[CONTRIBUTION FROM THE WESTERN UTILIZATION RESEARCH BRANCH, AGRICULTURAL RESEARCH SERVICE, UNITED STATES DEPARTMENT OF AGRICULTURE]

Reaction of Fructose with Benzylamine

BY JOHN F. CARSON

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Reaction of anhydrous D-fructose with excess benzylamine yields crystalline fructosylbenzylamine (I), which rearranges in methanol solution to 2-benzylamino-2-deoxy-D-glucose. The latter compound has been proved to have the D-glucose configuration by a catalytic hydrogenolysis to the D-glucosamine. The difference between the molecular rotations of the anomeric forms of the 2-benzylamino-2-deoxy-D-glucose hydrochlorides does not agree with values predicted from isorotation rules. Reaction of phenyl isothiocyanate with 2-alkylamino-2-deoxyglucoses yields crystalline derivatives assumed to be derivatives of 2-imidazolidinethione (IV).

Previous investigations[1,2] have shown that D-fructose will react with primary aliphatic amines under very mild conditions and yield the corresponding rearranged 2-alkylamino-2-deoxy-aldohexoses in low yields. With ethylamine, however, the intermediate fructosylethylamine could be isolated; in methanol at room temperature it rearranged to 2-ethylamino-2-deoxyhexose. Although evidence was presented which strongly suggested the glucose configuration for the rearranged products, rigorous proof was lacking.

In extension of these studies, fructose has now been allowed to react with benzylamine to yield crystalline fructosylbenzylamine (I). An isopropylidene fructosylbenzylamine, assumed to have structure II, has also been isolated from the mother liquor after crystallization of I from acetone. Fructosylbenzylamine, like the corresponding ethylamino derivative,[2] rearranges in methanol solution to 2-benzylamino-2-deoxy-D-glucose (III), the configuration of which has now been established by catalytic hydrogenolysis. The α- and β-forms of the hydrochloride have anomalous molecular rotations.

Heyns, Eichstedt and Meinecke[3] have recently reported that reaction of fructose with benzylamine or with *n*-butylamine, in the presence of small quantities of the amine hydrochloride, yielded after long standing, the corresponding rearranged 2-amino-2-deoxy-D-glucosylamines. The intermediate fructosylbenzylamine was not isolated, probably because the amine hydrochloride catalyzed the rearrangement of the precursor. These investigators established the D-glucose configuration of their benzylamine derivative by hydrogenolysis to D-glucosamine.

Reaction of D-fructose with excess benzylamine first at 0° and then at 25°, followed by removal of excess amine by extraction with petroleum ether and ether, yields a sirup that crystallizes on addition of acetone and yields fructosylbenzylamine (I) in 40–50% yields. In dilute acid, the compound rapidly hydrolyzes to fructose and benzylamine. The compound is similar in reactions to the previously reported fructosylethylamine,[2] although it is slightly more stable to polar solvents. No conclusions concerning the configuration or ring structure can be obtained from rotational observations, because the compound decomposes in pyridine and alcohols. In methanol solution at room temperature, fructosylbenzylamine rearranges to 2-benzylamino-2-deoxy-D-glucose isolable in 5–10% yields; in addition, a dark resinous material is formed. In the presence of acetic acid in methanol, the yield of crystalline rearranged product is increased to 50%.

Crystalline 2-benzylamino-2-deoxy-D-glucose is obtained as the β-anomer ($[\alpha]D$ +79° → +84.5° in pyridine; $[\alpha]D$ +60° → +75.7° in 0.1 *N* hydrochloric acid) in contrast to the previously described 2-alkylaminoglucose derivatives, which were obtained as the α-anomers. The hydrochloride of the benzylamino sugar, on the other hand, crystallizes as the α-form ($[\alpha]D$ +78.5° → +66.6° in water). Evidence that the mutarotations are probably α-β changes rather than pyranose–furanose transformations was obtained from the relative insensitivity of the equilibrium rotations to temperature. A change of 4° in each case produced no observable change in equilibrium rotation. Figure 1 shows mutarotation curves for 2-benzylamino-2-deoxy-β-D-glucose in hydrochloric acid calculated as the β-hydrochloride and for the isolated crystalline α-hydrochloride. Table I gives the molecular rotations and the $2A$ and $2B$ values for the benzylamino-glucose hydrochlorides and, for comparison, the corresponding values for D-glucosamine hydrochloride, D-galactosamine hydrochloride, D-glucose and D-mannose. The $2A$ value (mol. rotation α − mol. rotation β) for the benzylamino sugar hydrochlorides, 8,100, is close to the $2A$ value for D-mannose, 8,340, and far from the corresponding values for D-

