Studies on the Leaves of the Family Salicaceae. II.[1] Quercetin-3-glucosiduronic Acid from *Populus grandidentata* Leaves[2]

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In the continuing studies on the evaluation of the lead salts obtained during the purification of glucosides of *Populus* species leaves,[1] the precipitated lead salts obtained by treatment of the hot water extractives of *P. grandidentata* leaves were processed to yield a yellow crystalline compound. Upon hydrolysis with dilute sulfuric acid this compound yielded quercetin and glucuronic acid, and analysis corresponded with a monoglucosiduronic acid of quercetin. The compound is identical with querciturone, a quercetin-glucosiduronic acid of undetermined glycoside substitution, isolated from the leaves of the French bean, *Phaseolus vulgaris*, by Endres and co-workers[3] and by Marsh[4] and with purified miquelianin (quercetin-3-glucosiduronic acid) isolated in a somewhat impure state from the leaves of the Japanese evergreen shrub, *Gaultheria miqueliana*, by Sasaki and Watanabe.[5] Thus, the structure of the quercetin-monoglucosiduronic acids from the three botanical species is established as quercetin-3-glucosiduronic acid, and we suggest that this name be applied to all three products.

Experimental[6]

Quercetin-3-glucosiduronic Acid from *P. grandidentata* Leaves.—An amount of 820 g. (oven-dry basis) of leaves freshly obtained from a bigtooth aspen (*P. grandidentata*) felled in Oneida County, Wisconsin, on June 14, 1962, was digested with 40 l. of boiling water, filtered through cloth, and processed with lead subacetate exactly as described earlier.[1] The filtered lead precipitate was suspended in 3 l. of water with vigorous stirring, saturated with hydrogen sulfide, heated to boiling, and filtered hot through a Celite pad. The dark red filtrate was concentrated to 200-ml. volume and allowed to stand at room temperature. Crystalline material separated after a few days. After several weeks, the reddish orange crystals were filtered. The yield was 3.03 g. This crude product was recrystallized several times from water in the presence of decolorizing carbon to give pale yellow needles (2.01 g.) shrinking at 135°, melting at about 170° with gas evolution, solidifying at about 190°, and finally decomposing to a black melt at about 260–265°. Paper chromatography in 4:1:5 butanol–acetic acid–water followed by spraying with 2% ethanolic sodium hydroxide indicated three materials which gave yellow spots fluorescing strongly under ultraviolet light. The crude product was dissolved in 25 ml. of boiling 95% ethanol, treated with decolorizing carbon, filtered hot, diluted with 10 ml. of chloroform, and allowed to stand in the refrigerator. Orange colored crystals separated after a short time and were filtered. These melted at 160°. The pale yellow filtrate was allowed to evaporate spontaneously, and the yellow residue was recrystallized from water to give 1.11 g. of pale yellow crystals. These were dehydrated *in vacuo* in a drying pistol at 100° over phosphorus pentoxide to yield 1.00 g. of light yellow crystals melting at 193–195° with gas evolution, resolidifying immediately to a yellow product which turned brown at 210° and finally melted with decomposition at 260–262°, $[\alpha]^{25}D$ −48.1° (*c* 1.67 in 50% pyridine), $[\alpha]^{26}D$ −21° (*c* 1.0 in absolute ethanol). The infrared absorption spectrum contained bands at 2.95, 5.62, 6.03, 6.23, 6.38, 6.68, 6.86, 7.36, 7.74, 8.30, 8.63, 8.90, 9.30, 9.50, 9.81, 10.05, 10.62, 11.42, 12.25, 12.50, and 12.70 μ, and was identical with those of authentic querciturone[7] and authentic miquelianin[8] which had been purified further by the ethanol–chloroform procedure employed for our product. Marsh[4] reported $[\alpha]D$ −50° (in 50% pyridine), and Sasaki and Watanabe[5] reported $[\alpha]^{10}D$ −22.93° (in anhydrous ethanol) for their somewhat impure product.

Hydrolysis of the compound with *N* sulfuric acid for 90 min. yielded yellow crystals melting at 309–310° and not depressing the melting point of a mixture with authentic quercetin. The infrared spectra of the yellow compound and of quercetin were identical. The aqueous filtrate from the quercetin was neutralized with excess barium carbonate and filtered. The filtrate was concentrated, and the concentrate gave a strong uronic acid test with naphthoresorcinol. Paper chromatography indicated glucuronic acid. The orginal quercetin-glucosiduronic acid liberated carbon dioxide from sodium bicarbonate solution.

Infrared Spectra.—Infrared absorption spectra were obtained with a Perkin-Elmer Model 21 recording spectrophotometer using a sodium chloride prism and potassium bromide pellets prepared by hand grinding with sample before pressing.

(1) For paper I of this series, see I. A. Pearl, S. F. Darling, and O. Justman, *J. Org. Chem.*, **27**, 2685 (1962).

(2) A portion of a paper presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., March 31–April 5, 1963.

(3) C. Endres, R. Huttel, and L. Kaufmann, *Ann.*, **537**, 205 (1939).

(4) C. A. Marsh, *Nature*, **176**, 176 (1955).

(5) T. Sasaki and Y. Watanabe, *J. Pharm. Soc. Japan*, **76**, 1893 (1956).

(6) All melting points are uncorrected. Infrared absorption spectra were determined by Mr. Lowell Sell of The Institute of Paper Chemistry Analytical Department.

(7) Kindly supplied by Dr. C. A. Marsh of Rowett Research Institute, Bucksburn, Aberdeen, Scotland.

(8) Kindly supplied by Dr. Toyosaku Sasaki, Hyogo University of Agriculture, Sasayama, Hyogo-ken, Japan.