The closest intermolecular distances are 3·53 and 3·54 Å between C(4) and C(7) and between C′(3) and C′(5), respectively.

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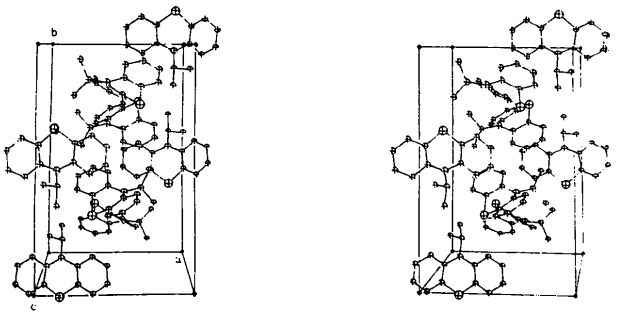

Fig. 4. The stereoscopic drawing of molecular packing of *N*-isopropylphenothiazine, excluding H atoms, in the unit cell.

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The Crystal Structures of the α- and β-Anomers of D-Galactose

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The structures of α- and β-D-galactose have been determined by direct methods. Refinement was by least squares with anisotropic temperature factors for the C and O atoms to produce a final R of 0·0820 for 572 reflexions (α) and 0·0318 for 821 reflexions (β). The space groups are $P2_12_12_1$ with $Z=4$ and the cell parameters are (α) $a=15{\cdot}7806$ (38), $b=7{\cdot}8783$ (15), $c=5{\cdot}9436$ (20) Å and (β) $a=7{\cdot}6992$ (8), $b=7{\cdot}7726$ (8), $c=12{\cdot}6408$ (17) Å. The molecules have the configurations 1*a*2*e*3*e*4*a* and 1*e*2*e*3*e*4*a* respectively with hydrogen-bonding systems which involve the five hydroxyl groups of each molecule.

Crystals of the α- and β-anomers of D-galactose were originally prepared to resolve the question of the unit-cell dimensions (Sheldrick, 1961). The crystal structures of both forms are now reported.

Experimental

α-D-*Galactose*

Confirmation of the cell dimensions was obtained by least-squares refinement of 41 measurements of 2θ taken at room temperature with Cu $K\alpha_1$ monochromatic radiation.

Crystal data

$C_6H_{12}O_6$, F.W. 180·15, space group $P2_12_12_1$, $a=15{\cdot}7806$ (38), $b=7{\cdot}8783$ (15), $c=5{\cdot}9436$ (20) Å, $V=738{\cdot}4$ Å^3, $D_m=1{\cdot}60$ (in a mixture of $C_2H_2Cl_4$ and C_2Cl_4), $D_x=1{\cdot}62$ g cm^{-3} for $Z=4$, Cu $K\alpha_1$ monochromatic, $\lambda=1{\cdot}54051$ Å, crystal size $=0{\cdot}2\times0{\cdot}2\times0{\cdot}002$ mm, crystal shape: flat plate.

Intensities were collected on an Enraf–Nonius CAD-4 diffractometer with a graphite crystal monochromator. Measurements were made in the range $3°<\theta\leq70°$, scanned in the ω–2θ mode. 572 independent reflexions were measured and 163 more were

too weak to be measured. The data were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1970) with an E_{min} of 1·00. Two of the 16 possible solutions gave significantly higher combined figures of merit and the E map from one of these showed sensible positions and bond relations for all the non-hydrogen atoms. Refinement of positional and isotropic temperature parameters gave $R=0·148$. Further refinement with anisotropic parameters reduced R to 0·0947; the H atoms were then found from a difference synthesis and included in the final structure factor calculation with $B=2·37$ Å^2 and no refinement of their parameters. This final calculation gave $R=0·0820$ for 572 measured reflexions.* The final atomic coordinates are listed in Table 1 and thermal parameters for the non-hydrogen atoms in Table 2.

* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31370 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

β-D-Galactose

The cell parameters were obtained by least-squares refinement of 59 measurements of 2θ at room temperature on a CAD-4 diffractometer with Cu $K\alpha_1$ monochromatic radiation.

Crystal data

$C_6H_{12}O_6$, F.W. 180·15, space group $P2_12_12_1$, $a=7·6992$ (8), $b=7·7726$ (8), $c=12·6408$ (17) Å, $V=756·5$ Å^3, $D_m=1·61$ (in a mixture of $C_2H_2Cl_4$ and C_2Cl_4), $D_x=1·58$ g cm^{-3} for $Z=4$, Cu $K\alpha_1$ monochromatic, $\lambda=1·54051$ Å, crystal size $0·15\times0·20\times0·15$ mm.

