A sample of the diene (VIII) in absolute alcohol was subjected to hydrogenation over Raney nickel at 50° and 160 atmospheres. The product after one recrystallization from methanol was pure IXb, m. p. 104–105°.

7,7'-Dimethoxy-1,1'-binaphthyl (X).—A mixture of the diene (VIII) with about 2.5% of its weight of palladized charcoal,[19] when heated at 290–300° for fifteen minutes, gave a practically quantitative yield of X which, after recrystallization from ethanol, formed colorless rectangular plates, m. p. 110.5–111.5°.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.08; H, 5.77. Found: C, 83.73; H, 5.64.

Similar treatment of the bitetralyl (IXa and IXb) gave in each case the same compound, identified by mixed m. p.

7,7'-Dihydroxy-1,1'-binaphthyl (XI).—The methyl ether (X) was smoothly demethylated in practically quantitative yield by the method of Prey.[20] A mixture of X with three times its weight of pyridine hydrochloride was heated at 200° for six hours, then poured into water. For analysis, the compound was converted to its diacetate by standard methods, because the free phenol was difficult to purify. The diacetate formed white crystals from ethanol, m. p. 173.5–174.5°. After three recrystallizations the compound gave the following analytical values.

Anal. Calcd. for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90. Found: C, 77.38; H, 4.66.

Perylene (XII).—A mixture of the binaphthol (XI) with five times its weight of zinc dust was heated in a distilling flask with a free flame. A yellow oil distilled out of the mixture and solidified in the cooler parts of the apparatus. This was removed and recrystallized from benzene; it formed yellow leaflets with a bronze luster, melting at 267–268°. This was identified as perylene by comparison with an authentic specimen prepared by heating 2,2'-dihydroxy-1,1'-binaphthyl (XIII)[21] with zinc, zinc chloride and water.[13] A mixture of the two samples melted at 267–268°. The picrate formed dark violet needles from benzene, m. p. 220° (reported[22] m. p. 221°). The sample of perylene obtained from XI gave the following analytical results.

Anal. Calcd. for $C_{20}H_{12}$: C, 95.21; H, 4.80. Found: C, 94.90; H, 4.65.

Summary

1. A procedure for the preparation of 6-methoxy-1-tetralone in 40–45% yields from anisole is described.

2. A by-product from the catalytic hydrogenation of 7-methoxy-1-tetralone or 7-methoxy-1-tetralol has been shown to be 7,7'-dimethoxy-1,1',2,2',3,3',4,4'-octahydro-1,1'-binaphthyl.

KALAMAZOO, MICHIGAN RECEIVED[23] AUGUST 27, 1947

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(19) Linstead and Thomas, *J. Chem. Soc.*, 1130 (1940).

(20) Prey, *Ber.*, **74B**, 1219 (1941).

(21) Julius, *Chem. Ind.*, **10**, 98 (1887).

(22) Brass and Tengler, *Ber.*, **64B**, 1650 (1931).

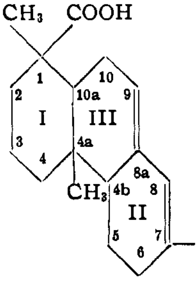
(23) Original manuscript received November 29, 1946.

[CONTRIBUTION FROM THE HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

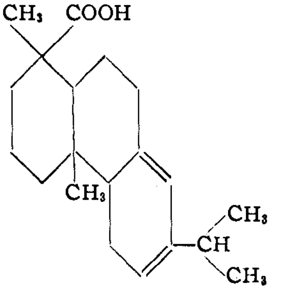
Resin Acids. I. An Improved Method of Isolation of Resin Acids; The Isolation of a New Abietic-Type[1] Acid, Neoabietic Acid

BY GEORGE C. HARRIS AND THOMAS F. SANDERSON

This is the first in a series of papers presenting recent developments made in these laboratories on the isolation and proof of structure of pure resin acids. This paper deals with improved methods of isolation of abietic acid (I)[2] and levopimaric acid (II)[3,4] the most familiar abietic-type acids; the isolation of neoabietic acid (III),[5] a new primary acid of this type, is also described.



I



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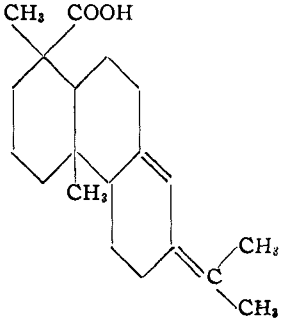

III

Abietic Acid

The difficulty in separating abietic acid from isomeromorphic resin acids has made its isolation from rosin a difficult problem. However, Palkin and Harris[6] were able to obtain a pure abietic acid according to the following procedure: (1) isomerizing rosin by boiling in glacial acetic acid to increase the abietic acid content, (2) concen-

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(1) We wish to designate by this term that type of resin acid that yields retene, 1-methyl-7-isopropylphenanthrene, upon complete dehydrogenation and has an isopropyl or isopropylidene group at C-7.

