The results of several runs are given in Table I.

TABLE I

ALKYLBENZENES FROM ESTERS AND BENZENE

Ester used	Nature of alkyl group in benzene	BF_3, g. used	Yield of alkylbenzenes, g. Mono	Di	Poly.
Ethyl formate	Ethyl	65.0	6.4		4.1
n-Propyl formate	Isopropyl	55.9	33.4	21.8	10.1
Isopropyl acetate	Isopropyl	65.0	16.4	7.8	4.4
Isopropyl trichloroacetate	Isopropyl	23.6	34.8	18.7	9.3
n-Butyl formate	*s*-Butyl	65.0	33.2	26.8	16.0
s-Butyl formate	*s*-Butyl	65.0	26.0	15.0	8.0
s-Butyl acetate	*s*-Butyl	60.3	29.6	16.4	18.9
Isobutyl formate	*t*-Butyl	65.0	30.6	29.4	7.4
Cyclohexyl acetate	Cyclohexyl	22.9	36.8	14.8	22.0
n-Butyl phosphate	*s*-Butyl	65.0	11.0	22.5	22.0
n-Propyl sulfate	Isopropyl	5.0	45	18	10
Isopropyl sulfate	Isopropyl	3.0	38	20	13

The physical properties of the alkylbenzenes checked those as previously reported,[4] the ethylbenzene had b. p. 134.5°, $n^{25}D$ 1.4949, sp. gr. 0.8629 (25°), in moderately good agreement with values recorded in the literature.

Summary

Benzene has been alkylated by various esters both organic and inorganic in the presence of boron fluoride.

Normal and secondary butyl esters both gave secondary substituted benzenes while isobutyl ester gave tertiary butylbenzenes.

A mechanism for the reaction has been proposed.

NOTRE DAME, INDIANA RECEIVED MARCH 30, 1937

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Glycofuranosides and Thioglycofuranosides. I. A Method of Preparation and its Application to Galactose and Glucose

BY JOHN W. GREEN[1] AND EUGENE PACSU

Twenty years after the synthesis[2] of the "normal" α- and β-methylglucosides, E. Fischer found that the sirupy by-product of the reaction was a third methylglucoside, which he designated as a "γ-form."[3] Extensive constitutional studies of the simple glycosides of the sugars by Haworth and co-workers[4] have shown that all the "normal" glycosides are related to the parent form, pyran, whereas the "γ-forms" are derivatives of the parent form, furan. Unlike the α- and β-pyranosides, which can be prepared in crystalline form by several methods, the α- and β-furanosides are only difficultly available substances, and frequently occur as uncrystallizable sirups.

A review of the literature reveals that only seven alkyl-furanosides, obtained by three distinct methods, are known in crystalline form. Fischer's original method, treatment of the sugar with alcoholic hydrogen chloride at room temperature, usually yields an inseparable sirupy mixture of isomeric glycosides. Although this method has been employed for almost all the monoses, only α-methylmannofuranoside[5] and α-methyl-[6] and α-benzylfructofuranoside[7] have been thus prepared in crystalline form. A second method, characterized by the temporary protection of the 5,6-positions in the sugars with a carbonate group, has been worked out by Haworth and co-workers. Crystalline α- and β-ethylglucofuranoside[8,9] representing the first α,β-pair in the furanoside series, crystalline α-methylglucofuranoside,[9] and also the previously mentioned α-methylmannofuranoside[10] have been obtained by this procedure. The third method, employed by Schlubach in the preparation of the crystalline β-ethylgalactofuranoside,[11] requires furanoid acetohalogenoses as starting materials.

Since these procedures are either involved or of no general applicability, further work in the field of the glycofuranosides will be aided by a method which makes this class of sugar derivatives more available for investigation.

In a preliminary report,[12] a brief outline of the

(1) This paper is based upon a thesis submitted by John W. Green, Chemical Foundation Research Assistant, to the Faculty of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Fischer, *Ber.*, **26**, 2400 (1893); **27**, 2478 (1894); **28**, 1145 (1895).

