



Synthesis and Structure of Novel Anhydrogalactosucrose Derivative

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A novel anhydrogalactosucrose derivative was prepared from sucrose. Its structure was determined by single crystal X-ray diffraction analysis. The crystals are monoclinic, space group $P2_1$ with $a = 5.40373(15)$, $b = 18.3877(5)$, $c = 7.68465(19)$ Å, $\alpha = 90.00^\circ$, $\beta = 103.299(3)^\circ$, $\gamma = 90.00^\circ$, $V = 743.08(4)$ Å³, $Z = 2$, $F(000) = 376.0$, $D_c = 1.614$ g/cm³, $\mu = 4.307$ mm⁻¹, the final $R = 0.0344$ and $wR = 0.0881$. A total of 6472 reflections were collected, of which 2732 were independent ($R_{int} = 0.0286$).

Keywords: Anhydrogalactosucrose, Synthesis, Crystal structure.

INTRODUCTION

Sucrose and its derivatives are of interest as potentially useful substrates in the chemical and biological fields, which attribute to its widespread existence in all photosynthetic plants and its biological importance. To improve the function of compounds with new and attractive characteristics, structural modifications of sucrose have been extensively investigated. Structural modifications can occur by dehydration and hydrolysis. Some work has been previously carried out on the synthesis of anhydrosucrose¹. In our earlier work, we reported a convenient method for synthesis of anhydrosucrose derivatives (1',4':3',6'-dianhydro- β -D-fructofuranosyl 3,6-anhydro-4-chloro-4-deoxy- α -D-galacto-pyranoside) from 4,6,1',6'-tetrachloro-4,6,1',6'-tetra-deoxy-galactosucrose². As a continued work, we obtained a novel anhydrogalactosucrose derivative and now we report the structure of title compound.

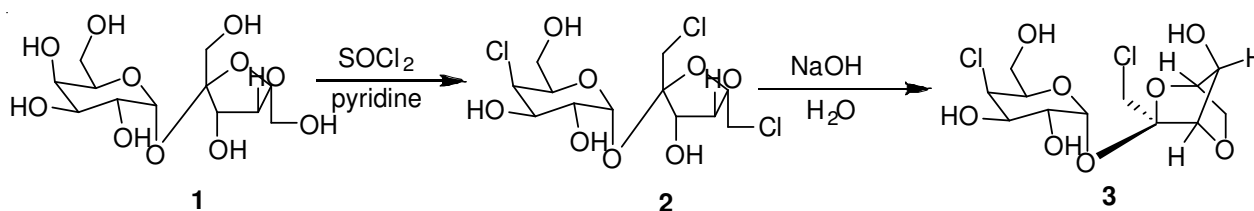
EXPERIMENTAL

Determination of crystal structure: The crystal of title compound with dimensions of $0.23 \times 0.20 \times 0.20$ mm was mounted on Xcalibur Eos Gemini diffractometer with a graphite-monochromated $\text{CuK}\alpha$ radiation ($\lambda = 1.54184$ Å) by using a ϕ and scan modes at 291.15(2) K in the range of $8.28^\circ \leq 2\theta \leq 134.04^\circ$. The crystal belongs to monoclinic system with space group $P2_1$ and crystal parameters of $a = 5.40373(15)$, $b = 18.3877(5)$, $c = 7.68465(19)$ Å, $\alpha = 90.00^\circ$, $\beta = 103.299(3)^\circ$, $\gamma = 90.00^\circ$, $V = 743.08(4)$ Å³, $Z = 2$, $F(000) = 376.0$, $D_c = 1.614$ g/cm³. The absorption coefficient $\mu = 4.307$ mm⁻¹. The final $R_1 = 0.0335(> 2\sigma(I))$ and $wR_2 = 0.0868$. A total of 6472

reflections were collected, of which 2732 were independent ($R_{int} = 0.0286$). The structure was solved by direct methods with SHELXS-974 and refined by the full-matrix least squares method on F_2 data using SHELXL-97⁵. The empirical absorption corrections were applied to all intensity data. H atom of N-H was initially located in a difference Fourier map and were refined with the restraint $\text{Uiso}(\text{H}) = 1.2 \text{ Ueq}(\text{N})$. Other H atoms were positioned geometrically and refined using a riding model, with $d(\text{C-H}) = 0.93\text{--}0.97$ Å and $\text{Uiso}(\text{H}) = 1.2 \text{ Ueq}(\text{C})$ or $1.5 \text{ Ueq}(\text{C-methyl})$. The final full-matrix least squares refinement gave 0.0344 and $wR = 0.0881$.

