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Note

Molecular and crystal structure of galactinol dihydrate [1-*O*-(α-D-galactopyranosyl)-*myo*-inositol dihydrate]

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Abstract

The crystal structure of galactinol dihydrate has been determined by X-ray diffraction. The crystal belongs to the orthorhombic system, space group $P2_12_12$, $a = 15.898(6)$, $b = 19.357(5)$, $c = 5.104(4)$ Å, and $Z = 4$. The structure was refined to $R = 0.044$ for 1818 observed structure amplitudes. The primary hydroxyl group exhibits twofold orientational disorder. The linkage conformation is close to those of α-(1→4) linkages in methyl α-maltotrioside tetrahydrate and erlose trihydrate. Although there is no interring hydrogen bond in galactinol, an *indirect* interring hydrogen bond including a water molecule is present. The observed conformation is additionally stabilized by the *indirect* interring hydrogen bond. The global minimum in the relaxed-residue energy map based on the MM3(92) force-field is close to the observed conformation in the crystal structure. All hydroxyl, ring and water oxygen atoms are involved in a complex three-dimensional hydrogen-bonding network.

Keywords: Galactinol; X-ray diffraction; Crystal structure; Conformation analysis

1. Introduction

Galactinol [1-*O*-(α-D-galactopyranosyl)-*myo*-inositol] is one of the galactosyl derivatives of cyclitols which are widely distributed in higher plants, especially leguminous seeds [1–3]. In the biosynthetic pathway of the raffinose family of oligosaccharides, such as raffinose (trisaccharide), stachyose (tetrasaccharide), and verbascose (pentasaccharide), the galactosyl group of galactinol is transferred to sucrose, raffinose, and stachyose, respectively [4,5]. These oligosaccharides have received a lot of attention since they have been proposed to be important in conferring protection against desiccation-induced damage in desiccation-tolerant seeds. In addition, galactinol in maturing seeds has been recently pro-

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posed as playing a role in stabilizing the structures of macromolecules and membranes during desiccation [3]. In the present study, we describe the molecular and crystal structures of galactinol using X-ray diffraction and molecular mechanics calculation and comparison with related oligosaccharides.

2. Results and discussion

The molecular structure of the title compound together with the numbering of atoms is illustrated in Fig. 1 [6]. There are two water molecules per galactinol in the crystal lattice. Bond lengths and bond angles (deposited) are in agreement with previously reported values for the geometry of the carbohydrate [7,8] except for the C-6–O-6 bond [C-6–O-6A = 1.374(6), C-6–O-6B = 1.365(8) Å]. Such shortening of the C-6–O-6A and C-6–O-6B bond distances are consistent with the observation of the twofold orientational disorder of the primary hydroxyl group [9]. One orientation corresponds to the *gg* conformation (O-6A) and the other corresponds to the *gt* conformation (O-6B). The occupancy factors of O-6A and O-6B are 0.64 and 0.36, respectively. In the case of the $^4C_1$-D-*galacto* configuration, the *gg* conformation seems to be unfavorable because of the '*peri*' or '1,3-*syndiaxial*' interaction [10]. In solution, the coupling constants between H-5 and the two H-6 atoms observed by NMR lead to rotameric distribution of the three staggered orientations (*gg*: *gt*: *tg*) around 20: 60: 20 [11]. In crystals, the unfavorable *gg* orientation in the galactopyranose ring was only observed in cases where an intramolecular hydrogen bond was formed between the O-4 and O-6 atoms [12]. The major conformation of O-6 observed in the present study is stabilized by the O-4–H-O4B···O-6A [2.662(4) Å] intramolecular hydrogen bond.