(3) Fischer, *ibid.*, **47**, 1980 (1914).

(4) W. N. Haworth, "The Constitution of Sugars," Edward Arnold & Co., London, 1929.

(5) Haworth, Hirst and Webb, *J. Chem. Soc.*, 651 (1930).

(6) Purves and Hudson, THIS JOURNAL, **56**, 708 (1934).

(7) Purves and Hudson, *ibid.*, **59**, 49 (1937).

(8) Haworth and Porter, *J. Chem. Soc.*, 2796 (1929).

(9) Haworth, Porter and Waine, *ibid.*, 2254 (1932).

(10) Haworth and Porter, *ibid.*, 649 (1930).

(11) Schlubach and Meisenheimer, *Ber.*, **67**, 429 (1934).

(12) Pacsu and Green, THIS JOURNAL, **58**, 1823 (1936).

method discussed in the present paper has already been given. This method represents a modification of a previous procedure,[13] by which the α-alkylpyranosides were prepared from the sugar mercaptals and mercuric chloride in the boiling solutions of the different alcohols. The reaction with, *e. g.*, glucose benzylmercaptal and ethyl alcohol, can be expressed in the following summary equation

$$C_6H_{12}O_5(SCH_2C_6H_5)_2 + 2HgCl_2 + C_2H_5OH \longrightarrow 2HCl + 2C_6H_5CH_2SHgCl + C_6H_{11}O_5OC_2H_5$$

This method was shown to yield a large quantity of α-alkylpyranosides accompanied by a slight quantity of the β-isomers. It should be noticed that acid is generated in the reaction.

Now it has been found that if the same reaction be carried out under neutral conditions, β-alkylfuranosides can be obtained. An excess of yellow mercuric oxide is used with vigorous stirring or shaking. The hydrogen chloride formed is immediately neutralized and at the end of the reaction there is still an excess of mercuric chloride present.

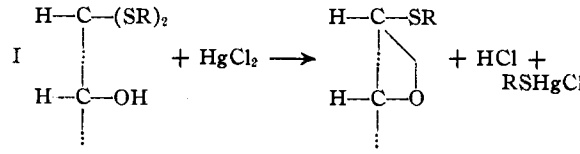
Galactose ethylmercaptal, shaken with two or three moles of mercuric chloride and an excess of yellow mercuric oxide in absolute ethyl alcohol at room temperature for two or three hours, gives a 70% yield of crystalline β-ethylgalactofuranoside, possessing the same melting point as reported by Schlubach,[11] but a higher specific rotation (−102°) in water solution. The excess of the mercuric chloride is conveniently removed with pyridine in the form of an insoluble molecular compound.

Galactose benzylmercaptal reacts similarly, but the yield is somewhat lower, due to the lesser solubility and hence slower reaction of this compound in alcohol.

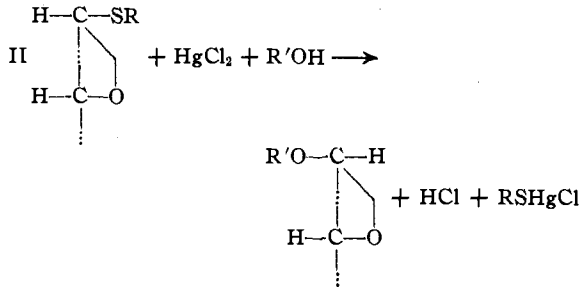
If the reaction with the ethyl mercaptal be carried out at 70°, a 35% yield of crystalline β-ethylgalactofuranoside results. From the mother liquor a sirup is obtained, which may contain the unknown α-form, and which is being investigated.

When methyl alcohol is substituted for ethyl alcohol, liquid β-methylgalactofuranoside, with a specific rotation of −85° in water solution, is obtained. So far it has not been isolated in the solid state.

