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.

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

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[1] L. Krober, *Heil-gewurz Pflanzen*, **12**, 131 (1930).

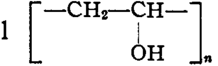
[2] F. P. Rey, *Rev. farm.* (*Buenos Aires*), **74**, 93 and 131 (1932).

[3] E. Wagner, *Seifensieder-Ztg.*, **68**, 35 (1941).

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



$\left[\begin{array}{c}-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-\end{array}\right]_n$

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-

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[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.

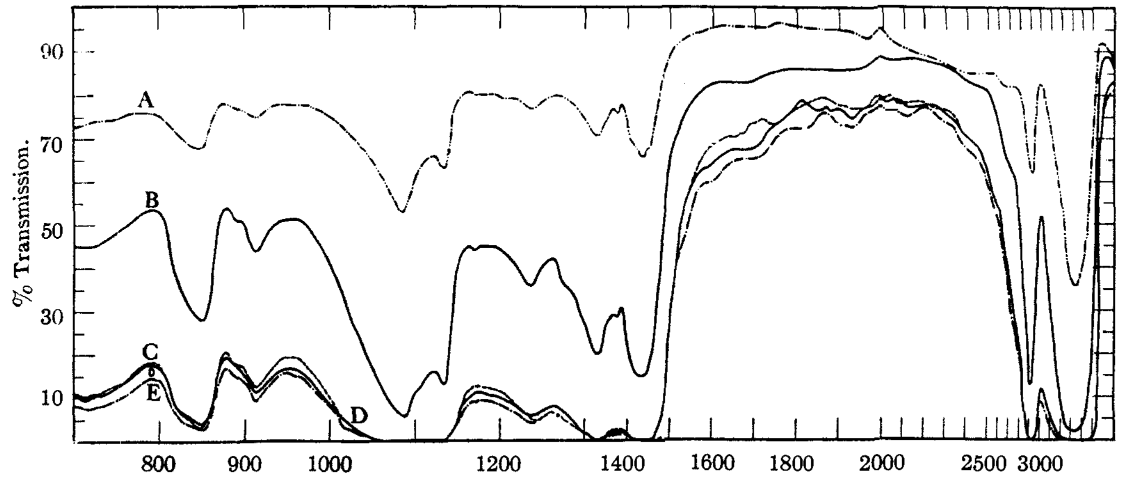

Fig. 1.—Polyvinyl alcohols after acid hydrolysis and drying: curve A, ··—··—··—, JRG-8200 (0.0002″ film); curve B, ————————, RH-391 (0.0003″ film); curve C, — — — — — — — —, RH-393 (0.001″ film); curve D, ———————, RH-391 (0.001″ film); curve E, ·—·—·—·, RH-349 (0.001″ film).

ated with the motions of the substituent groups in the material, the last band arising from stretching of the C—O bond.[7] The absorption bands below 1000 cm.$^{-1}$ cannot be identified except as due to motions of the carbon skeleton. We find that the band at 1240 cm.$^{-1}$ is not removed by acid hydrolysis although a band at 1265 cm.$^{-1}$ in unpurified samples is removed simultaneously with the 1710 cm.$^{-1}$ band. This fact suggests that the 1240 cm.$^{-1}$ band is not associated with the acetate groups of polyvinyl alcohol, as has been previously pointed out.[2]

It is interesting to note that the band at 1380 cm.$^{-1}$, which is present even after repeated acid hydrolysis, is located in the region characteristic of the symmetrical deformation frequency of the C—CH_3 group.[6,8,9] This suggests the possibility that either the polymer contains methyl groups branching off the chain, or the chain ends are methyl groups or perhaps both.

Experimental

Materials.—The various polyvinyl alcohols were obtained as white powders.[7,10] Since they are prepared by the hydrolysis of polyvinyl acetate, further purification was undertaken to assure complete absence of residual acetate groups. This was accomplished by hydrolyzing 5% aqueous solutions with 0.02 N hydrochloric acid for twenty-four hours at 90° followed by precipitation and thorough washing with ethanol. The material so obtained was air-dried, then dissolved in water (approximately 15% solution) and cast into thin films (0.0002″–0.001″ thick) on glass plates at room temperature. To remove the

