[CONTRIBUTION FROM THE VEGETABLE PROCESSING SECTION, WESTERN UTILIZATION RESEARCH BRANCH][1]

The Reaction of Fructose with Isopropylamine and Cyclohexylamine[2]

BY J. F. CARSON

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From the reaction of fructose with anhydrous isopropylamine at 25°, 2-isopropylamino-2-deoxyaldohexose (II, R = isopropyl) has been isolated in crystalline form. Reaction of fructose with anhydrous cyclohexylamine at 0° has yielded the crystalline 2-cyclohexylamino-2-deoxyaldohexose (II, R = cyclohexyl) and 2-cyclohexylamino-2-deoxy-aldohexosylcyclohexylamine (III). Evidence for the structure of the compounds is presented. The configuration of the number 2 carbon atom is in doubt and the compounds may be glucose or mannose derivatives. Although the ring structures and the configuration of the glycosidic carbon atoms are not known, the moderately high dextrorotation accompanied by mutarotation in the negative direction suggests an alpha configuration.

The preparation of crystalline condensation products from fructose and amines is difficult and except in a very few cases has not been successful in contrast to the corresponding glucose–amine condensation reactions. A wide variety of amines, both aliphatic and aromatic, have been treated with glucose and other aldoses to yield N-substituted glycosylamines.[3] The Amadori rearrangement of these compounds to the N-substituted 1-amino-1-deoxyketoses also has been studied intensively.[4]

The only well-defined amino derivatives, produced directly from fructose, that have been described are compounds prepared from several aromatic amines and most recently from ammonia. Sorokin[5] prepared the N-phenyl-; Kuhn and Birkofer,[3] the N-*p*-ethoxyphenyl-; Barry and Honeyman,[6] the N-*p*-tolyl-, and Helferich and Portz,[7] the N-*p*-hydroxyphenyl- and *p*-methoxyphenyl-D-fructosylamines. These N-fructosides, generally obtained in low yields, were prepared by heating fructose and the corresponding amine in alcoholic solutions in the presence of small quantities of zinc chloride or amine hydrochloride as catalysts. Erickson[8] has recently reported that reaction of sugars including fructose and sorbose with octadecylamine in aqueous isopropyl alcohol yields compounds in which several amino residues have been introduced into the sugar molecule but in the absence of more complete information, the constitution of these substances is still uncertain. Recently Heyns and Meinecke[9] have isolated D-glucosamine (2-amino-2-deoxyglucose) from the reaction of fructose with aqueous or anhydrous ammonia.

This investigation was initiated with the idea that the properties of amine–fructose condensation products might be relevant to the "Maillard reaction" or the non-enzymatic browning of foodstuffs. The formation of N-substituted glucosylamines from glucose and amino compounds followed by rearrangement to 1-amino-1-deoxy ketoses has been considered by Hodge[4,10] and by Gottschalk[11] to be a possible intermediate step in the non-enzymatic browning discoloration of foodstuffs. Of additional interest is the relationship that fructose–amine condensation products would have to the biologically interesting 2-amino sugar, glucosamine.

Reaction of fructose with excess anhydrous isopropylamine at room temperature produces a crystalline condensation product in 10–15% yields having the composition $C_9H_{19}NO_5$ (one-to-one condensation with the loss of one molecule of water). Reaction of fructose with excess anhydrous cyclohexyl amine at 0° yields the corresponding one-to-one condensation product $C_{12}H_{23}NO_5$ in yields of 12%. A second crystalline product is also obtained in approximately the same yield with the composition $C_{18}H_{34}N_2O_4$ in agreement with that of a compound formed by the reaction of one molecule of fructose with two molecules of amine accompanied by the loss of two molecules of water. The two cyclohexylamine condensation products are easily separated by their differing solubilities in alcohol and acetone. After excess cyclohexylamine is removed *in vacuo*, the resulting sirup yields the monoamino compound on the addition of methanol. The diamino compound is then obtained by adding acetone to the mother liquor. No diamino compound has been isolated from the fructose–isopropylamine reaction.

The formation of monoamino and diamino compounds of fructose and cyclohexylamine may be postulated as proceeding through the reactions shown on the following page.