Synthesis of compound 2: As shown in **Scheme-I**, sucrose (**1**) (0.5 mol) and thionyl chloride (1.5 mol) were added to a stirred solution of pyridine (500 mL) and stirred at 115°C for 8 h under nitrogen atmosphere. The solvent was evaporated under vacuum. Water (100 mL) was added to the residue and pH was adjusted to 7 with the saturated NaOH solution. The mixture was washed with toluene and concentrated under vacuum to obtained the compound **2** as a white solid with a 76 % yield. ¹H NMR (500 Hz, D₂O, ppm) δ : 5.48 (d, $J = 2.4$ Hz, 1H), 4.59 (dd, $J = 1.2$ Hz, 3.6 Hz, 1H), 4.56 (s, 1H), 4.47 (m, 1H), 4.46 (d, 3.6 Hz, 1H), 4.44 (d, $J = 1.2$ Hz, 1H), 4.31 (d, $J = 5.6$ Hz, 1H), 4.09 (d, $J = 10.4$ Hz, 1H), 4.02 (dd, $J = 2.8$ Hz, 10.4 Hz, 1H), 3.81 (d, $J = 7.6$ Hz, 1H), 3.92 (d, $J = 8.4$ Hz, 1H), 3.87 (d, $J = 8.4$ Hz, 1H) 3.74 (m, 1H), 3.70 (d, $J = 7.6$ Hz, 1H); ¹³C NMR (125 Hz, D₂O, ppm) 110.2, 90.4, 82.6, 82.2, 78.2, 77.6, 75.7, 72.5, 72.2, 70.2, 67.8, 58.2; HRMS: Calcd for $\text{C}_{12}\text{H}_{19}\text{O}_8\text{Cl}_3$ 396.0146; found 419.0046 [$\text{M} + \text{Na}$]⁺.

Synthesis of compound 3: To a solution of compound **2** (0.05 mol) in water (100 mL) was added a solution of NaOH



Scheme-I: Route for the synthesis of compound 3

(0.175 mol) in water (50 mL). The mixture was heated to 55 °C under stirring and kept for 2 h. After the compound 2 disappeared by TLC detection, the solution was evaporated under diminished pressure. The residue was dissolved with 2-PrOH (50 mL) and dried over anhydrous Na_2SO_4 . Evaporation of the dry solution gave 3 as a white foamy solid (89 % yield). ^1H NMR (500 Hz, D_2O , ppm) δ : 5.41 (d, $J = 4.1$ Hz, 1H), 4.51 (dd, $J = 1.2$ Hz, 3.6 Hz, 1H), 4.49 (dd, $J = 0.5$ Hz, 2.4 Hz, 1H), 4.46 (s, 1H), 4.44 (dd, $J = 1.1$ Hz, 6.5 Hz, 1H), 4.41 (d, $J = 2.3$ Hz, 1H), 4.15 (dd, $J = 3.6$ Hz, 10.3 Hz, 1H), 3.94-4.04 (m, 4H), 3.90 (dd, $J = 4.1$ Hz, 10.3 Hz, 1H), 3.67 (d, $J = 6.5$ Hz, 1H); ^{13}C NMR (125 Hz, D_2O , ppm) 108.6, 94.32, 81.64, 77.54, 75.52, 70.94, 70.51, 68.22, 67.99, 62.88, 60.81, 43.24; HRMS: Calcd for $\text{C}_{12}\text{H}_{19}\text{O}_8\text{Cl}_3$ 396.0146; found 419.0046 $[\text{M} + \text{Na}]^+$. HRMS: Calcd for $\text{C}_{12}\text{H}_{18}\text{O}_8\text{Cl}_2$ 360.0379; found 383.0278 $[\text{M} + \text{Na}]^+$.

RESULTS AND DISCUSSION

Slow evaporation of compound 3 in MeOH afforded colorless crystals suitable for X-ray analysis.

