

Citation:

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Chemistry. — "*The configuration of α -galactose and α -fructose.*"By Prof. J. BÖESEKEN, A. H. KERSTJENS and C. E. KLAMER.¹⁾

(Communicated in the meeting of March 25, 1916.)

In a previous article one of us has used the influence of the polyhydroxy-compounds on the conductivity of boric acid to determine the configuration of the α - and of the β -glucose. Starting from the assumption that a positive influence is caused by the formation of complex acids and that this is promoted by a favourable position of the hydroxyl-groups, it could be expected that cane sugar and raffinose should exert *no* positive influence; on the other hand their cleavage products might do so.

In the non-reducing polysaccharides the hydroxyl groups attached to adjacent C-atoms which form part of the furane-rings are nowhere situated at the same side of those rings; in the reducing cleavage products: glucose, fructose and galactose this may, however, be the case, namely in one of the mutarotation isomerides of each of those three sugars. In the other mutarotation isomeride, the position of the hydroxyl-groups is certainly more unfavourable.

Hence, we could expect:

1st. that the two mutarotation isomerides should exert a different influence on the conductivity of boric acid;

2nd. that that influence would change in aqueous solution and would decrease with the one isomeride and increase with the other;

3rd. that this phenomenon should run quite parallel to the mutarotation, i. e. that it would proceed under the same circumstances (in presence of boric acid) unimolecularly and with a same reaction-constant.

With the glucoses these demands have been completely fulfilled and as the α -glucose exerted a greater influence on the boric acid than the β -glucose, we could take the subjoined symbols as proved.²⁾

We have now also carried out this investigation with the α -galactose and the α -fructose (the β -galactose and the β -fructose have not yet been obtained in a sufficiently pure condition). From the symbols of the two mutarotation isomerides of the galactose we notice that they are constructed quite analogous to the glucose, only the tail CHOHCH_2OH occupies another position in regard to the furane-ring.

¹⁾ Some of the measurements described here have been executed by Mr. W. STURM

²⁾ In the Proceedings of the Meeting of Sat. June 29, 1912 pag. 221 these symbols. are given incorrectly.

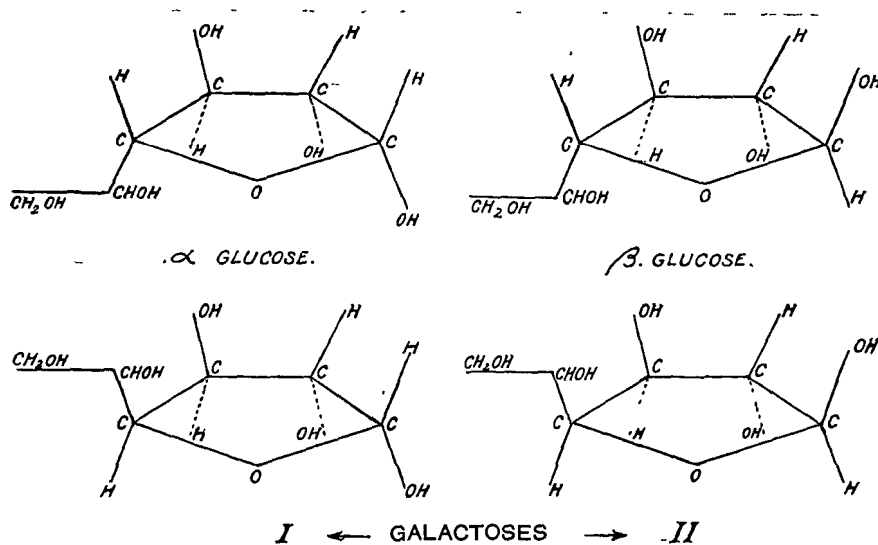


Fig. 1.

We may, therefore, expect here a same phenomenon as with the glucoses; the numerical values it is true will not be equal to those of the glucoses but still not differ much therefrom.

We have prepared the α -galactose from milksugar by hydrolysis with dilute acids and repeatedly recrystallised the same from alcohol; although the rotation was normal, the electric conductivity remained somewhat too high, namely 32×10^{-6} KHb for 0,5 mol. solution. The mutarotation was now determined successively in conductivity water and in a solution of 0,5 molar H_3BO_3 ; then the change in the conductivity for 0.5 mol. α -galactose + 0,5 mol. H_3BO_3 was determined. The latter had to be done as quickly as possible so as not to let the range of the slider on the scale turn out too small.

From these measurements it follows:

1st That the mutarotation constant is not or but little affected by boric acid.

2nd That the mutarotation constant is equal to the constant of the conductivity change, both considered as reversible unimolecular reactions seeking an equilibrium.

