replacing the viscometers in the thermostat the normal prior rate of polymerization was resumed. This evidence is not favorable to a thermal chain mechanism for the reaction. Nor did the failure of highly purified citral to polymerize under the influence of heat, ultraviolet light, etc., encourage the acceptance of the chain hypothesis.

Upon admitting air to the vacuum system after distilling styrene in it, a pronounced whitish luminescence was often noticed near the points at which styrene bulbs had been sealed off. This occurred only at small air pressures.

This work would suggest that the greatest care should be exercised in attempting to correlate propensity to polymerize with molecular structure, since granting the possibility of polymerization, catalysts appear to be the more important factor.

Summary

The polymerization of highly purified styrene, citral, and heptaldehyde has been investigated in the presence of and substantial absence of oxygen.

Citral and heptaldehyde are stable in the substantial absence of oxygen. Styrene continues to polymerize under these conditions but at a diminished rate. This polymerization is probably still governed by catalysts. The effect of some catalysts and inhibitors has been investigated.

The Tritylation of Sugar Mercaptals[1]

BY M. L. WOLFROM, JOSEPH L. QUINN AND CLARENCE C. CHRISTMAN

In view of the publication of Micheel and Spruck[2] on the triphenylmethyl (trityl) ether of galactose ethyl mercaptal, we wish to report the work completed in this Laboratory on the tritylation of a number of sugar mercaptals. The work herein reported was completed before the above article of Micheel and Spruck appeared and was also well under way before the appearance of the very important publication of Micheel and Suckfüll[3] on the action of mercuric chloride on 6-iodogalactose ethyl mercaptal tetraacetate.

In the latter, the advantage of introducing halogen on the C_6 atom in connection with the synthesis of derivatives of the free aldehydo form was indicated, while the preferential substitution of halogen by the trityl group is shown in the former.

All compounds now reported were obtained in crystalline form and were recrystallized to constant melting point and rotation.

In 1886 Kiliani[4] commented on the Tollens' ring structure for d-glucose by stating that this conception would greatly complicate hexose structure because ring closure on any one of five carbon atoms was a possibility. This was forgotten until much later, when the furanose and pyranose ring structures were established. The partially substituted sugar mercaptals offer the possibility of studying other rings than the furanose and pyranose structures. The first study of this nature was made by Brigl and co-workers[5] who showed that glucose 3,4,5,6-tetrabenzoate exhibited no apparent tendency to react in an ethylene oxide structure and was an open chain or aldehydo form. This derivative was obtained by hydrolysis of the ethylmercapto groups from glucose ethyl mercaptal 3,4,5,6-tetrabenzoate. Micheel and Suckfüll[6] have now established a (1,6) or septanose ring structure for derivatives of d-galactose. These workers prepared 6-iodogalactose ethyl mercaptal tetraacetate and on hydrolyzing the ethylmercapto groups with mercuric chloride and cadmium carbonate in moist acetone, the iodine was also rather unexpectedly hydrolyzed with the formation of a galactose tetraacetate hydrate, which was apparently an aldehydo form. On further acetylation of this substance ring closure on the sixth carbon atom was effected and well proved.

The tritylation procedure of Helferich and co-workers[7] affords a convenient method for obtain-

(1) A complete preliminary report of this work was published in THIS JOURNAL, **56**, 2789 (1934). The work herein recorded on the glucose compounds was reported completely at the 44th Meeting of the Ohio Academy of Science at Columbus, Ohio, March 30, 1934. Compounds I, II and III are recorded in the M.A. thesis of Mr. Clarence C. Christman, The Ohio State University, Dec. 15, 1933.

(2) F. Micheel and W. Spruck, Ber., **67**, 1665 (1934).

(3) F. Micheel and F. Suckfüll, Ann., **502**, 85 (1933).

(4) H. Kiliani, Ber., **19**, 767 (1886).

(5) P. Brigl, H. Mühlschlegel and R. Schinle, ibid., **64**, 2921 (1931).

(6) F. Micheel and F. Suckfüll, Ann., **507**, 138 (1933); Ber., **66**, 1957 (1933).

