5. From the method of preparation of isophenol-tetrachlorophthalein one hydroxyl group must be in the *ortho* position and the other in the *para* position to the methane carbon atom; that is, it is the tetrachloro derivative of isophenolphthalein in which the four chlorine atoms are in the phthalic acid residue.

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RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP.[1] XI[2] THE RELATED ROTATIONS OF AMYLOBIOSE, AMYLOTRIOSE AND GLUCOSE

BY C. S. HUDSON, H. PRINGSHEIM AND J. LEIBOWITZ

RECEIVED NOVEMBER 21, 1925 PUBLISHED JANUARY 8, 1926

It has been shown[3] that the rotations of many of the compound sugars can be mathematically expressed in terms of the rotations of the constituent sugars by formulas derived from the application of the Van't Hoff hypothesis of optical superposition. Doubtless, this method of correlating rotation with structure can eventually be applied to all compound sugars and polysaccharides since the extent of the applications that have so far been made of it have been limited only by the extent of our knowledge of the structures of compound sugars. It was successfully applied to the group of compound sugars that possess in common the "sucrose union" (namely, sucrose, raffinose, gentianose and stachyose), and from it conclusions were drawn concerning structural features of trehalose, lactose, cellobiose[3] and amygdalin.[4] It is the purpose of the present article to indicate the application of this method to the problem of the structures of amylobiose and amylotriose, the two sugars which have recently been shown to be the units from which the starch molecule is constructed.[5] It will be shown that if the structural formulas proposed by Pringsheim for these sugars are correct, and the Van't Hoff hypothesis holds for these substances, a certain simple numerical relationship should apply among the rotations of glucose, amylobiose and amylotriose. An experimental test verifies this theoretical deduction both for the case of the sugars themselves and for that of their acetates. The numerical relationship that is thus established may be regarded as a fact, independent of theory, with which any structural formulas that may be proposed for

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[1] Published by permission of the Director of the Bureau of Standards, U. S. Department of Commerce.

[2] Part X was published in THIS JOURNAL, **47,** 2052 (1925).

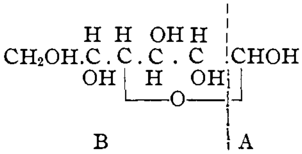
[3] Hudson, *ibid.*, **38,** 1566 (1916).

[4] Hudson, *ibid.*, **46,** 483 (1924).

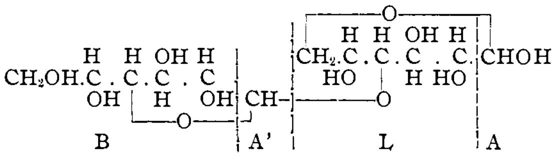
[5] Pringsheim, *Ber.*, **57,** 1581 (1924).

amylobiose and amylotriose must conform. The agreement of Pringsheim's structures with this fact does not necessarily prove their correctness but it constitutes evidence of a new kind supporting that which Pringsheim has already adduced from the peculiar chemical reactions of these sugars, particularly their quantitative conversion to maltose by enzymes.

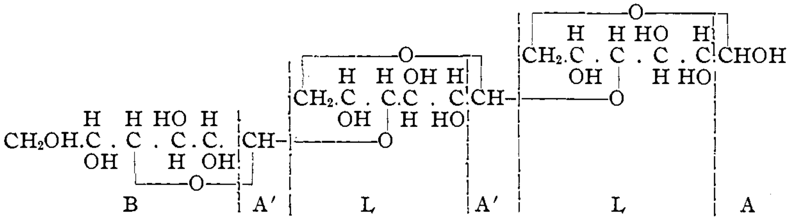
If the molecular rotation of α-glucose be separated[6] into the components $+A$ (rotation of Carbon 1) and $+B$ (rotation of the remainder of the structure, see (I)) the analogous separations for Pringsheim's structures of α-amylobiose (II) and α-amylotriose (III) are those indicated in the diagrams. From this formulation



I. Glucose, $[M] = B + A$.



II. Amylobiose, $[M] = B + A + (L + A')$



III. Amylotriose, $[M] = B + A + 2\,(L + A')$

it follows that the molecular rotations of the corresponding α (or β) forms of the three sugars are related by the expression

$$[M]_{(\text{amylotriose})} - [M]_{(\text{amylobiose})} = [M]_{(\text{amylobiose})} - [M]_{(\text{glucose})} \qquad (1)$$

Since amylobiose and amylotriose are not known as yet in pure α or β forms, only their final or equilibrium rotations having been determined, a test of Equation 1 must be limited at present to comparing the final rotations of the three sugars under the assumption that the equilibrium coefficient, $k = C_\alpha/C_\beta$, where C is the concentration, has the same value for the three sugars. It has previously been shown[6] that this coefficient has nearly a constant value for most sugars.

TABLE I

COMPARISON OF THE MOLECULAR (EQUILIBRIUM) ROTATIONS OF GLUCOSE, AMYLOBIOSE AND AMYLOTRIOSE IN WATER

$[M]_D$ (glucose) = (52.5) (180) = 9,500
$[M]_D$ (amylobiose) = (110) (342) = 37,600
$[M]_D$ (amylotriose) = (124) (504) = 62,500
$[M]_D$ (amylotriose) − $[M]_D$ (amylobiose) = 24,900
$[M]_D$ (amylobiose) − $[M]_D$ (glucose) = 28,100

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[6] Hudson, THIS JOURNAL, **31,** 66 (1909).