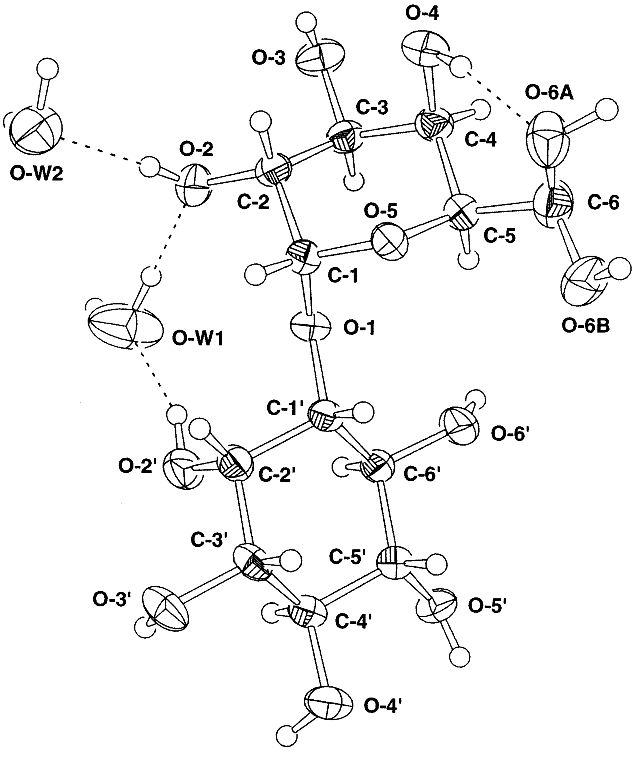

Fig. 1. Molecular structure of galactinol. Broken lines indicate hydrogen bonds. Thermal ellipsoids are drawn at the 50% probability level.

The α-D-galactopyranose ring is close to the ideal $^4C_1$ chair conformation, with Cremer–Pople puckering parameters [13] $Q = 0.564(4)$ Å, $\Theta = 1.5(4)°$ and $\Phi = 296.9(3)°$ (for the atom sequence O-5–C-1–C-2–C-3–C-4–C-5). The *myo*-inositol ring is also close to the ideal chair conformation ($Q = 0.588(4)$ Å, $\Theta = 2.4(4)°$ and $\Phi = 108.8(3)°$ for the atom sequence C-6′–C-1′–C-2′–C-3′–C-4′–C-5′).

The conformation about the linkage between the galactopyranose and *myo*-inositol rings is described by the torsional angles ϕ (O-5–C-1–O-1–C-1′) and ψ (C-1–O-1–C-1′–C-2′). The values obtained in the present study are $\phi = 66.8(3)°$ and $\psi = 87.6(3)°$. The value of the angle ϕ may be affected by the exo-anomeric effect, being close to the theoretical value of $+60°$ [14,15]. Another important parameter, the bridge angle C-1–O-1–C-1′, is 113.6(2)°. These torsional and bond angles are compared with those found in α-(1 → 3) and α-(1 → 4) linkages of the related oligosaccharides in Table 1. The linkage conformation of galactinol is close to those of methyl α-maltotrioside tetrahydrate [16] and erlose trihydrate [17], whereas it is different from those of the other oligosaccharides in which their molecular structures are stabilized by the interring hydrogen bonds between the O-2 and O-4′ atoms and the O-2 and O-3′ atoms in the α-(1 → 3) [18] and α-(1 → 4) [19–24] linkages, respectively. The hydroxyl oxygen atoms that participate in these interring hydrogen bonds

Table 1
Comparison of the linkage conformation of α-(1 → 3)- and α-(1 → 4)-linked oligosaccharides

Compound	Torsional angle (°)		Bond angle (°)	Distance (Å)	Linkage
	ϕ (O-5–C-1–O-1–C-X') [a]	ψ (C-1–O-1–C-X'–C-Y') [a]	τ (C-1–O-1–C-X') [a]	(O-2···O-Y′) [a]	
Methyl α-maltotrioside tetrahydrate [15]	82.7	88.6	115.5	3.87	Glc-α(1 → 4)-Glc
	82.3	93.0	114.7	3.63	Glc-α(1 → 4)-Glc
Erlose trihydrate [16]	68.7	90.3	115.0	4.14	Glc-α(1 → 4)-Glc
	51.1	73.8	116.7	4.91	Glc-α(1 → 4)-Glc
Methyl α-nigeroside [17]	99.9	104.2	116.2	2.84	Glc-α(1 → 3)-Glc
α-Maltose [18]	116.1	122.2	120.1	2.77	Glc-α(1 → 4)-Glc
β-Maltose [19]	121.7	132.7	117.9	2.79	Glc-α(1 → 4)-Glc
Methyl β-maltoside monohydrate [20]	109.9	129.2	117.6	2.82	Glc-α(1 → 4)-Glc
Phenyl α-maltoside [21]	110.0	100.3	116.5	2.79	Glc-α(1 → 4)-Glc
	108.5	102.2	116.9	2.67	Glc-α(1 → 4)-Glc
Erlose monohydrate [22]	107.2	108.3	117.0	2.75	Glc-α(1 → 4)-Glc
α,β-Panose [23]	96.8	104.3	113.9	2.93	Glc-α(1 → 4)-Glc

[a] α-(1 → 3)-linkage: $X = 3$, $Y = 4$; α-(1 → 4)-linkage: $X = 4$, $Y = 3$.

are in the equatorial positions in the plane of the pyranose rings. Since the O-2′ atom in the *myo*-inositol ring is in the axial orientation, such an interring hydrogen bonding was not found in galactinol. However, the *indirect* interring hydrogen bond including a water molecule is observed in the present case (O-2···H-W1A–O-W1···H–O2′–O-2′). Similar *indirect* interring hydrogen bonds have been reported in the crystal structures of disaccharides [25–27].