(2) L. Ruzicka, L. Sternbach and O. Jeger, *Helv. Chim. Acta*, **24**, 504 (1941).

(3) This word has purposely been written as one word since the compound is not stereoisomeric with dextropimaric acid as the prefixes *levo-* and *dextro-* would imply.

(4) L. Ruzicka and S. Kaufman, *Helv. Chim. Acta*, **23**, 1346 (1940); according to Ruzicka and Kaufman the double bonds may be at the positions indicated in Formula II or at positions 5–6 and 7–8, the former being preferred.

(5) G. C. Harris and T. F. Sanderson, Resin Acids. II., THIS JOURNAL, **69**, 339 (1947).

(6) S. Palkin and T. H. Harris, *ibid.*, **56**, 1335 (1934).

trating the abietic acid in the form of "Steele's" acid[7] by crystallizing the isomerized rosin from glacial acetic acid, (3) further concentrating the abietic acid by the preparation and recrystallization of the acid sodium salts ($C_{19}H_{29}COONa\cdot 3C_{20}H_{30}O_2$), and (4) fractionating the regenerated acids by the preparation and recrystallization of the diamylamine salts, a method first employed by Balas.[8] This procedure is effective but somewhat tedious and gives a relatively low recovery (*ca.* 12%) of the pure acid compared with the total abietic acid which can be shown to be present by ultraviolt absorption spectra. We have now found that diamylamine, the amine used by Balas[8] and Palkin and Harris,[6] not only offers a means of purification of abietic acid, $[\alpha]^{24}\mathrm{D}$ −98°, but is specific for the separation of abietic acid from the complex mixture of resin acids in rosin. Addition of a molar quantity of diamylamine to an acetone solution of isomerized rosin precipitates the crystalline amine salts high in abietic acid content from which the salt of abietic acid is readily separated by $[\alpha]^{24}\mathrm{D}$ fractional crystallization. The pure acid, $[\alpha]^{24}\mathrm{D}$ − 106°, m. p. 172–175°, was obtained by decomposition of the salt with a weak acid such as acetic or phosphoric to minimize isomerization of the regenerated acid. The yield amounted to 40% of the weight of the isomerized rosin which is in fair agreement with that indicated by the absorption spectra.

Ultraviolet absorption curves are of great value in determining the amount of abietic acid present in modified or unmodified rosins. Figure 1 shows the ultraviolet absorption spectra of pure abietic acid (curve 1) and isomerized rosin (curve 2) The difference, $\Delta\alpha$, in specific absorption coefficient between the maximum at 241 mμ and the inflection point at 248.5 mμ is a constant value characteristic of pure abietic acid and can well be used as a measure of the abietic acid content of a rosin. The ratio of this difference for isomerized rosin to that for the pure acid is a measure of the amount of pure acid in the isomerized rosin. On the basis of these ratios, isomerized rosin contains 47 ± 2% of abietic acid. This precision does not hold for a non-isomerized rosin which contains neoabietic acid whose most intense band of absorption is at 250 mμ.

The ultraviolet absorption spectrum of pure abietic acid was found to demonstrate its most intense band at 241 mμ, α (specific absorption coefficient)[8a] = 77.0. This value is in good accord with that reported by Sandermann[9] (240 mμ) and that calculated (242 mμ) according to a method postulated by Woodward[10] and in disagreement with the value of 237.5 mμ reported by Kraft.[11]

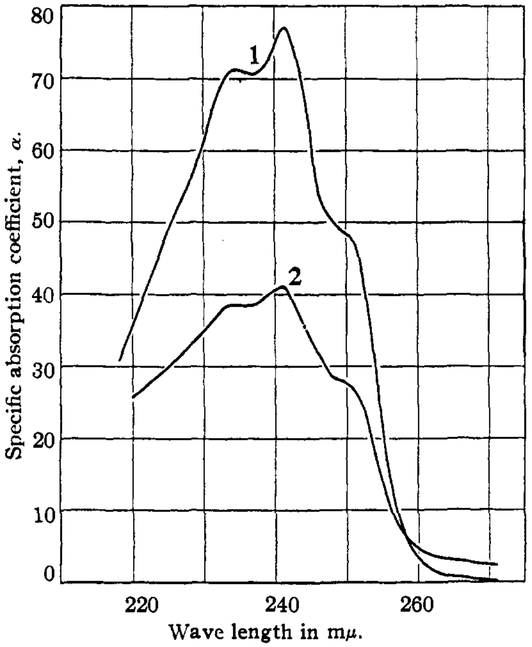

Fig. 1.—Ultraviolet absorption spectra: 1, abietic acid; 2, isomerized rosin.