Intensities were collected as for α-D-galactose to give 821 independent measured reflexions with 74 more too weak to be measured. The data were corrected for Lorentz and polarization effects but not for absorption.

Table 1. *Fractional atom coordinates* ($\times10^5$) *and e.s.d.'s in parentheses*

	α-D-Galactose			β-D-Galactose		
	x	*y*	*z*	*x*	*y*	*z*
C(1)	9524 (65)	−259 (116)	23269 (183)	97804 (34)	7106 (36)	60175 (22)
C(2)	2538 (60)	7212 (111)	8241 (188)	106335 (36)	21054 (35)	66861 (21)
C(3)	6200 (64)	12626 (115)	−13946 (181)	123790 (36)	21209 (36)	64637 (22)
C(4)	13246 (65)	25908 (118)	−10058 (197)	133568 (37)	3276 (36)	66064 (23)
C(5)	19797 (67)	18065 (113)	6031 (179)	123680 (36)	−9192 (37)	58933 (22)
C(6)	26588 (72)	30458 (134)	13237 (193)	129789 (42)	−27603 (38)	59928 (25)
O(1)	12823 (48)	−14621 (89)	12506 (137)	80384 (25)	5490 (27)	63080 (17)
O(2)	−4216 (40)	−4989 (74)	5900 (127)	99466 (26)	37470 (25)	63861 (16)
O(3)	−219 (49)	19466 (79)	−28175 (133)	134685 (27)	33475 (27)	71053 (19)
O(4)	9749 (47)	41520 (71)	−1995 (126)	132113 (27)	−1800 (27)	76941 (16)
O(5)	15832 (45)	12611 (81)	26341 (118)	105713 (24)	−9133 (24)	62097 (15)
O(6)	31329 (47)	35532 (87)	−5909 (137)	119211 (31)	−38635 (27)	53540 (17)
H(1)	7467	−3128	40070	98761	10162	51721
H(2)	−903	16845	16860	104294	18756	74924
H(3)	8177	1898	−22627	128124	24682	56338
H(4)	14819	25441	−25931	146835	3684	63898
H(5)	21812	10553	−1948	124647	−5075	50865
H(6)	28900	24098	25634	129354	−31217	67470
H(7)	23549	38638	22274	144343	−28481	57237
H(8)	8815	−19589	1670	76137	189	58190
H(9)	−9295	1856	5969	90633	39401	67354
H(10)	−3342	10243	−34658	127896	38176	75581
H(11)	7913	42677	13315	140737	−5630	78713
H(12)	33452	27964	−17379	113817	−43356	56404

Table 2. *Thermal parameters* ($\times10^5$)

The U_{ij}'s are defined by: $\exp[-2\pi^2(U_{11}h^2a^{*2}+\cdots+2U_{12}hka^*b^*+\cdots)]$.

	α-D-Galactose						β-D-Galactose					
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	1714	1434	2490	411	−89	−249	1453	1936	2606	−574	−60	330
C(2)	140	1036	3207	−156	80	362	1619	1571	2418	318	60	330
C(3)	1680	714	2371	−121	−980	232	1682	1625	2962	−236	168	−544
C(4)	1642	1499	2656	116	−144	454	1735	2179	2870	152	714	544
C(5)	2031	982	1782	27	−317	461	1920	1650	2731	−358	1126	452
C(6)	1860	2535	2751	−732	196	319	3102	1818	3614	−770	654	706
O(1)	3309	1875	3373	297	−82	−557	1528	3191	3147	−1740	−6	−398
O(2)	589	992	3339	223	87	319	2237	1446	3659	484	1260	832
O(3)	1859	1387	3515	−1262	−1184	1051	2042	2591	5324	−2988	−350	−1072
O(4)	1999	201	3359	204	198	−155	2195	3192	2823	926	−552	918
O(5)	1642	1834	2094	−606	−507	249	1745	1525	2853	−74	592	−88
O(6)	1970	1799	3839	−813	763	−734	3961	2046	3532	−1184	2828	−762