(7) B. Helferich and J. Becker, Ann., **440**, 1 (1924).

ing a partially substituted sugar mercaptal with the sixth position open. Helferich and co-workers showed that triphenylchloromethane (trityl chloride) reacts preferentially with primary hydroxyl groups, although Hockett and Hudson[8] have shown that under vigorous conditions a secondary hydroxyl group may also react. In the work which we have completed, glucose ethyl mercaptal was successively treated in pyridine solution with trityl chloride and benzoyl chloride to produce 6-trityl glucose ethyl mercaptal tetrabenzoate and a similar procedure produced the tetrabenzoate of 6-trityl galactose ethyl mercaptal. By substituting acetic anhydride for the benzoyl chloride there was obtained crystalline 6-trityl galactose ethyl mercaptal tetraacetate (m. p. 123-124°; $[\alpha]_D$ -22.5°, $CHCl_3$), trityl l-arabinose ethyl mercaptal triacetate, and trityl d-xylose ethyl mercaptal triacetate. The acetylated 6-trityl galactose ethyl mercaptal was obtained by Micheel and Spruck[2] as an impure sirup.

Helferich and co-workers have shown that the trityl ethers of the sugars are readily hydrolyzed by halogen acids with the formation of the trityl halide and regeneration of the sugar hydroxyl. However, all attempts to hydrolyze the trityl group in 6-trityl glucose ethyl mercaptal tetrabenzoate with hydrogen bromide always produced 6-bromoglucose ethyl mercaptal tetrabenzoate (m. p. 169-170°; $[\alpha]_D$ +39°, $CHCl_3$). This behavior is unusual. The position of the bromine atom was proved by the identity of this compound with the product obtained by benzoylation of the 6-bromoglucose ethyl mercaptal of E. Fischer.[9] The terminal position of the bromine atom in the latter compound was well established by Fischer through its reduction to the corresponding methylpentose.

The bromine atom in our compound was not sufficiently reactive and was replaced with iodine by sodium iodide in acetone according to the general procedure of Irvine and Oldham.[10] The 6-iodoglucose ethyl mercaptal tetrabenzoate (m. p. 165-166°; $[\alpha]_D$ +39°, $CHCl_3$) so produced had constants practically identical with those of the 6-bromo compound but its halogen atom was much more reactive. The iodine was removed with silver nitrate in dilute acetone and the ethylmercapto groups with mercuric chloride and

cadmium carbonate in moist acetone.[11] The product obtained was the glucopyranose tetrabenzoate of E. Fischer,[12] which has been related to β-methyl glucopyranoside. A benzoyl migration had accordingly occurred at some point. A priori, we do not know whether our compound shifted to a pyranose ring or whether the tetrabenzoate is really a septanose and shifted for Fischer in one of his reactions in relating the compound to β-methyl glucopyranoside through the acetobromo derivative. Of course, the probabilities are in favor of the shift to the more stable pyranose ring. Another example is thus given of a benzoyl migration in the sugar series. This work is being continued in this Laboratory using the methoxyl instead of the benzoate derivatives of glucose.

Micheel and Spruck[2] hydrolyzed the ethylmercapto groups from their 6-trityl galactose ethyl mercaptal tetraacetate with mercuric chloride and cadmium carbonate in moist acetone to produce the crystalline aldehydo-galactose 6-trityl tetraacetate aldehydrol and this on detritylation produced the galactose 2,3,4,6-tetraacetate hydrate of Micheel and Suckfüll.[3] We had obtained the same result through a different series of compounds. Cautious hydrolysis of 6-trityl galactose ethyl mercaptal tetraacetate with hydrogen bromide produced galactose ethyl mercaptal 2,3,4,5-tetraacetate. More vigorous hydrolysis produced 6-bromogalactose ethyl mercaptal tetraacetate. Hydrolysis of the ethylmercapto groups from galactose ethyl mercaptal 2,3,4,5-tetraacetate produced the galactose 2,3,4,5-tetraacetate hydrate of Micheel and Suckfüll,[3] who record the constants: m. p. 150°; $[\alpha]_D$ +8° ⟶ -20° (pyridine). When recrystallized from water this substance melts sharply at 168° and shows a specific rotation in pyridine solution of +10° ⟶ -38°.

