

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

Chemical Constitution and the Tanning Effect. II. Pentagallates of Glucose and Mannose

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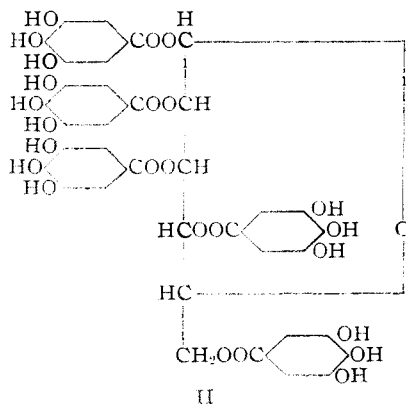
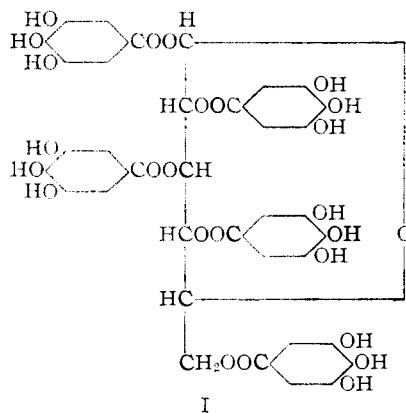
It has already been shown¹ that simple esters of gallic acid have no tanning properties, but that the polyesters of gallic acid with various polyhydric alcohols have tanning properties that are poor but definite and appear to improve as the alcohol series is ascended. Moreover, none of the simple initial materials used in the preparation of the various esters have tanning properties.

In the course of his extensive work on gallo-tannin Emil Fischer² prepared many more or less water soluble materials that precipitated gelatin (or glue) from aqueous solution. On the strength of this, such compounds have since been stated to have tanning properties. It is worth noting that Fischer himself made no such claim for any of his products; the faulty interpretation has found its way into the records due to careless translation and incomplete information. Thus in the case of diprotocatechuic acid Fischer and Freudenberg³ claimed only that the depside gave a precipitate with gelatin and quinine acetate; elsewhere it is stated⁴ that the compound has "tanning properties." The fact is that a natural organic tanning material will precipitate gelatin from aqueous solution, but the converse is not always true—a compound may well precipitate gelatin from aqueous solution and still, when applied to leather formation, have very questionable tanning properties. Many relatively simple sulfonic acids will do just this. It is true that precipitation of gelatin from solution in water is a good *preliminary* test for tanning properties; however, as has been emphasized before, the only safe, final, and reliable test for tanning properties is the making of a piece of leather.

It seems certain from Fischer's work that unaltered gallotannin from Chinese galls is pentam-digalloylglucose, and it may be inferred that if this compound were prepared synthetically in sufficient quantity for testing, it would show leather forming properties. Although it would be worth while repeating the synthesis of this com-

pound from the point of view of general interest, the repetition of the synthesis of such a complex compound would serve no useful purpose from the point of view of the present research since much simpler compounds with good tanning properties are likely to be found.

As a result of his work with Aleppo galls Fischer concluded² that the tanning material present was essentially pentagalloyl-*d*-glucose. Accordingly he carried out the synthesis of this compound and found that the synthetic product had gelatin precipitating properties. In the present communication there are described the syntheses of β -*d*-glucose-1,2,3,4,6-pentagallate (I), *d*-mannose pentagallate (II), β -*d*-glucose diethyl mercaptal pentagallate (III) (as an intermediate in the synthesis of the aldehyde form of glucose pentagallate), and aldehydo-*d*-glucose pentagallate (IV) and the examination of each of these for tanning properties. The preparation of

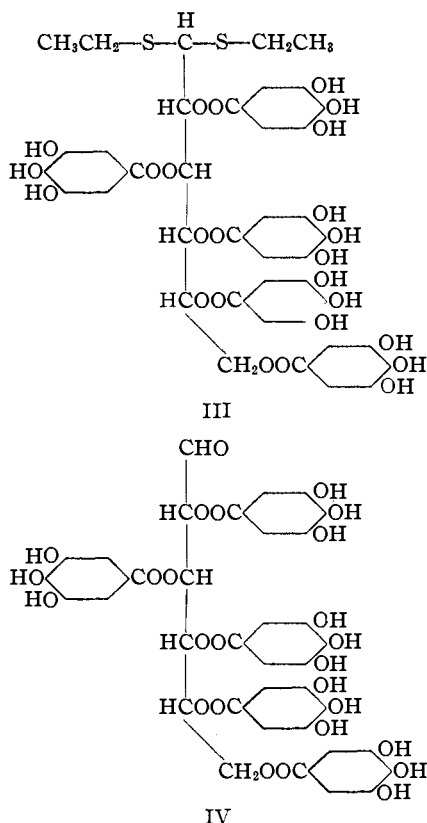


(1) Russell and Tebbens, *This Journal*, **64**, 2274 (1942).

(2) Emil Fischer, "Untersuchungen über Depside und Gerbstoffe," Julius Springer, Berlin, 1919.

(3) Fischer and Freudenberg, *Ann.*, **384**, 240 (1911).