3^d That in the α -galactose the hydroxyl groups are situated more favourably than in the β -galactose for the conductivity influence decreases so that it claims the cis-form (symbol I).

4th That the influence of the galactoses on the conductivity of boric acid is but trifling, still more so than that of the glucoses.

From the observed exaltations of the conductivity of the α - and β -glucose, as well as of the α -galactose and of the equilibrium mixture, it follows that the β -glucose as well as the β -galactose cause an

Measurements, all at 25°.

Capacity of the resistance vessel = 0.235

t in min.	0.5 mol. α -galactose		$K + K' = \frac{1}{t} \log \frac{r_\alpha - r_\infty}{r_t - r_\infty}$	0.5 mol. α -galactose + " " H_3BO_3		$K + K'$	Conductivity change		$K + K' = \frac{1}{t} \log \frac{K_\alpha - K_\infty}{K_t - K_\infty}$	
	Read- ing	Spec. Rot.		Reading	Spec. Rot.		R	a		$K \times 10^6$
0	54.6	118.6		53.4	116.0			491	81.1	0.013
5			0.0146			0.0137		494	80.2	
10	50.8	110.1		50.2	109.1			496.5	79.2	
20	48.0	104.3	142	47.5	103.2	152		500.3	78.2	15
30	46.2	100.2	140	45.9	99.7	149		505.0	76.7	16
40	44.6	96.9	142	44.7	97.1	148	3000	507.0	76.1	17
50	43.8	95.1	136	43.8	95.2	148				
60	43.1	93.6	133	43.3	94.1	143		509.6	75.4	17
80	42.0	91.2	139	42.6	92.6	138				
100	41.4	89.9	147	42.1	91.5					
∞	40.9	88.9		41.7	90.6			511.4	74.8	
		Mean = 0.0141			Mean = 0.0145				Mean = 0.015	

exaltation in the conductivity of the boric acid, though only but little.

In view of what has been found with canesugar, raffinose and α -methylglucoside, this was not to be expected.

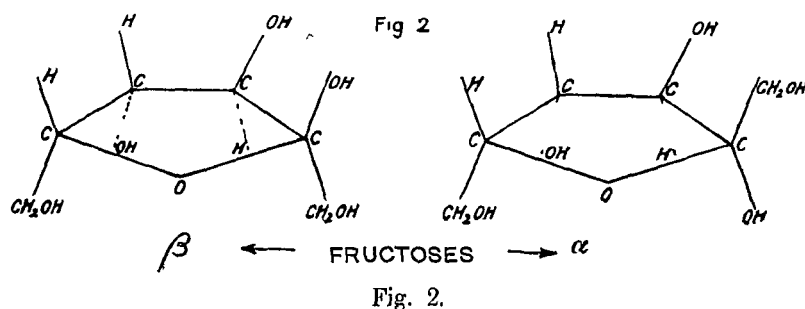
For these cause, in accordance with the unfavourable position of the OH-groups a slight *depression* of the conductivity.

The position of the OH-groups in β -glucose and β -galactose is equally unfavourable so that the positive influence must be connected with the greater mobility of the molecule of the reducing sugars.

It is not improbable that the mobile hydroxyl-group receives some support from the side of the furane-oxygen atom say in the sense that to this O-atom is still bound a molecule of water so that the number of hydroxyl groups is greater here and the chance for the fixing of boric acid is more favourable¹⁾.

In the non-reducing sugars and in the glucosides the furane-oxygen atom is present, but the mobile OH-group has disappeared, so that here the cause of the boric acid combination is cancelled.

If the explanation of this favourable influence of the furane-oxygen atom is correct, the fructose [in which the circumstances are still more favourable, because to the C-atom that carries the furane-oxygen



and the mobile OH-group (Fig. 2) are still attached *two* other OH-containing groups] will have to cause a much more powerful exaltation in the conductivity than the two investigated aldoses. This, indeed has now been proved to be correct.

For the increase in conductivity of the equilibrium mixtures of the glucoses, galactoses and fructoses were found the following figures ($T = 25^\circ$; the fructoses at 0° to 3°).

Mol. (α and β) glucose	+ 0.5	mol. H_3BO_3 =	95×10^{-6}	K.Hb.
"	+ 0.25	" "	$60 \times$	" "
"	+ 0.125	" "	$38 \times$	" "
0.5 mol. (α and β) galactose	+ 0.5	" "	$25 \times$	" "
mol. (α and β) fructose	+ 0.44	" "	$\pm 900 \times$	" "
"	+ 0.22	" "	$\pm 680 \times$	" "
"	+ 0.11	" "	$\pm 480 \times$	" "
"	+ 0.02	" "	$110 \times$	" "

Although a considerable exaltation in conductivity, as indicated above, might well be expected the amount of it was strikingly large.