Hydrolysis of the ethylmercapto groups from 6-trityl galactose ethyl mercaptal tetraacetate produced aldehydo-galactose 6-trityl tetraacetate, which we had isolated as its ethyl hemiacetal (m. p. 153°; $[\alpha]_D$ -28°; $CHCl_3$), and also as its crystalline semicarbazone.

Experimental[13]

6-Trityl d-Glucose Ethyl Mercaptal Tetrabenzoate (I).— Ten grams (1 mol) of glucose ethyl mercaptal, previously

(8) R. C. Hockett and C. S. Hudson, THIS JOURNAL, 53, 4456 (1931); 56, 945 (1934).

(9) E. Fischer, B. Helferich and P. Ostmann, Ber., 53, 873 (1920).

(10) J. C. Irvine and J. W. Oldham, J. Chem. Soc., 127, 2729 (1925).

(11) M. L. Wolfrom, THIS JOURNAL, 51, 2188 (1929).

(12) E. Fischer and H. Noth, Ber., 51, 321 (1918).

(13) The Experimental work in the glucose series was performed by Mr. Clarence C. Christman and the remainder was performed by Mr . Joseph L. Quinn.

dried under reduced pressure over phosphorus pentoxide, was dissolved in 40 cc. of dry pyridine, 9.8 g. (1 mol) of dry triphenylchloromethane added, and the solution kept at room temperature for thirty hours. It was then treated with 50 cc. of dry pyridine and 50 cc. of benzoyl chloride. The solution became red in color and a small amount of solid separated. The mixture was kept at room temperature for thirty hours and was then poured into ice and water. The thick sirup that formed was separated by decantation, dissolved in ether and the ethereal solution washed with aqueous solutions of sodium bisulfate, sodium bicarbonate and finally with water. The extract was dried with sodium sulfate and the ether removed under reduced pressure. The residual sirup was decolorized and crystallized by trituration with successive portions of methanol; yield, 23.1 g.; m. p. 159–160°. It was recrystallized from hot methanol; m. p. 161–162°; $[\alpha]_D^{24}$ +49° (c, 3; CHCl₃). The substance was moderately soluble in alcohol, practically insoluble in petroleum ether and water, and soluble in other common organic solvents.

Anal. Calcd. for $C_{37}H_{52}O_9S_2$: S, 6.79. Found: S, 6.73.

6-Trityl *d*-Galactose Ethyl Mercaptal Tetrabenzoate.— This substance was prepared from galactose ethyl mercaptal according to the directions cited for the corresponding glucose compound. It was crystallized by adding petroleum ether to the ethereal extract; yield, 44 g. from 20 g. of galactose ethyl mercaptal; m. p. 135–137°. It was purified by recrystallization from ether by the addition of petroleum ether; m. p. 138–139°; $[\alpha]_D^{30}$ −22.5° (c, 3.5; CHCl₃). The substance crystallized in long needles and its solubilities were similar to those of the corresponding glucose compound.

Anal. Calcd. for $C_{37}H_{52}O_9S_2$: S, 6.79. Found: S, 6.73.

6-Trityl *d*-Galactose Ethyl Mercaptal Tetraacetate.— Forty grams of galactose ethyl mercaptal was treated with pyridine and triphenylchloromethane as described for glucose ethyl mercaptal. After standing, 250 cc. of acetic anhydride was added to the solution, the mixture cooled in an ice-salt bath for an hour and then kept at room temperature for thirty hours. The slight precipitate that formed was removed by filtration and the filtrate poured into 12 liters of ice and water. The partially crystalline material that separated was removed by rapid filtration and crystallized from 600 cc. of 95% ethanol; yield, 77 g.; m. p. 119–121°. The substance was recrystallized in the same manner; m. p. 123–124°; $[\alpha]_D^{21}$ −22.5° (c, 4; CHCl₃). The compound is insoluble in petroleum ether and water, soluble in hot alcohol and in the other common organic solvents.

Anal. Calcd. for $C_{29}H_{32}O_5S_2(COCH_3)_4$: S, 9.21; acetyl, 5.74 cc. 0.1 N NaOH per 100 mg. Found: S, 9.17; acetyl, 5.69 cc.

