the difference between free benzophenone oxime, which does not rearrange, and its salts, which rearrange readily.

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[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. VI.[1] THE ROTATORY POWERS OF THE ALPHA AND BETA FORMS OF METHYL d-XYLOSIDE AND OF METHYL l-ARABINOSIDE

BY C. S. HUDSON[2]

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The rotatory powers of the alpha and beta forms of methyl *d*-glucoside and of methyl *d*-galactoside are known with precision from the careful reinvestigation of these substances by E. Bourquelot.[3] The present investigation was undertaken with the purpose of determining accurately the rotations of the alpha and beta forms of methyl *d*-xyloside and of methyl *l*-arabinoside as a supplement to Bourquelot's data so that the rotations of these four isomeric pairs of methyl glycosides of the four aldoses may be used for a more exact quantitative study of the relation between rotatory power and structure than has been possible in the past.[4] The principal problem in the obtaining of accurate data respecting such compounds is the purification of the substances themselves and particularly the thorough separation of isomeric forms by crystallization from suitable solvents.

The two forms of methyl xyloside and one of the forms of methyl arabinoside were discovered by Emil Fischer.[5] The present results agree with his values of the rotations of the methyl xylosides within about 0.5%. He did not record the rotation of the arabinoside. The second form of methyl arabinoside was discovered by Purdie and Rose[6] who measured not only its rotation but the rotation of the first form as well. The present results closely confirm their value of the rotation of the first, or Fischer's arabinoside, but give a greatly different value from theirs in the case of the second arabinoside ($[\alpha]_D^{20} = +17.3$ in place of $+73$). The difference is probably due to the presence of some of the first arabinoside in their compound, which is readily accounted for by the great difficulty of separating the two isomers, especially when only small quantities of material

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[1] Part V was published in THIS JOURNAL, **46**, 2591 (1924).

[2] This work was done in 1917 in the Carbohydrate Laboratory, Bureau of Chemistry, U. S. Department of Agriculture.

[3] Bourquelot, *Ann. chim.*, **7**, 219 (1917).

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

[5] Fischer, *Ber.*, **28**, 1145 (1895).

[6] Purdie and Rose, *J. Chem. Soc.*, **89**, 1204 (1906).

are subjected to purification. The new set of values of the rotations is used in the accompanying article (Part VII) in a comparison of the rotatory powers of nearly all the known methyl glycosidic derivatives of the various sugars.

The directions for preparing the methyl xylosides and methyl arabinosides specified in the present article are based upon many experiments undertaken to ascertain the best conditions for applying to xylose and arabinose Bourquelot's modification[7] of Fischer's method[5] for preparing methyl glucoside. By this method of preparation the use of sealed tubes or an autoclave is avoided and the combination of the sugar with the methyl alcohol is effected simply by boiling the slightly acidified solution for a few hours.

Preparation of the Alpha and Beta Forms of Methyl *d*-Xyloside

β-Methyl *d*-Xyloside.—Bourquelot[7] has shown that methyl glucoside may be prepared by boiling a solution of glucose in methyl alcohol containing 0.25% of hydrochloric acid, a method that offers advantage over the directions of Fischer[5] which require the heating of the solution at 100° in an autoclave or a sealed tube. After trying several strengths of acid and various times of boiling, we adopted the following directions for preparing the methyl xylosides by Bourquelot's procedure. One hundred g. of dextrorotatory *d*-xylose ($[\alpha]^{20}_{\mathrm{D}} = +18$) was boiled with 1 liter of pure anhydrous methyl alcohol containing 1% of dry hydrogen chloride on the steam-bath under a reflux condenser during six hours. A few pieces of porous plate insured steady boiling. The acid was then neutralized with silver carbonate and the solution was filtered, decolorized with active carbon, filtered again and concentrated to a thick sirup under reduced pressure. By treating the sirup with ethyl acetate 42 g. of crystalline β-methyl *d*-xyloside was obtained. The mother liquor was used for the preparation of the isomeric α-form, as will be described. The crystals of the β-xyloside were purified by recrystallization from absolute alcohol. After one recrystallization, $[\alpha]^{20}_{\mathrm{D}} = -65.6$ in aqueous solution (2.520 g. of substance, 25 cc. of solution, reading 6.61° to the left, in a 1-dm. tube), and after a second recrystallization from absolute alcohol $[\alpha]^{20}_{\mathrm{D}} = -65.5$, (3.430 g. of substance, 25 cc. of solution, reading 8.95° to the left in a 1-dm. tube). The melting point of the twice recrystallized substance was 157°. The corresponding values of Fischer are —65.8° and 157°.

α-Methyl *d*-Xyloside.—The mother liquor of the initial crystallization of the β-xyloside from ethyl acetate was placed in a vacuum desiccator and occasionally stirred. In the course of several weeks it became a semi-solid crystalline mass. The sirupy portion was thinned with a small amount of methylethyl ketone and the crystals of α-methyl *d*-xyloside were

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[7] Bourquelot, *Ann. chim.*, **3**, 298 (1915)

then separated by pressing the mass between several thicknesses of filter paper. After two recrystallizations from methylethyl ketone, $[\alpha]_D^{20}$ = + 152.8; after another, the value was + 153.7; and after a fourth it was + 153.9, (10.556 g. of substance, 100 cc. of aqueous solution, reading 32.50° to the right, in a 2-dm. tube). Fischer found + 153.2. The use of methylethyl ketone in place of the ethyl acetate that Fischer employed is of much advantage in the purification of α-methyl xyloside.

