin, is a sweet compound with bitter aftertaste.

The crystal structure analysis of phlorizin has been undertaken in an effort to study the conformational aspects of the flavonoid dihydrochalcones.

### Experimental

Transparent crystals of phlorizin (Sigma) were obtained by slow evaporation of an aqueous ethanol solution at room temperature. The orthorhombic space group  $P2_12_12_1$  was uniquely determined from the systematic absences. Accurate unit cell parameters were determined by a least-squares fit of the  $2\theta$  angles ( $20^\circ < 2\theta < 50^\circ$ ) for the 24 reflections centered on an automated Rigaku AFC diffractometer. Crystal data are as follows:

$C_{21}H_{24}O_{10} \cdot 2H_2O$ ; mol. wt. 472.4;  $F(000) = 1000$ ;  
 $a = 4.9094(2)$ ,  $b = 19.109(1)$ ,  $c = 23.275(4)$  Å;  
 $V = 2183.1 \text{ \AA}^3$ ; space group  $P2_12_12_1$ ;  $Z = 4$ ;  
 $\mu(\text{Cu K}\alpha) = 9.13 \text{ cm}^{-1}$ ;  $D_c = 1.437 \text{ g cm}^{-3}$   $D_m = 1.435 \text{ g cm}^{-3}$  by flotation in  $\text{CCl}_4$ -cyclohexane

Reflection data from a crystal with dimensions of  $0.5 \times 0.4 \times 0.2$  mm were collected with graphite-monochromated Cu K $\alpha$  radiation using the  $\omega$ - $2\theta$  scan technique over a range of  $(1.2 + 0.4 \tan \theta)^\circ$  in  $\omega$  at a scan rate of  $4^\circ/\text{min}$  and a 10-s background count at each end of the scan range. Three standard reflections were monitored after every 50 reflections. After corrected for Lorentz and polarization effects, the intensities were converted to structure factor amplitudes. Of the 1945 independent reflections measured within the range of  $2\theta \leq 120^\circ$ , 248 were considered unobserved as defined by  $F < 6\sigma(F)$ . No correction for the absorption and extinction effects was made.

The structure was solved by direct methods using the program SHELX76.<sup>4</sup> The H atoms were located on a difference Fourier map calculated at an intermediate stage of least-squares refinement after nonhydrogen atoms were refined anisotropically. In the final cycle of full-matrix least-squares refinement, isotropic thermal parameters for the H atoms were varied. The quantity minimized was  $\sum \omega (|F_o| - |F_c|)^2$ , where  $\omega = 1.0/(\sigma^2(F) + 0.0093(F)^2)$  in the last cycle of refinement. The final R value was 0.047 for the 1697 observed reflections. The weighted  $R_w$  was 0.050. All of the atomic scattering factors were from the International Tables for X-ray Crystallography.<sup>5</sup> The final atomic parameters are listed in Table 1.\*

TABLE 1: Fractional Coordinates ( $\times 10^4$  for non-H Atoms,  $\times 10^3$  for H Atoms), Thermal Parameters ( $\times 10^3$  for non-H Atoms,  $\times 10^2$  for H Atoms) and Bond Distances (Å) for H Atoms

Atom	x	y	z	Ueq <sup>a</sup>
C(1)	4151(9)	3545(2)	3462(2)	34(1)
C(2)	4525(8)	3491(2)	2864(2)	30(1)
C(3)	6372(9)	3896(2)	2568(2)	35(1)

\*Tables for the anisotropic temperature factors for the nonhydrogen atoms, the final observed and calculated structure factors, the bond angles involving the hydrogen atoms and the least-squares planes are available as supplementary materials from the author.