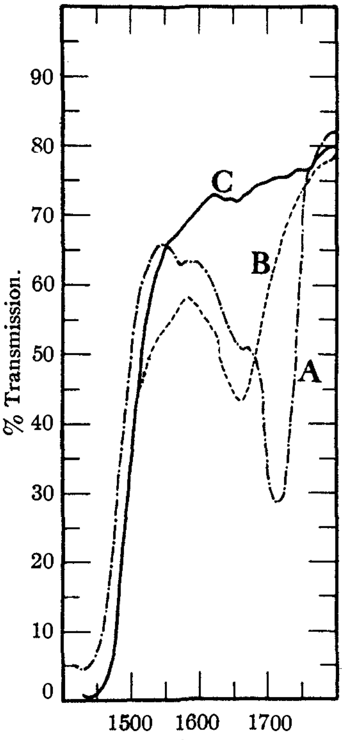

Fig. 2.—Polyvinyl alcohol (JRG-8200): curve A, ·—·—·—, cast as received (0.0006″ film); curve B, — — — — — —, cast after acid hydrolysis (0.001″ film); curve C, ————————, dried film cast after acid hydrolysis (0.001″ film).

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[7] *Cf.* analogous compounds in refs. 1 and 6.

[8] Thompson and Torkington, *Proc. Roy. Soc.* (*London*), **184**, 3 (1945).

[9] Fox and Martin, *ibid.*, **175**, 208 (1940).

[10] All polyvinyl alcohols referred to in this paper were obtained from E. I. du Pont de Nemours and Co. The designations used are those of the du Pont Co.

Grade	Viscosity	Approximate viscosity centipoises of 4% in aqueous solutions at 20°C.	%Residual[a] acetate
RH-393	Low	5	1
RH-349	Medium	24	1
RH-391	High	55	1
JRG-8200[b]	High	115	4

[a] After acid hydrolysis as described below there were no acetate groups detectable by saponification. [b] Experimental sample obtained through the courtesy of Dr. R. E. Burk, E. I. du Pont de Nemours & Co., Wilmington, Delaware.

5-10% of retained water the films were heated at 160° for one hour immediately before spectral analysis. Determinations showed that during the time it took to measure the spectra no appreciable absorption of moisture occurred.

Instrument.—The spectral measurements[11] were made on a Perkin–Elmer infrared spectrometer Model 12-A using a 40-cycle chopper, a Strong nickel-strip bolometer, an a. c. amplifier and a Brown Instrument Company potentiometer. The data were obtained on a point-to-point basis, the points being taken from 5 to 10 cm.$^{-1}$ apart at frequencies up to 1900 cm.$^{-1}$ and at larger intervals at higher frequencies.

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[11] We are indebted to Mr. Dwight Merrill for some of the spectral measurements.

CHEMICAL RESEARCH LABORATORY
POLAROID CORPORATION
CAMBRIDGE 39, MASSACHUSETTS RECEIVED JULY 18, 1947

A Convenient Synthesis of Octahydropyrrocoline and 2-(γ-Hydroxypropyl)-piperidine

BY V. BOEKELHEIDE AND S. ROTHCHILD[1]

It has been found that octahydropyrrocoline, which has previously been prepared in poor yield by procedures involving three or more steps,[2] can be obtained readily in excellent yield by the direct hydrogenation of 2-(γ-hydroxypropyl)-pyridine[3] at 200° and 2500 lb. pressure with Raney nickel catalyst.

When the reduction was carried out at 125° instead of 200°, the product was not octahydropyrrocoline but rather 2-(γ-hydroxypropyl)-piperidine. The yield of 2-(γ-hydroxypropyl)-piperidine is practically quantitative and this is undoubtedly the best method for its preparation.[4] At temperatures intermediate between 125 and 200° the reduction gave mixtures of octahydropyrrocoline and 2-(γ-hydroxypropyl)-piperidine. Although it is probable that 2-(γ-hydroxypropyl)-piperidine is an intermediate in the formation of octahydropyrrocoline, 2-(γ-hydroxypropyl)-piperidine is not readily affected by heat and can be distilled repeatedly without change.

Experimental[5]

Octahydropyrrocoline.—A mixture of freshly distilled 2-(γ-hydroxypropyl)-pyridine (9.0 g., 0.066 mole), Raney nickel (2 g.), and absolute alcohol (10 cc.) was heated at 200° with shaking under an initial pressure of 2540 p. s. i. of hydrogen. At the end of one hour the drop in hydrogen pressure corresponded to that calculated. After removal of the catalyst by filtration, the oily product was distilled yielding 6.4 g. (78%) of a colorless oil; b. p. 71–72° at 32 mm.; $n^{21.2}\text{D}$ 1.4702.