The differences are approximately equal, as the divergence corresponds to about 5 or 6 degrees only in the specific rotations of amylobiose and amylotriose.

This conclusion that Equation 1 holds is strongly supported by a comparison of the molecular rotations of the alpha forms of the fully acetylated derivatives of the three sugars. These acetates of the biose and triose were prepared[7] by the use of zinc chloride as a catalyst, a method which has been found in general to yield α-acetates.[8] The rotations of these substances have now been measured and are: for α-amylobiose octaacetate, $[\alpha]_D = (+2.04 \times 5)/0.0835 = +122$ (in $CHCl_3$); for α-amylotriose hendeka-acetate, $[\alpha]_D = (+2.52 \times 5)/0.0986 = +128$ (in $CHCl_3$).

TABLE II

COMPARISON OF THE MOLECULAR ROTATIONS OF THE ALPHA ACETATES OF GLUCOSE, AMYLOBIOSE AND AMYLOTRIOSE IN CHLOROFORM

$[M]_D$ (glucose) = (102) (390) = 39,800
$[M]_D$ (amylobiose) = (122) (678) = 82,700
$[M]_D$ (amylotriose) = (128) (966) = 123,600
$[M]_D$ (amylotriose) − $[M]_D$ (amylobiose) = 40,900
$[M]_D$ (amylobiose) − $[M]_D$ (glucose) = 42,900

The two differences for these acetates in chloroform solution (see Table II) are nearly the same, their divergence corresponding to only 2 or 3 degrees in the specific rotations. The acetates of the biose and triose are amorphous substances, and a more precise test of this rotatory relation could be made if it should prove possible to obtain the acetates in pure crystalline form.

The conclusions which we would draw from these results are (1) that the component (A′ + L) of the rotation of amylobiose occurs twice in the rotation of amylotriose or, in other words, that the radical (of rotation L) which has been proposed by one of us[5] as one of the structural elements of amylobiose occurs twice in the molecule of amylotriose, and (2) that the glycosidic linkage present in amylobiose (whether it be an alpha or beta union, being for the present left undecided) occurs twice in amylotriose and in both cases has the same configuration (α or β) as in amylobiose. This second conclusion is based upon the identity of the sign of the rotation (A′) of the Carbon 1 of these three linkages.

Summary

It is shown that the application of the Van't Hoff hypothesis of optical superposition to the structural formulas that have been proposed for amylobiose and amylotriose by Pringsheim leads to a simple numerical relation among the molecular rotations of glucose, amylobiose and amylotriose. Experimental test indicates that this relation holds for the rota-

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[7] Ref. 5, p. 1593.

[8] Hudson, *J. Ind. Eng. Chem.*, **8**, 379 (1916).

tions of the sugars themselves and for those of their acetates. From the results it is possible now to specify more precisely certain stereochemical features of the structures of the biose and triose. The rotations of the alpha forms of amylobiose octa-acetate and amylotriose hendeka-acetate (amorphous substances) in chloroform solution have been measured.

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NOTES

Acetyldiphenylamine from Ketene.—In a recent interesting article,[1] J. van Alphen concerned himself chiefly with reactions of the ketenes with hydrazines. In a digression from this topic, he stated[2] that ketene was entirely without action on a solution of diphenylamine in ether. Van Alphen expected the acetyl derivative to precipitate from the ether, and this it failed to do. His observation of the non-precipitation is correct, as would also have been a statement that diphenylamine does not react instantly with ketene. To state, however, that the two do not react is quite erroneous.

An excess of ketene was bubbled through an ice-cold solution of diphenylamine in ordinary ether. No precipitation ensued. The escaping gases were shown to contain much ketene by passing them into an ethereal solution of *p*-phenetidine. Phenacetin precipitated so readily that the wide-mouthed delivery tube soon became clogged.

To separate the unchanged diphenylamine from its acetyl derivative, dry hydrogen chloride was passed into the ethereal solution. Diphenyl-ammonium chloride separated. It was filtered off, and the filtrate was tested with more hydrogen chloride. In the absence of further precipitation, the solution was left to evaporate. Water was then poured on the oily residue. Gradually, this converted the oil to a solid, which was later collected upon a filter, rinsed, and pressed on a porous plate. With no further purification, the melting point was 98–100°, which indicated that the product was nearly pure. The best yield obtained was 33%, based on the original diphenylamine. A low yield of 8% was obtained when the reaction flask was not cooled with an ice-bath. The yield, instead of being bettered, was lessened when ketene was passed into pure molten diphenylamine.

The diphenylamine is, of course, easily recovered from its hydrochloride by suspending it in hot water, a reaction which proceeds more smoothly if a little hydroxide is added.

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RECEIVED SEPTEMBER 14, 1925
PUBLISHED JANUARY 8, 1926

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[1] van Alphen, *Rec. trav. chim.*, **43,** 826 (1924).

[2] Ref. 1, p. 860.