C(4)	8018(8)	4374(2)	2877(2)	33(1)
C(5)	7739(9)	4443(2)	3456(2)	39(1)
C(6)	5825(10)	4047(2)	3753(2)	38(1)
O(4)	9763(7)	4757(2)	2558(1)	42(1)
O(6)	5625(8)	4160(2)	4314(1)	56(1)
C(7)	2285(9)	3135(2)	3817(2)	36(1)
O(7)	2146(8)	3250(2)	4335(1)	61(1)
C(8)	510(9)	2550(2)	3592(2)	34(1)
C(9)	-1205(10)	2231(2)	4071(2)	39(1)
C(10)	-3021(9)	1629(2)	3899(2)	35(1)
C(11)	-3095(9)	1317(2)	3363(2)	40(1)
C(12)	-4865(10)	762(2)	3243(2)	39(1)
C(13)	-6579(9)	523(2)	3658(2)	35(1)
C(14)	-6521(11)	812(2)	4202(2)	45(1)
C(15)	-4766(10)	1354(2)	4320(2)	41(1)
O(13)	-8387(7)	-24(1)	3558(1)	47(1)
C(1')	3535(7)	2850(2)	2006(1)	30(1)
C(2')	2064(9)	2170(2)	1861(1)	33(1)
C(3')	2461(8)	1993(2)	1229(1)	32(1)
C(4')	1881(7)	2624(2)	849(1)	28(1)
C(5')	3390(7)	3267(2)	1062(1)	30(1)
C(6')	2768(9)	3918(2)	715(2)	42(1)
O(1')	2895(6)	3019(1)	2575(1)	34(0)
O(2')	3083(9)	1610(1)	2192(1)	62(1)
O(3')	675(8)	1436(1)	1094(1)	49(1)
O(4')	2675(6)	2464(1)	276(1)	37(0)
O(5')	2627(5)	3393(1)	1646(1)	31(0)
O(6')	-75(6)	4025(2)	659(1)	47(1)
O(W1)	2475(23)	5676(5)	3188(4)	74(3)
O(W2)	6600(24)	5584(5)	4585(4)	100(3)

Atom	x	y	z	U	C, O-H
H(1)	-214(13)	151(3)	297(3)	7(2)	1.10(6)
H(2)	-487(10)	53(2)	283(2)	4(1)	1.05(4)
H(3)	-884(19)	5(4)	318(3)	9(2)	0.93(8)
H(4)	-747(9)	69(2)	445(2)	2(1)	0.77(4)
H(5)	-502(9)	160(2)	465(2)	3(1)	0.90(4)
H(6)	3(10)	212(2)	439(2)	5(1)	0.99(5)
H(7)	-218(10)	261(3)	425(2)	6(1)	0.96(5)
H(8)	170(11)	222(2)	344(2)	3(1)	0.94(5)
H(9)	-45(10)	272(2)	327(2)	5(1)	0.94(4)
H(10)	636(8)	390(2)	218(2)	2(1)	0.91(4)
H(11)	1076(21)	493(4)	280(3)	14(3)	0.82(8)
H(12)	868(13)	482(3)	374(2)	6(1)	1.08(6)
H(13)	448(13)	387(3)	442(2)	12(2)	0.83(6)
H(14)	563(11)	271(2)	198(2)	5(1)	1.06(5)
H(15)	29(10)	230(2)	193(2)	4(1)	0.92(4)
H(16)	282(14)	169(3)	263(3)	11(2)	1.04(6)
H(17)	431(9)	182(2)	115(2)	3(1)	0.99(4)
H(18)	161(10)	125(2)	92(2)	4(1)	0.70(4)
H(19)	-1(9)	275(2)	83(2)	4(1)	0.96(4)
H(20)	147(10)	248(3)	0(2)	4(1)	0.88(5)
H(21)	535(10)	317(2)	105(2)	4(1)	0.98(4)
H(22)	346(11)	383(2)	32(2)	5(1)	1.01(5)
H(23)	357(11)	435(3)	88(2)	5(1)	0.98(5)
H(24)	-60(15)	435(4)	86(3)	10(2)	0.83(7)
H(25)	106(39)	579(8)	352(7)	21(7)	1.06(17)
H(26)	442(37)	583(8)	324(7)	12(6)	1.01(16)
H(27)	579(44)	572(9)	482(8)	16(7)	0.73(19)
H(28)	735(24)	541(6)	463(4)	6(4)	0.51(11)

$$^a U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* (\vec{a}_i \cdot \vec{a}_j)$$

