and the diffusion of benzyl chloride into the fiber body are of the same magnitude, so that diffusion and reaction go hand in hand. At higher temperatures, however, this is not the case. Because of the increase in the velocity of benzylation the outer layers of the fibers are rapidly benzylated. As the penetration (diffusion) of benzyl chloride is not increased appreciably, the outer layers have time to take up a larger number of benzyl groups before the next layer is attacked. The strongly organophilic higher substituted fiber portions gelatinize and thus insulate, in increasing degree, the remainder of the fibers. The lye set free by the originally hydrophilic layers, which have been converted into a hydrophobic condition, cannot escape radially, and is compelled to migrate toward the unattacked regions, diluting there the sodium hydroxide, and thus lowering the reactivity of those unattacked portions. In the meantime, the substitution of the outer layers, because of the higher reaction velocity, has increased to a point where solubility in benzyl chloride sets in. In this state, these layers can be dispersed readily by pressure (*e. g.*, on the cover glass under the microscope), or by agitation (in the batch). The remaining fiber fragments seem hardly attacked at all (as shown by their intense double refraction) and, what is worse, are in a rather inactive state because of the loss of their alkali content by what might be called "demercerization." It is difficult to introduce fresh alkali from without because of the presence of hydrophobic films, so that it takes a very long time to complete the benzylation.

Summary

Alkali cellulose prepared from cotton linters has been benzylated under conditions favorable to the preservation of the fiber structure.

A microscopic study of the changes within the fibers in the course of benzylation shows that the reaction is greatly influenced by the presence of two immiscible liquid phases (water and benzyl chloride), which causes diffusion difficulties. As alkali cellulose reacts with benzyl chloride, the originally hydrophilic system becomes hydrophobic, whereby aqueous lye is expelled and a dispersion is formed. This and the swelling of the increasingly organophilic system in benzyl chloride facilitate microscopic observation of the reaction.

The progress of the chemical conversion depends on the ratio between the reaction velocity and the speed of diffusion. At about 60°, the two are of the same magnitude; as a result, the reaction zone progresses continuously toward the center of the fiber. Even under these favorable conditions, the reaction is of the topochemical macroheterogeneous type, *i. e.*, starting at the surface of the fiber, it is propagated from layer to layer.

With rising temperature, the reaction velocity increases more rapidly than the rate of diffusion. In this way, differences in the degree of benzylation of the fiber layers arise. The highly substituted outer layers form an insulating jelly shell around the unreacted region, thus preventing diffusion, and the reaction comes to a stop unless the shell is mechanically broken.

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The Analysis of Fructoside Mixtures by Means of Invertase. VI. Methylated and Acetylated Derivatives of Crystalline β-Benzylfructopyranoside[1]

BY C. B. PURVES AND C. S. HUDSON

When α-methylfructofuranoside was dissolved in benzyl alcohol containing hydrogen chloride the optical rotation of the solution first diminished very rapidly and subsequently much more slowly. A previous article[2a] described the data used in plotting this decrease against a new time scale (Fig. 1, curve AA_1) and showed that the substances present in solution at the break in the curve (region A) were mainly benzylfuranosides.

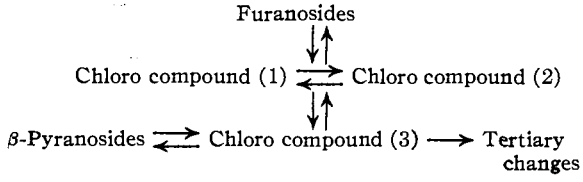
On the present occasion, when neutralization of the hydrogen chloride was delayed until the end of the slow, secondary optical change (region A_1), only 14% of the fructose remained as the benzyl derivative hydrolyzed by invertase. The bulk of the product comprised a sirup of a non-carbohydrate nature which was not investigated (up to 40%) and a new, crystalline glycoside, β-benzyl-

(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

(2) Purves and Hudson, THIS JOURNAL, (a) **59**, 49 (1937); (b) **56**, 702 (1934); (c) **56**, 708 (1934).