Trityl *l*-Arabinose Ethyl Mercaptal Triacetate.—This substance was prepared by tritylation and subsequent acetylation of *l*-arabinose ethyl mercaptal by a procedure analogous to that used for the corresponding galactose compound. The gummy mass that separated on pouring the acetylating mixture into ice and water was obtained crystalline from hot methanol and was recrystallized from

absolute ethanol; yield, 11.5 g. from 8 g. of *l*-arabinose ethyl mercaptal; m. p. 101–102°; $[\alpha]_D^{27}$ −24° (c, 5; CHCl₃). The substance crystallized in long needles, was insoluble in water, but was soluble in the common organic solvents, including warm petroleum ether.

Anal. Calcd. for $C_{34}H_{40}O_7S_2$: S, 10.26. Found: S, 10.32.

Trityl *d*-Xylose Ethyl Mercaptal Triacetate.—*d*-Xylose ethyl mercaptal[14] was tritylated and acetylated according to the methods previously described. The gummy mass that separated on pouring the acetylation mixture into ice and water was obtained crystalline from hot methanol, a relatively large amount being required. It was recrystallized from absolute ethanol; m. p. 149–150°; $[\alpha]_D^{21}$ −20.5° (c, 5; CHCl₃). The substance was composed of very beautiful and uniformly sized crystals. It was soluble in chloroform, acetone and benzene, moderately soluble in ether and alcohol and was practically insoluble in water and petroleum ether.

Anal. Calcd. for $C_{34}H_{40}O_7S_2$: S, 10.26. Found: S, 10.32.

6-Bromo-*d*-glucose Ethyl Mercaptal Tetrabenzoate (II).—6-Trityl *d*-glucose ethyl mercaptal tetrabenzoate (30 g.) was dissolved in 50 cc. of U. S. P. chloroform and a rapid stream of dry hydrogen bromide passed into the solution for fifteen minutes. The chloroform and hydrogen bromide were removed under diminished pressure and the dry solid residue was placed in a Soxhlet extractor and the trityl bromide extracted with petroleum ether. The crystalline residue was recrystallized twice from an acetone, ether and petroleum ether mixture; yield, 16.5 g.; m. p. 168–169°. The constants of the pure product were: m. p. 169–170°; $[\alpha]_D^{25}$ +39° (c, 4; CHCl₃). The substance is soluble in the common solvents except ether, petroleum ether and water.

Anal. Calcd. for $C_{36}H_{37}O_8S_2Br$: S, 8.38; Br, 10.43. Found: S, 8.38; Br, 10.44.

The above compound was identical with that obtained by the benzoylation of 6-bromoglucose ethyl mercaptal prepared according to E. Fischer, Helferich and Ostmaun.[9] We found it necessary to add water in small amounts to the final acid solution in order to effect a crystallization of the ethyl mercaptal of 6-bromoglucose. Two grams of 6-bromoglucose ethyl mercaptal was dissolved in a mixture of 15 cc. of pyridine and 8 cc. of benzoyl chloride, cooled and kept overnight at room temperature. The mixture was poured into ice and water, the semicrystalline product removed by filtration and dissolved in warm ether. The product crystallized on concentration of the ethereal solution to half volume and was recrystallized from chloroform by the addition of petroleum ether; m. p. 169–170° (mixed m. p. with the detritylation product unchanged); $[\alpha]_D^{24}$ +39° (c, 4; CHCl₃).

6-Iodo-*d*-Glucose Ethyl Mercaptal Tetrabenzoate (III).— 6-Bromoglucose ethyl mercaptal tetrabenzoate (33 g.) and 65 g. of sodium iodide were dissolved at room temperature in the minimum amount of acetone and the solution heated in sealed tubes at 115° for twenty-four hours. The contents of the tubes were concentrated to

(14) M. L. Wolfrom, Mildred R. Newlin and E. E. Stahly, THIS JOURNAL, **53**, 4379 (1931).

dryness under reduced pressure and the reddish-yellow residue dissolved in a mixture of water and chloroform. The chloroform layer was washed twice with an aqueous solution of sodium thiosulfate, thrice with water, dried with calcium chloride and concentrated under reduced pressure to approximately 25 cc. volume. Petroleum ether was then added gradually until no further crystallization was obtained; yield, 23 g. The product was recrystallized from chloroform by the addition of petroleum ether; m. p. 165–166°; $[\alpha]^{27}$D +39° (c, 3; CHCl$_3$). The solubilities of the substance were similar to those of the corresponding bromo compound.