The properties of the monocyclohexylamino and dicyclohexylamino compounds are consistent with expressions II and III, respectively. Similarly the isopropylamino condensation product is II, and not I (when R = isopropyl). The isolation of rearrangement products as N-cyclohexyl- or N-isopropyl-2-amino-2-deoxyaldohexoses rather than the expected fructosylamine derivatives is in agreement with Heyns and Meinecke's[9] isolation of D-glucosamine from the reaction of fructose and ammonia but is in contrast with results of other workers, in which N-substituted fructosylamines were obtained by reaction with aromatic amines in ethanol solution with added zinc chloride or amine hydrochloride.

In the reaction of glucose with aliphatic amines under anhydrous conditions, the glucosylamines are usually produced first and the preparation of the isomerized 1-amino-1-deoxyketoses usually re-

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(1) Presented at ACS meeting in New York, N. Y., Sept., 1954.

(2) Agricultural Research Service, U. S. Department of Agriculture.

(3) R. Kuhn and A. Dansi, *Ber.*, **69**, 1745 (1936); R. Kuhn and F. Weygand, *ibid.*, **70**, 769 (1937); R. Kuhn and L. Birkofer, *ibid.*, **71**, 621 (1938); E. Mitts and R. M. Hixon, THIS JOURNAL, **66**, 483 (1944); A. Mohammad and H. S. Olcott, *ibid.*, **69**, 969 (1947); J. Honeyman and O. R. Tatchell, *J. Chem. Soc.*, 967 (1950); G. P. Ellis and J. Honeyman, *ibid.*, 1940 (1952); S. Bayne and W. H. Holms, *ibid.*, 3247 (1952); J. E. Hodge and C. E. Rist, THIS JOURNAL, **74**, 1494 (1952).

(4) (a) F. Weygand, *Ber.*, **73**, 1259 (1940); (b) J. E. Hodge and C. E. Rist, THIS JOURNAL, **74**, 1494 (1952); **75**, 316 (1953).

(5) B. Sorokin, *J. prakt. Chem.*, **37**, 292 (1888).

(6) C. P. Barry and John Honeyman, *J. Chem. Soc.*, 4147 (1952).

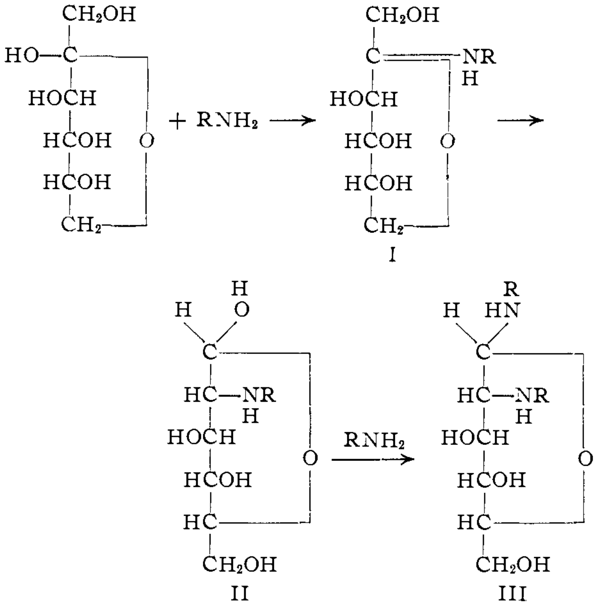
(7) B. Helferich and W. Portz, *Ber.*, **86**, 604 (1953).

(8) J. G. Erickson, THIS JOURNAL, **75**, 2784 (1953).

(9) K. Heyns and Karl-Heinz Meinecke, *Ber.*, **86**, 1453 (1953).

(10) J. E. Hodge, *J. Agr. and Food Chem.*, **1**, 928 (1953).

(11) A. Gottschalk and S. M. Partridge, *Nature*, **165**, 684 (1950); A. Gottschalk, *Biochem. J.*, **52**, 455 (1952).



quires acidic reagents, long standing of the glycosylamines, or heat. Whether the formation of the rearranged products with fructose is the result of an unusually facile isomerization of the presumed original fructosylamines (I) or whether the isomerization is greatly accelerated by other products in the complex fructose amine reaction is not known.