Levopimaric Acid

Although levopimaric acid is the major constituent of the gum oleoresin of several conifers, its isolation has always been difficult with yields of the order of 1% having been obtained by Ruzicka, *et al.*,[12] and Palkin and Harris[13] from the "galipot"[13a] of *Pinus maritima* and *Pinus palustris*, respectively. The method employed was based on the fractional crystallization of the sodium salts.

The application of the amine salt technique in this instance resulted in the much increased yield of 20% of pure levopimaric acid $[\alpha]^{24}\mathrm{D}$ −276°, from the "galipot" of *Pinus palustris*. The procedure is similar to that used for the isolation of abietic acid from rosin with the exception that butanolamine (2-amino-2-methyl-1-propanol, Commercial Solvents, Inc.) was used since it was found to be more specific for the precipitation of levopimaric acid than any other amine tried.

In the event that the whole oleoresin of *Pinus palustris* is used as the source of levopimaric acid, the total acids can be first separated from the turpentine by precipitation as amine salts. Cyclohexylamine was found most suitable for this purpose, since it results in a nearly quantitative precipitation of resin acids as the very insoluble cyclohexylamine salts from any medium in which they exist with non-resin acid material, *e. g.*, gum oleoresin or tall oil.[14] Formation of the butanol-

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[7] L. L. Steele, THIS JOURNAL, **44**, 1333 (1922).

[8] Fr. Balas, *Časopis Československeho Lékárnictva*, **7**, 320 (1927).

[8a] Defined in the experimental section.

[9] W. Sandermann, *Ber.*, **74**, 154 (1941).

[10] R. B. Woodward, THIS JOURNAL, **64**, 72 (1942).

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

[12] L. Ruzicka and R. G. R. Bacon, *Helv. Chim. Acta*, **20**, 1542 (1937).

[13] S. Palkin and T. H. Harris, THIS JOURNAL, **55**, 3677 (1933).

[13a] "Galipot" is a term used to describe the crystalline acids which settle out of the oleoresin, which, in turn, is a solution of resin acids in turpentine.

[14] G. C. Harris, U. S. Patent 2,419,211, April 22, 1947.

amine salt and regeneration of the acid as in the previous instance gave a yield of 15% based on the total acids or approximately 50% of the amount reported to be present. Recently, Fleck and Palkin[15] reported a value of 36% of levopimaric acid in the acids fraction of the oleoresin of *Pinus palustris* determined by the quantitative addition of maleic anhydride to levopimaric acid.

The ultraviolet absorption spectrum of pure levopimaric acid was found to demonstrate its most intense band at 272 mμ, α = 19.2 (Fig. 2), in good agreement with that reported by Kraft.[11]

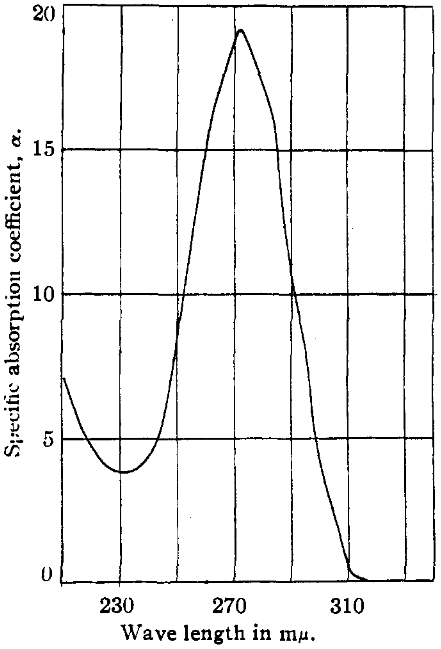

Fig. 2.—Ultraviolet absorption spectrum of levopimaric acid.

Neoabietic Acid

The presence of a dextrorotatory abietic-type acid in gum oleoresin has often been alluded to in the extensive literature on resin acids. The first serious attempt to isolate it was made by Kraft,[16] who was able to obtain only a mixture of acids with a positive rotation, $[\alpha]^{24}\text{D}$ + 11°.[17] R. F. Cox, of this Laboratory, also isolated a resin acid with positive rotation, $[\alpha]^{24}\text{D}$ +83°. This was obtained by the heat isomerization of abietic acid, $[\alpha]^{24}\text{D}$ −105°, at 180° in accordance with a postulation by Ruzicka[18] that dextrorotatory acids are formed in equilibrium with levorotatory acids when the latter are isomerized at elevated temperatures. Cox's method of isolation of the dextro acid consisted of crystallizing the unaltered abietic acid from the mixture to concentrate the former in the residue from which it was fractionally crystallized. It is not surprising that further purification of the dextro acid was not obtained because fractional crystallization of mixtures of resin acids, as pointed out by Duffour,[19] always results in the isolation of mixed crystals rather than pure compounds. It was apparent, then, from the two instances cited above, that the lack of a workable technique for the isolation of pure resin acids from mixtures impeded progress in this direction.

