tations of the last few fractions were 0°, +3°, +12°, +29°, +44°, +57°, +88° and +102°. From these rotations and the ultraviolet absorption curves of these fractions it was concluded that the first fraction was the salt of isodextropimaric acid, the last that of neoabietic acid, and the middle fractions were mixtures of salts of neoabietic and abietic acids and acids that do not demonstrate absorption in the ultraviolet region.

Summary

The composition of the acid fraction of American gum oleoresin from *Pinus palustris* has been determined fully for the first time using such techniques as the amine salt method, ultraviolet absorption spectrum technique, and the Diels–Alder addition of maleic anhydride. In addition to the already known levopimaric and dextropimaric acids and a dihydroabietic acid, the following acids were shown to be present as primary acids in oleoresin: neoabietic, abietic, isodextropimaric and dehydroabietic acids.

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[CONTRIBUTION FROM HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

Resin Acids. VI. Kraft's Proabietic Acid,[1] a Mixture of Primary Resin Acids

BY GEORGE C. HARRIS AND JACQUELINE SPARKS

The purity and homogeneity of Kraft's proabietic acid was suspected for the following reasons: (1) its preparation involved only the concentration of the dextrorotatory constituents in the oleoresin after removal of as much levopimaric acid as possible by fractional crystallization, a technique shown to be inoperable in resin acid chemistry, (2) the height of the maximum at 243 mμ, log $K_{\mathrm{molar}} = 3.86$, for the substance was too low for absorption maxima of pure resin acids in that region, 243 mμ, and (3) the irregularities in the ultraviolet absorption curve between 265 and 278 mμ indicated the presence of residual levopimaric acid and some dehydroabietic acid. In the light of the first reason, the isolation of the dextrorotatory neoabietic acid,[2] $[\alpha]^{24}\mathrm{D}$ +159°, from oleoresin in 15–20% yield cast further doubt on the homogeneity of proabietic acid.

The acid prepared in this Laboratory was similar in physical constants (melting point 159–162°, and rotation $[\alpha]^{24}\mathrm{D}$ + 10°) to that reported by Kraft with exception of the position of the intense band in the ultraviolet absorption spectrum of the substance. Kraft's acid demonstrated its most intense band of absorption at 243 mμ, $\alpha = 24.3$, and ours at 250 mμ, $\alpha = 27.0$. A discrepancy in the most intense band of absorption of abietic acid was also described in an earlier paper.[3] Kraft reports it as being at 237.5 mμ and we have found it repeatedly to be at 241 mμ.[2] These differences are not alarming inasmuch as Kraft's work was done on a Hilger-type apparatus whereby transmission was determined by measurements made on a photographic plate and ours was done with a Beckmann spectrophotometer which utilizes a photoelectric cell and gives accurate determinations below 250 mμ, the region in which a Hilger-type apparatus is inaccurate.

In working the oleoresin to obtain the crystalline acids, 80% aqueous acetone was used more effectively than petroleum ether[4] to obtain the same type of acid mixture with rotation $[\alpha]^{24}\mathrm{D}$ − 95°, and melting point 140–145°, in better yield. The ammonium salts were prepared as directed[1] in 1% aqueous ammonia solution and filtered. The resulting acids regenerated with carbon dioxide from the soluble ammonium salts in the filtrate, with rotation, $[\alpha]^{24}\mathrm{D}$ − 24°, were again treated with 1% ammonia and the unreacted acids regenerated with rotation, $[\alpha]^{24}\mathrm{D}$ + 10°. This material was crystallized from aqueous alcohol with the same rotation, melting point 159–162°, and ultraviolet absorption characteristics, Fig. 1, Curve 1.[5] Since the presence of levopimaric acid was suspected from the ultraviolet absorption curve[1] of the mixture, the material was treated under anhydrous conditions with maleic anhydride at room temperature in the absence of acid to obtain an unreacted fraction, with rotation $[\alpha]^{24}\mathrm{D}$ +39°, from which can be calculated 9–10% of levopimaric acid in Kraft's acid. An ultraviolet absorption curve, Fig. 1, Curve 2, was determined of the levopimaric acid-free acids to detect the presence and determine more accurately the amounts of neoabietic acid, with intense band at 250 mμ and slight bulge at 265 mμ, and abietic acid with intense band at 241 mμ. The amounts were determined according to a method described in an earlier paper[6] and found to be 25% of neoabietic and 10% of abietic acids.

Further attempts to resolve the mixture to pure constituents consisted of the preparation and fractional crystallization of the butanolamine salts according to the triangle scheme. The salt of isodextropimaric acid was obtained as the insoluble fraction, to show the presence of this acid in the mixture, and that of neoabietic acid as the more soluble fraction, to confirm its presence.

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[1] K. Kraft, *Ann.*, **524**, 1 (1936).

[2] G. C. Harris and T. F. Sanderson, "Resin Acids. I," THIS JOURNAL, **70**, 334 (1948).

[3] K. Kraft, *Ann.*, **520**, 133 (1935).

[4] F. Vocke, *Ann.*, **508**, 14 (1933).

[5] The ultraviolet absorption data were obtained by Dr. Evelyn V. Cook, of this Laboratory.

[6] G. C. Harris, "Resin Acids, V," THIS JOURNAL, **70**, 3671 (1948).

