Constituents of the Fruits of *Viburnam opulus*

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Fresh unripe fruits of the plant were used in this study. Although the fruits are quite bitter, no glycosides were found.

VIBURNUM is a genus of mostly ornamental trees and shrubs of the family *Caprifoliaceae*. However, the dried bark of *V. opulus* L. was listed at one time in the U.S.P. as a remedy for uterine disorders. *Viburnam opulus*, also called the European cranberry bush, is a large deciduous shrub which grows wild, reaches a height of about 12 ft., and bears heads of white flowers and bright red fruit when fully ripe.

In 1922, Heyl (1) reported the isolation of two phytosterols of molecular formulas, $C_{33}H_{56}O_6$ and $C_{27}H_{46}O$, and an acid, m.p. 200–202°, from the bark. A further study by Powers and Powers (2) led to the isolation of α- and β-amyrin from the bark. Egger (3) showed the presence of two flavonol glycosides, astragalin and paeonoside, in the blossoms.

The present investigation is a pursuance of a program of screening the flora of Connecticut for glycosidal principles.

Ethanol extraction of the fruits and subsequent concentration gave an aqueous solution which was continuously extracted with ether and ethyl acetate successively. From the ethyl acetate soluble fraction chlorogenic acid was isolated and identified. The ether soluble extractive yielded β-sitosterol and the triterpene acid, ursolic acid. Attempts to isolate glycosides from the aqueous portion by charcoal adsorption techniques (4) failed.

EXPERIMENTAL[1]

Extraction.—Fresh unripe fruits (1 Kg.) of *V. opulus* L. were homogenized in a blender with 95% ethanol (2 L.) and refluxed for 6 hr. The aqueous ethanol extract was concentrated to about 300 ml. and the solution was continuously extracted, first with ether (0.5 L.) and then with ethyl acetate (0.5 L.).

Isolation of Chlorogenic Acid.—The ethyl acetate extract was evaporated to give a dark brown gum which was re-extracted with 300 ml. of ethyl acetate saturated with water. Concentration of this solution to 75 ml. gave 2 Gm. of a slightly colored crystalline solid. Further crystallization from water (decolorizing with Norit) yielded chlorogenic acid, m.p. 212–213°. [Lit. (5) m.p. 208°.] The compound was identical in every respect (melting point, infrared, and ultraviolet data) with an authentic commercial sample.

Isolation of β-Sitosterol and Ursolic Acid.—The ether extract was washed with aqueous sodium bicarbonate (1 L. of 10%), with aqueous sodium hydroxide (1 L. of 2%), and finally with water. It was dried over sodium sulfate; the ether was evaporated, and the residue was chromatographed over 50 Gm. of neutral alumina. Elution with 1 L. of benzene and evaporation of the benzene yielded a gum which was crystallized from hexane and then from methanol to yield 40 mg. of β-sitosterol, m.p. 139°, $[\alpha]_D$ −33.5°; lit. (6) m.p. 140°, $[\alpha]_D^{25}$ −37°. The compound and its benzoate ester, m.p. 148°, $[\alpha]_D$ −12.4°, [lit. (6) m.p. 146–147°, $[\alpha]_D^{25}$ −13.8] were identical in all respects (melting point and infrared data) with authentic samples.

Acidification of the sodium bicarbonate washings gave only traces of a red oil which could not be crystallized.

Acidification of the sodium hydroxide washings and extraction with ether yielded a semisolid triterpene acid which gave successive colors of pink, blue, and green with the Liebermann-Burchard test. The acid was methylated with diazomethane (prepared from *N,N'*-dinitroso-*N,N'*-dimethyl terephthalamide, Dupont EXR-101, according to the manufacturers instructions), and the methyl ester was chromatographed over 50 Gm. of neutral alumina. Elution with 0.5 L. of benzene and evaporation of the solvent yielded a gum which was crystallized from aqueous ethanol to yield 100 mg. of methyl ursolate, m.p. 168–169°. [Lit. (7) m.p. 171°.] It was identical in every respect (melting point and infrared data) with an authentic sample.

An *acetate* of methyl ursolate was prepared in acetic anhydride and pyridine. Decomposition of the reaction mixture and crystallization of the product from ethanol yielded the acetate of methyl ursolate, m.p. 243–245°. [Lit. (7) m.p. 246–247°.] The compound was identical in every respect (melting point and infrared data) with an authentic sample.

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[1] Melting points are uncorrected. Optical rotations were determined in chloroform at room temperature. Infrared spectra were measured in potassium bromide disks.