(4) Perkin and Everest, "The Natural Organic Colouring Materials," Longmans, Green and Co., London, 1918.



aldehyde-*D*-glucose pentagallate was undertaken to make a comparison between a galloylated glucopyranose and the corresponding linear form of the same compound. It also allows a comparison to be made with the linear polyhydric alcohol derivatives already prepared.¹

The galloylation of the sugars followed the general procedure previously described¹ in which the anhydrous sugar was coupled with triacetyl-galloyl chloride in the presence of dry chloroform and quinoline. The deacetylation of the coupled products was accomplished by the use of sodium acetate and dilute sodium hydroxide following the method of Fischer.² The experimental tannages were carried out by the standard procedure previously described.¹

All the derivatives tested gave very good tannages; β -*D*-glucose pentagallate, *D*-mannose pentagallate, *D*-glucose diethyl mercaptal pentagallate, and aldehyde-*D*-glucose pentagallate each made leather exactly similar in quality to that given by pure gallotannin. The leather made with the first two synthetic products was neutral white in color (gallotannin leather is cream white), whilst that from the second two had an ivory shade.

Experimental

β -*D*-Glucose 1,2,3,4,6-pentagallate was prepared following the procedure of Fischer² by the deacetylation of the corresponding acetyl derivative in acetone-water solution with sodium acetate and 1 *N* sodium hydroxide solution. Runs were made using four times the quantities employed by Fischer with comparable yields, m. p. 133° (softens) 143° (sintered). The product gave a blue-black color with dilute ferric alum solution, a gelatin test, and was water soluble. *Anal.* Calcd. for C₄₁H₅₂O₂₈: C, 52.3; H, 3.43. Found: C, 52.3; H, 3.31. The average of three determinations of optical rotation in ethanol solution was $\alpha^{25D} +25.33^\circ$ ($c = 2$) which compares favorably with Fischer's value of +24°.

Penta-(triacetylalloyl)-*D*-mannose.—7.2 grams (0.04 mole) of finely powdered anhydrous *D*-mannose was taken up in 120 cc. of dry, freshly distilled chloroform and 36 g. of dry, freshly distilled quinoline; 72 g. of finely powdered triacetylalloyl chloride was added portionwise with shaking. The reaction mixture was tumbled for three days until entirely homogeneous. It was then washed successively with three 100-cc. portions of distilled water, three 100-cc. portions of cold 1% sulfuric acid and finally with four 100-cc. portions of distilled water (last wash neutral to litmus). The chloroform solution was dried overnight with anhydrous sodium sulfate, filtered and the drying agent washed with chloroform. The combined filtrate and chloroform washings were added dropwise with vigorous mechanical stirring to 700 cc. of methanol at 0° over a period of three hours. The granular white solid was collected on a filter and dried over phosphorus pentoxide and paraffin at 2 mm. and 56° for six days. The yield was 50.9 g. of white, odorless and tasteless solid which gave no gelatin test and no color with dilute ferric alum solution, m. p. 121° (sinters). *Anal.* Calcd. for C₇₁H₈₂O₄₁: C, 54.3; H, 3.98. Found: C, 54.1; H, 3.88. The optical rotation was determined in chloroform solution, $\alpha^{24D} -55.50^\circ$ ($c = 2$).

***D*-Mannose Pentagallate.**—The deacetylation of penta-(triacetylalloyl)-*D*-mannose was carried out as follows: 30.0 g. of the acetyl derivative was dissolved in 700 cc. of acetone under an atmosphere of oxygen-free nitrogen. A solution of 60.0 g. of crystalline sodium acetate in 400 cc. of distilled water was added and the whole refluxed (64°), with mechanical stirring, under a nitrogen atmosphere for 25 min., there was now added 60 g. of crystalline sodium acetate dissolved in 300 cc. of distilled water. After refluxing for one hour, the solution was chilled to 0° and 96 cc. of 1 *N* sodium hydroxide solution added with 400 cc. of water. The solution was refluxed three one-hour periods with chilling followed by the successive addition of 80 cc. and 60 cc. of 1 *N* sodium hydroxide solution. The reaction mixture was cooled to room temperature and allowed to stand overnight under a nitrogen atmosphere. The clear, straw-yellow solution was filtered and 320 cc. of 1 *N* sulfuric acid was added to the filtrate which was then concentrated under reduced pressure at 35–40° to a volume of 400 cc. The concentrate was made just acid to congo red paper by the addition of 5 *N* sulfuric acid and the acidified solution extracted with five 200-cc. portions of neutral ethyl acetate. The ethyl acetate extract was washed twice with 100-cc. portions of water, separated and concentrated

under reduced pressure to dryness. The friable solid so produced was further dried in an Abderhalden pistol over potassium hydroxide; yield 17.2 g., m. p. 161° (sinters). *Anal.* Calcd. for $C_{41}H_{32}O_{25}$: C, 52.3; H, 3.43. Found: C, 52.3; H, 3.59. The optical rotation in ethyl acetate solution was determined, $\alpha^{25}_D -72.38^\circ$ ($c = 2$).