In 1916 Schneider[14] prepared thioglucosides by treating glucose mercaptals with one mole of mercuric chloride in water, or aqueous alcoholic solution, neutralizing at intervals with alkali the acid liberated during the process



These strongly positive rotating substances he described as the α-forms of the β-thioglucosides. These β-compounds he had prepared by treating α-acetobromoglucose with the potassium salt of the mercaptans. The reaction given above is independent of the solvent. With more mercuric chloride the intermediate thioglycosides give rise to the free sugars in water solution, and should form alkylglycosides in alcoholic solution



Obviously, if the second stage of the reaction is faster than the first stage, no intermediate thioglycosides can be isolated. This appears to be the case, as already pointed out by Schneider,[14b] with galactose mercaptal in water solution. Attempts in the present investigation to isolate a thiogalactoside by the use of one mole of mercuric chloride in alcoholic solution also failed, since half of the mercaptal was converted into the glycoside, while the other half remained unchanged.

When glucose ethylmercaptal was shaken in water suspension at 0 or at 20° for several hours with the necessary amount of mercuric chloride in the presence of mercuric oxide, α-ethylthioglucoside was obtained. This substance was found to be identical with Schneider's compound,[14a] which he described as the α-form of the β-ethylthioglucoside. Since this β-ethylthioglucoside was prepared from acetobromoglucose, which is known at present to give rise to pyranosides, it was embarrassing to see the formation of an alleged thioglucopyranoside under the experimental conditions of the present method, which was believed to give only furanosides. At this stage of the

(13) (a) Pacsu, *Ber.*, **58**, 509 (1925); (b) Pacsu and Ticharich, *ibid.*, **62**, 3008 (1929).

(14) (a) Schneider and Sepp, *ibid.*, **49**, 2054 (1916); (b) Schneider, Sepp and Stiehler, *ibid.*, **51**, 220 (1918); (c) Schneider, Gille and Eisfeld, *ibid.*, **61**, 1244 (1928).

work, Hudson's rules of isorotation were consulted. From the molecular rotations of α- and β-ethylglucofuranosides (specific rotations 101° and −86°, respectively), the value of $B_{\text{gluc.}<1,4>} = 1560$ is obtained, and from the values of the corresponding ethylglucopyranosides (specific rotations 152 and −36.5°, respectively) $B_{\text{gluc.}<1,5>} = 12{,}000$. Since Schneider's β-ethylthioglucoside (specific rotation −60.1°) of molecular rotation −13,470, was prepared from the acetobromoglucose<1,5>, it must possess pyranoid structure, and, therefore, from the equation: $-13{,}470 = -A_{\text{SEt}} + 12{,}000$, the value for $A_{\text{SEt}} = 25{,}470$ is obtained. If Schneider's α-ethylthioglucoside were really of pyranoid structure, then its specific rotation would be (25,470 + 12,000)/224 = 167°, whereas if it were of furanoid structure, its specific rotation would be (25,470 + 1560)/224 = 120.7°. The perfect agreement between the latter value and the actually observed rotation (121°) leaves no element of doubt that Schneider's α-ethylthioglucoside possesses furanoid structure, and is not the α-form of the β-ethylthioglucopyranoside.

It is interesting to note that Schneider[14b] emphasized quite strongly that the α-ethylthioglucoside is much more sensitive to acid than is the β-compound. It has now been found that the former substance is hydrolyzed in 0.01 *N* hydrochloric acid at 98–100° very rapidly, the velocity constant, $k \times 10^5 = 6250$, being of the order given by furanosides.

If the α-ethylthioglucofuranoside be treated at 70° in ethyl alcoholic solution with mercuric chloride, and in the presence of mercuric oxide to neutralize the hydrogen chloride formed, a sirupy product, with a specific rotation of −54° in water solution, is obtained, which is β-ethylglucofuranoside, contaminated probably with its α-form. The hydrolysis constant of this sirup in 0.01 *N* hydrochloric acid at 98–100° is $k \times 10^5 = 8000$. The same product (−54°) can be obtained directly from glucose ethylmercaptal, if an excess of mercuric chloride and mercuric oxide is used at either elevated or room temperature.

