

have found that the liquid dimethyl 3:6-anhydro- α -methyl-*d*-galactopyranoside changes, by a brief contact with air containing a trace of hydrogen chloride, to the corresponding crystalline β -form, namely, 2:4-dimethyl 3:6-anhydro- β -methyl-*d*-galactopyranoside (m.p. 82°; $[\alpha]_D - 77^\circ$ in water, -87° in chloroform, -81° in methyl alcohol). Both forms appear, by ebullioscopic methods, to be monomeric, and this is confirmed for the β -form by X-ray examination.

The same isomeric change from α - to β -form was effected by the addition of a drop of a solution of hydrogen chloride in ethyl alcohol or in ether. The velocity of this change is apparent from the fact that with gaseous hydrogen chloride or hydrogen bromide the syrupy α -form appears to pass instantaneously into the crystalline β -form, although the solid mass of the product still contains some of the α -form. Inasmuch as there is no loss of methyl from the glycosidic group during these transformations, it is clear that the mechanism does not admit of a stage which passes through the free sugar. Moreover, we have prepared the same crystalline substance, namely, 2:4-dimethyl 3:6-anhydro- β -methyl-*d*-galactopyranoside by following the procedure observed for the α -form, except that we started from β -methylgalactopyranoside. It is evident, therefore, that the transformation product derived from the α -form is the true β -form. When either the α - or the β -form is treated with methyl-alcoholic hydrogen chloride (2 per cent), at room temperature or at boiling point, polarimetric observations show the rapid establishment of equilibrium of the two forms, and fission, if any, of the 3:6-anhydro-ring does not occur to an appreciable extent. The presence of the 2:4-dimethyl residues seems to stabilize the 3:6-anhydro-ring in the presence of acid reagents. The corresponding glucose derivative, 3:6-anhydro-methylglucopyranoside, does not display with acid reagents instability of the anhydro-ring.

Detailed examination of 3:6-anhydro-ring forms has recently assumed a new importance inasmuch as an enantiomorph in the *l*-galactose series has been isolated from a study of the hydrolytic products of agar-agar^{3,4}. Recognition of 2:4-dimethyl sugars in the form of their methylglycosides has become a live problem for the reason that we have required these sugars in order to identify the components having 1:3- and 1:6-glycosidic links which, in the course of our work during the past five years, have been found to occur in the polysaccharide derived from gum arabic. Both the α - and β -forms of 2:4-dimethyl 3:6-anhydro-methyl-*d*-galactopyranoside are rapidly hydrolysed by dilute acids. From the β -form, 2:4-dimethyl 3:6-anhydro-galactose, m.p. 112°, was isolated, and this gives the anilide, m.p. 123°, and also, by oxidation, the corresponding 2:4-dimethyl 3:6-anhydro-galactonic acid and its amide, m.p. 151°.

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3:6-Anhydro-*l*-galactose in Agar

IN continuation of our former communication¹ we are now able to confirm that the substance (X) derived from agar is a derivative of 3:6-anhydro-*l*-galactose as recently advanced by Hands and Peat². 3:6-Anhydro- β -methyl-*d*-galactoside, m.p. 118°, $[\alpha]_D^{20} = -113^\circ$ in water has now been synthesized from the crystalline triacetyl 6-*p*-toluenesulphonyl α -*d*-galactosyl-1-bromide ($[\alpha]_D = +157^\circ$) of Ohle and Thiel³ by treatment with silver carbonate and methyl alcohol followed by deacylation with sodium hydroxide. Methylation of this substance yielded quantitatively crystalline 2:4-dimethyl 3:6-anhydro- β -methyl-*d*-galactoside, m.p. 82°, $[\alpha]_D^{20} = -77^\circ$ in water, -86° in chloroform, which is undoubtedly the enantiomorph of (X), since the properties are the same but the sign of the rotation is reversed (mixed m.p. 65°). We have obtained further confirmation of this point by the preparation of the anilides of the dimethyl anhydro sugars, 2:4-dimethyl 3:6-anhydro-*d*-galactose anilide having m.p. 118°, whilst the corresponding derivative from agar had m.p. 117° strongly depressed on admixture with the *d*-anilide. Furthermore, the properties and stability of the lactones produced on oxidation are in agreement with these findings, so that the substance (X) must be regarded as 2:4-dimethyl 3:6-anhydro- β -methyl-*l*-galactoside.

The preparation of 2:4-dimethyl 3:6-anhydro- α -methyl-*d*-galactoside was described in our former letter¹ and isolated as an oil, $[\alpha]_D = +87^\circ$ in chloroform, and both this oil and the crystalline substance synthesized above reach the same equilibrium ($[\alpha]_D^{20} = +22^\circ$) in cold *N*-sulphuric acid. It has also been found that this oily 2:4-dimethyl 3:6-anhydro- α -methyl-*d*-galactoside is very sensitive to traces of acid; contact with cold methyl-alcoholic hydrogen chloride causes a remarkably rapid fall in optical rotation and the crystalline β -form can then be readily isolated.

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¹ Percival, Somerville and Forbes, *NATURE*, **142**, 797 (1938).

² Hands and Peat, *NATURE*, **142**, 797 (1938).

³ Ohle and Thiel, *Ber.*, **66**, 525 (1933).

"Methyl Epiglucosamine" and 2-Amino α -Methylaltrósíde

DURING recent years, a series of papers from this laboratory have shown that derivatives of glucose may be converted smoothly into derivatives of altrose, galactose and gulose by means of optical inversion within the molecule¹. In each case the key substance to such a conversion has been an anhydro-compound of the ethylene oxide type in which the ring is broken under the influence of alkali. For example, 2:3-anhydro 4:6-benzylidene α -methylalloside or 2:3-anhydro 4:6-benzylidene α -methylmannoside, in our experience, invariably yield derivatives of altrose when treated with alcoholic caustic potash or sodium methoxide solution.

We are now able to report that an analogous series of reactions may be carried out with derivatives of galactose, and that various crystalline derivatives of idose have thus been obtained (Robertson and Tetlow, unpublished result).

¹ Valentin, *Coll. Czech. Chem. Comm.*, **4**, 364 (1932).

² Ohle and Thiel, *Ber.*, **66**, 523 (1933).

³ Percival, Somerville and Forbes, *NATURE*, **142**, 797 (1938).

⁴ Peat and Hands, *Chem. and Ind.*, **57**, 937 (1938); *NATURE*, **142**, 797 (1938).