Penta-(triacetylalloyl)-*d*-glucose Diethyl Mercaptan.—Glucose diethyl mercaptan was made by the method of Fischer⁵ by treatment of anhydrous *d*-glucose with ethyl mercaptan in the presence of cold aqueous hydrochloric acid: 11.45 g. of anhydrous, powdered *d*-glucose diethyl mercaptan was treated with 72 g. of triacetylalloyl chloride in quinoline and chloroform exactly as described for the *d*-mannose derivative. The precipitation of the coupled product was made by addition to 90–100° petroleum ether rather than methanol; yield 65.5 g. of a white, amorphous, highly hygroscopic powder, m. p. 82° (sinters). The compound gave no color with dilute ferric alum solution. *Anal.* Calcd. for $C_{73}H_{72}O_{46}S_2$: S, 3.82. Found: S, 3.78. The optical rotation in chloroform solution was found: $\alpha^{25}_D +18.75^\circ$ ($c = 2$).

***d*-Glucose Diethyl Mercaptan Pentagallate.**—This ester was made from 42.8 g. of the corresponding acetyl derivative following the procedure outlined for *d*-mannose pentagallate. During the deacetylation there was no odor of mercaptan, indicating that the mercaptan linkage was stable under the conditions of hydrolysis; yield 22.4 g. of light tan friable solid, m. p. 167° (sinters), which gave a positive test with reagent gelatine and a deep blue color with alcoholic ferric alum solution. *Anal.* Calcd. for $C_{48}H_{42}O_{26}S_2$: S, 5.03. Found: S, 5.01. The optical rotation in neutral ethyl acetate was determined: $\alpha^{25}_D +11.13^\circ$ ($c = 2$).

Aldehyde-*d*-glucose Pentagallate.—The usual methods of demercaptalization using heavy metal salts were not

(5) Fischer, *Ber.*, **27**, 674 (1894).

attempted since heavy metal ions form insoluble precipitates with tannins; 4.25 g. (0.004 mole) of *d*-glucose diethyl mercaptan pentagallate was taken up in 100 cc. of water and 20 cc. of 1 *N* sulfuric acid and allowed to stand for two days. The yellow homogeneous solution smelled strongly of ethyl mercaptan. Oxygen-free nitrogen was passed through the solution for six days at room temperature at the end of which time there was no odor of mercaptan. The aqueous solution was extracted with neutral ethyl acetate, the ethyl acetate solution was washed with water and dried over anhydrous sodium sulfate. After filtering, the ethyl acetate solution was dried *in vacuo* and the residue was again taken up in ethyl acetate, filtered, and reduced to dryness. The product, after drying in an Abderhalden pistol, was a pale tan friable solid which was water soluble, gave a blue-black color with dilute ferric alum solution and a positive test with reagent gelatine; yield, 3.6 g., m. p. 113° (sinters). *Anal.* Calcd. for $C_{41}H_{32}O_{26}$: C, 52.3; H, 3.43. Found: C, 52.0; H, 3.61. The optical rotation in ethyl acetate solution was determined: $\alpha^{25}_D +10.13^\circ$ ($c = 2$).

Summary

The preparations of β -*d*-glucose pentagallate, *d*-mannose pentagallate, *d*-glucose diethylmercaptan pentagallate, and aldehyde-*d*-glucose pentagallate have been accomplished.

All four are transparent vitreous solids that cannot be crystallized. However, each one has been adequately characterized.

Each is a very good tanning material and forms leather strictly comparable, both for quality and color, to that given by natural gallotannin.

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Lead Tetraacetate Oxidations in the Sugar Group. IV.¹ The Rates of Oxidation of Trehalose, Levoglucosan, α -Methyl-L-sorbopyranoside, Polygalitol and Styracitol in Glacial Acetic Acid²

BY ROBERT C. HOCKETT, MARGARET T. DIENES AND HUGH E. RAMSDEN

Criegee's observation that *cis*-1,2-glycols are more rapidly oxidized by lead tetraacetate than *trans* glycols³ led the senior author and McClenahan⁴ to investigate correlations between oxidation rates and configurations in a series of

pyranosides which contained α,β,γ -triol structures with fixed spatial relationships among the hydroxyl groups. The findings of this research are reiterated below in a more explicit form for the sake of easy reference in subsequent publications:

(1) Number III of this series, *THIS JOURNAL*, **66**, 403 (1943).
 (2) The material in this paper is taken from theses submitted by Margaret T. Dienes and Hugh E. Ramsden in partial fulfillment of the requirements for the degree of Bachelor of Science in May, 1940, and in February, 1943, respectively. A similar paper was read before the Division of Organic Chemistry at the Detroit meeting of the American Chemical Society in September, 1940.

(3) Criegee, *Ann.*, **507**, 159 (1933).

(4) Hockett and McClenahan, *THIS JOURNAL*, **61**, 1667 (1936).

(1) Ultimately at least two moles of lead tetraacetate are consumed by a vicinal triol. Side reactions, such as the oxidation of formic acid, often prevent the consumption of oxidant from levelling off sharply at two moles.

(2) If two of the three hydroxyl groups bear a