The conformational energy of the title compound was calculated by using the MM3(92) force field [28–30]. The isoenergy contour map is shown in Fig. 2. A low-energy region extending vertically in the ψ-direction and centered about a conformation between ϕ values of 60 and 120° appears on the map. The general characteristics for this energy map are consistent with those of α-(1 → x)-linked disaccharides, where $x = 2$, 3 and 4 [31]. In particular, the isoenergy contour map obtained in the present study and that of α-kojibiose [α-(1 → 2)-linked disaccharide] [31] are quite similar because of the stereochemical similarity of the linkage regions between both compounds. In Fig. 2, there are three energy minima. The global minimum is located at $(\phi, \psi) =$ (84.8, 80.2) with a steric energy value of 23.3 kcal/mol, being close to the observed conformation in the crystal structure. The second and third lowest minima occurring at $(\phi, \psi) = (90.2, 163.1)$ and $(\phi, \psi) = (86.6, -65.0)$, have energy values of 23.8 and 27.7 kcal/mol, respectively. An interring hydrogen bond is formed between atoms O-5 and H(O-6′) (1.853 Å) for the second lowest energy minimum. Although similar hydrogen bonds have been expected from the conformational analyses of α-(1 → 2)-linked and α-(1 → 3)-

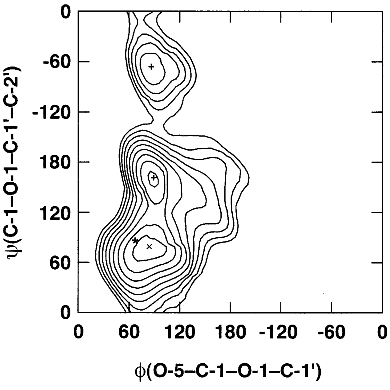

Fig. 2. Relaxed-residue steric energy map of galactinol. Contour lines are graduated in 1 kcal/mol increments above the global minimum: (×) global minimum; (+) local minima; (*) conformer in the crystal structure.

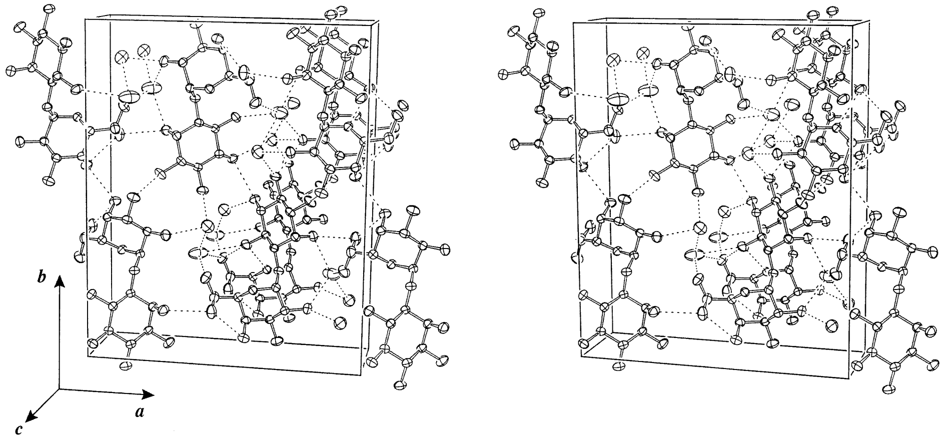

Fig. 3. Stereodrawing of the molecular packing of galactinol dihydrate. Broken lines indicate hydrogen bonds. Hydrogen atoms are not shown.