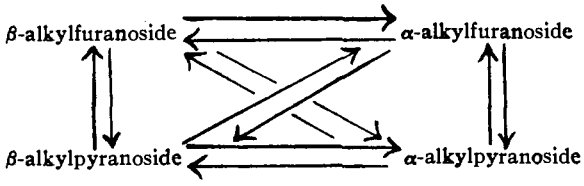
When the above experiments are repeated with glucose benzylmercaptal, crystalline α-benzylthioglucoside is isolated. This compound was described by Schneider[14b] as the α-form of the β-benzylthioglucoside derived from α-acetobromoglucose<1,5>. Although insufficient data prevent the calculation of its rotation by Hudson's rules, there is no doubt that this compound is similar in structure to the α-ethylthioglucoside and, contrary to Schneider's view, belongs to the furanoid series. Its rate of hydrolysis, $k \times 10^5 = 630$, in 0.01 *N* hydrochloric acid at 98–100°, is about one-tenth that of the α-ethylthioglucofuranoside, but it shows unmistakably that the compound is not pyranoside. In confirmation of this conclusion, α-benzylthioglucofuranoside, on treatment with mercuric chloride in ethyl alcoholic solution in the presence of mercuric oxide, is converted into the same sirupy β-ethylglucofuranoside (−54°), which was obtained from the α-ethylthioglucofuranoside.

As to the possible mechanism of the β-alkylfuranoside formation from the mercaptals, the assumed intermediate α-thiogalactofuranoside must react as fast as it is formed. The intermediate α-thioglucofuranoside, however, reacts so slowly that it can be isolated easily. Attempts to isolate a β-ethyl- or β-benzylthioglucofuranoside, or either of the thioglucopyranosides, from the reaction mixture, failed. At high temperature, or low temperature, with or without mercuric oxide, very curiously, only[15] the α-thioglucofuranosides were obtained from the glucose mercaptals. The conversion of the known (glucose), or assumed (galactose) α-thioglycofuranosides into the alkylglycofuranosides appears to be accompanied by only partial Walden inversion of the glycosidic carbon atom. The isolation of the β-ethylfuranoside in pure form is easy in the case of galactose, but is unsuccessful in the case of glucose. The lesser tendency of the furanosides to precipitate in crystalline form from a solution presents a serious technical difficulty, which will require special study to overcome.

Since the formation of the furanosides from the sugar mercaptals under neutral conditions appears to be a direct reaction, the formation of pyranosides[13a,b] from the same starting materials must be a secondary effect, due to acidity. It is a well-known fact that furanosides can be converted into pyranosides by the action of alcoholic hydrogen chloride. When pure β-ethylgalactofuranoside was refluxed for two hours with 1% ethyl alcoholic hydrogen chloride, crystalline α-ethylgalactopyranoside was isolated from the resulting

(15) From the combined mother liquors of several α-ethylthioglucofuranoside preparations, a small amount of a crystalline material was obtained. It reacts with mercuric chloride solution and its specific rotation is −37° in water. The compound is being investigated.

sirup. Similarly, from ethylglucofuranoside a small amount of α-ethylglucopyranoside resulted. Again, when α-ethylthioglucofuranoside was treated with mercuric chloride in boiling methyl alcohol, with no mercuric oxide present, 23% of pure α- and 15% of pure β-methylglucopyranoside were obtained. Under the same conditions, but with one and one-half hours of boiling, α-benzylthioglucofuranoside gave 34% of pure α- and 21% of pure β-methylglucopyranoside. From these preliminary experiments one may conclude that, starting from a pure β-alkylfuranoside in alcoholic hydrogen chloride solution, the following transformations occur with different velocities



Under these conditions the alkylpyranosides are the more stable, and, therefore, the β-furanosides change into an equilibrium mixture, in which the α-pyranosides dominate.

These investigations are being extended to the mercaptals of the other sugars. The possibilities of carrying out these reactions in inert solvents are also being investigated.