TABLE I

MOLECULAR ROTATIONS OF AMINO SUGARS COMPARED WITH D-GLUCOSE AND D-MANNOSE

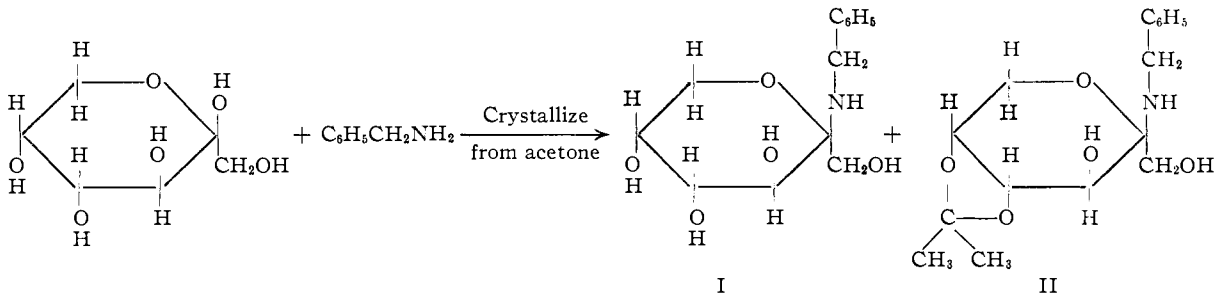
Sugar derivative	$[\alpha]D$	M_D	$2A$	$2B$
N-Benzyl-α-D-glucosamine hydrochloride	+78.5	24,000	8,100	39,900
N-Benzyl-β-D-glucosamine hydrochloride	52	15,900		
α-D-Glucosamine hydrochloride	100[a]	21,600	17,300	25,900
β-D-Glucosamine hydrochloride	20[b]	4,300		
α-D-Galactosamine hydrochloride	121[c]	26,100		
			16,500	35,700
β-D-Galactosamine hydrochloride	44.5[c]	9,590		
α-D-Glucose	112.2[d]	20,210	16,840	23,580
β-D-Glucose	18.7[d]	3,370		
α-D-Mannose	29.3[d]	5,280	8,340	2,220
β-D-Mannose	−17.0[d]	−3,060		

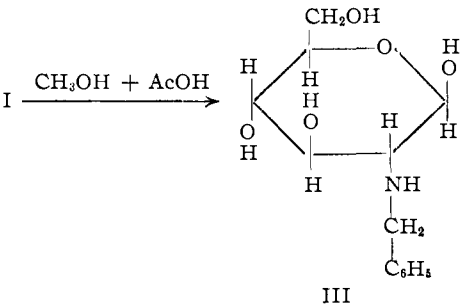
[a] A Neuberger and Rosalind Pitt-Rivers, *J. Chem. Soc.*, 122 (1939). [b] H. Hisamura and M. Kusono, *J. Biochem. Japan*, **27**, 378 (1938). [c] T. White, *J. Chem. Soc.*, 1498 (1938). [d] "Polarimetry, Saccharimetry and the Sugars," Circular of the Natl. Bureau of the Standards C440, Frederick J. Bates and Associates, 1942, p. 728, 746.

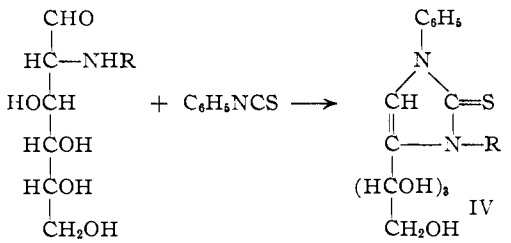
(1) J. F. Carson, THIS JOURNAL, **77**, 1881 (1955).

(2) J. F. Carson, *ibid.*, **77**, 5957 (1955).

(3) K. Heyns, R. Eichstedt and Karl-Heinz Meinecke, *Ber.*, **88**, 1551 (1955).







glucosamine hydrochloride, 17,300, or for D-glucose, 16,840.

