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MUTAROTATION OF *L*-SORBOSE

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## ABSTRACT

Optical-rotation measurements are reported on carefully purified *L*-sorbose at 0.4 and 20° C. In contradiction of the statements in various periodicals and text books, the results show that this sugar exhibits a small complex mutarotation.

Since the ketohexose, *L*-sorbose, has become of commercial importance, particularly as an intermediate in the synthesis of ascorbic acid, an accurate knowledge of its physical and chemical properties is desirable. The optical rotation of *L*-sorbose was studied by Lobry de Bruyn and Van Ekenstein,<sup>1</sup> who reported that no mutarotation was observable. Although the effect of temperature, concentration, and other factors on the equilibrium specific rotation have been studied,<sup>2</sup> it has been generally assumed, except for a statement by Riiber,<sup>3</sup> that the sugar does not mutarotate or else that the mutarotation is too rapid to be detected.<sup>4</sup>

We have made a number of measurements of the optical rotatory power of pure samples of anhydrous *L*-sorbose<sup>5</sup> in water solution and have found that neither of the earlier assumptions is correct, since the sugar exhibits a definite mutarotation in which the optical rotation increases slightly at first and then decreases, so that the initial and final rotations are not widely different. The observed change (about 0.7° S) is undoubtedly real and is not due to accidental impurities, because samples of the sugar which had been purified and then recrystallized 2, 3, 5, and 6 times from water gave the same characteristic mutarotation. On account of its complex character the mutarotation cannot be represented by the usual first-order equation but requires an equation containing two exponential terms. The measurements and equations representing the reactions at both 20 and 0° C are given in table 1.

<sup>1</sup> M. M. C. A. Lobry de Bruyn and W. A. Van Ekenstein, *Rec. trav. chim.* **19**, 6 (1900).

<sup>2</sup> R. H. Smith and B. Tollens, *Ber. deut. chem. Ges.* **33**, 1285 (1900).

<sup>3</sup> C. N. Riiber, *Saertrykk av Tidsskrift for kjemi og bergvesen*, no. 10, p. 16 (1932).

<sup>4</sup> Tollens-Elsner, *Kurzes Handbuch der Kohlenhydrate*, p. 383 (Johann Ambrosius Barth, Leipzig, 1935).

<sup>5</sup> The material used was furnished through the courtesy of the Bureau of Chemistry and Soils, U. S. Department of Agriculture.

TABLE 1.—Mutarotation of *l*-sorbitose in water<sup>1</sup>

11.3 g per 100 ml at 20.0° C in a 4-dm tube. $^{\circ}\text{S} = -1.13 \times 10^{-.040t} + .77 \times 10^{-.23t} - 56.77$ $[\alpha]_{\text{D}}^{20} = -.86 \times 10^{-.040t} + .59 \times 10^{-.23t} - 43.4$				
Time	Observed rotation	$m_1 \times 10^3$	Deviation	$m_2 \times 10^3$
Minutes	$^{\circ}\text{S}$			
0	(-57.124)	-----	(0.772)	-----
1.75	-57.446	-----	.282	290
2.69	-57.498	-----	.150	210
4.06	-57.451	-----	-----	-----
6.33	-57.404	-----	-----	-----
9.37	-57.246	-----	-----	-----
12.37	-57.129	-----	-----	-----
15.32	-57.049	37	-----	-----
19.64	-56.953	40	-----	-----
23.09	-56.898	41	-----	-----
26.14	-56.864	42	-----	-----
34.76	-56.801	-----	-----	-----
120	-56.768	-----	-----	-----
Average.....	-----	40	-----	250
11.6 g per 100 ml at 0.4° C in a 4-dm tube $^{\circ}\text{S} = -.74 \times 10^{-.0055t} + .40 \times 10^{-.030t} - 58.0$ $[\alpha]_{\text{D}}^{0.4} = -.55 \times 10^{-.0055t} + .30 \times 10^{-.030t} - 43.3$				
0	(-58.341)	-----	(0.400)	-----
4.66	-58.409	-----	.290	-----
9.16	-58.447	-----	.213	31
14.02	-58.461	-----	.159	28
19.93	-58.477	-----	.098	31
29.91	-58.478	-----	(.029)	-----
40.95	-58.429	-----	-----	-----
50.11	-58.407	-----	-----	-----
60.12	-58.365	-----	-----	-----
70.83	-58.301	-----	-----	-----
81.35	-58.265	5.2	-----	-----
89.88	-58.231	6.0	-----	-----
105.99	-58.190	5.6	-----	-----
205.08	-58.061	5.1	-----	-----
1,350	-57.998	-----	-----	-----
Average.....	-----	5.5	-----	30

<sup>1</sup> The equations and values for mutarotation constants,  $m_1$ , and  $m_2$ , are determined by the method described by Isbell and Pigman, J. Research NBS 18, 156 (1937) RP969. Each observed rotation represents the average of 10 consecutive readings.

The smallness of the mutarotation might arise from one of two possibilities: (1) Equilibrium might be established between isomers having only slightly different optical rotatory values, in which case the equilibrium solution would contain considerable quantities of these isomers, or (2) the known modification might greatly predominate in the equilibrium state and other modifications be present only in small quantities. In order to decide between these possibilities, solubility measurements were made of *l*-sorbitose in water at 0° C. An excess of finely powdered *l*-sorbitose was shaken with ice water for 3 minutes and filtered; after standing until equilibrium was reached, the solution read  $-127.52^{\circ}\text{S}$  in a 4-dm tube. A solution allowed to reach equilibrium at 0° C in the presence of an excess of *l*-sorbitose read  $-128.63^{\circ}\text{S}$  in a 4-dm tube. The small difference (0.87 percent) between the two values indicates that the equilibrium solution of

*l*-sorbitose is composed almost exclusively of that isomer which is known in the crystalline state.

The specific rotations for *l*-sorbitose in water were found to be  $[\alpha]_D^{0.4} = -43.3$  and  $[\alpha]_D^{20} = -43.4$  (12 g. of *l*-sorbitose in 100 ml). The equilibrium appears to be only slightly affected by temperature. This behavior resembles that of glucose, as might be expected from the analogous structures of the two sugars. The equilibrium specific rotation in 50-percent (in volume) ethyl alcohol was found to be  $[\alpha]_D^{20} = -43.4$  (0.6067 g made up to 25 ml read  $-12.18^\circ$  S in a 4-dm tube).

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