That the monoamino compounds are not fructose derivatives but are 2-amino-2-deoxyaldohexose derivatives is shown by their stability in dilute hydrochloric acid in contrast to the N-substituted fructosylamines which are known to hydrolyze readily with dilute acids.[6] The original compounds could be isolated from acid solutions by treatment with acid-absorbing ion exchangers or alternately the hydrochloride salts could be isolated. The equilibrium specific rotations of the monoamino hydrochlorides in water were in good agreement with the specific rotations of the free bases in 0.1 N hydrochloric acid when the latter were calculated to their hydrochloride content. As expected, the compounds give the Elson–Morgan[12] test for 2-amino sugars. They reduce Fehling solution and alkaline 2,6-dichlorophenolindophenol only on heating. This is evidence against the possibility that a carbonyl group might have formed at C_3 rather than C_1 of the hexose chain. Compounds with this structure would be expected to reduce Fehling solution and dichlorophenolindophenol rapidly at room temperature. That the monoamino compounds have their carbonyl and amine functions at the first two carbon atoms and that the configuration of the lower four carbon atoms is identical with fructose was shown by the isolation of phenyl-D-glucosazone when either the isopropylamino or cyclohexylamino derivative was reacted with phenylhydrazine under forcing conditions.

Since the formation of 2-amino-2-deoxyaldoses involves the asymmetric carbon atom no. 2 and makes carbon no. 1 asymmetric in the ring form, the configuration of these two carbon atoms is in doubt; *i.e.*, the compounds may be derivatives of glucose or of mannose with α- or β-forms. The moderately high dextrorotation of the free bases as well as their hydrochlorides accompanied by mutarotation in the negative sense suggests that the configuration of the glycosidic carbon in these derivatives is alpha. It is not known whether the ring forms are pyranose or furanose or whether the compounds are glucose or mannose derivatives. The investigations of Heyns and Meinecke,[9] in which D-glucosamine and not 2-amino-2-deoxymannose was isolated in reactions of fructose and ammonia, support the supposition that these compounds are also of the glucose configuration.

The structure of the dicyclohexylamino compound is shown to be III or 2-cyclohexylamino-2-deoxyglucosyl- or mannosylcyclohexylamine by interconversion reactions with the monoamino compound II. Treatment of II with anhydrous cyclohexylamine yields the diamino compound III. Hydrolysis of III in hydrochloric acid yields II or its hydrochloride. Moreover, the specific rotation of the dicyclohexylamino compound in hydrochloric acid changes to an equilibrium value agreeing with a value calculated from the monoamino hydrochloride content.

The mutarotations of these compounds are of interest. The hydrochlorides of the monocyclohexylamino and isopropylamino derivatives show approximately first-order mutarotation throughout most of the reaction (Fig. 1). Since the rates of mutarotation at pH 5 and pH 1 are nearly identical (Fig. 2), the reaction is not significantly catalyzed by acids when the amino group is in the salt form. The positive charge on the nitrogen may hinder the approach of protons by an electrostatic shield[13] or by acting through adjacent carbon atoms to reduce the electron availability on the glycosidic or ring oxygen. On the other hand, glucose has approximately a constant mutarotation rate over the range from pH 2.5 to 6.5[14] as a result of a very small hydrogen ion catalysis and a relatively large water catalysis.[15]

The 2-isopropylamino-2-deoxyaldose as the free base in water (pH 9.4) shows an unusually slow mutarotation where $[\alpha]^{26}\text{D}$ +65.6 → +44.9. Approximately three weeks are required for the attainment of equilibrium (Fig. 3) in contrast to glucose where hydroxyl ion catalysis is strong and equilibrium is reached in minutes and D-glucosamine which mutarotates to an equilibrium value in 20–30 minutes.[16] The 2-cyclohexylamino-2-deoxyaldose shows a marked complex mutarotation in pyridine as shown by a minimum in the curve, $[\alpha]^{26}\text{D}$ +132.7 → +102.8 (11 hours) → +106.5 (constant, 31 hours).

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[12] L. A. Elson and W. T. J. Morgan, *Biochem. J.*, **27**, 1825 (1953).

[13] R. C. G. Moggridge and A. Neuberger, *J. Chem. Soc.*, 745 (1938), have used this argument to explain the stability of methyl glycosides of 2-aminoglucose to acid hydrolysis.