## Results and Discussion

The conformation of the phlorizin molecule and the numbering of the atoms are shown in Figure 1. Bond distances and angles are given in Table 2. The average C-C distances in the benzene rings 1 and 2 are 1.398 (0.027) and 1.384 (0.016) Å respectively. Each ring is planar within 0.010 Å. The two highly substituted benzene rings show characteristic deformation from the ideal  $D_{6h}$  symmetry. For example, the endocyclic bond angles opposite to the carbon substituents are 116.2 (3) and 116.9 (4)° for the rings 1 and 2 respectively. Decrease in this angle from the ideal value of 120° is a characteristic feature in the  $C_6H_5-C$  type structures.<sup>6,7</sup> The exocyclic C(6)-O(6), 1.327 (5) Å, and C(4)-O(4), 1.349 (5) Å, bonds are considerably shorter than normal 1.38 Å observed in phloroglucinol.<sup>8</sup> This shortening may be due to delocalization of the benzene  $\pi$  electrons through the C-O bonds. The lengthening of the C(1)-C(6) bond and the shortening of the C(1)-C(7) and C(6)-O(6) bonds may be the result of forming of an acyclic six membered ring through the strong O(6)-H...O(7) intramolecular hydrogen bond.

In the  $\beta$ -D-glucose moiety, the average C-C and exocyclic C-O distances are 1.520 (4) and 1.412 (8) Å, respectively. These values are in excellent agreement with those in the O(1')-substituted  $\beta$ -D-glucose derivatives.<sup>9-12</sup> The bond distances in the acetal sequence of bonds C(5')-O(5')-C(1')-O(1')-C(2) display the characteristic variation observed in the  $\alpha$ - and  $\beta$ -pyranosides, in that the anomeric C(1')-O(1') and C(1')-O(5') bonds are shorter.<sup>13</sup> However, C(1')-O(1') is longer by 4 $\sigma$  and C(1')-O(5') is shorter by 5 $\sigma$  than the

mean values 1.384 and 1.427 Å observed in 12  $\beta$ -pyranosides.<sup>11</sup> The bridge angle C(1')-O(1')-C(2) is 118.8 (3)° which is very larger than the values (113~115°) in the other  $\beta$ -D-glucose derivatives. This widening may be due to the presence of the bulky phenyl group.

The selected torsion angles in the phlorizin molecule are listed in Table 3. The dihydrochalcone moiety is fully extended and nearly planar. The dihedral angle between the two phenyl groups is 171°. The ring torsion angles of the

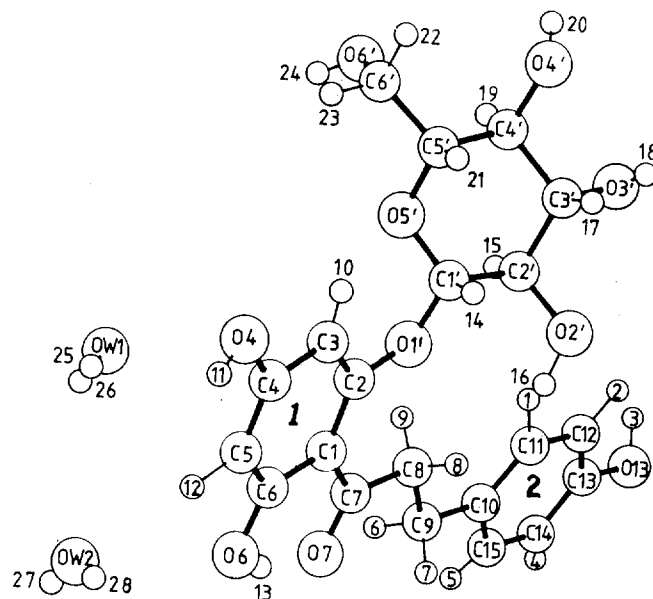


Figure 1. Conformation and atom notation for phlorizin dihydrate.