fructopyranoside, m. p. 157°, which had a specific levorotation of −130° in water (10%). The new glycoside was easily prepared in quantity from fructose by a method which had the advantage of recovering, in 5% yield, the α-benzylfuranoside formed as a byproduct. When the easily accessible β-benzylpyranoside was dissolved in methyl alcoholic hydrogen chloride and the acid was removed at the end of the initial, very rapid optical change (Fig. 1, curve B, region B), an 80% yield of recrystallized β-methylfructopyranoside was isolated. This synthesis of the β-methyl derivative was probably even more advantageous for preparative purposes than the one discovered by Hudson and Brauns.[3] If the action of the hydrogen chloride was prolonged, a maximum was created in the optical curve (region B) and a final, nearly constant specific rotation of −150.4° was observed for the methylfructoside produced. As an independent experiment showed that the rotation of the pure β-methyl glycoside, observed in the same acid solvent, diminished from the initial value of −172 to −142° (not plotted), the above final rotation was due to the slight instability of the glycoside in the experimental conditions. β-Benzylfructopyranoside, dissolved in benzyl alcoholic hydrogen chloride, underwent a similar obscure tertiary optical change to a marked extent (Fig. 1, curve C).

Reasons were given[2a] for assuming that in acid benzyl alcohol the replacement of α-methyl- by a mixture of benzylfuranosides (Fig. 1, curve A, region A) was due to the formation of a copper reducing chloro compound (1) which very rapidly came into equilibrium with another similar compound (2). These then swiftly recondensed with the alcoholic solvent to form the glycosides isolated. In similar fashion, it was now assumed that (1) and (2) were slowly replaced in solution by a third chloro derivative which corresponded to the β-benzylpyranoside recovered at the end of the slower secondary reaction (region A_1). A probably oversimplified outline of the course taken in these transformations suggested itself



The gradual accumulation of derivatives of the chloro-fructose (3) at the expense of those from (1) and (2) pointed to the former as being most stable. The high yield of β-methyl from β-benzylfructopyranoside dissolved in acid methyl alcohol was also evidence that the hypothetical intermediate (3) did not isomerize readily (Fig. 1, curve B, region B). On the other hand, a rather slow isomeric change or decomposition was indicated by the definite instability of the β-benzylpyranoside dissolved in acid benzyl alcohol (curve C).

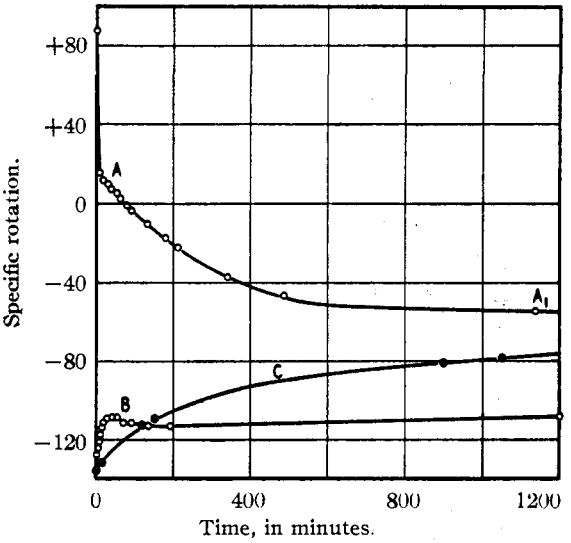


Fig. 1.—Fructosides in 0.03 normal alcoholic hydrogen chloride at 20°: curve AA_1, α-methylfuranoside in acid benzyl alcohol; curve B, β-benzylpyranoside in acid methyl alcohol; curve C, β-benzylpyranoside in acid benzyl alcohol.

Tetraacetyl-β-benzylfructopyranoside was a crystalline substance, m. p. 69–69.5°, with a specific levorotation of −139.8° in chloroform. The corresponding tetramethyl derivative, a viscous liquid with a refractive index of $n^{20}D$ 1.5045 and a levorotation of −110.3°, gave on hydrolysis a nearly quantitative yield of tetramethyl fructopyranose.[4] These benzyl derivatives therefore possessed the 2,6 or pyran ringed structure. As aldosides of this ring type were hydrolyzed by hydrochloric acid one hundred to five hundred times as slowly as sucrose or aldofuranosides,[5] it was surprising to discover that β-methyl[4] and β-benzylfructopyranoside were only 1.3[6] and 0.8

(3) Hudson and Brauns, THIS JOURNAL, **38**, 1216 (1916).

(4) Haworth, Hirst and Learner, *J. Chem. Soc.*, 1040 (1927). This work established the constitution of β-methylfructopyranoside.

(5) Haworth, *Ber.*, **61A**, 50 (1932); Haworth, Porter and Waine, *J. Chem. Soc.*, 2257 (1932); Knoop, *Ann.*, **520**, 35 (1935), cited other references and gave data for the inulins.