Structure of the title compound: The title compound 3 has been confirmed by single crystal X-ray diffraction analysis. Crystallographic and refinement parameters are given in Table-1. The selected bond lengths and bond angles are listed in Tables 2-4, respectively. The weak hydrogen bonds of the O-H...O (dotted lines) in the crystal structure of the title compound are listed in Table-5. The structure was solved by direct methods. Anisotropic displacement parameters were applied to all nonhydrogen atoms in full-matrix least-square refinements based on F^2 . The hydrogen atoms were set in calculated positions with a common fixed isotropic thermal parameter.

The molecular structure and the packing view of the title complex are shown in Figs. 1 and 2, respectively.

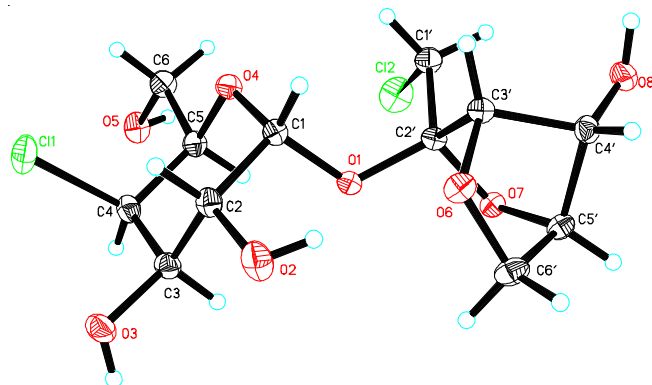


Fig. 1. Molecular structure of the title compound

TABLE-1
CRYSTAL DATA AND STRUCTURE
REFINEMENT OF TITLE COMPOUND

Items	Values
Empirical formula	$\text{C}_{12}\text{H}_{18}\text{O}_8\text{Cl}_2$
Formula weight	361.16
Crystal system	Monoclinic
Unit cell dimensions	
a/Å	5.40373(15)
b/Å	18.3877(5)
c/Å	7.68465(19)
Unit cell angles (°)	
$\alpha/^\circ$	90.00
$\beta/^\circ$	103.299(3)
$\gamma/^\circ$	90.00
Volume (Å ³)	743.08(4)
Z	2
Temperature (K)	291.15
Space group	P2_1
Calculated density (g/cm ³)	1.614
$\mu(\text{mm}^{-1})$	4.307
F(000)	376.0
Crystal size (mm ³)	0.23 × 0.20 × 0.20
2 θ Range for data collection	9.62 to 144.68°
Reflections collected	6472
Independent reflections	2732 [$R_{\text{int}} = 0.0286$]
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0335$, $wR_2 = 0.0868$

TABLE-2
SELECTED BOND LENGTHS [Å] OF TITLE COMPOUND

Bonds lengths	X-ray crystal	Bonds lengths	X-ray crystal
C11-C4	1.808(3)	O1-C2'	1.414(3)
C12-C1'	1.782(2)	O2-C2	1.418(3)
O1-C1	1.418(3)	O3-C3	1.415(3)
O6-C6'	1.464(3)	O4-C1	1.406(3)
O6-C3'	1.451(3)	O5-C6	1.419(3)

TABLE-3
SELECTED BOND ANGLES [°] AND TORSIONAL
ANGLES [°] OF TITLE COMPOUND

Bonds angles	X-ray crystal	Bonds angles	X-ray crystal
C2'-O1-C1	116.67(16)	O5-C6-C5	111.0(2)
C5'-C4'-C3'	90.71(18)	O6-C6'-C5'	103.15(17)
C3'-O6-C6'	104.81(16)	O7-C5'-C6'	109.1(2)
C2'-O7-C5'	105.93(14)	O7-C5'-C4'	102.40(16)
O6-C3'-C4'	101.10(17)	O6-C3'-C2'	106.58(17)
O1-C2'-O7	104.90(16)	O7-C2'-C1'	111.83(16)

The title compound crystallizes in the monoclinic space group P2_1 . The unit cell contains two molecules of title compound. As can be seen in Fig. 1, the molecular structure consists of one pyrane ring (C1, C2, C3, C4, C5, C6) and one bridge ring on the anhydrofructose moiety of compound 3. Two furan rings (C2'-C3'-C4'-C5'-O7 and C3'-C4'-C5'-C6'-O6)