Experimental Part

Chemicals.—Yellow mercuric oxide was prepared by dissolving 100 g. of mercuric chloride in 1000 cc. of hot water, cooling the solution to 40°, and pouring it slowly, with stirring, into a solution of 40 g. of sodium hydroxide in 625 cc. of water. The precipitate was washed with water, first by decantation, then on a filter until free of alkali, and dried in an oven at 60°.

Dimethylaniline was tried in place of mercuric oxide, but the results were not satisfactory, due to the slight acidity of the hydrochloride salt formed.

Galactose benzylmercaptal was prepared according to Pacsu and Ticharich.[13b] Galactose ethylmercaptal was prepared by a procedure of Wolfrom,[16] slightly modified in that the reaction mixture, after the addition of ice water and subsequent filtration, was stirred up in a small amount of ice-cold ethyl alcohol, then sharply filtered and washed with ether. It was then recrystallized as usual. An improved yield of 60% was obtained.

Glucose benzylmercaptal was prepared according to Pacsu[17] and the ethylmercaptal by the method of Fischer.[18]

For the preparation of absolute ethyl alcohol, 1000 cc. of 95% alcohol was refluxed for two to three hours over 550 g. of lime and then distilled. Unless otherwise stated, this grade of alcohol was used throughout the experiments given below. The methyl alcohol used was the synthetic grade, dried over drierite.

Preparation of β-Ethylgalactofuranoside.—(a) A mixture of 11.4 g. of galactose ethylmercaptal (1 mole) with 21.8 g. of mercuric chloride (2 moles) and an excess of yellow mercuric oxide (17 g.) was shaken in a total volume of 200 cc. of absolute ethyl alcohol at 20° for two hours. The mixture was filtered and 5 cc. of pyridine added to the filtrate. The molecular compound of pyridine and mercuric chloride precipitated almost immediately. After standing overnight at 0°, the solution was filtered and evaporated *in vacuo* at 35° to a sirup. This was dissolved in a little water and the solution filtered from a small amount of pyridine-mercuric chloride. The filtrate was neutralized with a few drops of dilute sodium hydroxide to phenolphthalein, and evaporated *in vacuo* at 50°. The residue was dissolved in a little ethyl alcohol, the solution obtained filtered and evaporated to dryness. This procedure was repeated. The sirup slowly crystallized in a few hours. It was dissolved in 100 cc. of boiling ethyl acetate and cooled to room temperature. The clear solution was decanted from a small amount of sirup and let stand overnight at 0°. The crystals deposited were filtered, and recrystallized from 125 cc. of ethyl acetate; yield 5.8 g. or 70% of the theoretical; m. p. 85–86°; specific rotation[19] −102° (0.0500 g. of substance, in 10 cc. of water; 2-dm. tube; rotation 1.02° to the left).

With galactose benzylmercaptal, after shaking for three hours at 20°, the yield was 5.0 g. or 60% of the theoretical.

(b) To a solution of 11.4 g. of galactose ethylmercaptal and 17 g. of mercuric oxide in 100 cc. of ethyl alcohol at 70°, a second solution of 21.8 g. of mercuric chloride in 80 cc. of ethyl alcohol was added, slowly with rapid stirring, over a period of one to two hours. The mixture was cooled to room temperature and filtered. To the filtrate 5 cc. of pyridine was added, and the solution was worked up as in (a); yield 3.0 g., or 35% of the theoretical. The mother liquor contained a sirup of slight positive rotation.

Preparation of α-Ethylthioglucofuranoside.—(a) To 28.4 g. of glucose ethylmercaptal and an excess of mercuric oxide (21 g.) in 200 cc. of ice water, a solution of 13.6 g. of mercuric chloride (0.5 mole) in 400 cc. of ice water was added. The mixture was shaken for one hour at 0°. It was then filtered and a few drops of pyridine added to the filtrate. The solution, after standing overnight at 0°, was filtered from any pyridine-mercuric chloride, and neutralized with dilute sodium hydroxide to phenolphthalein. The solution was then evaporated *in vacuo* at 50° to dryness. The residue was dissolved in 130 cc. of hot ethyl alcohol, filtered hot, and kept overnight at 0°. The resulting crystals were filtered and recrystallized from 130 cc. of ethyl alcohol; yield 11.5 g. or 55% of the theoretical. The m. p. 153–153.5° and specific rotation 121° in water solution agreed closely with the values given by Schneider.[14a]

