

Citation:

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Chemistry. — "*d*-Sorbinose and *l*-sorbinose (*ψ*-tagatose) and their configurations." By Prof. C. A. LOBRY DE BRUYN and Mr. W. ALBERDA VAN EKENSTEIN, communicated by Prof. LOBRY DE BRUYN.

The configuration of *d*-sorbinose, a substance which has been known for a long time, has not up to the present been made out with certainty. It is only known that this sugar is a ketose, that it yields *d*-sorbite on reduction and that it can be formed again from this latter alcohol by oxidation.

d-Sorbinose which was formerly difficult to prepare in a tolerably large quantity, is now more easily obtained by the method of BERTRAND¹⁾. According to the interesting method of this chemist, sorbite can be oxidised to sorbinose by means of *Bacterium xylinum* (and *B. aceti*). By this method we have obtained yields of 25 to 30 percent²⁾; we are indebted to the courtesy of Mr. BEYERINCK of Delft for the pure cultures of *Bact. xylinum*.

The final experiments with *d*-sorbinose were brought to a conclusion in the beginning of 1898; they proved that, on reduction with sodium amalgam, *d*-idite is formed as well as *d*-sorbite. The former alcohol was recognised, in the form of its tribenzal-compound, as the optically opposite form of tribenzal *l*-idite prepared from *l*-idonic acid.³⁾

This result was obtained many months before the publication, at a meeting of the Société chimique, by G. BERTRAND from the fact that on reducing *d*-sorbinose a second hexite is produced, in addition to sorbite, which according to BERTRAND must be *d*-idite.⁴⁾ The publication of our work was, however, postponed because in the course of an investigation of *ψ*-tagatose (a new ketose which is formed along with tagatose by the action of alkalis on galactose⁵⁾) it was becoming more and more probable that this sugar was to be regarded as *l*-sorbinose. More than a year ago, the two ketoses were submitted to a comparative crystallographic examination; Mr. VAN LIER was good enough to make this examination in the laboratory of Prof. SCHROEBER VAN DER KOLK at Delft. The result

¹⁾ Bull. Soc. chim. 15, 1196, 627.

²⁾ 200 gr. sorbite gave 50 to 60 grams of pure sorbinose.

³⁾ Recueil 18, 50.

⁴⁾ Report of the meeting of March 11. 1898; Bull. 19. 259. In the publication relating to this communication (Bull. 19, 347) no details are given about the reduction of *d* sorbinose to idite or about its configuration; BERTRAND has also not returned to the subject.

⁵⁾ Recueil 16, 267.

was that the two substances behave crystallographically and optically in exactly the same way.

At that time we still hesitated, however, to assume that ψ -tagatose was *l*-sorbinose; on reduction some *l*-dulcitol was always obtained along with *l*-sorbitol and *l*-iditol. The specific rotatory power of ψ -tagatose to the right remained, even after repeated crystallisations from water, methyl- and ethylalcohols, about 4° less than that of *d*-sorbinose to the left; the crystals were never quite clear but always slightly turbid.

After many attempts to convert ψ -tagatose into a crystalline compound from which the pure ketose could be regenerated, we attained our object by the employment of aniline. It was then found that *d*-tagatose crystallises together with ψ -tagatose in a very persistent way, but forms an anilide much more readily than its isomer so that the latter is deposited in well formed, clear crystals from an alcoholic solution containing aniline. The ψ -tagatose purified in this way was then proved with certainty to be the optical opposite of *d*-sorbinose and it is therefore henceforth to be regarded as *l*-sorbinose. A short summary of the comparative experiments which place this view beyond doubt follows.

The melting points are the same (about 154°); from a mixture of equal quantities of the two ketoses a well crystallised racemic compound is obtained with approximately the same melting point and a somewhat higher specific gravity.

The specific gravities and the solubilities in water and methyl- and ethylalcohols are the same.

For *d*-sorbinose, $\alpha_{17} = -42^\circ.7$, for *l*-sorbinose $\alpha_{17} = +42^\circ.3$ (4 percent solutions at 17°). Both solutions show the same slight birotation.

It has already been remarked that the two ketoses are crystallographically identical; hemihedral faces will be again sought for.

