d-Glucose-semicarbazone Penta-acetate.—Four and one-half g. (1 mol.) of pure μ-glucose penta-acetate was dissolved in 45 cc. of warm water, cooled to room temperature, and a mixture of 1.1 g. of semicarbazide hydrochloride (0.9 mol.) and 1.8 g. of potassium acetate (1.6 mols.) was added in the solid form. In a few minutes the solution became cloudy and an oil was gradually deposited. On standing overnight at room temperature this solidified. This was filtered and washed with cold water, 3.6 g. being obtained. The material was dissolved in methyl alcohol, treated with decolorizing carbon, filtered and water added. On standing at ice-box temperature 1.4 g. of crystals (m. p. 148–150°) in the form of minute elongated prisms was deposited. These were removed by filtration, washed with water and a further crop of 1.3 g. (m. p. 148–150°) obtained from the filtrate by further addition of water. On two further recrystallizations the substance melted at 150–151° and on two more (5) melted at 150°.

Anal. Subs., 0.2055: N_2, 18.83 cc. (751.5 mm., 28°). Calcd. for $C_7H_{10}O_6N_3$-$(CH_3CO)_5$: N, 9.40. Found: N, 9.87. Calcd. for 0.2019: 22.6 cc. 0.1 *N* KOH. Found: 22.7 cc. Calcd. for 0.2074: 23.2 cc. 0.1 *N* KOH: Found: 23.1 cc.

The writer wishes to acknowledge his indebtedness to Professor W. L. Evans for his inspirational counsel and advice.

Summary

1. A new form of d-glucose penta-acetate has been prepared in pure condition.
2. Evidence is given that this compound possesses the open-chain, free aldehyde structure and the suggestion is made that the name μ-d-glucose penta-acetate be applied to the substance.
3. The crystalline semicarbazone of this aldehyde has been prepared in pure form.

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PREPARATION OF SOME METHYLATED GALLIC ACIDS

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During the course of a study of some anthocyan pigments it was desired to have samples of certain methylated gallic acids, since these are produced by degradation of the anthocyanidin. The compounds desired were: 3,5-dimethylgallic acid, 3,4-dimethylgallic acid and 3-methylgallic acid. The first of these, syringic acid, is easily prepared by the method of Bogert and Ehrlich,[1] and its properties and derivatives[2] have been thoroughly studied. However, the data available in the literature on the other two methylgallic acids are very meager. The 3,4-dimethylgallic acid has been previously prepared by Zincke and Francke[3] and Her-

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[1] Bogert and Ehrlich, This Journal, **41**, 798 (1919).

[2] Bogert and Coyne, *ibid.*, **51**, 569 (1929).

[3] Zincke and Francke, *Ann.*, **293**, 191 (1896).

zig and Pollak,[4] and 3-methylgallic acid by Vogl.[5] Since the methods used in the present work for the preparation of these last two compounds differed from those previously used and since the properties of the compounds obtained do not agree with those recorded in the literature, it was thought that a brief report of their preparation would be of interest.

Vanillin was the starting material for the preparation of both of these compounds. The 3,4-dimethylgallic acid was obtained as a result of the following series of preparations: Vanillin ⟶ 5-bromovanillin ⟶ 5-bromo-3,4-dimethoxybenzaldehyde ⟶ 5-bromo-3,4-dimethoxybenzoic acid ⟶ 3,4-dimethylgallic acid. The product crystallized from alcohol in long white needles and melted at 184–185°. Zincke and Francke[3] gave no melting point at all, while Herzog and Pollak[4] reported 189–192°. It was free from bromine and gave only a light yellow color with ferric chloride, which indicates the absence of gallic acid and 3-methylgallic acid which might be produced by the action of the alkali in the last step.

The 3-methylgallic acid was prepared from 5-bromovanillin by heating the latter with alkali and copper powder. After careful purification the 3-methylgallic acid was obtained in the form of needles which melted constantly at 131–132°. The previously reported value[5] was 199–200°. Dilute ferric chloride produced a light green color quite distinct from the blue produced by gallic acid itself.