Since the 2-benzylamino-2-deoxy sugar has now been shown to have the D-glucose configuration, Hudson's first rule of isorotation,[4] although applicable to D-glucosamine and D-galactosamine hydrochlorides, cannot be extended to this compound.

Another diagnostic test for configuration, the Levene salt–acid rule,[5] was applied. Oxidation of 2-benzylamino-2-deoxy-D-glucose with mercuric oxide in aqueous suspension yielded the corresponding gluconic acid which had $[\alpha]^{26}D$ +50.1° in sodium hydroxide solution and $[\alpha]^{26}D$ +14.4 → +16.7° in dilute hydrochloric acid. This agrees with the rule[5] that a hexonic acid with the hydroxyl or amino group on the number 2 carbon atom to the right in a Fischer projectional formula should be more dextrorotatory as the sodium salt than as the free acid. A similar conclusion resulted from rotational measurements of the 2-*n*-butylamino-2-deoxyhexonic acid previously described.[2] Opposite conclusions would therefore be drawn from the two rules. Conclusive proof of configuration was obtained by catalytic hydrogenolysis of the benzylamino sugar to yield 2-amino-2-deoxy-D-glucose isolated as its hydrochloride.

The second crystalline compound II obtained in 10–14% yields from the acetone mother liquor after crystallization of I corresponds in its reactions to an isopropylidene fructosylbenzylamine. Although the most probable structure is considered to be a 4,5-isopropylidene derivative, no evidence for the positions of linkage of the acetone group has been obtained. In dilute acid, the compound hydrolyzes to acetone, benzylamine and fructose. In methanol containing acetic acid, the compound rapidly decomposes and yields dark resinous material, and no crystalline rearranged product could be isolated. In pyridine, in contrast to fructosylbenzyl amine, the compound is stable and mutarotates in a positive direction, suggesting a β-configuration. The spontaneous formation of an isopropylidene derivative under these conditions is surprising, since at no time was the acetone solution heated and no acidic or dehydrating catalyst was added. Moreover, attempts to convert the isolated fructosylbenzylamine into the corresponding isopropylidene derivative by heating in acetone or by long storage of acetone solutions at room temperature or at 0° have failed to yield anything but starting material.

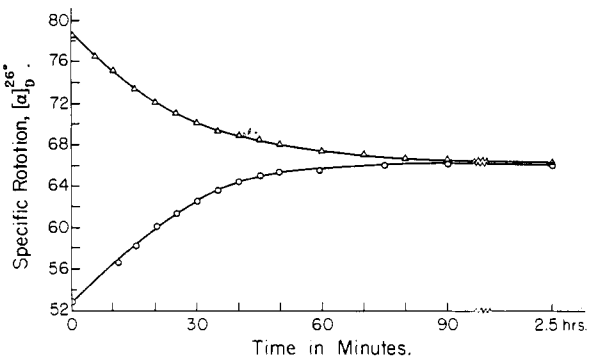


Fig. 1.—Mutarotation of 2-benzylamino-2-deoxy-α- and β-D-glucose hydrochlorides in water, *p*H 5.0: α-anomer (Δ), β-anomer (O).

Acetylation of fructosylbenzylamine, the isopropylidene derivative and 2-benzylamino-2-deoxyglucose have not yielded crystalline products. A crystalline tribenzoate and a crystalline pentabenzoate have been obtained by benzoylation in pyridine at low temperature of isopropylidene fructosylbenzylamine and 2-benzylamino-2-deoxyglucose, respectively.

Crystalline derivatives have been obtained, in some cases by reaction of 2-alkylamino-2-deoxyhexoses with phenyl isothiocyanate in aqueous acetone. These products are considered to be derivatives of 2-imidazolidinethione (IV) by analogy with the reactions of 2-amino-2-deoxy-D-glucose with phenyl isocyanate and with phenyl isothiocyanate. The former yields a derivative of hydroxyimida-

(4) "Polarimetry, Saccharimetry and the Sugars," Circular of the National Bureau of Standards C440, Frederick J. Bates and Associates, 1942, p. 432.

(5) P. A. Levene, *J. Biol. Chem.*, **63**, 95 (1925).