Preparation of the Alpha and Beta Forms of Methyl *l*-Arabinoside

β-Methyl *l*-Arabinoside.—After trials with various percentages of acid and times of boiling, the following directions were adopted for preparing the two forms of methyl *l*-arabinoside. One hundred g. of dextrorotatory *l*-arabinose ($[\alpha]_D^{20}$ = + 104 to + 105) was boiled with 1 liter of pure anhydrous methyl alcohol containing 1.5% of dry hydrogen chloride on the steam-bath under a reflux condenser during three hours. The acid was neutralized with silver carbonate and the solution filtered, decolorized with active carbon and filtered again. On boiling down the solution under reduced pressure, β-methyl *l*-arabinoside crystallized and the crystals were filtered off; yield, 30 g. These crystals were extracted with boiling ethyl acetate to remove as much sirupy impurity as possible and were then recrystallized from absolute alcohol. The product from this first recrystallization gave $[\alpha]_D^{20}$ + 243.1. After repeating the extraction with ethyl acetate and the crystallization from absolute alcohol the value of $[\alpha]_D^{20}$ rose to + 245.6, but a third extraction and recrystallization gave crystals of the same rotation, $[\alpha]_D^{20}$ = + 245.5, (1.813 g. of substance, 25 cc. of aqueous solution, reading 33.60° to the right in a 1-dm. tube), which is taken as the specific rotation of pure β-methyl *l*-arabinoside. The melting point was 169°. Purdie and Rose found the values + 245.7 and 166°. Fischer found a melting point of 169–171°.

α-Methyl *l*-Arabinoside.—This substance is contained in the methyl alcoholic mother liquor from the original crystallization of the β-arabinoside. The solution was evaporated under reduced pressure to a thin sirup and kept in a vacuum desiccator, where it slowly crystallized. At successive stages of the crystallization the crystals were filtered off by suction; the $[\alpha]_D^{20}$ values of the successive crops were about the same, approximately + 49, a rotation which seemed to indicate that the crystals were a mixture of the two isomers. The separation of the pure α-isomer from this mixture was at last accomplished through the use of boiling ethyl acetate as a solvent, as it was found that the α-isomer was more soluble than the β-form. On successive fractional recrystallizations from ethyl acetate the more slowly crystallizing portions regularly showed lower specific rotations, which became constant at $[\alpha]_D^{20}$ = + 17.3, (0.8536 g. of substance, 25 cc. of aqueous solution, reading 1.18° to the right in a

1-dm. tube). This is taken as the specific rotation of pure α-methyl *l*-arabinoside.

The melting point of pure α-methyl *l*-arabinoside is 131°. A preparation showing $[\alpha]^{20}_D = +20$ melted at 130°, one showing $[\alpha]^{20}_D = +49$ at 123°. Fractions giving $[\alpha]^{20}_D$ higher than + 60 did not melt sharply. Purdie and Rose reported 115–117° as the melting point of their preparation. Proof that their product having $[\alpha]^{20}_D = +73$ was in all probability a mixture is given by the fact that on successive recrystallizations of a fraction having approximately this rotation, the $[\alpha]^{20}_D$ values of the recrystallized products gave the series $+75 \longrightarrow +34 \longrightarrow +20 \longrightarrow +17.7 \longrightarrow +17.3$.

Anal. Subs. ($[\alpha]^{20}_D = +17.3$), 0.2728: H_2O, 0.1745; CO_2, 0.4420. Calcd.: C, 44.18; H, 7.15. Found: C, 43.88; H, 7.37.

Summarizing, the following values have been found for the specific rotations of the four pure substances in dilute aqueous solution: α-methyl *d*-xyloside, $[\alpha]^{20}_D = +153.9$, α-methyl *l*-arabinoside, $[\alpha]^{20}_D = +17.3$; β-methyl *d*-xyloside, $[\alpha]^{20}_D = -65.5$, β-methyl *l*-arabinoside, $[\alpha]^{20}_D = +245.5$.

My thanks are expressed to Dr. D. H. Brauns for the skilful assistance that he has rendered in the course of the experiments.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE POLARIMETRY SECTION OF THE BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE[1]]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. VII.[2] THE METHYL GLYCOSIDIC DERIVATIVES OF THE SUGARS

BY C. S. HUDSON

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The developments that have followed from the discovery of the methyl glycosides[3] in 1893 by Emil Fischer[4] are of much historical interest. His study of the composition and reactions of these crystalline compounds which result from the union of the reducing sugars with methyl alcohol led him to conclude that they are not of the acetal type of structure, which he had expected they would prove to be, but that the semi-acetal ring structure should be assigned to them. He then drew from the van't Hoff-LeBel theory of the asymmetric carbon atom the deduction that

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

[2] Part VI immediately precedes this article.

[3] Following the practice of several writers the word "glycoside" is here used as a convenient class name for the various aldosides (glucosides, galactosides, maltosides, etc.) and ketosides (fructosides, sorbosides, etc.).

[4] Fischer, *Ber.*, **26**, 2400 (1893).