TABLE 2: Bond Distances (Å) and Angles (°) for Phlorizin Dihydrate

C(1) -C(2) 1.409(6)	C(1) -C(6) 1.434(6)	C(1) -C(7) 1.461(6)	C(2) -C(3) 1.375(6)
C(2) -O(1') 1.380(5)	C(3) -C(4) 1.416(6)	C(4) -C(5) 1.361(6)	C(4) -O(4) 1.349(5)
C(5) -C(6) 1.391(6)	C(6) -O(6) 1.327(6)	C(7) -O(7) 1.227(6)	C(7) -C(8) 1.512(6)
C(8) -C(9) 1.524(6)	C(9) -C(10) 1.509(6)	C(10) -C(11) 1.383(6)	C(10) -C(15) 1.403(6)
C(11) -C(12) 1.399(6)	C(12) -C(13) 1.359(6)	C(13) -C(14) 1.382(6)	C(13) -C(13) 1.392(5)
C(14) -C(15) 1.375(6)	C(1') -C(2') 1.524(5)	C(1') -O(1') 1.400(4)	C(1') -O(5') 1.407(4)
C(2') -C(3') 1.523(5)	C(2') -O(2') 1.410(5)	C(3') -C(4') 1.522(5)	C(3') -O(3') 1.413(4)
C(4') -C(5') 1.518(5)	C(4') -O(4') 1.422(4)	C(5') -C(6') 1.515(5)	C(5') -O(5') 1.430(4)
C(6') -O(6') 1.416(5)			
C(1) -C(2) -C(3) 122.6(4)	C(1) -C(2) -O(1') 116.9(4)	C(1) -C(6) -C(5) 121.0(4)	
C(1) -C(6) -O(6) 122.1(4)	C(1) -C(7) -O(7) 119.6(4)	C(1) -C(7) -C(8) 124.2(4)	
C(2) -C(1) -C(6) 116.2(4)	C(2) -C(1) -C(7) 127.0(4)	C(2) -C(3) -C(4) 119.0(4)	
C(2) -O(1') -C(1') 118.8(3)	C(3) -C(2) -O(1') 120.5(4)	C(3) -C(4) -C(5) 120.5(4)	
C(3) -C(4) -O(4) 115.7(4)	C(4) -C(5) -C(6) 120.6(4)	C(5) -C(4) -O(4) 123.8(4)	
C(5) -C(6) -O(6) 116.9(4)	C(6) -C(1) -C(7) 116.8(4)	C(7) -C(8) -C(9) 111.1(4)	
O(7) -C(7) -C(8) 116.2(4)	C(8) -C(9) -C(10) 115.9(4)	C(9) -C(10) -C(11) 125.6(4)	
C(9) -C(10) -C(15) 117.5(4)	C(10) -C(11) -C(12) 121.6(4)	C(10) -C(15) -C(14) 121.7(4)	
C(11) -C(10) -C(15) 116.9(4)	C(11) -C(12) -C(13) 119.8(4)	C(12) -C(13) -C(14) 120.3(4)	
C(12) -C(13) -O(13) 122.0(4)	C(13) -C(14) -C(15) 119.8(4)	C(14) -C(13) -O(13) 117.7(4)	
C(1') -C(2') -C(3') 110.1(3)	C(1') -C(2') -O(2') 110.9(3)	C(1') -O(5') -C(5') 111.0(2)	
C(2') -C(1') -O(1') 107.5(3)	C(2') -C(1') -O(5') 110.3(3)	C(2') -C(3') -C(4') 111.2(3)	
C(2') -C(3') -O(3') 107.6(3)	C(3') -C(2') -O(2') 108.4(3)	C(3') -C(4') -C(5') 111.1(3)	
C(3') -C(4') -O(4') 108.8(3)	C(4') -C(3') -O(3') 110.6(3)	C(4') -C(5') -C(6') 113.1(3)	
C(4') -C(5') -O(5') 108.7(3)	C(5') -C(4') -O(4') 110.3(3)	C(5') -C(6') -O(6') 111.5(3)	
C(6') -C(5') -O(5') 108.3(3)	O(1') -C(1') -O(5') 108.8(3)		

