alkyl groups: s-butyl < 2-cyanoethyl < ethyl and *n*-butyl < isobutyl. The pyrolysis of appropriate acrylic and methacrylic esters constitutes a convenient method for preparing the corresponding unsaturated acids.

The acidolysis of methyl acrylate with formic acid is described.

PHILADELPHIA, PA.

Received July 5, 1944

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Chemical Constitution and the Tanning Effect. III. The Synthesis and Examination of Fructose Pentagallate, d-Arabinose Tetragallate and α -Methyl-d-glucoside Tetragallate

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The work already on record¹ describing the preparation, and examination for tanning properties, of the more easily available fully galloylated aldohexoses has now been extended to include a fully galloylated ketohexose (fructose pentagallate I), a fully galloylated aldopentose (d-arabinose tetragallate II) and α -methyl-d-glucoside tetragallate III. Each forms a brittle transparent vitreous mass, is water soluble and, in aqueous solution, gives a typical precipitate with gelatin solution. d-Arabinose tetragallate has very good tanning properties and forms leather strictly comparable with that given by gallotannin. α -Methyl-d-glucoside tetragallate has good leather forming properties—only slightly inferior to those of gallotannin.

Fructose pentagallate is not a tanning material. This result was so surprising that the entire tedi-



(1) Russell, Tebbens and Arey, THIS JOURNAL, 65, 1472 (1943).



ous synthesis of the compound was carried out a second time. However, the second preparation was identical with the first, the final product gave a typical gelatin precipitate in aqueous solution but would not make leather.

It would be idle at the present stage in this investigation to speculate as to why, on the one hand, a fully galloylated aldohexose (pyranose or aldehyde form) or an epimeric form¹ should be a very good tanning material and, on the other, the isomeric fully galloylated ketohexose should have no tanning properties. One minor point is emphasized by the examination of fructose pentagallate—a positive test with gelatin is not always evidence of tanning properties since fructose pentagallate gives the test.

Experimental

Penta-(triacetylgalloyl)-fructose.—7.2 g. (0.04 mole) of anhydrous, finely powdered fructose was suspended in 120 cc. of dry, freshly distilled chloroform and 36 g. of dry, freshly distilled quinoline; 72 g. of freshly distilled triacetylgalloyl chloride was added portionwise with shaking and cooling. After tumbling for three days the pale yellow reaction mixture was completely homogeneous. It was washed three times with 100-cc. portions of water, three times with 100-cc. portions of cold 1% sulfuric acid and four times with 100-cc. portions of cold water (second wash neutral to litmus). The chloroform solution was dried over sodium sulfate and then added slowly with vigorous mechanical stirring over a period of three hours to 800 cc. of anhydrous 90–100° petroleum ether at 0°. The cream-colored amorphous solid so produced was dried at 56° and 1 mm. over phosphorus pentoxide and paraffin for three days; yield 57.2 g., m. p. 88° (sintered). It was tasteless and odorless and gave no color with ferric alum solution. The optical rotation was determined on chloroform solutions of samples prepared in two separate preparations made under the same conditions: α^{24} D +11.50°, α^{34} D +11.63° (c = 2). Anal. Calcd. for C₇₁H₅₂O₄₁: C, 54.3; H, 3.98. Found: C, 54.0; H, 4.00. Fructose Pentagallate.—This hydrolysis was run on 40 g.

Fructose Pentagallate.—This hydrolysis was run on 40 g. of the acetyl compound using precisely the same procedure, but appropriate quantities, as previously described¹ for the corresponding derivative of *d*-mannose; yield, 12.7 g. of cream-colored amorphous powder after drying for six days at 76° and 1 mm. over solid potassium hydroxide, m. p. 136° (sintered).

A second run using 50.0 g. of the acetyl compound gave 22.5 g. of comparable product, m. p. 134° (sintered). Both products were water soluble, gave good gelatin tests, and blue-black coloration with ferric alum solution. The optical rotation was determined on ethyl acetate solutions of the two samples: $\alpha^{23}D + 15.75^{\circ}$, $\alpha^{24}D + 16.00^{\circ}$ (c = 2). Anal. Calcd for C₄₁H₃₂O₂₈: C, 52.3; H, 3.43. Found: C, 52.5; H, 3.34. Tetra-(triacetylgalloyl)-d-arabinose.-7.5 g. of finely