On closer examination of the fructose molecule we notice, however,

¹⁾ E. F. ARMSTRONG (Die einfachen Zuckerarten und die Glucosiden" pag. 22—27) calls the oxygen atom of the furane-ring, when taking up one molecule water, quadrivalent and thus considers the sugar hydrates as oxonium compounds.

some resemblance with an α -hydroxy-acid and as these acids cause an enormous increase of the conductivity ¹⁾, the considerable increase caused by the fructose is not so strange.

Moreover, the formation of a comparatively strong fructose-boric acid, even at very weak boric acid concentrations is a further proof that boron must be considered as an important element in nature's household.

In consequence of these strongly acid properties and the circumstance that the mutarotation is accelerated by H-ions, great difference was found here in the values of the mutarotation-constant determined with and without addition of boric acid (with glucose and galactose this difference kept within the experimental errors).

This great difference with the fructose, moreover, corroborated the probability of the entire hypothesis, as the constant of the reaction at which the α -fructose-boric acid was transformed into the ($\alpha + \beta$) fructose-boric acid mixture, agreed with this increased mutarotation constant. In order to determine this constant, dilute boric acid solutions had to be used and the temperature had to be kept low (0°).

With a molar- α -fructose + 0.44 m. boric acid solution, the conductivity at 0° altered so rapidly that the equilibrium was already practically attained after a few minutes.

A solution of one molecule of fructose in 0.22 mol H₃BO₃ exhibited the following change of the specific conductivity ($t = 0^\circ$).

$R_s = 200 \Omega$; Cap. resistance v. = 0.1661. Mutarotation 50% fruct. sol. + 0.22 m. H₃BO₃.

t'	Reading scale	$K \times 10^6$	$K+K' = \frac{1}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$	t'	Rot.	$K+K' = \frac{1}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$
12	559.5	658		7.5	-32.4	
16	552	678	0.0541	9.5	-31.5	0.044
20	548.5	687	0.0456	11.5	-30.9	0.040
25	545.5	695	0.0442	13.5	-30.3	0.040
30	544	700	0.0405	16.5	-29.6	0.038
40	543	702	0.0308	19.5	-29.2	0.041
∞	541.5	709		24.5	-28.5	0.037
				∞	-27.5	

The change in the conductivity was still difficult to follow; for

¹⁾ Rec. 35 211 and 313 (1915).

a solution of one molecule of fructose in 0.11 m. H_3BO_3 , the following result was obtained.

$R = 400 \Omega$; Cap. = 0.1661.

$R = 400 \Omega$; Cap. = 0.1629.

t'	Reading scale	$K \times 10^6$	$K + K'$	t'	a	$K \times 10^6$	$K + K'$
10	511	400		10	504	403	
14	493	429	0.040	14	488.5	429	0.036
18	481	450	0.041	18	476	451	0.039
23	472.5	465	0.039	23	466.5	469	0.041
30	464.5	481	0.042	30	461	480	0.039
35	462	486	0.041	40	455	491	0.042
∞	460	490		∞	452	496	

Hence, there is a fairly satisfactory agreement between the constant of the mutarotation and that of the conductivity change; both are still considerably higher than that of the mutarotation of the α -fructose at 0° in pure water. (Found = 0.0124).

0.5 mol. fructose in 0.02 mol. H_3BO_3 , gave as constant for the conductivity change 0.032.

From our measurements it will be seen that the conductivity at the transformation $\alpha \rightarrow \beta$ -fructose rises; from this it follows that in the ordinary fructose the distribution of the hydroxyl-groups is less favourable than in its mutarotation isomeride. With this the configuration of the two fructoses is now known; it is indicated in the above symbols.

Delft, March 1916.

Physics. — “*The viscosity of liquefied gases. IV. Apparatus and method. V. Preliminary measurements on liquid mixtures of oxygen and nitrogen.*” By Prof. J. E. VERSCHAFFELT and Dr. CH. NICAISE. Communication 149b from the Physical Laboratory at Leiden. (Communicated by H. KAMERLINGH ONNES).

(Communicated in the meeting of March 25, 1916).

IV. Apparatus and method.

1. Introduction.

In the three preceding communications of this series (Comm. 148b c and d) one of us has developed the theory of the rotational oscillations of a sphere in a viscous liquid, with a view to an experimental investigation concerning the viscosity of liquid gases at low temperatures, especially of liquid hydrogen, which we have under-