$\beta$ -D-glucose moiety vary from 48.4 to 66.1° with the mean value of 57.2°. The average deviations of atoms from the three least-squares planes through opposite bonds are 0.65 Å from plane C(1'), C(2'), C(4'), C(5'), 0.67 Å from C(3'), C(4'), O(5'), C(1') and 0.66 Å from C(2'), C(3'), C(5'), O(5'). The ring-puckering parameters are  $q_2 = 0.082$  Å,  $q_3 = 0.569$  Å,  $\theta = 8.2^\circ$ ,  $\phi_2 = 174.8^\circ$  and  $Q = 0.575$  Å.<sup>14</sup> These indicate a distorted <sup>4</sup>C<sub>1</sub> chair form for the  $\beta$ -D-glucose ring. The conformation about exocyclic C(5')-C(6') is *gauche-gauche* identical to those of the relevant molecules. The other exocyclic torsion angles have values close to 60 or 180° which correspond to the ideal *gauche* or *trans* arrangements respectively. The glycosidic torsion angle C(2)-O(1')-C(1')-O(5') is -78.6° and larger than the ideal 60° staggered angles. This is consistent with the conformational potential-energy curves calculated by Jeffrey, Pople & Radom.<sup>15</sup>

The stereoscopic view of the crystal packing is presented in Figure 2. The extensive system of the hydrogen bonds is described in Table 4. There are three unique intermolecular hydrogen bonds between the phlorizin molecules and six hydrogen bonds involving the two water molecules. Each water molecule forms three hydrogen bonds with the hydroxyl groups of the phlorizin molecules. All of the molecules in the *ab* plane are strongly interconnected by the seven hydrogen bonds (types 1 to 7) to form an infinite two-dimensional molecular stack perpendicular to the *c* axis. Two hydrogen bonds (types 8 and 9) interweave these stacks along the *c* direction to form a three-dimensional hydrogen bonding network. There is a strong intramolecular hydrogen bond between the hydroxyl O(6) and keto O(7) atoms. The close contact between the hydroxyl O(1') and bridge O(2') atoms can marginally be considered as a weak intramolecular hydrogen bond due to the poor geometry (see Table 4). Hydrogen bonding to the bridge oxygen has not been observed in the di- and higher saccharides thus far studied.<sup>12</sup> An unusual

"hydrogen-bonding interaction" exists between the ring

TABLE 3: Selected Torsion Angles (°) in Phlorizin Dihydrate and Comparison for the Glucopyranose Moiety in the Relevant Molecules

	I	II	III	IV
C(2)-C(1)-C(7)-C(8)	3.0			
C(1)-C(7)-C(8)-C(9)	-179.8			
C(7)-C(8)-C(9)-C(10)	-178.7			
C(8)-C(9)-C(10)-C(11)	5.1			
C(1)-C(2)-O(1')-C(1')	-167.9			
C(2)-O(1')-C(1')-C(2')	162.0			
C(2)-O(1')-C(1')-O(5')	-78.6			
C(1')-C(2')-C(3')-C(4')	-48.4	-51.3	-60.9	-54
C(2')-C(3')-C(4')-C(5')	49.6	49.2	64.3	52
C(3')-C(4')-C(5')-O(5')	-56.8	-51.7	-63.2	-54
C(4')-C(5')-O(5')-C(1')	65.8	60.6	61.1	63
C(5')-O(5')-C(1')-C(2')	-66.1	-63.3	-58.3	-68
O(5')-C(1')-C(2')-C(3')	56.2	56.3	57.3	62
O(5')-C(5')-C(6')-O(6')	-69.5	-53.6	-61.8	-69

I; present study, II; Gentiobiose<sup>12</sup>, III; 4-O- $\beta$ -D-Glucopyranosyl-D-glucitol<sup>11</sup>, IV; Methyl  $\beta$ -D-glucopyranoside hemihydrate<sup>10</sup>.

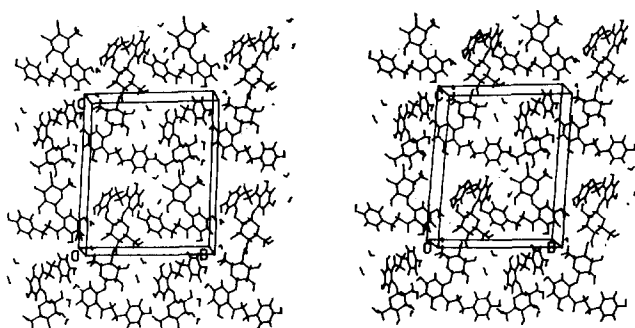


Figure 2. Stereoscopic PLUTO<sup>16</sup> packing diagram for phlorizin dihydrate.