Table 2
Hydrogen bond parameters for galactinol dihydrate

Donor	Acceptor	Distance (Å)		Angle (°)	Acceptor symmetry code [a]
(D–H)	(A)	D···A	H···A	D–H···A	
Intramolecular					
O-4–H-O4B	O-6A	2.663(4)	1.80	157	
Intermolecular					
O-3–H-O3	O-3′	2.892(4)	2.03	167	3556
O-4–H-O4A	O-4	2.725(5)	1.84	172	2675
O-6A–H-O6A	O-2′	2.797(5)	1.98	146	4566
O-3′–H-O3′	O-3	2.888(4)	2.02	163	3545
O-4′–H-O4′	O-2	2.848(3)	2.05	154	3545
O-5′–H-O5A′	O-5′	2.797(4)	1.93	167	2665
O-6′–H-O6′	O-6B	2.727(8)	1.94	143 [b]	1554
O-6′–H-O6′	O-5	2.927(3)	2.23	132 [b]	1554
Including water molecules					
O-2–H-O2	O-W2	2.681(4)	1.83	165	1555
O-6B–H-O6B	O-W1	2.906(9)	2.03	158	4566
O-2′–H-O2′	O-W1	2.725(4)	1.92	155	1555
O-W1–H-W1A	O-2	2.708(5)	1.79	169	1555
O-W1–H-W1B	O-W2	2.888(5)	2.05	148	1554
O-W1–H-W1B	O-6B	2.827(9)	2.37	110	4465
O-W1–H-W1B	O-6′	2.975(5)	2.67	100	4465
O-W2–H-W2A	O-4′	2.773(4)	1.89	156	3556
O-W2–H-W2B	O-5′	2.789(4)	2.03	156	4465

[a] Symmetry code. The last three digits give the unit cell translation in the a, b, and c directions with respect to 555; the first digit specifies one of the following operations: 1; x, y, z; 2: $-x$, $-y$, z; 3: $-x+1/2$, $y+1/2$, $-z$; 4: $x+1/2$, $-y+1/2$, $-z$.

[b] The summation of three angles, O-6′–H-O6′···O-6B, O-6′–H-O6′···O-5 and O-6B···H-O6′···O-5 (= 85°), is 360°.

linked disaccharides [31], no crystal structure containing such an interring hydrogen bond has been reported so far. Since an energy difference of just 0.5 kcal/mol exists between the second and the global minima, the molecular structure observed in this study is additionally stabilized by the already mentioned *indirect* interring hydrogen bond.

The packing of the molecules is shown in Fig. 3. The molecules are roughly parallel to the *ab*-plane and are stacked along the *c*-direction. The details of hydrogen bondings are listed in Table 2. All the hydroxyl groups and water molecules participate in hydrogen bonding, acting as both proton donors and acceptors. The ring oxygen atom (O-5) accepts a hydrogen bond, and the linkage oxygen atom (O-1) does not take part in hydrogen bonding. Each hydroxyl group, except for O-2 and O-6′, forms two hydrogen bonds. The O-2 oxygen atom accepts two bonds from O-4′ and O-W1, and donates one to O-W2. The O-6′ hydroxyl group donates a three-center hydrogen bond to O-6B and O-5, and accepts one bond, which is the component of the four-center bond from O-W1–H-W1B. The H-O6′ atom is in the plane of the three oxygens (O-6′, O-6B and O-5) of the three-center bond. The water molecule O-W1 has six oxygen nearest neighbors, accepting two two-center bonds and donating one two-center and one four-center bond. O-W2 has the more common fourfold environment. The O-4 and O-5′ hydroxyl groups are located near crystallographic twofold axes and one of the disordered hydrogen atoms of each hydroxyl group forms a O-4···O-4 or O-5′···O-5′ hydrogen bond. A schematic diagram of the hydrogen bonding in the crystal is given in Fig. 4. Two out of three infinite hydrogen bond chains (O-6B···O-W1··· and O-2···O-W2···O-4′···) along the *c*-direction and finite chains (O-6A···O-2′···O-W1 and O-W1···O-6′···O-5) are crosslinked into a net through the hydrogen bonds including water molecules and O-4···O-4 and O-5′···O-5′ hydrogen bonds on the crystallographic twofold axes. In addition, there is a separate infinite hydrogen bond chain (O-3···O-3′···) along the *c*-axis. We believe that this type of extensive water-mediated hydrogen-bonding network helps to prevent dehydration in seeds.