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1970) with an $E_{min}=1{\cdot}00$. One of the 16 possible solutions gave a high combined figure of merit and the *E* map from this showed positions for 10 of the 12 non-hydrogen atoms. An additional Fourier synthesis revealed the two remaining atoms. Isotropic refinement of the non-hydrogen atoms gave $R=0{\cdot}094$. Further refinement with anisotropic temperature factors reduced *R* to 0·065. The H atoms were then found from a difference synthesis and included with isotropic temperature factors. It was not possible to refine the temperature factors of the H atoms and two cycles were carried out with a fixed $B=0{\cdot}8$ Å^2 to give a final $R=0{\cdot}032$.* Including the 74 weak reflexions with a value of half the minimum observed gave $R=0{\cdot}039$. The final atomic coordinates are listed in Table 1 and the thermal parameters for the non-hydrogen atoms in Table 2.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). In all stages of refinement unit weight was assigned to each measurement. The structure factor refinements and Fourier synthesis calculations were carried out on the ICL 1906A computer of the Leeds University Centre for Computer Studies with a modified version of the program suite originally written by Cruickshank, Pilling, Bujosa, Lovell & Truter (1961). Bond lengths and angles, with their related e.s.d.'s, with the atom numbering shown in Fig. 1 [the positions of H(1) and O(1) should be interchanged for the β-anomer], were

* See previous footnote.

Table 3. *Bond lengths* (Å) *and e.s.d.'s in parentheses*

	α	β
C(1)–O(1)	1·400 (12)	1·396 (4)
C(1)–O(5)	1·433 (12)	1·422 (4)
C(2)–O(2)	1·442 (11)	1·432 (4)
C(3)–O(3)	1·425 (13)	1·426 (4)
C(4)–O(4)	1·431 (12)	1·434 (4)
C(5)–O(5)	1·426 (13)	1·440 (4)
C(6)–O(6)	1·419 (14)	1·432 (4)
C(1)–C(2)	1·536 (14)	1·523 (4)
C(2)–C(3)	1·501 (15)	1·524 (4)
C(3)–C(4)	1·544 (14)	1·528 (4)
C(4)–C(5)	1·538 (15)	1·526 (4)
C(5)–C(6)	1·511 (15)	1·512 (4)

Table 4. *Bond angles* (°) *and e.s.d.'s in parentheses*

	α	β
O(1)–C(1)–O(5)	111·83 (80)	106·66 (22)
O(1)–C(1)–C(2)	108·11 (83)	109·43 (22)
C(2)–C(1)–O(5)	107·55 (73)	110·63 (22)
C(1)–C(2)–C(3)	110·07 (81)	109·16 (22)
C(1)–C(2)–O(2)	109·34 (73)	107·89 (22)
O(2)–C(2)–C(3)	112·90 (85)	109·10 (24)
C(2)–C(3)–C(4)	109·77 (86)	111·86 (24)
C(2)–C(3)–O(3)	110·79 (81)	110·77 (24)
O(3)–C(3)–C(4)	110·14 (75)	110·88 (24)
C(3)–C(4)–C(5)	107·75 (77)	109·48 (25)
C(3)–C(4)–O(4)	110·78 (80)	110·60 (25)
O(4)–C(4)–C(5)	113·36 (87)	108·30 (25)
C(4)–C(5)–O(5)	110·64 (83)	113·37 (26)
C(4)–C(5)–C(6)	113·15 (79)	108·26 (24)
O(5)–C(5)–C(6)	105·42 (83)	106·19 (24)
C(5)–C(6)–O(6)	109·18 (88)	110·07 (27)

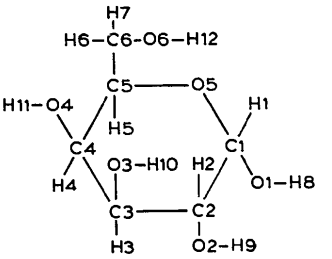

Fig. 1. Atomic numbering for α-D-galactopyranose.

