scribed by Fletcher and Hudson,[14] was mixed with 1.65 g. of dry, finely powdered silver oxide and 17 ml. of methanol and shaken at 20° for seven hours. The solid phase was then removed by filtration and the filtrate concentrated *in vacuo* to a sirup. From a solution in 10 ml. of ethanol this product deposited 1.31 g. of fine needles; a second crop of 0.25 g. raised the yield to 69%. Recrystallized twice from methanol and once from a mixture of ether and pentane the material melted at 93–96°. A mixed melting point with the material obtained in (**a**) above was undepressed.

(c) **From Tribenzoyl-α-D-xylopyranosyl Bromide with Methanol.**—Two grams of pure tribenzoyl-α-D-xylopyranosyl bromide was dissolved in 20 ml. of anhydrous methanol by boiling for five minutes. Cooled to room temperature, seeded and left at +5° overnight, the reaction mixture yielded 0.95 g. of material melting at 94–96°. Concentration of the mother liquor led to the isolation of 0.55 g. more material (m. p. 91–95°), raising the yield to 83% of theory. Recrystallized from methanol and then from a mixture of ether and pentane the product melted at 93–96° either alone or in admixture with a sample of methyl β-D-xylopyranoside tribenzoate prepared as described in (a).

The Rate of Reaction of Tribenzoyl-α-D-xylopyranosyl Bromide with 1:9 Dioxane–Methanol at 20°.—This measurement was conducted in the same manner as that employed for the arabinose analog described above. The bromide (0.2191 g.) was dissolved in 2.50 ml. of pure anhydrous dioxane and diluted with anhydrous methanol to 25.0 ml., the changing rotation of the resulting solution being observed in a 1-dm. tube at 20° and listed in Table II. The extrapolated rotation at zero time (+1.04°) corresponds to a specific rotation of +118.0°, *i. e.* close to the specific rotation of +118.7° recorded[14] for tribenzoyl-α-D-xylopyranosyl bromide in chloroform. The reaction was essentially completed in one hundred and eight minutes, the final rotation being identical to that (−0.23°) which may be calculated from the specific rotation of methyl β-D-xylopyranoside tribenzoate in 1:9 dioxane–methanol (−28.4° (*c*, 0.77)), upon the assumption that this product was formed in quantitative yield.

Summary

Tribenzoyl-β-D-arabinopyranosyl bromide reacts with anhydrous methanol to give methyl α-D-arabinopyranoside tribenzoate in good yield. Similarly tribenzoyl-α-D-xylopyranosyl bromide reacts with methanol to give methyl β-D-xylopyranoside tribenzoate.

In the absence of an acid acceptor all the benzoylated glycopyranosyl halides thus far investigated which have a benzoyloxy group at carbon 2 *trans* to the halogen, react with methanol without net Walden inversion while those halides having a *cis* relationship between the groups on carbon atoms 1 and 2 react with inversion at carbon 1. These facts are in accord with current concepts of the influence of neighboring groups in replacement reactions.

The value of the reaction as a preparative method has been demonstrated through the synthesis of benzyl α-D-arabinopyranoside.

BETHESDA, MARYLAND RECEIVED FEBRUARY 8, 1950

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[14] H. G. Fletcher, Jr., and C. S. Hudson, THIS JOURNAL, **69**, 921 (1947).

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

The Isolation of Quercitrin from Peanut Hulls

BY CARL D. DOUGLASS, WILLIAM L. HOWARD[1] AND SIMON H. WENDER

In a search for abundant sources of vitamin P active flavonoid pigments,[2,3] quercitrin, the 3-rhamnoside of quercetin (3,5,7,3′,4′ pentahydroxyflavone) has been isolated from waste peanut hulls.

Lavollay and Neumann[4] report that this substance arrests the autoxidation of epinephrine. Richardson, El-Rafey and Long[5] found quercitrin to be an effective antioxidant for lard and for milk fat.