Experimental

5-Bromovanillin.—A solution of 105 g. of bromine in 200 cc. of glacial acetic acid was added to 100 g. of vanillin dissolved in 200 cc. of glacial acetic acid. The bromovanillin separated at once. It was filtered off and recrystallized from 95% alcohol. Colorless cubic crystals which soon turned yellow on standing were obtained; yield, 118 g. or 77.6% of the theoretical. It melted sharply at 163–164°, which agrees with the melting point recorded by Dakin.[6]

5-Bromo-3,4-dimethoxybenzaldehyde.—A solution of 10.5 g. of 5-bromovanillin in 75 cc. of 2.5% sodium hydroxide solution was stirred vigorously and 10 cc. of dimethyl sulfate added. As soon as the solution became acid to litmus another 10 cc. of dimethyl sulfate was added with sufficient alkali to render the solution alkaline. In this manner four more successive portions of dimethyl sulfate were added, keeping the temperature between 45 and 50°. After the addition of the last portion the solution was boiled for two hours and then cooled. The methylated bromovanillin was filtered off and recrystallized from 80% alcohol. Nine g. (80% of the theoretical) of white flocculent crystals was obtained melting at 61–62°. This agrees with the value reported by Jones and Robinson.[7]

5-Bromo-3,4-dimethoxybenzoic acid.—A hot solution of 22 g. of potassium permanganate in 500 cc. of water was added with vigorous stirring to a boiling mixture of 30 g. of 5-bromo-3,4-dimethoxybenzaldehyde and 300 cc. of water containing 35 g. of potassium carbonate. After refluxing for one hour the solution was cooled and filtered.

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[4] Herzig and Pollak, *Monatsh.*, **23**, 704 (1902).

[5] W. Vogl, *ibid.*, **20**, 395 (1899).

[6] Dakin, *Am. Chem. J.*, **42**, 493 (1909).

[7] Jones and Robinson, *J. Chem. Soc.*, **111**, 922 (1917).

The filtrate was acidified, the white precipitate filtered and recrystallized from hot water; yield, 30 g. of white crystals, m. p. 190–192°, which agrees with the melting point reported by Dakin.[6]

3,4-Dimethylgallic acid.—Ten g. of 5-bromo-3,4-dimethoxybenzoic acid, 200 cc. of 8% sodium hydroxide and 2 g. of copper powder were placed in an iron pipe fitted with lead-seated screw caps. The bomb was heated to 200° for one hour. After cooling the contents were acidified with dilute sulfuric acid and extracted with four 100-cc. portions of ether. The ether was distilled and the residue recrystallized from alcohol. Long colorless needles were obtained melting at 184–185°. Recrystallization from hot water or alcohol did not change the melting point. It gave a very light yellow color with ferric chloride; yield, 1.5 g. (20% of the theoretical).

Anal. Subs., 0.1118: CO_2, 0.2228; H_2O, 0.0520. Calcd. for $C_9H_{10}O_5$: C, 54.52; H, 5.09. Found: C, 54.45; H, 5.20.

The acetyl derivative was prepared by acetylation with acetic anhydride and a drop of perchloric acid according to the general method of Conant and Hall.[8] The acetate was crystallized from alcohol. Needles melting at 137–138° were obtained.

Anal. Subs., 0.0702: CO_2, 0.1415; H_2O, 0.0325. Calcd. for $C_{11}H_{12}O_6$: C, 55.00; H, 5.01. Found: C, 54.98; H, 5.18.

3-Methylgallic Acid.—The simultaneous removal of bromine and oxidation of the aldehyde group of 5-bromovanillin was accomplished by heating 5 g. of the latter with 100 cc. of 8% aqueous sodium hydroxide and 2 g. of copper powder at 200–210° for one hour. The reaction mixture was cooled, acidified with dilute sulfuric acid and extracted with ether. The ether was distilled and the residue treated with sodium bicarbonate solution. The insoluble material, consisting of unreacted 5-bromovanillin and some condensation products, was filtered and the filtrate acidified. The material which separated was recrystallized several times from benzene and melted sharply at 131–132°; yield, 1.0 g. Ferric chloride gives a light green coloration. It was acetylated by the method used above and the diacetate obtained after crystallization from benzene in the form of colorless plates melting at 102–103°.

Anal. Subs., 0.1621: CO_2, 0.3180; H_2O, 0.0654. Calcd. for $C_{12}H_{12}O_7$: C, 53.71; H, 4.52. Found: C, 53.50; H, 4.48.

Summary

The preparation and properties of 3,4-dimethylgallic acid and 3-methylgallic acid are described.

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[8] Conant and Hall, THIS JOURNAL, **49**, 3047, 3062 (1927).