TABLE II

REACTION PRODUCTS OF 2-ALKYLAMINO GLUCOSES WITH PHENYL ISOTHIOCYANATE

Alkylaminoglucose (R in IV)	M.p., °C.	$[\alpha]^{25}D$ pyridine	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
Ethyl	165–166.5	+22.2	55.54	55.4	6.21	6.45	8.64	8.22
n-Propyl	139–140	+17.1	56.78	57.0	6.55	6.52	8.28	8.12
Isopropyl	191–192 (dec.)	+21.3	56.78	56.9	6.55	6.49	8.28	8.27
n-Butyl	163–164	+19.7	57.93	58.1	6.86	6.91	7.95	7.87
Benzyl	144–145	+83.8	62.15	61.9	5.74	5.77	7.25	7.17

zole,[6] the latter a derivative of 2-mercaptoimidazole.[7] The ethyl-, *n*-propyl-, isopropyl-, *n*-butyl- and benzylamino-2-deoxyglucoses have yielded the corresponding crystalline 5-(D-*arabo*-tetrahydroxybutyl)-3-phenyl-1-alkyl-2-imidazolidinethiones (IV), the analyses of which are reported in Table II. As expected, the compounds are non-reducing and do not mutarotate in solution.

Experimental

Fructosylbenzylamine.—Thirty grams (0.167 mole) of anhydrous D-fructose and 135 g. (1.26 moles) of benzylamine were placed in a stoppered 500-ml. flask and kept at 0° for 24 hours and at room temperature for 3 days. Excess benzylamine was then removed with petroleum ether and ether as follows: 300 cc. of petroleum ether (60–70°) was stirred into the solution and the suspension allowed to settle at 0° for one hour. The hydrocarbon layer was decanted and the process was repeated 3 times with fresh petroleum ether. The light yellow oil was then washed in the same manner 4 times with 250-cc. portions of ether. The decanted ether fractions were saved and allowed to settle at 0°, since some of the product becomes emulsified and would otherwise be lost. The stiff yellow oil combined with material separating from the ether washings was dissolved in 250 cc. of absolute methanol and concentrated *in vacuo* at low temperature to a stiff sirup. Acetone, 250 cc., was added and the solution again concentrated *in vacuo* to a sirup. The sirup was dissolved in 100 cc. of acetone, seeded and allowed to crystallize for one day at 0°, then an additional 100 cc. of acetone was added and the mixture crystallized further at −20° for 2 days. Filtration yielded 21.7 g. (48%) of white crystalline product. The mother liquor, after concentration to 100 cc. and storage at −20° for 2 days, yielded a second crop, 1.5 g., to give a total yield of 51%. The compound was recrystallized from acetone to give the pure derivative in a 40% yield, dec. 107–108° (preheated to 100°). Fructosylbenzylamine is unstable and should be kept at 0° or lower.

Anal. Calcd. for $C_{13}H_{19}NO_5$: C, 57.98; H, 7.11; N, 5.20. Found: C, 58.0; H, 7.24; N, 5.09.

Specific rotations were: $[\alpha]^{26}D$ −42.5 (12 min.) → +6.2° (48 hours dec.) in methanol (*l* 2, *c* 1.07); $[\alpha]^{26}D$ −140° (0) → +3.9° (5 hours) → −2.2° (96 hours dec.) in pyridine (*l* 2, *c* 1.18). $[\alpha]^{26.5}D$ −58.85° (const. 15 min.) in 0.1 *N* hydrochloric acid (*l* 2, *c* 1.07); calcd. for complete hydrolysis to *D*-fructose $[\alpha]^{26.5}D$ −87.9°; calcd. from the Vosburgh[8] formula for fructose solutions, $[\alpha]^{26.5}D$ −87.84°.

Chromatography of the acid solution on paper[9] showed D-fructose to be the only reducing material. The characteristic 2,4-dinitrophenylhydrazone of D-fructose[9] was also prepared from the acid solution.

Isopropylidene Fructosylbenzylamine.—The acetone mother liquor remaining after removal of the second crop of fructosylbenzylamine, when stored for a week at 0°, yielded a bulky white crystalline material, 2.55 g. Concentration of the mother liquor *in vacuo* to 60 cc. and storage for a week at −20° yielded a second crop, 2.35 g. A third crop, 0.6 g., was obtained to give a combined yield of 10.5% of crude product. Recrystallization from acetone gave the pure compound as white fluffy fibrous crystals, dec. (gas) 124–125° (preheated to 118°).