[14] H. S. Isbell and W. W. Pigman, *J. Research Natl. Bur. Standards*, **20**, 773 (1938).

[15] The mutarotation coefficient ($k_1 + k_2$) in the equation $k_1 + k_2 = 1/t \log (r_0 - r_\infty)/(r_t - r_\infty)$ (where r_0 = rotation at $t = 0$, r_t = rotation at time t, and r_∞ = equilibrium rotation) has the values 0.015 and 0.017 for the isopropylamino and monocyclohexylamino hydrochloride derivatives, respectively. For glucose at pH 4 and 20° $k_1 + k_2 = 0.00632$ (H. S. Isbell and W. W. Pigman, *J. Research Natl. Bur. Standards*, **18**, 141 (1937)).

[16] O. Westphal and H. Holzmann, *Ber.*, **75**, 1274 (1942).

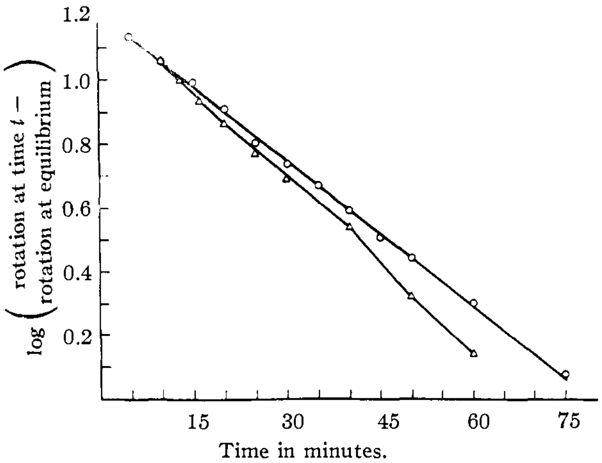

Fig. 1.—Mutarotation of 2-isopropylamino-2-deoxyaldohexose hydrochloride in water, *p*H 5.0 (O); of 2-cyclohexylamino-2-deoxyaldohexose hydrochloride in water, *p*H 5.2 (Δ).

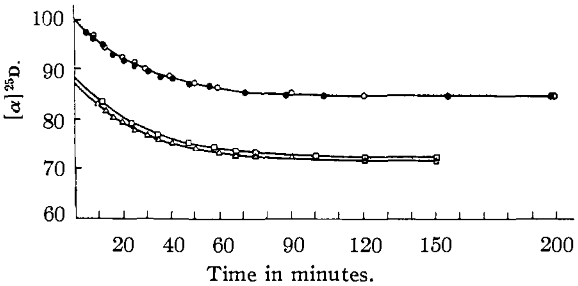

Fig. 2.—Mutarotation of 2-isopropylamino-2-deoxyaldohexose hydrochloride in water, *p*H 5.0 (O), *p*H 1.1 (●); of 2-cyclohexylamino-2-deoxyaldohexose hydrochloride in water, *p*H 5.2 (□), *p*H 1.0 (Δ).

Experimental

Reaction of Fructose with Cyclohexylamine.—Anhydrous D-fructose, 25 g. (0.14 mole) was dissolved in 60 g. (0.61 mole) of anhydrous cyclohexylamine by shaking mechanically for 30 minutes (external cooling). The clear colorless solution was kept at 0° for 48 hours and then concentrated *in vacuo* (25°) to a pale amber sirup which was then covered with 50 ml. of methanol and stored at 0°. On the following day when crystallization had begun, 75 ml. of methanol was added and the suspension allowed to crystallize for 5 days at 0°. Filtration yielded 3.7 g. of the monocyclohexylamine condensation product. Concentration of the mother liquor *in vacuo* to a sirup, addition of 50 ml. of methanol, and storage for a week at 0° yielded a second crop, 1.05 g. The combined product was recrystallized from 200 ml. of methanol, yielding 4.3 g. (12%) of 2-cyclohexylamino-2-deoxyaldohexose as white fibrous fluffy crystals, dec. 157–158° (gas) when preheated to 145°.

Anal. Calcd. for $C_{12}H_{23}NO_5$: C, 55.15; H, 8.80; N, 5.35. Found: C, 55.2; H, 8.87; N, 5.36.