(6) The data of Irvine and Patterson, *J. Chem. Soc.*, 2696 (1922), corresponded to a half-time period of about eighty-nine days for the

times as stable, respectively, as sucrose, which is itself a fructofuranoside. The pyran ring in the former two fructosides was thus as sensitive toward aqueous acid as those present in 2-desoxymethylglucoside or cellobioside[7] or as the furan systems of the inulins.[5] Since the α-methyl[8] and α-benzylfructofuranosides[2a] were only ten to thirteen times as readily hydrolyzed as the corresponding β-pyranosides and since this small difference might reasonably be attributed to the reversal in glycosidic configuration, it was concluded that at 20° fructosides of both ring types had very nearly the same slight resistance to hydrolytic scission.[9] An attempt to determine whether their relative stability varied with temperature[10] is in progress, as such data might elucidate the cause of the large, well-known decrease in levorotation observed on warming an aqueous fructose solution. The approximate equivalence of the 2,5 and 2,6 fructosides toward aqueous acid also meant that the method of selective hydrolysis previously used[2b] did not distinguish sharply between the two kinds of oxygen bridge linking. In consequence, a pyranose or 2,6 structure was not excluded for "the readily hydrolyzed, gamma fructoside (b), not more dextrorotatory than 28°" of an earlier article.[2c] The simplest interpretation to put upon all the facts available was that the fructoside (b) was a highly impure specimen of β-methylfructopyranoside, that fructose, condensed with an acid alcohol, gave initially α- and β-furanosides in nearly equal amount[8] and that invertase hydrolyzed the β-isomer.[2b,11] Sucrose is thus almost certainly α-glucopyranosido-β-fructofuranoside and isosucrose,[12] β-glucopyranosido-α-fructofuranoside.[13]

Experimental

All optical observations were made in sodium light.

Prolonged Action of Benzyl Alcoholic Hydrogen Chloride on α-Methylfructofuranoside (see Fig. 1, curve AA_1, region A_1).—The 7.8% solution of the glycoside in the 0.03 *N* alcoholic acid was kept for fourteen hundred minutes at 20° or until the specific rotation was about −50°. After the product had been recovered in aqueous solution,[2a] 37.5% of the theoretical amount of fructose escaped the usual analysis,[2b] 3% was in a reducing condition and 14% was hydrolyzed by invertase. The bulk of the mixture was fermented with yeast and recovered as a sirup which partly crystallized when kept over sulfuric acid. Purification left the crystalline β-benzylpyranoside in 10% yield; $[\alpha]^{20}D$ −128.5° in water, m. p. 152.5° and mixed m. p. with an authentic specimen, 154°.

Preparation of β-Benzylfructopyranoside from Fructose.—Twenty-five grams of the dry, very finely sifted sugar was shaken vigorously at 20° for sixty minutes with 500 cc. of newly fractionated benzyl alcohol made 0.2 *N* with dry hydrogen chloride. After filtering off undissolved ketose (1 to 4 g.) the solutes in 10 cc. were recovered for analysis in aqueous solution.[2a] Found: fructose, 15 mol. %; benzyl derivative hydrolyzed by invertase, 4.5%; other readily hydrolyzed but nonreducing derivatives, 40% and unestimated, 40%. The bulk of the filtrate was promptly extracted with 200 cc. of 5% aqueous sodium bicarbonate to remove all the acid, most of the fructose and, incidentally, 2 to 3 g. of the benzylfructosides. The emulsion was broken down on the centrifuge and the lower, occasionally upper, benzyl alcoholic layer separated (450 to 455 g., *p*H 7.5). This was dried by evaporation at 60° (20 mm.) before the residue, 410 g., was reduced to 35 to 40 g. by further distillation in the vacuum of an oil pump. A 1-liter short-necked still, a still-head 1 cm. in diameter and a receiver and worm condenser efficiently cooled in ice made it possible to keep the bath temperature below 100° and to recover 80% of the benzyl alcohol. Benzene, 50 to 100 cc., was used to wash the hot, extensively crystallized residue from the distillation into an accumulation from previous runs. After filtration the crystalline portion was extracted with cold benzene until nearly colorless, the combined benzene liquors being retained (see below), and was recrystallized in succession from three parts of hot water and three times from five parts of hot methyl alcohol. The yield of pure β-benzylfructopyranoside was 25 to 30%.

Anal. (Sample dried over soda lime at 25° at 1 mm.). Calcd. for benzylfructoside, $C_{13}H_{18}O_6$: C, 57.8; H, 6.7. Found: C, 57.7; H, 6.6. A 1.5% solution in 0.25 *N* aqueous acid had, after complete hydrolysis, a reduction of 0.98% and a levorotation of −10.73°V., observed at 20° in a 4-dm. tube. Calcd. for fructose: 1.00% and −10.68°.