Anal. Calcd. for C$_{38}$H$_{37}$O$_8$S$_2$I: S, 7.89; I, 15.62. Found: S, 8.05; I, 15.54.

This substance differed from 6-bromoglucose ethyl mercaptal in its greater speed of reaction with an aqueous acetone solution of silver nitrate. A mixed melting point with the bromo compound (m. p. 169–170°) melted as the iodide (m. p. 165–166°).

Hydrolysis of the Iodine and Ethylmercapto Groups of 6-Iodo-*d*-glucose Ethyl Mercaptal Tetrabenzoate.—6-Iodoglucose ethyl mercaptal tetrabenzoate (20 g.) was dissolved in 180 cc. of hot acetone and a solution of 10 g. of silver nitrate in 40 cc. of water added. In a few seconds the solution became canary yellow and silver iodide began to separate. The mixture was refluxed for one hour and the silver iodide removed by filtration of the hot solution. The gummy mass that separated on pouring the filtrate into 500 cc. of ice and water was dissolved in chloroform and the extract washed with water and dried with sodium sulfate. The sirup obtained after chloroform removal was dissolved in 100 cc. of acetone and 75 g. of powdered cadmium carbonate added. The mixture was stirred mechanically and a solution of 75 g. of mercuric chloride dissolved in 150 cc. of acetone was added slowly along with 25 cc. of water. This mixture was refluxed for one hour and was then held at room temperature for twenty-four hours, vigorous mechanical stirring being maintained throughout. The mixture was filtered into a flask containing a small amount of cadmium carbonate and the precipitate washed with warm acetone. The filtrate and washings were concentrated to dryness under reduced pressure at 40° and in the presence of cadmium carbonate. The residue was extracted with several portions of warm chloroform and the residual sirup obtained after solvent removal was crystallized from methanol; yield, 5.3 g.; m. p. 93–95°. The material was recrystallized from methanol; m. p. 95–96°; $[\alpha]^{21}$D +81° (c, 3; CHCl$_3$; no mutarotation). The product was then recrystallized to constant melting point from heptane; m. p. 118–119°; $[\alpha]^{25}$D +69.6° (c, 2; absolute EtOH; no mutarotation). This product is identical with the glucose tetrabenzoate prepared by E. Fischer and Noth[12] from benzobromoglucose. For the tetrabenzoate prepared by their method and purified from heptane we found the constants: m. p. 118–119° (mixed melting point with our product unchanged); $[\alpha]^{25}$D +69° (c, 1; absolute EtOH; no mutarotation). E. Fischer and Noth[12] record the constants: m. p. 119–120°; $[\alpha]$D +70.6°, no mutarotation (c, 4; EtOH). No mutarotation was exhibited by the products we prepared by both methods and it was thus apparently an equilibrated α,β-mixture. Further benzoylation of the

tetrabenzoate obtained from the mercaptal produced α-*d*-glucopyranose pentabenzoate; m. p. 184–185° (mixed m. p. unchanged); $[\alpha]^{25}$D +134.5° (c, 2; CHCl$_3$). Levene and Meyer[15] record the constants: m. p. 187°; $[\alpha]$D +138.5° (CHCl$_3$). We were unable to duplicate exactly these constants obtained by Levene and Meyer after repeated purification. However, an authentic specimen of the pentabenzoate purified in the same manner gave the above constants found by us.

***d*-Galactose Ethyl Mercaptal 2,3,4,5-Tetraacetate.—**6-Trityl galactose ethyl mercaptal tetraacetate (15 g.; 1 mol) was dissolved in 30 cc. of glacial acetic acid by warming on a water-bath. All acetic acid used was previously recrystallized several times. The solution was cooled to 15° and 3 cc. of a cold solution of 11 g. of hydrogen bromide (0.9 mol) in 20 g. of acetic acid was added rapidly with stirring. The yellow precipitate of trityl bromide that formed immediately was removed by rapid filtration and washed with a small amount of cold acetic acid; yield of trityl bromide, 4.9 g. (71%). The filtrate was poured on a mixture of ice and sodium bicarbonate, the sirup that separated extracted with chloroform and the extract washed with a cold aqueous solution of sodium bicarbonate and with ice-water, dried and evaporated to dryness under reduced pressure. The last traces of chloroform were removed by distilling several portions of absolute ethanol from the sirup under reduced pressure. Since it was not desirable to have a complete reaction, in order to avoid formation of the 6-bromo compound, the product at this point consisted of a number of substances which were readily separated.