Anal. Calcd. for $C_{16}H_{23}NO_5$: C, 62.12; H, 7.49; N, 4.53. Found: C, 62.2; H, 7.48; N, 4.52.

Specific rotations were: $[\alpha]^{25.5}D$ −64.5(0) → +14.6° (23 hours) in pyridine (*l* 2, *c* 1); $[\alpha]^{25}D$ −52.1 (constant after 10 min.)[10] in 0.1 *N* hydrochloric acid (*l* 2, *c* 1.03).

The presence of D-fructose as the only reducing material in the acid solution was demonstrated as with fructosylbenzylamine. The presence of acetone was demonstrated by the isolation of its 2,4-dinitrophenylhydrazone in 75% yield. The presence of benzylamine was shown by the isolation of benzylamine hydrochloride in 74% yield and confirmed by the preparation of the 5-nitrobarbiturate.

Isopropylidene Fructosylbenzylamine Tribenzoate.—To a mixture of 7 g. of benzoyl chloride in 100 cc. of pyridine at 0°, 0.8 g. of isopropylidene fructosylbenzylamine was added and the mixture kept at −20° for 48 hours. The thick red mush was poured into 500 g. of chopped ice containing 25 g. of sodium bicarbonate. After standing overnight, the yellow granular product was filtered, washed with saturated sodium bicarbonate solution and then with water, and dried *in vacuo*, yield 2.0 g. The product was recrystallized twice from 50 parts of absolute ethanol to yield 1.12 g. (70%) of long-bladed crystals, m.p. 125–125.5° dec. (preheated to 115°).

Anal. Calcd. for $C_{37}H_{35}NO_8$: C, 71.48; H, 5.68; N, 2.25. Found: C, 71.4; H, 5.70; N, 2.24.

Specific rotations were: $[\alpha]^{25.5}D$ −5.0° in ethyl acetate (*l* 2, *c* 1.07). The compound showed no observable rotation $[\alpha]^{25}D$ in 1% pyridine solution.

Rearrangement of Fructosylbenzylamine to 2-Benzylamino-2-deoxy-β-D-glucose.—A solution of 5 g. of fructosylbenzylamine in 400 cc. of absolute methanol, containing one ml. of acetic acid, was allowed to stand from 40–48 hours at 24–26°. The amber solution was concentrated *in vacuo* to 25 cc., whereupon 50 cc. of absolute ethanol was added, and the solution was again concentrated *in vacuo* to 20 cc. Addition of 60 ml. of acetone and seeding led to rapid crystallization. After storage for 2 days at 0°, the mixture was filtered to yield 2.75 g. (55%) of crystalline 2-benzylamino-2-deoxyglucose. Recrystallization from 50 parts of ethanol–acetone (1:1) gave the pure product (48% yield) as fine white prisms, dec. (gas) 157–158°.

Anal. Calcd. for $C_{13}H_{19}NO_5$: C, 57.98; H, 7.11; N, 5.20. Found: C, 57.8; H, 7.15; N, 5.15.

Specific rotations were: $[\alpha]^{24}D$ +79.0 (15 min.) → +84.5° (48 hours) in pyridine (*l* 2, *c* 1.0); $[\alpha]^{26}D$ +59° (0) → +75.6° (2 hours) in 0.1 *N* hydrochloric acid (*l* 2, *c* 0.9); calcd. as the hydrochloride, $[\alpha]^{26}D$ +52° (0) → +66.6° (equil.).

That the compound is probably the pure β-isomer was shown by the fact that the variation in extrapolated initial rotation in hydrochloric acid was not more than 1° for samples crystallized from ethanol alone or from ethanol–acetone mixtures and also from a second fraction from the ethanolic mother liquor.

2-Benzylamino-2-deoxy-α-D-glucose Hydrochloride.—A solution containing 0.9 g. of benzylamino glucose in 100 cc. of 0.1 *N* hydrochloric acid was concentrated *in vacuo* to 10 cc. Absolute ethanol, 100 cc., was added and the solution concentrated *in vacuo* to a dry solid, which was dissolved in 25 cc. of boiling ethanol. Addition of 50 cc. of acetone led

(6) H. Steudel, *Z. physiol. Chem.*, **33**, 223 (1901); **34**, 353 (1902).

(7) C. Neuberg and H. Wolff, *Ber.*, **36**, 618 (1903).