Quercitrin has previously been isolated from several sources, such as *Quercus tinctoria*[6] and golden rod.[7]

Experimental

Isolation.—The peanuts were grown on a farm near Norman and were harvested about September 1, 1948. They were shelled within a week after harvesting. One thousand ninety grams of peanut hulls was extracted exhaustively with boiling 95% ethanol. After the extract was filtered with suction, using Johns–Manville Celite as a filter-aid, it was concentrated to one-twelfth of its original volume in a flash-type evaporator.[8] The concentrate was next filtered, and water was added dropwise to precipitate a brown resinous material. This brown material was removed by swirling the flask vigorously. The resin adhered to the walls of the flask and the clear, straw-colored supernatant liquid was decanted. More water was added to the supernatant liquid until a yellow precipitate formed. After remaining in the cold for several days, this precipitate was filtered off and dissolved in acetone. Water was added to the acetone solution until incipient precipitation had occurred. The cloudy solution was set aside for three days and then filtered—the precipitate being discarded. To the filtrate, water was again added, this time until a yellow precipitate formed. The precipitate was filtered off and resuspended in water. The suspension was heated on the water-bath until only a small amount of undissolved matter remained. This undissolved material was removed by filtration. On cooling the filtrate, a yellow precipitate separated. This precipitate was recrystallized twice from boiling water.

The resulting yellow solid, after air drying, melted at 185° uncor. Moore reports that quercitrin melts at 185°.[9]

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[1] At present, Rhodes Scholar, Oxford University, Oxford, England.

[2] Rusznyak and Szent-Gyorgy, *Nature*, **138**, 27 (1936).

[3] Bentsath, Rusznyak and Szent-Gyorgy, *ibid.*, **138**, 789 (1936).

[4] Lavollay and Neumann, *Compt. rend.*, **212**, 251 (1941).

[5] Richardson, El-Rafey and Long, *J. Dairy Sci.*, **30**, 397 (1947).

[6] Bolley, *Ann.*, **37**, 101 (1841).

[7] Guthrie, O'Connor, Stansberg and Savich, THIS JOURNAL, **66**, 1794 (1944).

[8] Ciereszko, presented before the Fifth Southwestern Regional Meeting of the American Chemical Society at Oklahoma City, December, 1949.

[9] Moore, *Proc. Chem. Soc.*, **26**, 182 (1910).

From the 1090 g. of hulls, 1.188 g. of the pigment was obtained. This corresponds to a minimal yield of 0.109%.

Color Tests.—The isolated material gave the usual flavonol color tests.

The colors observed in ultraviolet light when the "chromogenic reagent" technique of Wender and Gage[10] was applied, agree with those obtained by these workers. An authentic sample of quercitrin gave identical results.

Absorption Spectrum.—A solution containing 1.4 mg. of the isolated pigment per one hundred ml. of 95% ethanol was used for the determination of the ultraviolet absorption spectrum. The pure solvent was used as a blank in the Beckman Model DU spectrophotometer. The ultraviolet absorption spectrum of authentic quercitrin of like concentration was also determined. Both gave absorption maxima at 255 and 352.5 mμ. Minima were observed at 235 and 280 mu.

Paper Chromatographic Analysis.—When the isolated substance was subjected to the paper chromatographic technique of Wender and Gage,[10] R_f values were observed which corresponded to those of quercitrin in the solvent systems used (phenol, ethyl acetate, *n*-butanol–acetic acid).

Hydrolysis Products.—The pigment was hydrolyzed by boiling a very small portion of it with 0.6% sulfuric acid for one and one-half hours.

L-Rhamnose was identified in the filtrate from the hydrolysis mixture by paper chromatography in *n*-butanol–acetic acid–water. The aglycone, quercetin, was likewise identified in the reaction mixture by this method. It was possible to distinguish quercetin from unhydrolyzed quercitrin by use of the chromogenic sprays.[10]

Acknowledgment.—This investigation was supported by a grant from the Division of Research Grants and Fellowships of the National Institutes of Health, U. S. Public Health Service.