The sirup was dissolved in methanol, water added to incipient turbidity and the mixture kept in the ice box for twenty-four hours. Two grams of crystalline material was removed by filtration. This consisted essentially of starting material, 1.1 g. of pure 6-trityl galactose ethyl mercaptal tetraacetate being obtained on further recrystallization. On further addition of water in small portions to the original dilute methanol mother liquor, a second crop of crystals was obtained; yield, 4.5 g.; m. p. 83–86°. Large and characteristic spear-shaped crystals of high density were obtained on further recrystallization of this fraction from heptane. The constants of this material after further purification from heptane were: m. p. 96–97°; $[\alpha]$D −6.8° (c, 4; CHCl$_3$).

Anal. Calcd. for C$_{10}$H$_{18}$O$_5$S$_2$(COCH$_3$)$_4$: S, 13.9; acetyl, 8.8 cc. 0.1 N NaOH per 100 mg. Found: S, 14.4; acetyl, 8.9 cc.

Further acetylation of the above substance with pyridine and acetic anhydride produced *d*-galactose ethyl mercaptal pentaacetate,[16] identified by its melting point and rotation.

6-Bromo-*d*-galactose Ethyl Mercaptal Tetraacetate.—In the removal of the trityl group from 6-trityl galactose ethyl mercaptal tetraacetate as described previously, experiments would occasionally produce the 6-bromo mercaptal tetraacetate and considerable deacetylation would occur. This substance would appear in the first material separating from the methanol and water mixture. One 15-g. run of the 6-trityl compound produced 1.6 g. of

(15) P. A. Levene and G. M. Meyer, *J. Biol. Chem.*, **76**, 513 (1928).

(16) M. L. Wolfrom, THIS JOURNAL, **52**, 2464 (1930).

this crude product. After several recrystallizations from methanol by the addition of water followed by more recrystallizations from heptane, a small amount of material showing a maximum melting point of 110–111° was obtained. This contained bromine and its analysis was in agreement with that required for the 6-bromo compound.

Anal. Calcd. for $C_{10}H_{17}O_4S_2Br(COCH_3)_4$: S, 12.40; acetyl, 7.73 cc. 0.1 N NaOH per 100 mg. Found: S, 12.36; acetyl, 7.73 cc.; Br, present.

Preparation of *d*-Galactose 2,3,4,5-Tetraacetate Hydrate from *d*-Galactose Ethyl Mercaptal 2,3,4,5-Tetraacetate.—A solution of 6 g. of galactose ethyl mercaptal 2,3,4,5-tetraacetate in 50 cc. of acetone and 8 cc. of water was mixed with 12 g. of powdered cadmium carbonate and to this was added slowly a solution of 10.5 g. of mercuric chloride in 36 cc. of acetone, vigorous mechanical stirring being maintained. The stirring was continued for twenty-four hours at room temperature. The mixture was filtered into a flask containing cadmium carbonate, the residue washed with cold acetone and the filtrate concentrated to dryness under reduced pressure in the presence of cadmium carbonate. This residue was dried by distilling several portions of absolute ethanol from it under reduced pressure. The dried residue was extracted with several portions of chloroform and the extract washed with water and dried. After solvent removal, the resulting sirup was obtained crystalline by standing under water for several days in the ice box; yield, 1.3 g.; m. p. 148–150°. In common with other aldehydo hydrates, the substance is soluble in hot water and is readily purified by dissolving in small portions of hot water, cooling rapidly to room temperature, and allowing to stand overnight in the ice box. After a few recrystallizations the melting point is sharp and constant at 168°. The substance is soluble in pyridine and insoluble in dioxane. It crystallizes from water in elongated rectangular plates. A product of melting point 162° showed a rotation change in pyridine solution of $[\alpha]^{25}D$ +10° $\longrightarrow$ −38° (c, 2). Micheel and Spruck[2] record the constants: m. p. 140°; $[\alpha]D$ +10° $\longrightarrow$ −25° (pyridine).