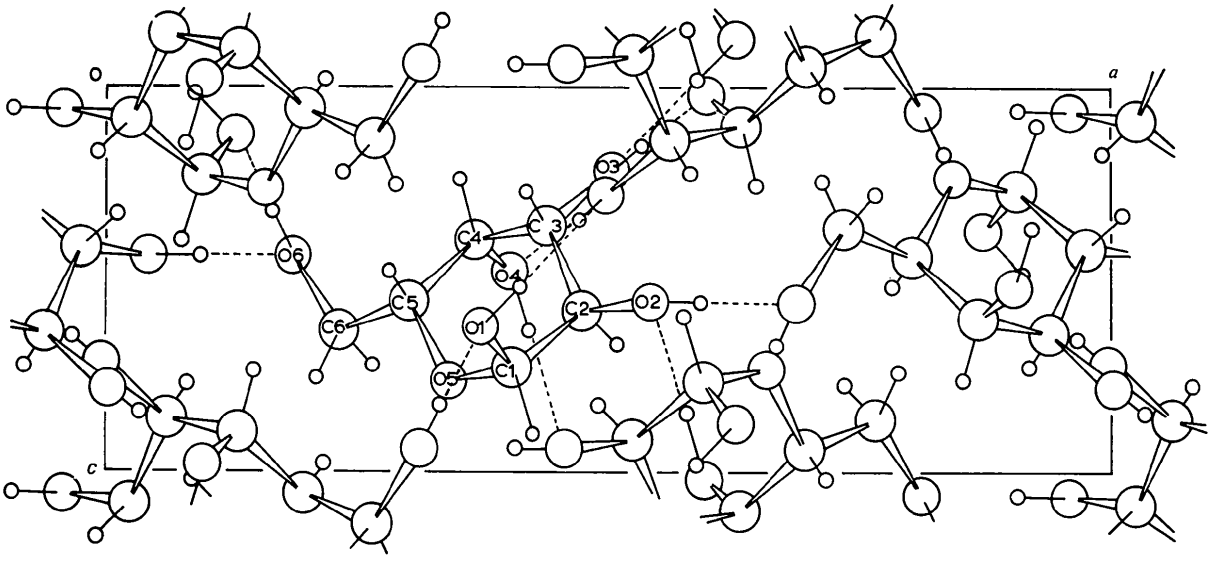

Fig. 2. *b*-Axis projection of α-D-galactopyranose.

calculated by a program written by Dr W. S. McDonald and the results are listed in Tables 3 and 4.

Projections of the structures are shown in Figs. 2 (*b* projection of α-D-galactose) and 3 (*a* projection of β-D-galactose).

Discussion

The configurations are 1*a*2*e*3*e*4*a* and 1*e*2*e*3*e*4*a* respectively with little or no detectable strain. The C–C bonds have an average length of 1·526 (α) and 1·522 (β) Å

Table 5. C–C *and* C–O *bond lengths in hexoses*

	Av. C–C length (Å)	Av. C–O length excluding C(1)–O(1) (Å)	C(1)–O(1) (Å)	Reference
α-D-Glucose	1·54	1·40	1·32	McDonald & Beevers (1952)
α-D-Glucose	1·524	1·426	1·39	Brown & Levy (1965)
β-D-Glucose	1·5274 (10)	1·4438 (9)	1·404 (10)	Ferrier (1963)
β-D-Glucose	1·520 (2)	1·425 (2)	1·383 (4)	Chu & Jeffrey (1968)
α-D-Glucose monohydrate	1·532	1·433	1·38	Killean, Ferrier & Young (1962)
α-Methyl-D-galactoside 6-bromohydrin	1·516 (15)	1·434 (13)	1·430 (14)	Robertson & Sheldrick (1965)
Methyl 6-*O*-acetyl-β-D-galactoside	1·516 (6)	1·429 (5)	1·374 (6)	Lindberg, Garegg & Swahn (1973)
Methyl β-maltopyranoside (disaccharide)	1·520 (8)	1·427 (8)	1·375 (8)	Chu & Jeffrey (1967)
Methyl α-D-glucopyranoside	1·519 (25)	1·424 (15)	1·411 (4)	Berman & Kim (1968)
Methyl α-D-galacto-pyranoside monohydrate	1·518	1·428	1·405	Gatehouse & Poppleton (1971*a*)
Methyl α-D-altro-pyranoside	1·517	1·431	1·405	Gatehouse & Poppleton (1971*b*)
α-D-Galactose	1·526 (15)	1·429 (12)	1·400 (12)	This paper
β-D-Galactose	1·522 (4)	1·431 (4)	1·396 (4)	This paper