In an hydrolysis experiment, 0.5914 g. of pure α-ethylthioglucofuranoside was dissolved in 100 cc. of 0.01 *N*

(16) Wolfrom, THIS JOURNAL, **52**, 2464 (1930).
(17) Pacsu, *Ber.*, **57**, 849 (1924).
(18) Fischer, *ibid.*, **27**, 673 (1894).

(19) Unless otherwise stated, the rotations given are all for sodium light and 20°.

hydrochloric acid. The solution rotated 2.79° in a 2-dm. tube at 20°. On heating the solution at 100°, the following rotations were observed at 20° from samples withdrawn after three and a half, five and a quarter, eight and a half, twelve, fifteen and a half, and twenty-five minutes, respectively: 2.47, 2.15, 1.72, 1.44, 1.26, and 1.22°. The calculated final rotation was 1.00°, based on the theoretical amount of glucose present in the solution. From these data, according to the unimolecular law, $k \times 10^5 = 6250$ was obtained as a mean value. It is interesting to note that the final calculated rotation has never been reached. After the last reading, the rotation started slowly to rise, undoubtedly due to the recombination of the liberated mercaptan with the free sugar. After three hours of heating at 100° in a closed vessel, the observed rotation passed the initial value, to reach that of 2.88°. This effect might be due to the formation of the α-thioglucopyranoside and will be investigated further.

(b) Glucose ethylmercaptal (7.1 g.) and 6.8 g. of mercuric chloride (1 mole) were shaken with 125 cc. of 95% ethyl alcohol at 0° for two hours, the solution filtered and worked up as described in (a) for β-ethylgalactofuranoside. A 40% yield of the α-ethylthiofuranoside resulted. The solid matter filtered from the original reaction mixture was extracted with 100 cc. of water at 20°. The water extract was neutralized with a few drops of dilute sodium hydroxide to phenolphthalein, and evaporated *in vacuo* at 50° to dryness. The residue was crystallized from 25 cc. of ethyl alcohol, yield 0.8 g.; specific rotation −37° (0.0500 g. substance; 10 cc. of water solution; 2-dm. semi-micro tube; rotation 0.37° to the left). The substance reacted with mercuric chloride solution and possessed an unsharp m. p. of 115–120°. It will be investigated further.

(c) A similar experiment, but at 70° and with absolute ethyl alcohol, gave a poor yield of the α-ethylthiofuranoside.

Preparation of α-Benzylthioglucofuranoside.—Glucose benzylmercaptal (16.4 g.), one-half mole of mercuric chloride (5.5 g.), and 9 g. of mercuric oxide were shaken with 200 cc. of 95% ethyl alcohol at 20° for four hours. The mixture was filtered, and the filtrate treated with pyridine, etc., as in (a) for β-ethylgalactofuranoside. After a final recrystallization from ethyl acetate, 3.8 g. of the α-thioglucoside was obtained. It showed the correct m. p. 112–114° and specific rotation 176.1° in water solution, as given by Schneider.[14b]

In an hydrolysis experiment, 0.3645 g. of pure α-benzylthioglucofuranoside was dissolved in 100 cc. of 0.01 *N* hydrochloric acid. The solution rotated 2.56° at 20° in a 2-dm. tube. On heating the solution at 100°, the following rotations were observed at 20° from samples withdrawn after five, ten and a half, twenty, forty, sixty, and one hundred and fifty minutes, respectively: 2.42, 2.27, 2.02, 1.82, 1.62, 1.33, and 0.78°. The calculated final rotation was 0.48°, based on the theoretical amount of glucose present in the solution. From these data, according to the unimolecular law, the velocity constant $k \times 10^5 = 630$ was obtained as a mean value.