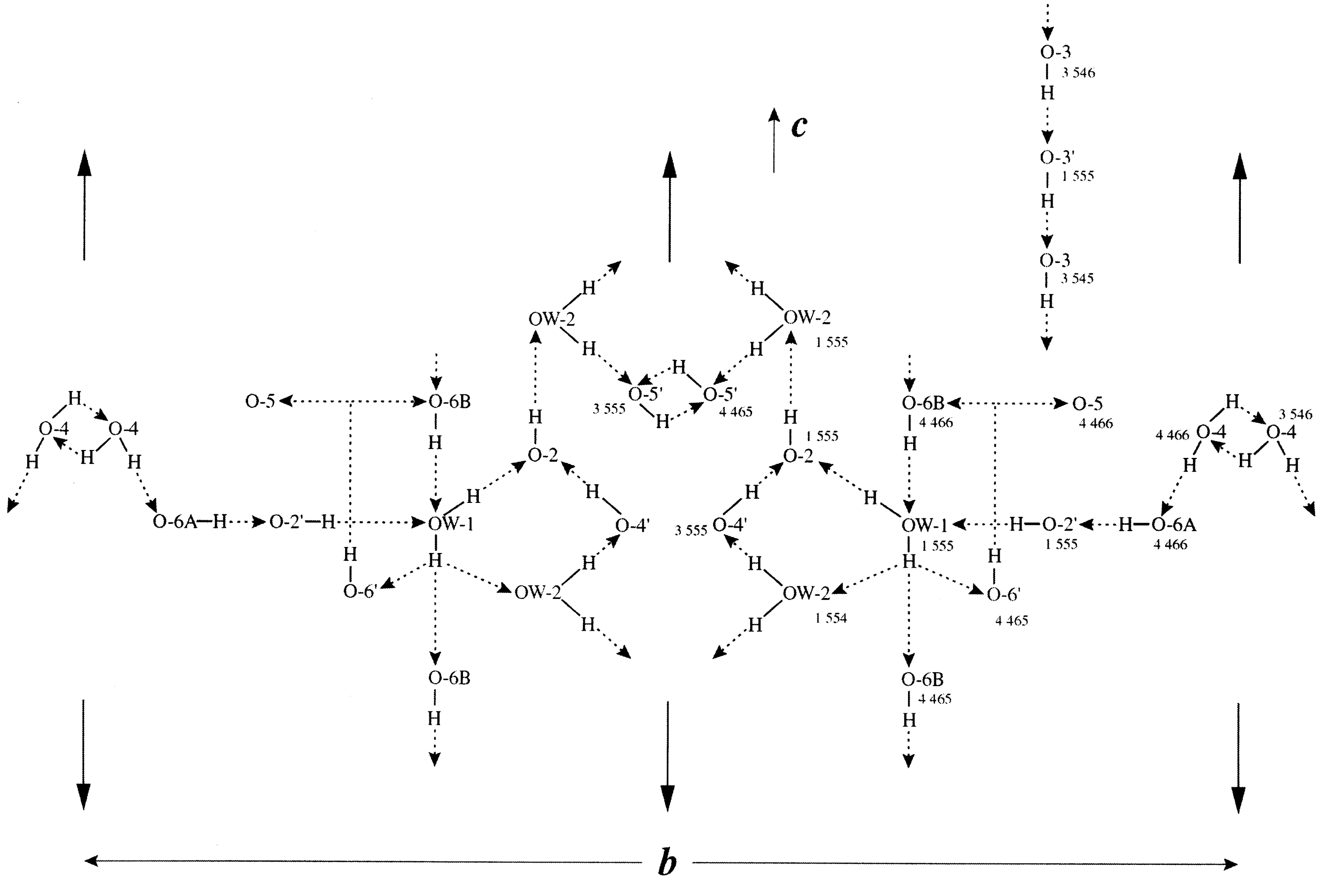

Fig. 4. The hydrogen-bonding scheme in the crystal structure of galactinol dihydrate.

Table 3
Crystal data and structure refinement of galactinol dihydrate

Molecular formula	$C_{12}H_{22}O_{11}\cdot 2H_2O$
Molecular weight	378.33
Temperature	293
Crystal system	orthorhombic
Space group	$P2_12_12$
Unit cell dimensions	
a (Å)	15.898(6)
b (Å)	19.357(5)
c (Å)	5.104(4)
Volume (Å^3)	1570(1)
Z	4
D_{calcd} (g·cm^{-3})	1.600
μ (cm^{-1})	12.91
F(000)	808
Crystal size (mm)	$0.6\times 0.2\times 0.2$
2θ Range for data collection (°)	3.5–150
Scan mode	ω–2θ
Scan speed (°·min^{-1})	4
Index range	$0\leq h\leq 19$; $0\leq k\leq 24$; $0\leq l\leq 6$
No. of reflections measured	1840
No. of independent reflections	1818
Refinement method	full-matrix least-squares on F^2
Function minimized	$\Sigma w(F_o^2-F_c^2)$ [a]
Data/parameters	1818/282
Goodness of fit on F^2	1.064
Final R value	
R_1 (on F)	0.0435
wR_2 (on F^2)	0.1132
Largest difference peak and hole (e·Å^{-3})	0.24, −0.28

[a] $w = 1/[\sigma^2(F_o^2)+(0.0594\times P)^2+1.06\times P]$, where $P = [\max(F_o^2, 0)+2\times F_c^2]/3$.