6-Trityl-*aldehydo-d*-Galactose Tetraacetate Ethyl Hemiacetal.—6-Trityl galactose ethyl mercaptal tetraacetate (20 g.) was dissolved in 125 cc. of acetone and 31 cc. of water and 40 g. of powdered cadmium carbonate added. With vigorous mechanical stirring, a solution of 40 g. of mercuric chloride in 65 cc. of acetone was added slowly and the stirring continued for forty-eight hours at room temperature. The stirring was then stopped and water added to the mixture to bring the volume to approximately 2 liters and this held in the ice box for several hours. The precipitate was removed by filtration, dried by washing with cold ethanol and with ether and extracted with warm chloroform. The extract was washed with water, dried, diluted with an equal volume of ethanol and evaporated to dryness under reduced pressure, the residue being crystalline; yield, 14 g. The substance was obtained pure after several recrystallizations from ethanol; m. p. 153°; $[\alpha]^{25}D$ −28° (c, 4; CHCl₃). The substance did not mutarotate in chloroform but showed a rotation change in methanol ($[\alpha]^{25}D$ −29.5° at twelve minutes

$\longrightarrow$ −16.5° at twenty-four hours). The compound was soluble in hot ethanol, acetone and chloroform, was very slightly soluble in acetic acid and methanol at room temperature and was practically insoluble in water.

Anal. Calcd. for $C_{27}H_{28}O_7(COCH_3)_4$: acetyl, 6.29 cc. 0.1 N NaOH per 100 mg. Found: acetyl, 6.18 cc.; S, absent; OEt, present.

6-Trityl-*aldehydo-d*-galactose Semicarbazone Tetraacetate.—Five grams (1 mol) of 6-trityl-*aldehydo*-galactose tetraacetate ethyl hemiacetal was dissolved in 25 cc. of hot 95% ethanol and to the hot solution was added a solution of 0.8 g. (0.9 mol) of semicarbazide hydrochloride and 1.4 g. (1.8 mol) of potassium acetate in 20 cc. of 50% ethanol. On cooling the solution to room temperature and adding water a sirup separated which hardened on standing overnight in the ice box; yield, 5.5 g. The substance was obtained crystalline by repeated precipitation from methanol by the addition of water. The melting point of this substance was unreliable but the rotation was constant at $[\alpha]^{27}D$ + 20.0° (c, 4; CHCl₃).

Anal. Calcd. for $C_{28}H_{29}O_6N_3(COCH_3)_4$: acetyl, 6.17 cc. 0.1 N NaOH per 100 mg. Found: acetyl, 6.0 cc.; N, present.

Summary

1. 6-Trityl *d*-glucose ethyl mercaptal tetrabenzoate, 6-trityl *d*-galactose ethyl mercaptal tetrabenzoate and tetraacetate, trityl *l*-arabinose ethyl mercaptal triacetate and the corresponding *d*-xylose derivative have been synthesized in crystalline condition.

2. 6-Trityl *d*-glucose ethyl mercaptal tetrabenzoate yielded 6-bromo-*d*-glucose ethyl mercaptal tetrabenzoate on detritylation with hydrogen bromide.

3. The position of the bromine atom in the above derivative has been proved to be on the sixth carbon.

4. 6-Bromo-*d*-glucose ethyl mercaptal tetrabenzoate was converted into the 6-iodo compound and this on complete hydrolysis produced the ordinary form of glucose tetrabenzoate.

5. 6-Trityl *d*-galactose ethyl mercaptal tetraacetate was converted into the 6-hydroxy compound and this was hydrolyzed to produce the *d*-galactose 2,3,4,5-tetraacetate hydrate of Micheel and Suckfüll.

6. 6-Bromo-*d*-galactose ethyl mercaptal tetraacetate and *aldehydo-d*-galactose 6-trityl tetraacetate have been synthesized and the latter isolated as its ethyl hemiacetal and semicarbazone.