The new glycoside occurred as well-built stout tablets melting sharply at 157° when quickly heated. A few milligrams could be sublimed with little change (m. p. 149–156°, bath 150° at 0.05 mm.) but decomposition occurred slowly in air at 100°. For this reason the m. p. usually observed was 151–152°. β-Benzylfructopyranoside was freely soluble in cold pyridine, in hot water, and in hot methyl or ethyl alcohol. It dissolved in hot dioxane but was nearly insoluble in the remaining common organic solvents. Invertase and the other enzymes of yeast did not affect it. The following specific levorotations were from observations made at 21° in a 2-dm. tube: in water, −130.0° (*c*, 2; V., −15.02°); in dioxane, −109.9°

hydrolysis of β-methylfructoside in 0.009 normal acid at room temperature. This is not necessarily inconsistent with the above ratio because the present authors found a half-time period of 6.9 days for sucrose in 0.0263 normal acid at 20°.

(7) Bergmann and Breuers, *Ann.*, **470**, 38 (1929); Levene and Mikeska, *J. Biol. Chem.*, **88**, 791 (1930).

(8) Purves, THIS JOURNAL, **56**, 1969 (1934).

(9) Glycosides of the keto sugar fructose are therefore an exception to the statement of Armstrong and Armstrong, "The Carbohydrates," Longmans, Green and Co., London, 1934, p. 181.

(10) Moelwyn-Hughes, *J. Gen. Physiol.*, **13**, 317 (1930).

(11) *Cf.* Schlubach and Rauchalles, *Ber.*, **58**, 1842 (1925).

(12) Irvine, Oldham and Skinner, THIS JOURNAL, **51**, 1279 (1929); Irvine and Oldham, *ibid.*, **51**, 3609 (1929).

(13) *Cf.* Georg, *Helv. Chim. Acta*, **17**, 1566 (1934).

(*c*, 1; V., −6.35°) and in methyl alcohol, −128.0° (*c*, 1.017; V., −7.52°).

Recovery of Tetraacetyl α-Benzylfructofuranoside.—The benzene liquors retained in the above condensation of 200 g. of fructose were concentrated in the still already described to a viscid, highly colored residue, 103 g., which formed two layers when shaken with 600 cc. of benzene. After standing overnight to allow a little of the β-benzyl pyranoside to crystallize, the remaining sirup and supernatant solution were extracted with four 150-cc. volumes of water; water-insoluble non-carbohydrate material remaining in the benzene layer. A fermentation removed 11.7 g. of the benzyl glycoside unstable to invertase from the aqueous fraction and after recovery the unfermented portion was acetylated, 30 g., with acetic anhydride and pyridine. The dark colored, partly crystalline acetate, when dissolved in a little ether, slowly deposited impure crystals of tetraacetyl α-benzylfructofuranoside. Two recrystallizations from hot methyl alcohol left 18 g. of the pure substance, m. p. 83°, mixed m. p. 84° and $[\alpha]^{20}D$ 65.9° in methyl alcohol. The yield was 6%.

Tetramethyl β-Benzylfructopyranoside.—An absolute alcoholic solution, containing 9.1 g. (1 mol.) of the β-benzylfructoside in 350 cc., was mixed at 30° with two mols of ethereal thallous ethylate and the methylation of the resulting dithallium glycoside was completed[2a] to give a 92% yield of a viscid, pale orange dimethyl derivative, $n^{19}D$ 1.5235 and $[\alpha]^{20}D$ −114° in dioxane (*c*, 1.377).

Anal. (Sample heated at 50° at 0.1 mm.) Calcd. for a dimethyl benzylfructoside, $C_{15}H_{22}O_6$: C, 60.4; H, 7.4; OCH_3, 20.8. Found: C, 60.4; H, 7.6; OCH_3, 21.9.

The remaining two hydroxyl groups in 8 g. of this dimethyl derivative were then completely methylated[2a] and the tetramethyl β-benzylfructopyranoside so produced in 93% yield was dried at 40° (0.1 mm.). The uncrystallized substance was insoluble in water, was soluble in organic solvents with the exception of petroleum ether, had a refractive index of $n^{20}D$ 1.5045 and the following specific levorotations, observed at 20° in a 2-dm. tube: in chloroform, −110.3° (*c*, 3.1; V., −19.75°); in dioxane, −111.8° (*c*, 3.013; V., −19.45°) and in methyl alcohol, −115.5° (*c*, 1.453; V., −9.70°).

