under the above conditions but benzoquinone (and perhaps the intermediate quinones) can be. If the concentration of cupric ion is significantly diminished such oxidations take place and the yield is less. In the presence of 0.01 mole of cupric acetate the oxygen-absorption was about the same but the bisaminoquinone was then obtained in 72–76% yield.

THE WELLCOME RESEARCH LABORATORIES
TUCKAHOE 7, NEW YORK RECEIVED OCTOBER 14, 1947

Isolation of a Saponin from the Leaves of *Solidago canadensis* L.

BY R. C. BURRELL AND FORREST G. HOUSTON

In the course of the investigation of the chemical composition of several common weeds, leaves of *Solidago canadensis* L. were examined for the possible presence of a saponin. There are several reports of the recognition of both acid and neutral saponins in various other species of goldenrod,[1,2,3] but none of actual isolation.

Experimental

Method of Isolation.—Leaves of *Solidago canadensis* L. were gathered in late July, 1946, dried at room temperature, and ground to a fine powder. A 230-g. sample of this powder in a small cloth bag was exhaustively extracted, first with acetone, then with ether and finally twice with 95% ethyl alcohol. The combined alcoholic extracts were concentrated to a small volume (about 100 cc.) and 5 volumes of ether added with shaking. This produced a gummy, white precipitate. After decanting the ether, this precipitate was dissolved in the least possible amount of hot methanol. This solution, which had a light yellow color, was treated with acetone added from a large pipet while shaking the mixture vigorously. A flocculent white precipitate formed from which the liquid was decanted. The precipitate was once more dissolved in hot methanol and the acetone precipitation repeated. The final white flocculent precipitate was amorphous and very hygroscopic. It produced a stable creamy foam with water and stabilized an emulsion of kerosene in water. Fehling solution showed no reduction.

Preparation of the Sapogenin.—The moist saponin preparation was brought into solution in 50 cc. of 10% hydrochloric acid, 25 cc. of 95% ethyl alcohol added to reduce foaming and this solution refluxed for three hours. A grainy precipitate formed which consisted of microscopic, colorless needles. The supernatant liquid gave a positive Fehling reaction. The crystals were filtered off and brought into solution by refluxing with methanol. This solution was concentrated to about 50 cc. and on cooling some 500 mg. of colorless needles were isolated, representing a yield of 0.22% of the dried leaves.

Properties of the Sapogenin.—The crystals, which melted at 310–315° with decomposition, were slightly soluble in ethanol methanol, acetone, ether and ethyl acetate, insoluble in water, but dissolved easily in cold concentrated sulfuric acid, giving a faintly yellow colored solution which became deep red on warming or on the addition of a few drops of acetic anhydride, suggesting the behavior of a triterpene. The Rast method indicated a molecular weight of approximately 500.

Anal. Calcd. for $C_{30}H_{50}O_5$ (490.4): C, 73.41; H, 10.28. Found: C, 72.97; H, 10.02.

Insolubility in hot alkali and a neutral reaction in alcoholic solution indicates the absence of a carboxyl group. The acetate was prepared as flat rectangular crystals which melt at 182–183°. A search of the literature failed to reveal a compound approximating $C_{30}H_{50}O_5$ which possesses the above properties.

(1) L. Krober, *Heil-gewurs Pflanzen*, **12**, 131 (1930).
(2) F. P. Rey, *Rev. farm. (Buenos Aires)*, **74**, 93 and 131 (1932).
(3) E. Wagner, *Seifensieder-Ztg.*, **68**, 35 (1941).

CONTRIBUTION FROM THE
DEPARTMENT OF AGRICULTURAL CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO RECEIVED SEPTEMBER 27, 1947

The Infrared Spectrum of Polyvinyl Alcohol

BY ELKAN R. BLOUT AND ROBERT KARPLUS

Despite two previously reported measurements on the infrared spectrum of polyvinyl alcohol[1,2] we should like to record some of our data, using carefully purified samples, because of their possible bearing on the details of the molecular structure of this material. The presence of chemical groups and arrangements other than those of the poly-1,3-glycol $\left[\text{—CH}_2\text{—CH(OH)—}\right]_n$ has been shown by chemical investigation. For example, terminal acetal,[3] keto or ketal[4] and 1,2-glycol groups[5] have been shown to be present in low percentage in the material known as polyvinyl alcohol.

The infrared spectra for the region 700–4000 cm.$^{-1}$ of carefully purified and dried films of polyvinyl alcohols of various degrees of polymerization are shown in Fig. 1. These spectra correspond in most salient features to those reported by Thompson and Torkington[2] except that there is no evidence of a band at 1650 cm.$^{-1}$. Other samples prepared so that water was not rigidly excluded at the time of measurement show a characteristic absorption band in this region. Another band typical of incompletely hydrolyzed polyvinyl alcohol is seen at 1710 cm.$^{-1}$ in Fig. 2, curve A. This figure also shows the effect of careful acid hydrolysis (removal of residual acetate groups) and drying on the spectrum in the region 1400–1800 cm.$^{-1}$.

It is difficult to correlate absorption bands definitely with molecular structure except through mathematical analysis. In the spectra shown in Fig. 1 the assignments of the bands above 1400 cm.$^{-1}$, *viz.*, 3350 cm.$^{-1}$ (O—H stretching), 2940 cm.$^{-1}$ (C—H stretching) and 1435 cm.$^{-1}$ (C—H bending) seem reasonable, based on analogy with the spectra of simple molecules and on the calculated characteristic frequency of various molecular groups.[6] In the region 1000 cm.$^{-1}$ to 1400 cm.$^{-1}$ five bands are observed at 1380, 1330, 1240 1135 and 1085 cm.$^{-1}$ which are probably associ-

(1) Barnes, Liddel and Williams, *Ind. Eng. Chem., Anal. Ed.*, **15**, 659 (1943).
(2) Thompson and Torkington, *Trans. Far. Soc.*, **41**, 246 (1945).
(3) Marvel and Inskeep, THIS JOURNAL, **65**, 1710 (1943).
(4) Clarke and Blout, *J. Pol. Sci.*, **1**, 419 (1946).
(5) Flory and Leutner, "The Occurrence of Head-to-Head Arrangements of the Structural Units in Polyvinyl Alcohol and Acetate," paper presented at the New York meeting of the American Chemical Society, September 15, 1947.
(6) Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., New York, N. Y., 1945.