3. Experimental

Crystal structure analysis.—The title compounds were extracted from the solid part of beet sugar molasses, which contains 1.5–3.5 wt.% galactinol. The details of purification have been reported elsewhere [32]. Single crystals suitable for X-ray work were grown by slow evaporation of an ethanolic solution. A crystal with dimensions of 0.6 × 0.2 × 0.2 mm^3 was used for the X-ray measurements at 293 K. Diffraction data were collected using a four-circle diffractometer (AFC5R, Rigaku Co.) with graphite-monochromated Cu K$_\alpha$ radiation ($\lambda = 1.5418$ Å). Cell constants and orientation matrix for data collection were determined by a least-squares refinement using 25 carefully centered reflections in the range of $57° < 2\theta < 60°$. The crystal data, the details of the data collection and structure determination, and refinement data are given in Table 3. The observed intensity data were corrected for Lorentz and polarization effects. Absorption corrections ($\mu = 12.91$ cm^{-1}) by the experimental method (ψ-scan) and decay corrections by using a polynomial correction factor were applied.

The structure was solved by the direct method with the program SIR88 [33] and refined by full-matrix least-squares using the program SHELXL-97 [34]. The non-hydrogen atoms were refined anisotropically. Some of the hydrogen atoms were located on the difference Fourier map, and their positions were refined. The other hydrogen atoms were introduced by geometrical calculations and allowed to ride on their parent atoms. The isotropic temperature factors of hydrogen atoms were held equivalent to those of the corresponding parent atoms. The primary hydroxyl group was shown to be disordered at two positions. The occupancy factors of O-6A and O-6B were obtained in the refinement, assuming these atoms have the same temperature factors. Two hydrogen bonds between the O-4 and O-5′ atoms pass through crystallographic twofold axes. Therefore, each hydrogen atom of these hydroxyl groups was considered to have two possible positions with equal occupancy. The final R factor (calculated based on F) and R_w factor (calculated based on F^2) are 0.044 and 0.113, respectively. The final atomic parameters are listed in Tables 4 and 5. Atomic scattering factors were taken from the International Tables for X-ray Crystallography, vol. IV [35]. All computations were performed using the TEXSAN crystallographic software package of the Molecular Structure Corporation [36] and SHELXL-97 [34].

Molecular modeling.—The conformational energy map of galactinol was calculated by using MM3(92) force field developed by Allinger and co-workers [28–30]. The molecular geometry obtained in this study was used for the initial structure. Starting conformations for exocyclic side groups were constructed according to the procedure used for the disaccharide molecules [31,37]. Three staggered conformations (*gg*, *gt*, *tg*) were considered for the primary hydroxyl group in the galactopyranose residue. The clockwise (*c*) and the reverse-clockwise (*r*) orientations were applied for the secondary hydroxyl groups, where all the OH vectors are oriented to the same direction that enables the formation of a partial hydrogen bonding ring around the pyranose ring [38]. These four orientations of the secondary hydroxyl groups combined with the three orientations of the primary hydroxyl group yield the 12 starting conformations. The strategic and technical details of the relaxed energy calculations of carbohydrates were discussed by French et al. [39]. The torsional angles ϕ and ψ were varied systematically with 5° intervals. Each structure at a given (ϕ, ψ) point was fully optimized except for the rotation of ϕ and ψ. Throughout the calculation, the dielectric constant was set at 4.0, as suggested by French et al. [40]. The lowest energy value from the 12 optimized starting conformers was used at each grid-point to construct the energy map. The MM3 program was purchased from Japan Chemistry Program Exchange.

Table 4
Fractional coordinates and equivalent isotropic temperature factors for non-hydrogen atoms of galactinol dihydrate