TABLE 4: Hydrogen Bonds in Phlorizin Dihydrate

Type	D	H	A	DA (Å)	HA(Å)	<DHA(°)	Symmetry* of A
Intermolecular							
1	O(13)-H(3)	.....	O(4)	2.718(4)	1.86(8)	153(7)	3,0 $\bar{1}$ 0
2	O(4)-H(11)	.....	O(W1)	2.646(11)	1.88(8)	154(8)	1,100
3	O(3')-H(18)	.....	O(W2)	2.634(11)	1.95(5)	165(5)	3,1 $\bar{1}$ 0
4	O(6')-H(24)	.....	O(13)	2.683(4)	1.87(7)	168(7)	3,100
5	O(W1)-H(25)	.....	O(3')	2.702(10)	1.75(17)	146(14)	3,000
6	O(W1)-H(26)	.....	O(2')	2.953(11)	2.19(16)	132(12)	3,100
7	O(W2)-H(28)	.....	O(6)	2.833(11)	2.64(11)	107(13)	1,000
8	O(W2)-H(27)	.....	O(6')	2.714(11)	2.04(19)	155(15)	2,010
9	O(4')-H(20)	.....	O(4')	2.774(3)	1.97(5)	152(5)	4,100
Intramolecular							
	O(6)-H(13)	.....	O(7)	2.438(5)	1.66(6)	156(6)	1,000
	O(2')-H(16)	.....	O(1')	2.838(4)	2.54(5)	96(4)	1,000
	C(3)-H(10)	.....	O(5')	2.985(5)	2.42(4)	120(5)	1,000

\*The first number denotes the symmetry operator while the second group of numbers indicates lattice translation. Symmetry operators are:

$$1 : x, y, z; \quad 2 : \frac{1}{2} - x, -y, \frac{1}{2} + z; \quad 3 : -x, \frac{1}{2} + y, \frac{1}{2} - z; \quad 4 : \frac{1}{2} + x, \frac{1}{2} - y, -z.$$

O(5') and C(3) atoms. Besides the crystal packing forces, these two weak hydrogen-bonding interactions involving O(1') and O(5') contribute to determine the overall conformation of the phlorizin molecule and the degree of puckering of the glucopyranose ring.

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## Transport Mechanisms of Holmium Sesquioxide-Yttrium Sesquioxide System

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Electrical conductivities of polycrystalline yttrium sesquioxides containing 1.6 and 3.2 mol % of holmium sesquioxides have been measured from 650 to 1050°C under oxygen partial pressures of  $1 \times 10^{-5}$  to  $2 \times 10^{-1}$  atm. Plots of log conductivity vs.  $1/T$  at constant oxygen partial pressures are found to be linear away from the two inflection points. The low- and high-temperature dependences of conductivity show different defect structures of yttrium sesquioxide. The plots of log conductivity vs. log  $P_{O_2}$  are found to be linear at  $P_{O_2}$ 's of  $10^{-5}$  to  $10^{-1}$  atm. The electrical conductivity dependences on  $P_{O_2}$  are found to be  $1/5.3$  at 950-1050 °C,  $1/6$  at 800-950 °C and  $\frac{1}{6.2} - \frac{1}{6.5}$  at 650-800 °C, respectively. The defect structures and conduction mechanisms have been suggested.

### Introduction

Yttrium sesquioxide is the only known oxide in the Y-O system.  $Y_2O_3$  exhibits small deviations from stoichiometry under normal conditions of temperature and pressure. Miller and Danne<sup>1</sup> reported that  $YO_{1.491}$  may be prepared

by arc melting the sesquioxide. The oxygen diffusion in  $YO_{1.491}$  is performed by the oxygen vacancies<sup>2,3</sup>. Berard *et al.*<sup>4,5</sup> have reported yttrium self-diffusion in  $Y_2O_3$ . They found that bulk diffusion predominated.

Tallan and Vest<sup>6</sup> have studied the electrical conductivity as a function of the partial pressure of oxygen. For tempera-