For purposes of identification, there were prepared the following derivatives: picrate, m. p. 228–9° (lit.,[2] m. p. 226°, 231–232°); gold chloride double salt, m. p. 188–192° (lit.,[2] m. p. 191–193°).

The methiodide of octahydropyrrocoline was formed in benzene and proved to be unstable in the presence of air. The amorphous solid, obtained from benzene, decomposed at 280–283° and was analyzed directly without further purification.

Anal. Calcd. for $C_9H_{18}NI$: C, 40.46; H, 6.79. Found: C, 40.00; H, 7.10.

2-(γ-Hydroxypropyl)-piperidine.—A mixture of freshly distilled 2-(γ-hydroxypropyl)-pyridine (14.0 g., 0.102 mole), Raney nickel (2 g.), and absolute alcohol (4 cc.) was heated at 125° with shaking under an initial pressure of 2500 p. s. i. of hydrogen. At the end of four hours the pressure drop corresponded to that calculated. After removal of the catalyst and solvent, the product was distilled yielding 12.5 g. (85%) of a colorless oil; b. p. 101–102° at 3 mm.; $n^{21.5}\text{D}$ 1.4882.

For identification there was prepared the hydrochloride, m.p. 128–129° (lit.,[2b] m. p. 127–128°), and the mercuric chloride complex, m. p. 180–182° (lit.,[2a] m. p. 182–183°).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROCHESTER
ROCHESTER, NEW YORK RECEIVED NOVEMBER 14, 1947

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[1] Aided by a Grant from the National Foundation for Infantile Paralysis.

[2] (a) Loeffler and Kaim, *Ber.*, **42**, 94 (1909); Loeffler and Flugel *ibid.*, **42**, 3423 (1909), and Tullock and McElvain, THIS JOURNAL, **61**, 961 (1939); (b) Clemo and Ramage, *J. Chem. Soc.*, 2969 (1932); (c) Wibaut and Beets, *Rec. trav. chim.*, **60**, 905 (1940); (d) Diels and Alder, *Ann.*, **498**, 16 (1932).

[3] 2-(γ-Hydroxypropyl)-pyridine is available from Reilly Tar and Chemical Co., Indianapolis, Indiana.

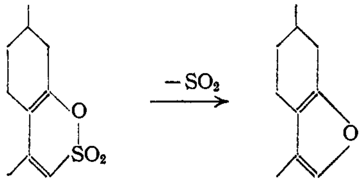
[4] Previous methods for preparing 2-(γ-hydroxypropyl)-piperidine are given in ref. (2a).

[5] Analysis by Mrs. G. L. Sauvage. All melting points are corrected.

The Sulfonation of Mesityl Oxide

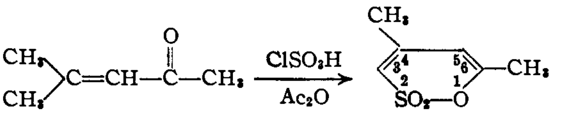
BY RICHARD H. EASTMAN AND DON GALLUP[1]

In seeking a convenient method for the synthesis of alkylated furans we have sought to extend to simple α,β-unsaturated ketones and aldehydes the observation of Treibs[2] that pulegone on treatment in acetic anhydride at ice temperature with concentrated sulfuric acid yields cyclopulegenol-sulfonic ester (I) from which menthofuran (II) is obtained in excellent yield on pyrolysis with zinc oxide at atmospheric pressure.



I II

We have attempted the sulfonation under varied conditions of concentration and temperature, using both sulfuric acid and chlorosulfonic acid, of crotonaldehyde, cyclohexylidenecyclohexanone, 3,4-dimethylhexene-3-on-2 and mesityl oxide. A clean-cut reaction was obtained only in the case of the sulfonation of mesityl oxide which on sulfonation with chlorosulfonic acid in acetic anhydride gave the cyclic sulfonic ester III in good yield. Pyrolysis of the cyclic sulfonic ester of mesityl oxide (III) at atmospheric pressure,



III

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[1] The work reported here is taken from a thesis presented by Don Gallup to Stanford University in partial fulfillment of the requirements for the degree of Master of Science.

[2] W. Treibs, *Ber.*, **70B**, 85 (1937).