Anal. Calcd. for tetramethylbenzylfructoside, $C_{17}H_{26}O_6$: C, 62.5; H, 8.0; OCH_3, 38.0. Found: C, 62.4; H, 8.1; OCH_3, 37.0. *Subs.*, 0.145 g., took 0.0 cc. of 0.1 *N* alkali, so that esters were absent.

Hydrolysis of Tetramethyl-β-benzylfructopyranoside.—The specific levorotation of 6.9 g. of the water-insoluble glycoside, dissolved in 150 cc. of 0.03 *N* methyl alcoholic hydrogen chloride at 20°, decreased within seventeen hours to a constant value of −89.6°, whereupon the water-soluble methylated methyl glycosides produced were isolated and completely hydrolyzed within fifteen minutes by 0.1 *N* hydrochloric acid at 100°. After recovery the product soon crystallized to a solid mass of thin square plates, m. p. 85–90°, increased to 97–99° by recrystallization. This m. p. and the specific rotation in water of −125.5°, changing to a final value of −122.3°, were in good agreement with the constants accepted for tetramethyl fructopyranose.[6]

Tetraacetyl β-Benzylfructopyranoside.—Attempts to prepare this acetate in a crystalline state were unsuccessful until the pyridine, 60 cc., the acetic anhydride, 35 cc., and the glycoside, 5 g., were specially purified before being mixed at 0° and kept for five days at 0°. Two fractional recrystallizations from 30 cc. of hot alcohol left the substance pure and in 80% yield.

Anal. (Sample dried at 30° at 0.1 mm.) Calcd. for tetraacetylbenzylfructoside, $C_{21}H_{26}O_{10}$: C, 57.5; H, 5.9. Found: C, 57.7; H, 6.1. In an acetyl estimation, 0.2364 g. took 21.5 cc. of 0.1 *N* alkali. Calcd. for four acetyl groups, 21.6 cc. A trace of sodium methylate deacetylated 1.0 g. dissolved in methyl alcohol to 0.614 g. of β-benzylfructopyranoside, m. p. and mixed m. p. 156–157°, $[\alpha]^{20}D$ −128.3° in water. Calcd. 0.616 g.

The well built stout prisms of tetraacetyl β-benzylfructopyranoside, m. p. 69–69.5°, had the following specific levorotations, determined from 4% solutions observed at 25° in a 4-dm. tube: in chloroform, −139.8° (V., −64.59°); in dioxane, −138.4° (V., −63.95°) and in methyl alcohol, −128.4° (V., −59.33°). The solubilities of the substance were those to be expected.

Behavior of β-Benzylfructopyranoside in Methyl Alcohol Containing Hydrogen Chloride.—A 1.017% solution was observed in a 2-dm. tube and the specific rotations in Table I were attributed to benzyl glycoside. The copper reduction of the solution remained negligible throughout.

TABLE I

OPTICAL ROTATION OF β-BENZYLFRUCTOPYRANOSIDE IN 0.03 *N* METHYL ALCOHOLIC HYDROGEN CHLORIDE AT 20°[a]

Min.	V.° obsd.	$[\alpha]^{20}D$	Min.	V.° obsd.	$[\alpha]^{20}D$
0	−7.16 (calcd.)	−128	12	−6.50	−116
2.2	7.10	127	15	6.38	114
3.2	6.90	125	18	6.30	113
4	6.90	125	20	6.22	111
5.2	6.92	126	25	6.15	110[b]
6.3	6.80	123	30	6.10	109
7.2	6.73	122	50	6.11	109
8	6.70	122	90	6.25	112
9	6.65	119	190	6.30	113
10	6.60	118	1230	6.05	108[c]

[a] See Fig. 1, curve B. [b] Recalculated as methylfructoside, −153°. [c] Recalculated as methylfructoside, −150°.