Atom	*x*	*y*	*z*	U_{eq}
C-1	0.3353(2)	0.7964(2)	0.4099(7)	0.0298(6)
C-2	0.3036(2)	0.8700(2)	0.3574(7)	0.0312(7)
C-3	0.3665(2)	0.9117(1)	0.2001(7)	0.0323(7)
C-4	0.4518(2)	0.9095(2)	0.3346(7)	0.0320(7)
C-5	0.4782(2)	0.8348(2)	0.3817(7)	0.0312(7)
C-6	0.5601(2)	0.8292(2)	0.5288(9)	0.0433(9)
O-1	0.3376(1)	0.76004(9)	0.1708(5)	0.0306(5)
O-2	0.2249(1)	0.8689(1)	0.2252(6)	0.0417(6)
O-3	0.3394(2)	0.9813(1)	0.1691(6)	0.0433(6)
O-4	0.4450(2)	0.9461(1)	0.5784(5)	0.0411(6)
O-5	0.4152(1)	0.7991(1)	0.5330(5)	0.0307(5)
O-6A	0.5538(3)	0.8557(2)	0.7779(9)	0.0483(10)
O-6B	0.5873(4)	0.7648(3)	0.597(2)	0.0490(18)
C-1′	0.3550(2)	0.6874(1)	0.2007(7)	0.0274(6)
C-2′	0.2740(2)	0.6470(2)	0.2448(7)	0.0319(7)
C-3′	0.2941(2)	0.5704(1)	0.2737(7)	0.0311(7)
C-4′	0.3391(2)	0.5441(1)	0.0309(7)	0.0296(7)
C-5′	0.4185(2)	0.5854(1)	−0.0207(7)	0.0286(6)
C-6′	0.3997(2)	0.6626(1)	−0.0433(7)	0.0290(6)
O-2′	0.2181(2)	0.6539(1)	0.0293(6)	0.0429(6)
O-3′	0.2197(2)	0.5319(1)	0.3304(6)	0.0432(6)
O-4′	0.3614(2)	0.4735(1)	0.0606(6)	0.0416(6)
O-5′	0.4558(1)	0.5624(1)	−0.2590(5)	0.0358(5)
O-6′	0.4760(1)	0.6981(1)	−0.0844(6)	0.0453(7)
O-W1	0.1505(3)	0.7783(2)	−0.1061(9)	0.0905(14)
O-W2	0.0913(2)	0.8842(2)	0.5407(7)	0.0565(7)

Table 5
Fractional coordinates for hydrogen atoms of galactinol dihydrate

Atom	*x*	*y*	*z*
H-1	0.296	0.773	0.528
H-2	0.296	0.893	0.527
H-3	0.372	0.891	0.026
H-4	0.494	0.932	0.223
H-5	0.484	0.812	0.212
H-61A	0.577	0.781	0.539
H-62A	0.604	0.854	0.434
H-61B	0.604	0.851	0.423
H-62B	0.555	0.856	0.688
H-O2	0.188(2)	0.873(2)	0.350(7)
H-O3	0.329(3)	0.994(2)	0.332(6)
H-O4A	0.477(4)	0.984(3)	0.57(2)
H-O4B	0.477(4)	0.920(3)	0.69(1)
H-O6A	0.603(3)	0.871(3)	0.86(1)
H-O6B	0.615(3)	0.762(4)	0.755(8)
H-1′	0.392	0.681	0.352
H-2′	0.246	0.664	0.405
H-3′	0.332	0.565	0.423
H-4′	0.302	0.549	−0.120
H-5′	0.458	0.578	0.124
H-6′	0.363	0.670	−0.195
H-O2′	0.209(2)	0.698(1)	0.016(9)
H-O3′	0.195(2)	0.524(2)	0.176(6)
H-O4′	0.322(2)	0.450(2)	−0.012(8)
H-O5B′	0.437(2)	0.593(2)	−0.380(5)
H-O5A′	0.479(4)	0.521(2)	−0.24(2)
H-O6′	0.491(2)	0.728(2)	−0.217(7)
H-OW11	0.1772(7)	0.8130(9)	−0.010(3)
H-OW12	0.113(2)	0.802(1)	−0.217(6)
H-OW21	0.105(3)	0.923(2)	0.639(8)
H-OW22	0.063(2)	0.901(2)	0.425(8)