Specific rotations were: $[\alpha]^{26}\text{D}$ (pyridine) +132.7 (0) → +102.8 (11 hours) → +106.5 (constant 31 hours) (*c* 0.75, *l* 2); $[\alpha]^{25}\text{D}$ (0/1*N* HCl) +100 (0) → +82.2 (constant 2.5 hours) (*c* 1.5, *l* 2), calcd. as hydrochloride $[\alpha]\text{D}$ +72.1 (equilibrium).

Evaporation of the pyridine solutions *in vacuo* to a white solid and crystallization from methanol yielded the starting material. The original compound could be isolated from acid solutions by stirring with an acid exchanger (Permutit A)[17] in the carbonate form followed by concentration of the solution *in vacuo* to a white solid and recrystallization from methanol. The compound is insoluble in hot acetone or hot ethyl acetate and moderately soluble in boiling methanol. The free base is only slightly soluble in water.

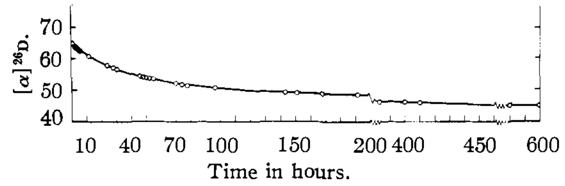

Fig. 3.—Mutarotation of 2-isopropylamino-2-deoxyaldohexose in CO_2-free water, *p*H 9.4.

The mother liquor, after removal of the monocyclohexylamino compound, was concentrated *in vacuo* to a semi-solid brown sirup which was then dissolved in 75 ml. of acetone and allowed to crystallize for 3 days at 0°. Filtration yielded 5.6 g. of white crystalline solid. By storing the mother liquor for two weeks at 0°, an additional crop, 3.3 g., of tan crystalline product was recovered. Recrystallization of the two fractions from 200 ml. of acetone yielded 5.8 g. (12%) of the dicyclohexylamino compound as white fibrous crystals, dec. 116–117°.

Anal. Calcd. for $C_{18}H_{34}N_2O_4$: C, 63.12; H, 10.01; N, 8.18. Found: C, 63.2; H, 9.99; N, 8.17. $[\alpha]^{24}\text{D}$ (pyridine) +117 (o) → +73.4 (const. 12 hr.) (*c* 0.86, *l* 2); $[\alpha]^{25}\text{D}$ (*N*/10 HCl) +64.2 (10 min.) → +62.8 (const. 1.5 hr.) (*c* 1.25, *l*, 2). The equilibrium rotation (+62.8) when calculated as the monocyclohexylamino compound gave the value +82.3 in agreement with the value, previously obtained, +82.2. Treatment of the acid rotation solution with Permutit A[17] in the carbonate form followed by concentration *in vacuo* to a white solid and recrystallization from methanol yielded the monoamino-condensation product identified by optical rotation and crystallographic properties. The dicyclohexylamino-condensation product is very soluble in methanol, hot or cold, moderately soluble in warm acetone, and sparingly soluble in cold acetone.

2-Cyclohexylamino-2-Deoxyaldohexose Hydrochloride.—The monocyclohexylamino condensation product, 1.5 g., was dissolved in 150 ml. of methanol containing 1 ml. of 10 *N* HCl and the solution was concentrated *in vacuo* to 25 ml. An additional 100 ml. of methanol was added and the solution reconcentrated *in vacuo* to 15 ml., whereupon 60 ml. of acetone was added and the solution allowed to crystallize at −20° for one week, yielding 1.51 g. (89%) of white crystalline product, dec. (gas) 189–190° (preheat to 145°).

Anal. Calcd. for $C_{12}H_{23}NO_5HCl$: Cl, 11.91; N, 4.70. Found: Cl, 12.0; N, 4.72. $[\alpha]^{26}\text{D}$ (H_2O, *p*H 5.1) +87.8 (0) → +71.7 (const. 2.5 hours) (*c* 1.65, *l* 2).