Preparation of β-Methyl from β-Benzylfructopyranoside.—A solution containing 5.8 g. of the benzyl glycoside in 133 cc. of dry 0.03 *N* methyl alcoholic hydrogen chloride was kept at 20° for forty minutes, when its optical rotation had become nearly constant. After neutralizing the acid with silver oxide, the filtrate was made just alkaline with a drop of *N* aqueous caustic soda, the brown silver coagulum was removed with absorbent carbon and the filtrate was reduced to a thick, nearly colorless sirup which was kept at 25° (0.1 mm.) until it commenced to crystallize. Two recrystallizations from hot alcohol left an 80% yield of pure β-methylfructopyranoside with the correct carbon, hydrogen and fructose analyses. The m. p. of 117° (uncorr.) and the specific rotation of $[\alpha]^{24}D$ −171.0° were in good agreement with the accepted constants, m. p. 119–120° and $[\alpha]^{20}D$ −172.1° in water.[3] Other specific rotations incidentally determined at 24°

were −172.4° in methyl alcohol (*c*, 1.067) and −156.4° in dioxane (*c*, 1.268).

Optical Rotation of β-Methylfructopyranoside Dissolved in 0.03 *N* Methyl Alcoholic Hydrogen Chloride at 25°.—The specific levorotation of a 1.2% solution in the absence of the acid was −172.4°. With the hydrogen chloride present, rotations of −164.6, −161.9, −157.1, −156.5 and −142.3° were observed after 5, 10, 25, 45 and 1680 minutes, respectively.

Optical Rotation of β-Benzylfructopyranoside Dissolved in 0.03 *N* Benzyl Alcoholic Hydrogen Chloride at 20° (see Fig. 1, curve C).—The specific levorotation of an 0.972% solution of the fructoside in the acid-free solvent was −135.4°. With 0.032 *N* hydrogen chloride present, the rotations observed after 15, 120, 150, 900 and 1050 minutes were −132.4, −113.0, −109.4, −80.8 and −79.1°, respectively. After forty hours the acidity of the solution had diminished to 0.024 *N*, probably owing to the gradual formation of benzyl chloride.

Hydrolysis of β-Benzylfructopyranoside by 0.25 *N* Hydrochloric Acid at 20°.—A 1.5% solution was observed on the saccharimeter and examined for increase in the copper reducing power by the usual method.[2b] The unimolecular velocity constant of the hydrolysis, determined optically, for the range 3–97% completion was given by $10^4K = 5.35 \pm 0.3$ (in minutes and decimal logarithms). The same constant, determined over the same range from the increase in reduction, was $10^4K = 5.87 \pm 0.3$. As the corresponding value for sucrose was 4.3, the hydrolysis of the β-benzylfructopyranoside was approximately 1.3 times as rapid.

Hydrolysis of β-Methylfructopyranoside and of Sucrose by 0.33 *N* Hydrochloric Acid at 25°.—Equimolecular solutions of the fructoside and of sucrose, 1.197 and 2.11%, respectively, were made up and observed alternately on the saccharimeter. In the region 40–90% hydrolysis, the unimolecular velocity constant lay between the limits $10^4K = 10.65 \pm 0.45$ (in minutes and decimal logarithms) in the first case and $10^4K = 12.9 \pm 0.2$ in the second. The β-methylfructopyranoside was therefore hydrolyzed with approximately 0.8 times the rapidity of sucrose.

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Summary

1. When α-methyl or α-benzylfructofuranoside was dissolved in benzyl alcoholic hydrogen chloride, the initial products were slowly and partially replaced by β-benzylfructopyranoside, m. p. 157° and $[\alpha]^{20}D$ −130° in water. The crystalline β-benzyl tetraacetate, m. p. 69–69.5°, $[\alpha]^{20}D$ −139.8° in chloroform, and the liquid tetramethyl derivative, $n^{20}D$ 1.5045 and $[\alpha]^{20}D$ −110.3° in chloroform, were also prepared. Hydrolysis of the latter to tetramethyl fructopyranose established the structure of these substances.

2. The α-benzylfuranoside and the β-benzylpyranoside were prepared, in yields of 5 and 30%, respectively, directly from fructose and acid benzyl alcohol. An easy synthesis of β-methylfructopyranoside from the readily accessible β-benzyl glycoside was effected by dissolving the latter in methyl alcohol containing hydrogen chloride.

3. Data derived exclusively from the aldose series led to the generalization that glycosides with the pyran ring structure were one hundred to five hundred times as resistant to acid hydrolysis as the corresponding furanosides.[5] The present work showed that at 20° β-methyl- and β-benzylfructopyranosides were hydrolyzed by hydrochloric acid 0.8 and 1.3 times, respectively, as rapidly as sucrose, which is itself a fructofuranoside. Glycosides of the keto sugar fructose therefore differ from those of the aldoses in that both ring types possess very nearly the same slight stability toward aqueous acid and thus cannot reliably be distinguished from each other by methods depending upon selective hydrolysis.

WASHINGTON, D. C.
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