Preparation of Ethylglucofuranoside.—(a) To a solution of 11.4 g. of glucose ethylmercaptal and 17 g. of mercuric oxide in 100 cc. of ethyl alcohol at 70°, a second solution of 21.8 g. of mercuric chloride (2 moles) in 80 cc. of ethyl alcohol was added slowly with stirring, over a period of two hours. The solution was cooled, filtered, and worked up as in (a) for β-ethylgalactofuranoside. A non-reducing sirup, of specific rotation −54° in water solution, resulted.

For the determination of the hydrolysis constant, 0.4763 g. of the sirup was dissolved in 50 cc. of 0.01 *N* hydrochloric acid. The solution rotated 0.92° in a 2-dm. tube at 20°. On heating at 100°, the following rotations were observed at 20° from samples withdrawn after two and a half, seven, ten, thirteen, eighteen, and forty-five minutes, respectively: −0.42, +0.07, 0.27, 0.45, 0.52, 0.58, and 0.72°. From these data, the average value of $k \times 10^5 = 8000$, calculated from the unimolecular law, was obtained.

(b) To a solution of α-ethylthioglucofuranoside (5.5 g.) and 11 g. of mercuric oxide in 130 cc. of ethyl alcohol at 70°, a solution of 13.6 g. of mercuric chloride (2 moles) in 40 cc. of ethyl alcohol was added slowly over a period of an hour with rapid stirring. After forty minutes more stirring, the mixture was filtered, pyridine added, and the solution worked up as in (a), to yield a non-reducing sirup of specific rotation −54° in water solution.

(c) α-Benzylthioglucofuranoside (1.43 g.) and 4.1 g. of mercuric chloride (3 moles) and an excess of mercuric oxide (4.5 g.) were shaken in 30 cc. of ethyl alcohol at 20° for one hour, then heated for ten minutes on the water-bath. The solution was then filtered and worked up as in (a). The sirup obtained had a specific rotation of −52.1° in water solution.

Preparation of α- and β-Methylglucopyranosides from α-Thiofuranosides.—(a) A solution of 4.5 g. of α-ethylthioglucofuranoside and 10.8 g. of mercuric chloride (2 moles) in 65 cc. of absolute methyl alcohol was refluxed for fifteen minutes. The solution was filtered and treated with hydrogen sulfide. After the removal of the mercuric sulfide, the filtrate was shaken with an excess of silver carbonate, then filtered. The resulting solution was evaporated *in vacuo* at 35° to a sirup, which had a specific rotation of 42° in water solution. From this sirup 0.9 g. of α- and 0.6 g. of β-methylglucopyranoside were obtained by fractional crystallization from ethyl alcohol.

(b) To 2.9 g. of α-benzylthioglucofuranoside in 20 cc. of boiling absolute methyl alcohol, a solution of 5.4 g. of mercuric chloride (2 moles) in 15 cc. of absolute methyl alcohol was added. After a few seconds a sudden precipitation occurred. After ten minutes' boiling the solution was filtered and the precipitate washed with 5 cc. of methyl alcohol. The combined filtrate and washings showed a specific rotation of 6.8°. The solution was refluxed for ninety minutes, when the specific rotation increased to 76.5°. From this solution 0.65 g. of recrystallized α- and 0.4 g. of recrystallized β-methylglucopyranoside were obtained.

Conversion of Glycofuranosides into Glycopyranosides.—(a) β-Ethylgalactofuranoside (2.8525 g.) was dissolved in 100 cc. of 1% ethyl alcoholic hydrogen chloride, and the solution refluxed for five hours. The specific rotation changed from an initial value of −125 to +60.4°. After five hours of additional refluxing, it had only shifted to 62.4°. Ninety cc. of the solution was then shaken with an excess of silver carbonate and filtered. The

filtrate was evaporated to a sirup and the latter dissolved in 75 cc. of hot ethyl acetate and filtered hot. The clear solution, after two days at 0°, deposited a small quantity of crystalline material. This was recrystallized from 50 cc. of ethyl acetate, and finally from a few cc. of ethyl alcohol. The final product possessed the correct m. p. (140–141°) and specific rotation (186° in water solution) of α-ethylgalactopyranoside.

