cells permitted the extension of the data to longer wave lengths. Also, it should be noted that Coblentz made his measurements with melted samples while in the present study sugar solutions were used. Furthermore, small bands were found at 6.0 μ and 6.3 μ which were not reported by Coblentz. In the case of levulose, agreement between Coblentz' data and those reported here is still less satisfactory. There is agreement on the 3.3 μ band, but Coblentz reports a band at 5.85 μ which is not noted here, and another at 5.3 μ reported here is not shown by Coblentz. Again, thinner cells permitted the extension of this study to longer wave lengths.

The effect of the solvent on the absorption of the sugars is very slight; also, no variation of the spectra of the solutions with time was detected.

Summary

The infrared absorption spectra for four furan derivatives, four pentoses and four hexoses between 2 and 12 μ have been mapped and the results compared with Raman and infrared data from other sources. Several bands were common to all the furans. Data on sugar solutions are in fair agreement with earlier results obtained in studies of melted compounds. No pronounced differences occurred between the spectra of any of the sugars studied.

GAINESVILLE, FLA. RECEIVED JULY 28, 1938

[CONTRIBUTION FROM NAVAL STORES RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

The Dihydroabietic Acids from So-called Pyroabietic Acids

BY E. E. FLECK AND S. PALKIN

In a previous paper it has been shown that so-called "α-pyroabietic acid" prepared from *l*-abietic acid by the catalytic method, was a mixture of dehydro-, dihydro- and tetrahydroabietic acids.[1] It was pointed out, however, with regard to the *di*hydro acid ($[\alpha]^{20}\text{D}$ $-3°$) isolated, that while the combustion data were in good agreement with those calculated for the dihydro compound, the rotation did not conform to that indicated by the Biot relationship[2] in that the latter pointed to a dihydroabietic acid of high positive rotation.

This compound ($[\alpha]^{20}\text{D}$ $+108°$) has now been isolated by first removing the tetrahydroabietic acid as the insoluble ammonium salt and then the dehydroabietic acid as the crystalline methyl ester. The non-crystalline residue of methyl esters was saponified with 10% *n*-butyl alcoholic potassium hydroxide to obtain the new dihydroabietic acid.

Another dihydroabietic acid ($[\alpha]^{20}\text{D}$ $+ 9.0°$, m. p. 193–194°) from α-pyroabietic acid mixture prepared by heat, without catalyst has been reported recently by Ruzicka *et al.*[3]

Further work on the previously reported dihydro compound ($[\alpha]^{20}\text{D}$ $-3°$, m. p. 130–131°), which was isolated by partial sulfonation of the non-crystalline portion of the mixed methyl esters and subsequent hydrolysis of the unsulfonated part, has now been found to be a lactone, as it took up no alkali on direct titration. This lactone was found to be identical with that reported by Hasselstrom, *et al.*,[4] who also obtained it as a sulfonation by-product, and with that reported earlier by Ruzicka, *et al.*,[5] who prepared it by the action of hydrobromic acid on dihydroabietic acid.

By treatment with butyl alcoholic potassium hydroxide, the lactone yielded hydroxytetrahydroabietic acid, m. p. 164–165°, identical with that reported by the above authors.

Experimental Part

Fifty grams of *l*-abietic acid was converted into "pyroabietic" acid mixture at 225° as previously described.[1] The yield was 47 g. of a product that melted at 166–168° and showed $[\alpha]^{20}\text{D}$ $+62°$ in absolute alcohol. This mixture was dissolved in 180 cc. of alcohol and 425 cc. of 0.4 *N* ammonium hydroxide. On standing overnight at room temperature fine needles separated which consisted chiefly of tetrahydroabietic acid. These were removed by filtration. A second and third crop of crystals was obtained from the mother liquor at intervals of several days. The crystalline ammonium salts were recrystallized and the mother liquors were united with the original filtrate. The combined mother liquors were evaporated to dryness on the

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(1) Fleck and Palkin, THIS JOURNAL, **60**, 921 (1938).

(2) *Ibid.*, citation 11, p. 924.

(3) Ruzicka, Bacon, Sternbach and Waldmann, *Helv. Chim. Acta*, **21**, 595–596 (1938).

(4) Hasselstrom, Brennan and McPherson, THIS JOURNAL, **60**, 1267 (1938).

(5) Ruzicka, Meier, Waldmann and Hösli, *Helv. Chim. Acta*, **5**, 333 (1922); **16**, 139 (1933).

steam-bath. The residue was taken up in ether and shaken, first with dilute hydrochloric acid, and then with water. The ether was distilled and the residue (19.5 g.) was esterified with diazomethane in the usual manner.