(8) W. C. Vosburgh, THIS JOURNAL, **42**, 1696 (1920).

(9) I am indebted to L. M. White for paper chromatography and for the preparation of the dinitrophenylhydrazone of D-fructose.

(10) Both the fructosylbenzylamine and the isopropylidene derivative showed unusual polarimetric behavior in acid. An apparent constant rotation was obtained as soon as the solutions could be read (10 minutes) in spite of the fact that in the case of the second compound, acetone is being split off, the amine is being removed by hydrolysis and supposedly the liberated fructose would mutarotate to its equilibrium mixture. In contrast, fructosylethylamine in hydrochloric acid required from 45 minutes to an hour for equilibrium.[2]

to rapid crystallization as needles, and after further crystallization overnight at 0°, a yield of 0.8 g. of hydrochloride was obtained. An additional 0.2 g. was obtained from the mother liquor. The pure compound dec. at (gas) 192° (preheated to 175°).

Anal. Calcd. for $C_{18}H_{20}NO_6Cl$: N, 4.58; Cl, 11.60. Found: N, 4.60; Cl, 11.6.

Specific rotation was $[\alpha]^{26}D$ +78.5° (0) → +66.6 (2 hours) in 0.1 *N* hydrochloric acid (*l* 2, *c* 0.9).

The variation in initial extrapolated values for the specific rotation was within 1° for samples crystallized rapidly or slowly and for samples obtained as second crops from the mother liquor. This narrow range suggests that the compound is a pure α-form.

2-Benzylamino-2-deoxy-D-glucose Pentabenzoate.—2-Benzylamino-2-deoxy-β-D-glucose, 1.3 g., was suspended in 70 ml. of pyridine, previously cooled to 0°. The suspension then was cooled rapidly in an acetone–Dry Ice bath, 10 g. of benzoyl chloride was added, and the mixture was kept at −20° for 4 days. The deep red mush was then poured into a mixture of 1500 g. of chopped ice and 25 g. of sodium bicarbonate and allowed to stand overnight. The pale yellow, partially granular product was filtered and washed repeatedly with saturated sodium bicarbonate solution followed by distilled water. Yield after drying *in vacuo* was 4 g. The compound was crystallized by adding 125 cc. of ethanol to a solution of the compound in 50 cc. of hot ethyl acetate and concentrating by boiling to 75 cc. The pentabenzoate rapidly crystallized on cooling to yield 1.49 g. (39%) of fine white prisms, m.p. 238–239.5°.

Anal. Calcd. for $C_{48}H_{39}NO_{10}$: C, 72.99; H, 4.98; N, 1.77. Found: C, 72.8; H, 5.03; N, 1.76; $[\alpha]^{25}D$ +70.0° (in chloroform, *l* 2, *c* 1.02).

2-Benzylamino-2-deoxy-D-gluconic Acid.—A suspension of 1.3 g. of 2-benzylamino-2-deoxy-D-glucose and 6.5 g. of red mercuric oxide in 150 ml. of water was heated in a boiling water-bath for 30 minutes and refluxed for 5 minutes. The amino sugar dissolved without formation of color and with no observable precipitation of mercury. The suspension was filtered hot. The filtrate was treated with hydrogen sulfide and a heavy precipitate of mercuric sulfide formed. After aeration and filtration with carbon, the clear colorless filtrate was concentrated *in vacuo* to 15 ml. with slight crystallization. The aqueous solution was heated to dissolve the precipitate, an equal volume of ethanol was added, and the solution was allowed to crystallize at 0° for 3 days. A yield of 545 mg. (39%) was obtained. Recrystallization from 50% ethanol yielded the pure acid as needles, dec. (gas) 221° (preheated to 200°)

Anal. Calcd. for $C_{18}H_{19}NO_6$: C, 54.73; H, 6.71; N, 4.91. Found: C, 54.7; H, 6.61; N, 4.90.

Specific rotation was $[\alpha]^{26}D$ +50° in 0.1 *N* sodium hydroxide (*l* 2, *c* 1.03). Twenty ml. of this solution was diluted with 5 ml. of 1.0 *N* hydrochloric acid, $[\alpha]^{26}D$ +14.4° (7.5 min.) → +16.7° (94 hr.).