Therefore, in conclusion, with the aid of the ultraviolet absorption and amine salt techniques[2] it has been shown that Kraft's proabietic acid is a mixture of levopimaric, neoabietic, abietic and isodextropimaric acids. In addition to these there are other acids present such as dextropimaric and a dihydroabietic acid, found in oleoresin acids, to account for the large fraction of acids that do not demonstrate absorption in the ultraviolet region as shown by the low log K_{molar} of the absorption curve of Kraft's preparation. Proabietic acid is, then, another example of what Duffour[7] described as isomorphous-mixed crystals that were obtained by the recrystallization of mixtures with virtually no separation to pure constituents.

Experimental[8,9]

Isolation of Proabietic Acid from *Pinus palustris*.—Many kilograms of gum oleoresin were suspended, in small batches, in 80% acetone and stirred to obtain a homogeneous suspension which was centrifuged. This operation was repeated at least twice to obtain colorless crystals which were dissolved in acetone, freed of foreign material by filtration, and crystallized by the addition of water to the acetone solution at 60°. The crystals which melted at 140–145° and had a specific rotation, $[\alpha]^{24}\text{D}$ $-95°$, were dissolved at 60° in 1% ammonia. After standing overnight at 0–3° the whole mass formed a paste of fine needles which was removed by centrifuging. The acids were regenerated from the mother liquor with carbon dioxide and redissolved in 1% ammonia. The regenerated acids with rotation $[\alpha]^{24}\text{D}$ $-18°$, were again dissolved in the minimum amount of 1% ammonia and the salts centrifuged. The regenerated acids from the filtrate had a rotation $[\alpha]^{22}\text{D}$ $+10°$, and were crystallized from aqueous alcohol with the same rotation and melting point, 159–162°.

Determination of Levopimaric Acid Content.—A solution of 20.0 g. of acids in 20 g. of *n*-pentane was treated with 3.2 g. of triply distilled maleic anhydride in 3 g. of acetone. The reaction was exothermic. At the end of two hours of agitation, the solution was poured slowly into a 3% solution of aqueous alkali containing a sufficient amount of alkali (4.0 g.) to neutralize the acids. The solution was diluted to a total volume of 3 liters and solid boric acid was added during rapid agitation to a *p*H of 6.2. Sodium sulfate, 60 g., was added to coagulate the precipitated acids that were filtered and washed well with water. The rotation of these acids was $[\alpha]^{24}\text{D}$ $+39°$. Using the Biot principle the per cent. of levopimaric acid was calculated to be 9–10%.

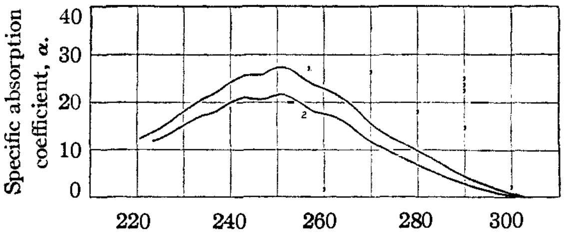

Fig. 1.—Ultraviolet absorption spectra: 1, Kraft's acid; 2, levopimaric acid-free Kraft's acid.

Investigation of the Levopimaric Acid-Free Acids.—The acids (18 g.) were dissolved in 40 g. of acetone and treated with 4.5 g. of butanolamine (2-amino-2-methyl-1-propanol) in 5 g. of acetone. The salts were filtered and fractionally crystallized to obtain (1) the more insoluble fraction with rotation $[\alpha]^{24}\text{D}$ $0°$, from which isodextropimaric acid was isolated and (2) the more soluble fraction with rotation $[\alpha]^{24}\text{D}$ $+103°$, from which neoabietic acid was isolated, both in small yield.

Summary

Kraft's proabietic acid was found to be a mixture of the following primary resin acids: levopimaric, abietic, neoabietic, isodextropimaric and others that do not demonstrate characteristic absorption maxima in the ultraviolet region and were not separated by the amine salt method.

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[7] M. A. Duffour, *Compt. rend.*, **175**, 109 (1922).

[8] All melting points are corrected.

[9] All rotations are of 1% solutions in absolute ethanol.

[10] Original manuscript received August 9, 1946.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Cashew Nut Shell Liquid. III. The Cardol Component of Indian Cashew Nut Shell Liquid with Reference to the Liquid's Vesicant Activity[1]

BY DAVID WASSERMAN[2] AND CHARLES R. DAWSON

India and Brazil are the chief sources of supply of raw cashew nut shell liquid which has found important commercial usage in this country as a phenolic raw material for the manufacture of certain resins and plastics possessing unusual electrical and frictional properties. The raw cashew nut shell liquid has the objectionable property, however, of causing a severe irritation or poison-ivy like dermatitis after coming in contact with the skin.[3]

Working with a solvent extracted oil from the shell of the cashew nut (*Anacardium occidentale*) grown in Java and Surinam, Backer and Haack[4] found, as had Städeler[5] many years earlier, that the oil is almost completely phenolic in character, being made up of two major components, anacardic acid and cardol. By means of quantitative hydrogenation and oxidative degradation experiments, the structures of anacardic acid and cardol, except for the positions of the olefinic linkages in the side chains, were deduced as 2-carboxy-3-pentadecadienylphenol and 5-pentadecadienylresor-

[1] For the second article in this series, see Sletzinger and Dawson, THIS JOURNAL, **68**, 345 (1946).

[2] Present address: Irvington Varnish and Insulator Co., Irvington, N. J.

[3] Keil, Wasserman and Dawson, *Ind. Med.*, **14**:**11**, 825 (1945).

[4] Backer and Haack, *Rev. trav. chim.*, **60**, 661 (1941).

[5] Städeler, *Ann. Chem. Pharmacie*, **68** 137 (1847).