The solvents were removed under reduced pressure and the residue was taken up in methyl alcohol. The solution was cooled to 0° and water was added until the solution became cloudy. On standing several days at 0° the crystalline methyl ether of dehydroabietic acid was deposited. By addition of more water to the filtrate a semi-crystalline deposit was obtained. The supernatant liquid was decanted and the methyl alcohol distilled under reduced pressure.

Nine grams of the resulting oil was refluxed for three hours with 90 cc. of *n*-butyl alcohol and 9 g. of potassium hydroxide. The butyl alcohol was removed by steam distillation. When the residue was cooled an amorphous potassium salt separated. Ether was added to the mixture and the aqueous layer was removed. This aqueous layer did not contain an appreciable amount of potassium salt of dihydroabietic acid. The ether solution was then shaken out with 0.25 *N* sodium hydroxide. The aqueous extract was shaken twice with fresh ether and then the dihydroabietic acid was isolated by addition of dilute hydrochloric acid, extraction with ether and evaporation of the solvent.

Eight grams of this light yellow product was dissolved in 35 cc. of alcohol and 50 cc. of 0.4 *N* ammonium hydroxide. On standing overnight 1.3 g. of stout prisms separated. The free acid was liberated as outlined above and the residue was recrystallized from alcohol. The final product melted at 174-176° and gave a yellow color with tetranitromethane: $[\alpha]^{20}_{D}$ +108°; *c*, 2.043% in absolute alcohol.

Anal. Calcd. for $C_{20}H_{32}O_2$: C, 78.88; H, 10.60; neut. equiv., 304.3. Found: C, 78.70, 79.00; H, 10.55, 10.32; neut. equiv., 310.

52.1 mg. of substance was dissolved in 10 cc. of alcohol and directly titrated with 0.1 *N* sodium hydroxide against phenolphthalein: neutralization equivalent, 310; calcd., 304.3.

Hydroxytetrahydroabietic Acid.—A solution of 50 mg. of the lactone in 10 cc. of 10% *n*-butyl alcoholic potassium hydroxide was refluxed for five hours. The butyl alcohol was removed by steam distillation, the aqueous solution diluted with water and extracted three times with ether to remove any neutral material. The aqueous solution was then made acid to litmus and neutral to congo red by addition of dilute acetic acid. The crystalline precipitate which separated was extracted with ether, the ether solution washed with water and the solvent evaporated. The residue after recrystallization from dilute methyl alcohol had a melting point of 164–165°.

Anal. Calcd. for $C_{20}H_{34}O_3$: C, 74.47; H, 10.63. Found: C, 74.25; H, 10.88.

Summary

A dihydroabietic acid of high positive rotation has been isolated from so-called "α-pyroabietic acid" prepared by the catalytic method.

Another compound of the same elemental composition, previously thought to be a dihydro compound, was found to be a lactone.

WASHINGTON, D. C. RECEIVED JULY 29, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Vinyl Halide Polysulfones. Peracetic Acid as a Catalyst for the Reaction between Sulfur Dioxide and Olefins[1]

BY C. S. MARVEL AND F. J. GLAVIS

Polysulfones have been obtained from many common olefins and olefin derivatives and sulfur dioxide by using various organic peroxides to catalyze the reaction. However, up to this time no descriptions of the polysulfones prepared from vinyl chloride and vinyl bromide have appeared. Solonina[2] and Staudinger and Ritzenthaler[3] report failures to obtain the addition reaction between vinyl chloride and sulfur dioxide. Recently Frey, Fitch and Snow[4] intimate that the reaction occurs readily although they do not give the details of the preparation or a complete description of the product.

We have found that vinyl chloride and vinyl bromide will combine with sulfur dioxide to give polysulfones which have two vinyl units for each sulfur dioxide unit. In this respect they differ from all other olefins, olefin derivatives, or acetylenes which have been examined previously.

The addition reaction appears to require an especially effective catalyst and in our early experiments could only be brought about in the presence of an unusually "active" sample of paraldehyde which contained peroxides.

A closer examination of the paraldehyde samples which were tried as catalysts showed that the ones which would cause the reaction to run smoothly not only contained peroxides but also were strongly acidic and showed absorption

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[1] Paper No. VIII. For the seventh communication see THIS JOURNAL, **60**, 1450 (1938).

[2] Solonina, *J. Russ. Phys.-Chem. Soc.*, **30**, 826 (1898); *Chem. Zentr.*, **70**, I, 248 (1899).

[3] Staudinger and Ritzenthaler, *Ber.*, **68B**, 455 (1935).

[4] Frey, Fitch and Snow, U. S. Patent 2,114,292 (1938).