Conversion of the Monocyclohexylamino Compound to the Dicyclohexylamino Compound.—2-Cyclohexylamino-2-deoxyaldose, 1.23 g., was shaken with 12 g. of cyclohexylamine for 4 hours at 25° when complete solution was obtained. The colorless solution was allowed to stand for 3 days at 20–25° and then concentrated *in vacuo* to a waxy white solid. The solid was dissolved in 15 ml. of methanol. Several days at 0° yielded 30 mg. of the starting material. The mother liquor was concentrated *in vacuo* to a yellow oil which was dissolved in 30 ml. of hot acetone and then kept at 0° for 5 days. Filtration yielded 1.38 g. of crystalline product, dec. 109–111°. Recrystallization from acetone yielded 970 mg. of pure dicyclohexylamino condensation product identified by elemental analyses and specific rotation.

Reaction of D-Fructose with Isopropylamine.—D-Fructose, 25 g. (0.139 mole), was dissolved in 70 g. (1.2 moles) of anhydrous isopropylamine and the solution left at 0° for 2 days and then at room temperature for 5 days. The pale amber solution was concentrated *in vacuo* to a thick sirup, dissolved in 75 ml. of absolute ethanol and allowed to crystallize at 0° for a week to yield 3.1 g. of crystalline material. The mother liquor on standing an additional week yielded 2.7 g. of white crystalline product. The combined crops (19% of theory) were recrystallized from 200 ml. of absolute ethanol to yield 4.45 g. (14.5%) of analytically pure 2-isopropylamino-2-deoxyaldohexose.

The product crystallizes from alcohol as colorless coarse

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(17) The Permutit Co., 330 West 42nd Street, New York. Mention of this product does not constitute endorsement by the Department of Agriculture over others of a similar nature not mentioned.

stubby needles, dec. 156–157° (gas) colors 150° (preheat 145°); $[\alpha]^{26.5}_{\mathrm{D}}$ (pyridine) +147° (0 time) → +121° (const. 24 hours); $[\alpha]^{25}_{\mathrm{D}}$ (0.1 *N* HCl) +103.7° (21 min.) → +98.7° (const. 2 hours); (*c* 2, , *l* 2.0) calcd. as hydrochloride, $[\alpha]_{\mathrm{D}}$ +84.5° (equilibrium).

Hydrochloride of the Isopropylamine-Fructose Condensation Product.—This derivative was prepared by the same procedure as the hydrochloride of the cyclohexylamino condensation product. It was obtained as coarse colorless prisms when recrystallized from methanol–acetone (1/3) at −20°, dec. (gas) 185–186° (preheat to 150°).

Anal. Calcd. for $C_9H_{19}NO_5HCl$: Cl, 13.33; N, 5.44. Found: Cl, 13.7; N, 5.41; $[\alpha]^{25}_{\mathrm{D}}$ +100° → +84.7 (const. 2 hours) [*c* 1.2 *l* 2 (water or 0.1 *N* hydrochloric acid)].

The mutarotation curves are shown in Figs. 1 and 2. Evidence for the purity of the hydrochloride and of the free base was obtained by fractional crystallization. Fractional crystallization of the isopropylamine condensation product from ethanol yielded 4 fractions with the equilibrium rotations in 0.1 *N* hydrochloric acid of +99.1, 99.2, 99.0 and 98.1. The hydrochloride of the original sample was separated into three fractions by adding various amounts of acetone to the methanol solution. The isolated salts had similar mutarotation curves with the equilibrium rotations, +84.7, 84.5 and 84.8. Attempts to obtain a crystalline anomeric form of the free base or of the hydrochloride by varying conditions of crystallization have not been successful.

Preparation of Phenyl-D-glucosazone from 2-Cyclohexylamino-2-deoxyaldohexose.[18]—Eight hundred mg. of 2-cyclohexylamino-2-deoxy aldose hydrochloride, 1.5 g. of phenylhydrazine hydrochloride, 2.5 g. of sodium acetate and 0.5 g. of sodium bisulfite in 30 ml. of water was refluxed for 6 hours. A precipitate was observed after 4 hours. The mixture was cooled and the yellow-brown solid filtered and washed with acetone to remove resinous material. The filtrate was refluxed again for two 6-hour periods, filtering and washing with acetone each time. A total of 99 mg. (10%) of phenyl-D-glucosazone was obtained. On recrystallization from methanol–water, the derivative melted at 207–208°. The identity of the compound as phenylglucosazone was confirmed by the preparation of the phenyl-D-glucosotriazole, m.p. 194–195°, by the procedure of Hann and Hudson.[19]

Acknowledgments.—The author gratefully acknowledges the assistance of L. M. White and G. E. Secor for elementary analyses and F. T. Jones for microscopic examinations.