(b) Four grams of ethylglucofuranoside sirup (−54°) was dissolved in 100 cc. of ethyl alcoholic hydrogen chloride. After one hour's refluxing, the observed rotation shifted from an initial value of −4.55 to +8.65° in a 2-dm. tube. After one more hour of refluxing, the solution was neutralized with silver carbonate and filtered. The filtrate was evaporated to a sirup, which was dissolved in 10 cc. of ethyl alcohol. After two days at −10°, the solution crystallized to a solid mass. The crystals were filtered and recrystallized from 25 cc. of acetone. After being dried at 15 mm. and 58°, the crystals melted at 70–72° and had a specific rotation of 138° in water. Further recrystallizations did not change this value, which agreed closely with that given by Fischer[20] in his first preparation of α-ethylglucopyranoside.

Summary

A new synthesis for alkylfuranosides has been found. From galactose ethylmercaptal, β-ethylgalactofuranoside can be prepared in 70% yield by treatment with mercuric chloride and mercuric oxide at 20° in absolute ethyl alcohol. The benzylmercaptal will give a similar yield.

The same reaction with glucose mercaptals apparently goes in two stages. The first, to an α-alkylthioglucofuranoside, goes very fast, even at 0°. The second stage, to the glucofuranoside, is slow at 20°, but goes fairly fast at 70°. A sirupy mixture of α- and β-ethylglucofuranoside results.

The α-ethyl- and α-benzylthioglucosides isolated in the first stage of the reaction are furanosides, and not of normal structure as earlier workers believed. This is shown by acid hydrolysis constants, conversion into ethylglucofuranoside, and calculations from Hudson's rules of isorotation.

The effect of acidity on these reactions has been shown by the conversion of furanosides into pyranosides in alcoholic hydrogen chloride.

(20) Fischer, *Ber.* **27**, 2480 (1894).

PRINCETON, NEW JERSEY RECEIVED APRIL 28, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF HAWAII]

The Properties of Bagasse Lignin Extracted by the Dilute Nitric Acid Method

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The ease with which lignin can be extracted from bagasse by the use of dilute nitric acid[2] renders the method of definite value in studying the composition of lignin from this source. Since any extraction method probably brings about some change in the lignin,[3] the change produced by dilute nitric acid, which involves mild nitration, is undoubtedly not greater than that produced by more drastic reagents.[4] Furthermore the introduction of a small amount of nitrogen in the form of nitro groups renders the lignin molecule more soluble in many organic solvents, and furnishes a method of estimating the empirical molecular weight.

It was found[2] that bagasse, which had been freed from gums, waxes, and water-soluble compounds, undergoes practically no change when heated to a temperature of 98–100° for several hours with 1.25% nitric acid. If the concentration of nitric acid is increased to 1.50%, however, definite reaction occurs. After one hour the bagasse is uniformly orange in color, and subsequent boiling with 1% sodium hydroxide dissolves the lignin, leaving the cellulose free. Upon acidification of the sodium hydroxide solution, the lignin is precipitated as a dark brown sticky mass. With concentrations of nitric acid above 1.50% the results are similar except that there is evidence of greater nitration, and greater decomposition of cellulose occurs; 1.40% nitric acid was found to be the minimum concentration which would effect uniform nitration of the bagasse, and which would cause the lignin to go into solution in 1% sodium hydroxide solution.

These results seem to indicate that a definite minimum concentration of nitric acid is necessary to bring about nitration of the lignin. The lignin thus nitrated is soluble in dilute sodium hydroxide solution. The orange color of the nitrated bagasse is due only in part to the color of the nitro-

(1) University of Hawaii Graduate Scholar.
(2) Payne, *Ind. Eng. Chem.*, **26**, 1339 (1934).
(3) Wright and Hibbert, THIS JOURNAL, **59**, 125 (1937).
(4) Hilpert and co-workers, *Ber.*, **67**, 1551 (1934); **68**, 16, 371, 380 (1935).