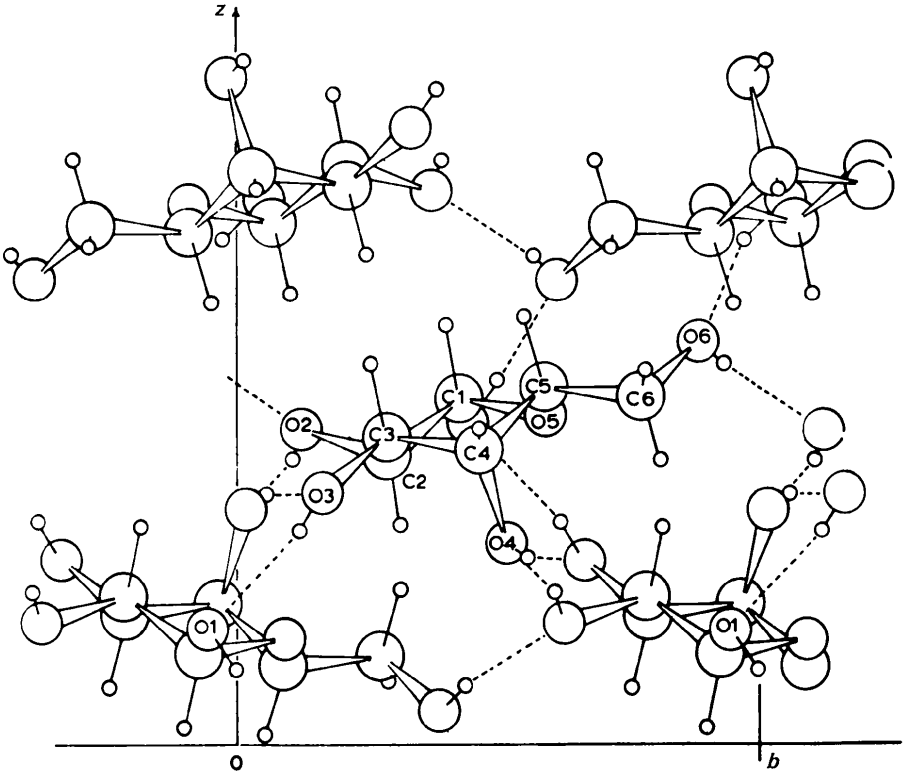

Fig. 3. *a*-Axis projection of β-D-galactopyranose.

and the C–O bonds [excluding C(1)–O(1)] an average of 1·429 (α) and 1·431 (β) Å. These values are consistent with those previously published for hexoses (Table 5). The estimated standard deviations are 0·012 and 0·004 Å respectively for C–C and 0·015 and 0·004 Å for C–O; the marked difference of the e.s.d.'s between the two structures is thought to be due to differences in crystal shape and mosaic spread.

C(1)–O(1) at 1·400 and 1·3961 Å show lower values than the average which occurs in previously published structures, with the exception of α-methyl-D-galactoside 6-bromohydrin, but this difference is only $2{\cdot}4\sigma$ for α. In β, however, the difference of 0·035 Å corresponds to nearly 9σ. No other C–O bond differs from the average by more than about 2σ. These variations of C–O lengths in the pyranose sugars have been discussed by Berman, Chu & Jeffrey (1967) and there appears to be no doubt that C(1)–O(1) is significantly shorter than the average. In methyl-substituted O(1) structures six C–O lengths have been reported, one of which shows no shortening while the others, in which O(1) is axial, are as listed in Table 5.

Table 6. H *bond distances* (Å) *and e.s.d.'s in parentheses*

α			β
O(1)–H(8)—O(3)	3·111 (12)	–O(6)	2·619 (3)
O(2)–H(9)—O(6)	2·748 (9)	–O(4)	2·820 (3)
O(3)–H(10)–O(4)	2·915 (9)	–O(1)	2·879 (3)
O(4)–H(11)–O(2)	2·888 (11)	–O(3)	2·812 (3)
O(6)–H(12)–O(1)	2·662 (11)	–O(2)	2·732 (3)

The hydrogen-bonding system is complete in both structures in that each O atom, with the exception of the ring O, acts as a donor and an acceptor, with the O···O distances shown in Table 6. Most are acceptable, but the value of 3·11 Å between O(1) and O(3) in α-D-galactose is rather long. The fact that the ring O atoms do not take part in the hydrogen-bonding system appears to violate the first of the rules postulated by Jeffrey & Rosenstein (1964) applicable to hydrogen bonds in pyranose structures. The actual situations conform to their second rule that each hydroxyl O atom acts as both donor and acceptor.

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