[18] Based on procedure of F. A. Kuehl, Jr., E. H. Flynn, F. W) Holly, R. Mozingo and K. Folkers (THIS JOURNAL, **69**, 3032 (1947). for conversion of N-methyl-L-glucosamine to phenyl-L-glucosazone.

[19] R. M. Hann and C. S. Hudson, *ibid.*, **66**, 735 (1944); **68**, 1769 (1946).

ALBANY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, PURDUE UNIVERSITY]

2-*O*-α-D-Xylopyranosyl-L-arabinose from Hemicellulose-B of Corn Cob[1,2]

BY ROY L. WHISTLER AND D. I. MCGILVRAY

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Mild acid hydrolysis of corn cob hemicellulose-B yields a number of neutral oligosaccharides which are distinct from the β-D-1 → 4 xylobiose polymer homologous series. One of these oligosaccharides has been isolated and characterized as 2-*O*-α-D-xylopyranosyl-L-arabinose.

In work toward elucidating the structure of hemicellulose-B of corn cob considerable reliance is placed on the method of fragmentation analysis, wherein the polysaccharide is hydrolyzed to oligosaccharides whose structures can be determined exactly. The nature of adjoining monosaccharide units and the glycosidic linkages between them thereby becomes fixed with a high degree of certainty. This method for the determination of polysaccharide structures is of great assistance in dealing with complex molecules.

From the hemicellulose-B of corn cob several acidic oligosaccharides have already been characterized after isolation from the polysaccharide partial hydrolyzate.[3-5] Attention is now turned to neutral oligosaccharides. These are produced in highest yield when hemicellulose-B is subjected to mild hydrolysis such as by dilute sulfuric acid at room temperature, or by autolysis through boiling, in water, the naturally acidic hemicellulose. Neutral oligosaccharides so obtained are not members of the β-D-1 → 4 xylobiose polymer homologous series. They are readily isolated by successive charcoal[6] and cellulose[7] column chromatography.

One of the neutral disaccharides, isolated in 1.5% yield, is described here. It reduces Fehling solution and hydrolyses to D-xylose and L-arabinose. On oxidation with bromine water, followed by hydrolysis and paper chromatography, only D-xylose is found. Thus L-arabinose is at the reducing end of the molecule. Since no osazone is isolated after reaction of the disaccharide with phenylhydrazine acetate a 1 → 2 linkage is indicated. Methylation with dimethyl sulfate, first at 0° then at higher temperatures produces a fully methylated product which on hydrolysis gives rise to 2,3,4-tri-*O*-methyl-D-xylose, 3,5-di-*O*-methyl-L-arabinose and 3,4-di-*O*-methyl-L-arabinose. From this it is concluded that the linkage is 1 → 2 and that the initial low temperature methylation caused the fixation in the L-arabinose portion of a mixture of furanoside and pyranoside structures. The positive rotation (+39.8°) of the disaccharide suggests that the glycosidic linkage is α-D. Thus the structure 2-*O*-α-D-xylopyranosyl-L-arabinose may be proposed. This disaccharide is not produced when a mixture of D-xylose and L-arabinose are subjected to the hydrolytic conditions used in the depolymerization of hemicellulose-B.

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[1] Journal Paper No. 819 of the Purdue Agriculture Experiment Station.

[2] Paper presented before the Division of Carbohydrate Chemistry at the 126th Meeting of the American Chemical Society at New York, N. Y., September, 1954.

[3] R. L. Whistler and L. Hough, THIS JOURNAL, **75**, 4918 (1953).

[4] R. L. Whistler, H. E. Conrad and L. Hough, *ibid.*, **76**, 1668 (1954).

[5] R. L. Whistler and D. I. McGilvray, *ibid.*, in press.

[6] R. L. Whistler and D. F. Durso, *ibid.*, **72**, 677 (1950).

[7] L. Hough, J. K. N. Jones and W. H. Wadman, *J. Chem. Soc.*, 2511 (1949).