The osazones have the same melting point (150 to 151°), the same solubility and equal and opposite rotatory powers.

l-Sorbinosazone is, as a comparison shows, identical with *l*-gulosazone.¹⁾

On reduction with sodium amalgam, *d*-sorbitol and *d*-iditol are formed from *d*-sorbinose, *l*-sorbitol and *l*-iditol from *l*-sorbinose; these

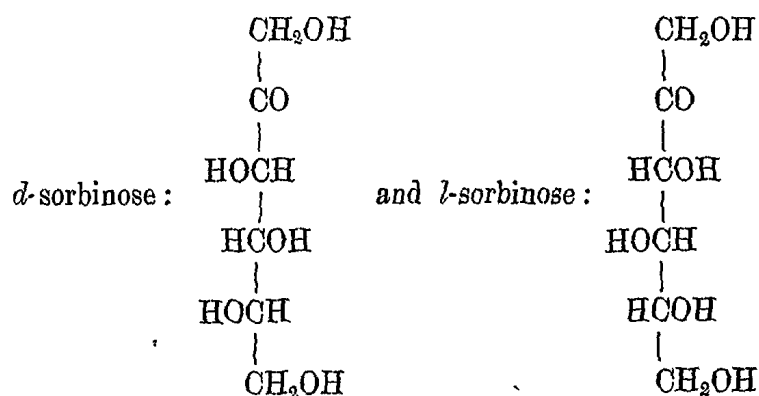
¹⁾ The statement in VON LIPP MANN'S "Chemie der Zuckerarten", p. 534, that sorbinosazone is not identical with gulosazone is, according to a communication from the author, a mistake.

hexites were recognised in the form of the benzal-¹⁾ and formal-derivatives.

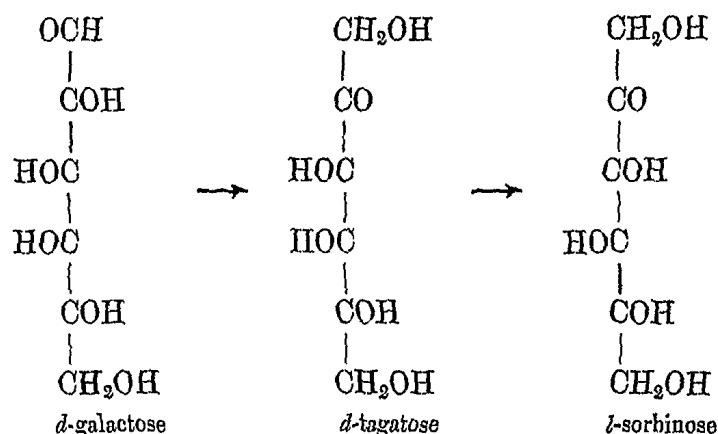
Both *d*- and *l*-sorbite have been prepared from the benzalcompounds and obtained in the crystalline form.

Crystalline methyl-*l*-sorbinoside was prepared by E. FISCHER's method from *l*-sorbinose; its specific rotation is equal and opposite to that of the known methyl-*d*-sorbinoside (88°.5).²⁾

The results obtained, including the production of idite along with sorbite by reduction and the identity of *l*-sorbinosazone with *l*-gulosazone enable us to give the two sorbinoses the following configurations:



The formation of *l*-sorbinose from *d*-galactose under the influence of alkalis is an example of a direct transition from the dulcitate series of the hexoses to the mannite series. This can be best represented by assuming the intermediate formation of *d*-tagatose; the OH and H attached to the third carbon atom must then change places in the transformation



¹⁾ Recueil 18, 150. A tribenzalsorbite was obtained as well as the mono- and di-benzalsorbites.

²⁾ E. FISCHER, Ber. 28, 1159.

We shall try to determine whether pure tagatose readily yields *L*-sorbinose under the influence of alkalis.

We have also again taken up the investigation of the probable formation of a new ketose (called, for the present, ψ -fructose¹⁾ by the reciprocal transformation of glucose, fructose and mannose under the influence of alkalis

The following triplets of hexoses (two aldoses and a ketose) are now known which give the same osazone:

d- and *l*-glucose, — fructose and — mannose

d- and *l*-gulose, — sorbinose and — idose

d-galactose, — tagatose and — talose.²⁾

A complete account of this investigation will be published in the "Recueil".

Chemistry. — "On the action of sodiummono- and -disulphides on aromatic nitro-compounds." By Mr. J. J. BLANKSMA. (Preliminary communication). Communicated by Prof. C. A. LOBRY DE BRUYN.

It has been shown for orthodinitrobenzene by LAUBENHEIMER³⁾ and for paradinitrobenzene by LOBRY DE BRUYN⁴⁾ that the nitrogroup can be readily replaced by other groups. The investigation of the behaviour of the alkalisulphides, although promised⁵⁾, has not been taken up until the present. Some positive result may be expected from this study since NIETZKI and BOTHOFF⁶⁾ have proved that the corresponding dinitrodiphenylsulphides are formed from *o*- and *p*-chloronitrobenzene and sodiummonosulphide.

It has now been found that orthodinitrobenzene reacts not only with sodium monosulphide but also with the disulphide in a similar

¹⁾ Recueil, 16, 278.

²⁾ The *d*-tagatose has yielded *d* talite along with dulcitol.

³⁾ Ber. 9, 1828; 11, 1155.

⁴⁾ Recueil 13, 121.

⁵⁾ Recueil 13, 105—106.

⁶⁾ Ber. 27, 3261, 29, 2774.