powdered, anhydrous d-arabinose was taken up in 120 cc. of dry, freshly distilled chloroform and 38 g. of dry, freshly distilled quinoline. To the suspension was added 78.6 g. of finely powdered triacetylgalloyl chloride and the whole was shaken for three days until homogeneous. The pale yellow chloroform solution was washed as usual with water, dilute sulfuric acid and then with water until the wash was neutral to litmus. The chloroform solution was dried over sodium sulfate and, after removal of the drying agent, the dried solution was added dropwise with mechanical stirring over a period of three hours to 600 cc. of absolute methanol at 0°. The white flocks produced by this again precipitated by methanol. The product was dried at 56° and 1 mm. over phosphorus pentoxide and paraffin; yield 44.0 g. of white, granular, amorphous powder which was odorless and tasteless, m. p. 87° (sintered). Soluble in ethanol, acetone, chloroform and insoluble in petroleum ether and water. Anal. Calcd. for CorHsuOss: C, 58.8; H, 4.33. Found: C, 58.2; H, 4.19. d-Arabinose Tetragallate.—20.0 g. of the acetyl deriva-

d-Arabinose Tetragallate.—20.0 g. of the acetyl derivative was dissolved in 400 cc. of acetone and a solution of 28 g. of crystalline sodium acetate in 180 cc. of water was added. The solution was refluxed on a steam-bath with stirring in an oxygen-free nitrogen atmosphere. After thirty minutes, 24 g. of sodium acetate in 120 cc. of water was added and the solution refluxed for one hour after which time it was chilled to 0° and 40 cc. of 1 N sodium hydroxide solution was added with 200 cc of water. The reaction mixture was refluxed for one hour, again chilled to 0° and 38 cc. of 1 N sodium hydroxide solution was added. The solution was alternately refluxed and chilled for intervals of one and one-half hours, and one hour while there was added 36 cc. and 28 cc. of 1 N sodium hydroxide solution. The solution was allowed to stand overnight at room temperature in a nitrogen atmosphere.

The solution after standing was filtered and 160 cc. of 1N sulfuric acid was added to the filtrate. This solution was concentrated under reduced pressure at 35° to a volume of 200 cc. and the concentrate was made acid to congo red with 5 N sulfuric acid and extracted with four 100-cc. portions of neutral ethyl acetate. The ethyl acetate extracts were combined and washed twice with 50-cc. portions of water and brought to dryness under reduced pressure. The product, a light tan amorphous solid, after drying over potassium hydroxide at 56° and 1 mm. for six days, weighed 11.8 g., m. p. 127-128° (sintered). This compound was water soluble and gave a good gelatin test and a blue-black color with ferric alum solution. The optical rotation in ethyl acetate solution was $\alpha^{25}D - 132.0^{\circ}$ (c = 2). Anal. Calcd. for $C_{23}H_{25}O_{21}$: C, 52.3; H, 3.45. Found: C, 51.9; H, 3.39.

Tetra-(triacetylgalloyl)- α -methyl-d-glucoside.—Fischer and Freudenberg² previously reported the preparation of tetra-(triacetylgalloyl)- α -methyl-d-glucoside and its hydrolysis to α -methyl-d-glucoside tetragallate. The acetyl derivative was made from 9.7 g. (0.05 mole) of α methyl-d-glucoside by the usual treatment of the sugar in chloroform and quinoline with triacetylgalloyl chloride. The purified chloroform solution was added to petroleum ether to precipitate the acetate as a granular, white amorphous solid which, after drying at 56° and 1 mm. over phosphorus pentoxide and paraffin, gave 64.0 g. of a white powder which was water insoluble, tasteless and odorless and which gave no color with alcoholic ferric alum solution, m. p. 92° (sintered). The optical rotation in chloroform solution was: α^{21} D +27.38° (c = 2). Anal. Calcd. for C₁₉H₅₄O₃₄: C, 54.2; H, 4.16. Found: C, 53.8; H, 3.99.

a-Methyl-d-glucoside Tetragallate.—By the hydrolysis procedure outlined above, but with appropriate quantities, 44.9 g. of the polyacetate gave 21.5 g. of water soluble light tan friable solid, m. p. 141° (sintered). This substance gave a positive test with reagent gelatin and a blue-black color with ferric alum solution.

The optical rotation was determined in ethyl acetate solution: $\alpha^{25}D + 60.88^{\circ}$ (c = 2). For comparison with the compound reported by Fischer and Freudenberg,² who used a solution of 0.076 g. of the compound in 100 cc. of water and found $\alpha^{20}D + 26.39^{\circ}$ (= 0.5°), the rotation of 2.000 g. of the compound prepared by the above deacetylation gave $\alpha^{23}D + 60.18^{\circ}$. Anal: Calcd. for $C_{38}H_{30}O_{22}$: C, 52.3; H, 3.77. Found: C, 52.0; H, 4.00.

Summary

Fructose pentagallate, *d*-arabinose tetragallate and α -methyl-*d*-glucoside tetragallate have been prepared, characterized and tested for leather forming properties.

d-Arabinose tetragallate and α -methyl-d-glucoside tetragallate have good tanning properties. Fructose pentagallate does not have tanning properties.

CHAPEL HILL, N. C. RECEIVED AUGUST 18, 1944

(2) Fischer and Freudenberg, Ber., 45, 934 (1912).