4. Supplementary material

Tables of anisotropic temperature factors, bond distances, bond angles and torsional angles have been deposited with the Cambridge Crystallographic Data Centre. These data may be obtained free of charge, on request, from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] R.J. Beveridge, C.W. Ford, G.N. Richards, *Aust. J. Chem.*, 30 (1977) 1583–1590.
[2] T.F. Schweizer, I. Horman, P. Wursch, *J. Sci. Food Agric.*, 29 (1978) 148–154.
[3] M. Horbowicz, R.L. Obendorf, *Seed Sci. Res.*, 4 (1994) 385–405.
[4] S.A. Blackman, R.L. Obendorf, A.C. Leopold, *Plant Physiol.*, 100 (1992) 225–230.
[5] Y. Chen, J.S. Burris, *Crop Sci.*, 30 (1990) 971–975.
[6] M.N. Burnett, C.K. Johnson, *ORTEP-III: A FORTRAN Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations*, *ORNL-6895*, Lockheed Martin Energy Research Corporation, Oak Ridge National Laboratory, July 1996.
[7] S. Arnott, W.E. Scott, *J. Chem. Soc.*, *Perkin Trans. 2*, (1972) 324–335.
[8] F.H. Allen, *Acta Crystallogr.*, *Sect. B*, 42 (1986) 515–522.
[9] G.A. Jeffrey, Y.J. Park, *Acta Crystallogr.*, *Sect. B*, 28 (1972) 257–267.
[10] O. Hassel, B. Ottar, *Acta Chem. Scand.*, 1 (1947) 929–942.
[11] H. Ohrui, Y. Nishida, H. Higuchi, H. Hori, H. Meguro, *Can. J. Chem.*, 65 (1987) 1145–1153.
[12] A. Neuman, H. Gillier-Pandraud, F. Longchambon, D. Rabinovich, *Acta Crystallogr.*, *Sect. B*, 31 (1975) 474–476.
[13] D. Cremer, J.A. Pople, *J. Am. Chem. Soc.*, 97 (1975) 1354–1358.
[14] S. Pérez, R.H. Marchessault, *Carbohydr. Res.*, 65 (1978) 114–120.
[15] E.E. Astrup, *Acta Chem. Scand.*, 25 (1971) 1994–1995.
[16] W. Pangborn, D. Langs, S. Pérez, *Int. J. Biol. Macromol.*, 7 (1985) 363–369.
[17] T. Taga, E. Inagaki, Y. Fujimori, S. Nakamura, *Carbohydr. Res.*, 251 (1994) 203–212.
[18] A. Neuman, D. Avenel, F. Arene, H. Gillier-Pandraud, J.R. Pougny, P. Sinaÿ, *Carbohydr. Res.*, 80 (1980) 15–24.
[19] F. Takusagawa, R.A. Jacobson, *Acta Crystallogr.*, *Sect. B*, 34 (1978) 213–217.
[20] M.E. Gress, G.A. Jeffrey, *Acta Crystallogr.*, *Sect. B*, 33 (1977) 2490–2495.
[21] S.S. Chu, G.A. Jeffrey, *Acta Crystallogr.*, 23 (1967) 1038–1048.
[22] I. Tanaka, N. Tanaka, T. Ashida, M. Kakudo, *Acta Crystallogr.*, *Sect. B*, 32 (1976) 155–160.
[23] T. Taga, E. Inagaki, Y. Fujimori, S. Nakamura, *Carbohydr. Res.*, 240 (1993) 39–45.
[24] G.A. Jeffrey, De-bin Huang, *Carbohydr. Res.*, 222 (1991) 47–45.
[25] M.E. Gress, G.A. Jeffrey, D.C. Rohrer, *Acta. Crystallogr.*, *Sect. B*, 34 (1978) 508–512.
[26] G.M. Brown, D.C. Rohrer, B. Berking, C.A. Beevers, R.O. Gould, R. Simpson, *Acta. Crystallogr.*, *Sect. B*, 28 (1972) 3145–3157.
[27] K. Noguchi, K. Okuyama, S. Kitamura, K. Takeo, *Carbohydr. Res.*, 237 (1992) 33–43.
[28] N.L. Allinger, Y.H. Yuh, J.H. Lii, *J. Am. Chem. Soc.*, 111 (1989) 8551–8566.
[29] J.H. Lii, N.L. Allinger, *J. Am. Chem. Soc.*, 111 (1989) 8566–8575.
[30] N.L. Allinger, M. Rahman, J.H. Lii, *J. Am. Chem. Soc.*, 112 (1990) 8293–8307.
[31] M.K. Dowd, J. Zeng, A.D. French, P.J. Reilly, *Carbohydr. Res.*, 230 (1992) 223–244.
[32] N. Wakiuchi, T. Tarui, H. Tamaki, S. Kishihara, S. Fujii, *J. Agric. Chem. Soc. Jpn.*, 67 (1993) 253.
[33] M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, D. Viterbo, *J. Appl. Crystallogr.*, 22 (1989) 389–393.
[34] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
[35] *International Table for X-ray Crystallography*, Vol. IV, Kynoch, Birmingham, UK, 1974, p. 71.
[36] TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, 1985 and 1992.
[37] M.K. Dowd, A.D. French, P.J. Reilly, *Carbohydr. Res.*, 233 (1992) 15–34.
[38] S.N. Ha, L.J. Madsen, J.W. Brady, *Biopolymers*, 27 (1988) 1927–1952.
[39] A.D. French, V.H. Tran, S. Pérez, *ACS Symp. Ser.*, 430 (1990) 191–212.
[40] A.D. French, R.J. Rowland, N.L. Allinger, *ACS Symp. Ser.*, 430 (1990) 120–140.