Summary

Quercitrin has been found to be present in waste peanut hulls. A method for its isolation has been described.

NORMAN, OKLAHOMA RECEIVED MARCH 6, 1950

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[10] Wender and Gage, *Science*, **109**, 287 (1949).

[CONTRIBUTION FROM THE CENTRAL LABORATORIES, GENERAL FOODS CORPORATION]

Isochlorogenic Acid. Isolation from Coffee and Structure Studies[1]

BY H. M. BARNES, J. R. FELDMAN AND W. V. WHITE

Early workers on the chemistry of coffee interpreted the green color formed upon the addition of ferric chloride to extracts of unroasted coffee as evidence for the presence of tannic acid. Prior to 1900, this fraction of coffee was known as "caffetannic acid" and was later called "chlorogenic acid" in view of the green color formed when solutions of the acid were made slightly alkaline and exposed to air. In 1907, Gorter[2] isolated the crystalline complex, potassium caffeine chlorogenate, from which he prepared the pure acid. The structure proposed by Gorter for the compound was later disproved by Freudenberg,[3] who proposed a structure that was subsequently established by Fischer and Dangschat[4] and is illustrated in Fig. 1.

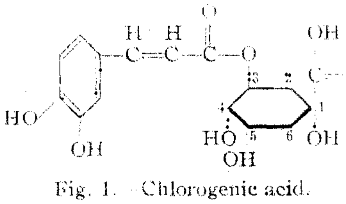

Fig. 1.—Chlorogenic acid.

The usual methods[5] of analysis indicated that the amount of this acid in coffee was about 6%, although neither Gorter[6] nor later workers could isolate more than two-thirds of this amount. Work in this laboratory has indicated that at least one-sixth of the material which shows up in the analyses as chlorogenic acid is markedly different in properties from that described by Gorter. This material has been isolated and purified, and the name "isochlorogenic acid" and the following structure are proposed for it

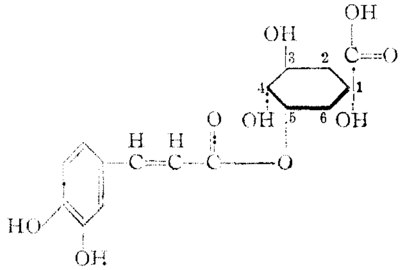

Fig. 2.—Isochlorogenic acid.

Isochlorogenic acid does not form a complex analogous to the crystalline potassium caffeine chlorogenate but is isolated from green coffee extracts by acidification with mineral acid and extraction with butyl acetate, a solvent in which chlorogenic acid is nearly insoluble. The crude acid is further purified by re-extraction of the acid from a solution buffered at *p*H 4.7.

The purity of the preparation is difficult to establish by classical criteria as neither the compound nor any derivative could be obtained in a crystalline form. The reactions tried included partial and exhaustive methylation, acetylation,

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[1] Presented in part at the Atlantic City Meeting of the American Chemical Society in April, 1947.

[2] K. Gorter, *Bull. Dept. Agr. Indes Neerland.*, **14**, 162 (1907); *Ann.*, **358**, 327–348; *ibid.*, **359**, 217–244 (1908).

[3] Karl Freudenberg, *Ber.*, **53B**, 232–239 (1920).

[4] H. O. L. Fischer and Gerda Dangschat, *Ber.*, **65B**, 1037–1040 (1932).

[5] Iodometric method, K. H. Slotta and K. Neisser, *ibid.*, **71B**, 1616 (1938); ultraviolet absorption method, R. G. Moores, D. L. McDermott and T. R. Wood, *Anal. Chem.*, **20**, 620 (1948).

[6] K. Gorter, *Ann.*, **379**, 110 (1911).