Hydrogenolysis of 2-Benzylamino-2-deoxyglucose.—A solution of 1.1 g. of benzylaminoglucose in 50 cc. of absolute methanol containing 735 mg. of palladium-on-carbon (5%) was shaken with hydrogen at atmospheric pressure and 27° for 4 hours, about 90% of the absorption occurring during the first 2 hours. A net total of 118 cc. (S.T.P.) of hydrogen was absorbed equivalent to 1.29 moles H_2 per mole of compound. After filtration, 3 cc. of 5 *N* hydrochloric acid was added dropwise to the solution. After storage for several hours at 0°, 470 mg. of D-glucosamine hydrochloride was obtained. An additional 100 mg. was obtained from the mother liquor to give a combined yield of 65%. The identity of the compound as α-D-glucosamine hydrochloride was established by comparison of X-ray powder diagrams[11] with authentic material.

Reaction of 2-Alkylamino-2-deoxyhexoses with Phenyl Isothiocyanate.—In a typical procedure, 1.0 g. of 2-*n*-butylamino-2-deoxyglucose was dissolved in 25 cc. of water to which was added 3.0 g. of phenyl isothiocyanate, followed by 100 cc. of acetone. The clear colorless solution turned a pale green in a few minutes but gradually faded to its original color. After standing for 40 hours at room temperature, the solution was concentrated *in vacuo* to a white solid which was extracted once with 25 cc. of chloroform and washed 4 times with 20-cc. portions of benzene. Crystallization of the residue from ethanol yielded 925 mg. (66%) of 5-(D-*arabo*-tetrahydroxybutyl)-3-phenyl-1-*n*-butyl-2-imidazolidinethione as white fibrous crystals. The corresponding ethyl, isopropyl and *n*-propyl derivatives were recrystallized from ethyl acetate, and the benzyl derivative was recrystallized by addition of petroleum ether (60–70°) to an ethyl acetate solution. Yields were generally 50–60%.

Acknowledgment.—I am grateful to Miss Geraldine Secor and L. M. White for elemental analyses.

(11) I am indebted to K. J. Palmer of this Laboratory for X-ray measurements.

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[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, U. S. NAVAL POWDER FACTORY]

Effect of Aqueous Sulfuric Acid on Sugars. II. Spectrophotometric Studies on the Hexoses; Identification of the Ether-soluble Products Formed[1]

BY F. A. H. RICE AND LAWRENCE FISHBEIN

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When a number of reducing hexoses were each heated under the same conditions with aqueous sulfuric acid, the ultraviolet absorption spectrum which developed was the same for each of the hexoses studied. However, the rate at which the ultraviolet spectrum developed and the steady state, as measured by the ultraviolet absorption spectra, were characteristic of the individual hexose. The hexoses were found to react at 100° in 4 *N* sulfuric acid in the following order: D-gulose > D-talose > D-galactose > D-altrose > D-mannose > D-glucose. In 20 *N* sulfuric acid at room temperature, however, the order was D-talose > D-mannose > D-galactose > D-glucose > D-altrose. The pentoses under the same conditions in 20 *N* sulfuric acid reacted in the order: D-xylose > D-ribose > D-lyxose > D-arabinose. The formation of the ultraviolet spectrum was found to be primarily due to the production of compounds which could be extracted from aqueous sulfuric acid by means of ether. These compounds were separated by the chromatography of their 2,4-dinitrophenylhydrazones on silicic acid and identified as acetaldehyde, propionaldehyde, formaldehyde and 5-(hydroxymethyl)-2-furaldehyde. Another compound as yet unidentified also was isolated.

In previous studies on the effect of aqueous sulfuric acid on the aldopentoses,[2] it was found that each of the aldopentoses developed the same ultraviolet spectrum under all the conditions of temperature and concentrations studied. The rate at which the spectrum developed and the final steady state, however, were found to be characteristic of the individual pentose. The apparent differences in the ultraviolet spectrum of individual pentoses,[3,4] when examined after identical treatment for a speci-

(1) Published with permission of the Bureau of Ordnance, Navy Department. The opinions and conclusions are those of the authors.

(2) F. A. H. Rice and L. Fishbein, THIS JOURNAL, **78**, 1005 (1956).

(3) R. M. Love, *Biochem. J.*, **55**, 126 (1953).

(4) Miyoshi Ikawa and C. Niemann, *Arch. Biochem. and Biophys.*, **31**, 62 (1951); *J. Biol. Chem.*, **180**, 923 (1949).