TABLE-4
 SELECTED BOND TORSIONAL ANGLES [°] OF TITLE COMPOUND

Bonds angles	X-ray crystal	Bonds angles	X-ray crystal
C11-C4-C5-O4	68.4(2)	O6-C6'-C5'-O7	-72.0(2)
C11-C4-C5-C6	-50.4(3)	C6'-C5'-C4'-C3'	-55.38(19)
O1-C1-C2-O2	54.9(2)	C3'-O6-C6'-C5'	3.2(2)
C2-C3-C4-C11	-71.4(2)	C5'-C4'-C3'-O6	58.86(17)
O1-C2'-C1'-C12	-60.2(2)	C5'-C4'-C3'-C2'	-50.93(17)
O3-C3-C4-C11	50.3(2)	C4'-C3'-C2'-O7	29.5(2)
O3-C3-C4-C5	173.34(19)	C4'-C3'-C2'-C1'	-90.5(2)
C6'-O6-C3'-C4'	-39.9(2)	C2'-O7-C5'-C4'	-42.8(2)
C6'-O6-C3'-C2'	66.2(2)	O7-C5'-C4'-C3'	57.00(18)

 TABLE-5
 HYDROGEN BONDS OF TITLE COMPOUND

D-H-A	d(D-H) (Å)	d(H-A) (Å)	d(D-A) (Å)	D-H-A (°)
O2-H2-O6	0.82	2.08	2.895(3)	171.8
O3-H3-O8 ¹	0.823(18)	1.914(19)	2.735(3)	175(4)
O5-H5-O2 ²	0.842(19)	2.10(3)	2.876(3)	153(4)
O5-H5-O3 ²	0.842(19)	2.56(4)	3.107(3)	123(4)
O8-H8-O5	0.840(19)	1.85(2)	2.653(3)	159(4)

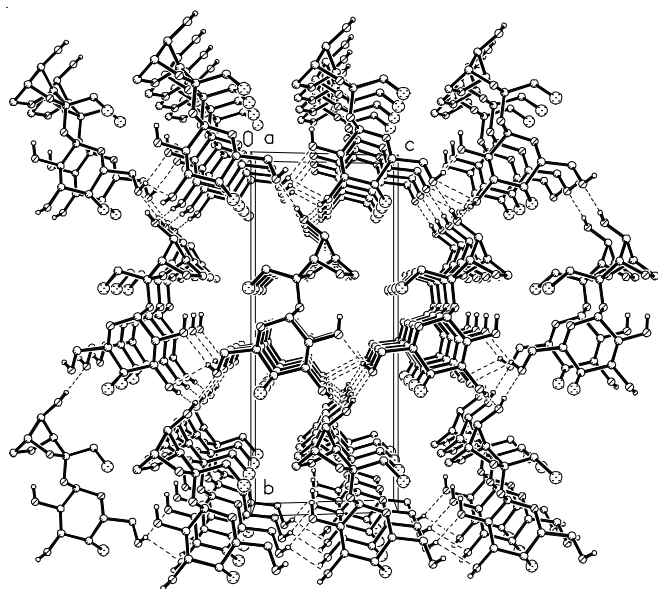
¹-X, 1/2 + Y, 1-Z; ²-1 + X, + Y, -1 + Z; ³-X, -1/2 + Y, -Z


Fig. 2. Crystal packing for the title compound

fused along the C3'-C4'-C5' bond, allowed a V-shaped molecule with ring 1 (Cremer-Pople puckering parameters⁴ for this rings are $Q = 0.612(3)$ Å and $F = 70.2(2)^\circ$) and ring 2 (Cremer-Pople puckering parameters for this rings are $Q = 0.584(2)$ Å and $F = 113.5(2)^\circ$). The six-member dioxane (O6-C3'-C2'-O7-C5'-C6') keep a V-shaped molecule (Cremer-Pople puckering parameters⁴ for this rings are $Q = 0.925(2)$ Å and $F = 247.00(13)^\circ$, $\Phi = 91.55(12)^\circ$). The six-member pyranoid ring keep a chair-confirmation ($Q = 0.553(2)$ Å, $\theta = 1.2(2)^\circ$, $F = 32(11)^\circ$)

As shown in Fig. 2, The structure exhibits an intermolecular hydrogen bond of the type O-H...O. The molecules are regularly bounded by the intermolecular hydrogen bonds between the oxygen atoms in the dianhydrofructose moiety

of one molecule and the -OH in the anhydrogalactose moiety of the next one. Finally, the molecules are bounded by the supramolecular interactions to form a regular threedimensional network.

Supplementary material: CCDC 1008746 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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