Before employing the amine salt technique for the isolation of the dextrorotatory acid from the gum oleoresin of *Pinus palustris*, it was considered best to attempt its isolation from the simpler mixture of acids obtained in heat-isomerized abietic acid. Abietic acid, for this purpose, was heated[18] at 300° for twenty minutes, and the unreacted abietic acid (76%) separated from the mixture as its insoluble diamylamine salt. In this manner, a highly dextrorotatory residue was obtained which was treated with butanolamine in acetone to obtain two crops of crystalline salts. The first with rotation $[\alpha]^{24}\text{D}$ +24° was discarded, the second with rotation $[\alpha]^{24}\text{D}$ +100° was recrystallized from acetone to a constant rotation, $[\alpha]^{24}\text{D}$ +102°. The salt was decomposed with boric acid to obtain a new resin acid, termed neoabietic acid, with rotation $[\alpha]^{24}\text{D}$ +159°, and melting point 167–169°. Neoabietic acid, like levopimaric acid, was found to be highly susceptible to mineral acid and isomerizes almost completely to abietic acid in the presence of a trace of strong acid.

This acid was isolated in 5% yield from the resin acids of gum oleoresin by alternate fractional crystallization of the diethylamine and butanolamine salts. Neoabietic acid can also be prepared from commercial gum rosin of any color grade by using the diethylamine salt to obtain initial concentration and butanolamine to effect final purification.

The homogeneity of neoabietic acid was established by preparation and recrystallization of the methy ester, m. p. 61.5–62°, and also of the butanolamine salt, $[\alpha]^{24}\text{D}$ + 102°, and regeneration in each case of acid identical with the original in optical rotation and ultraviolet absorption. The ultraviolet absorption spectrum of pure neoabietic acid demonstrates its most intense band at 250 mμ, α = 80.0 (Fig. 3).

Experimental[20,21]

Abietic Acid

Acid Isomerization of Wood Rosin.—The extent to which rosin was isomerized to produce the maximum amount of abietic acid was determined as follows: A sample of rosin was heated under reflux in alcohol with concentrated hydrochloric acid. Samples were taken at intervals and the ultraviolet absorption characteristics and specific rotation of each determined. As shown in

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[15] E. E. Fleck and S. Palkin, *Ind. Eng. Chem., Anal. Ed.*, **14**, 146 (1942).

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

[17] The composition of Kraft's proabietic acid is the subject of a future publication; G. C. Harris and T. F. Sanderson, Resin Acids, VI.

[18] L. Ruzica and J. Meyer, *Helv. Chim. Acta*, **5**, 338, 342 (1922).

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

[20] All melting points are corrected.

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

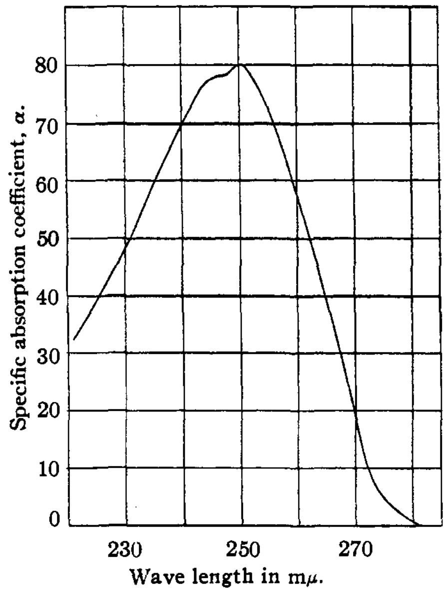

Fig. 3.—Ultraviolet absorption spectrum of neoabietic acid.

Fig. 4, the absorption curves of samples taken at one hour or after were the same and attained the highest value for specific absorption coefficient, α, at 241 mμ, indicating the production of the maximum amount of abietic acid, 47 ± 2%, at the end of one hour. The specific rotation of the samples, Fig. 5, also reached a constant value, $[\alpha]^{24}\mathrm{D}$ $-35°$, after one hour of heating, again indicating the formation of the equilibrium mixture at the end of this time.

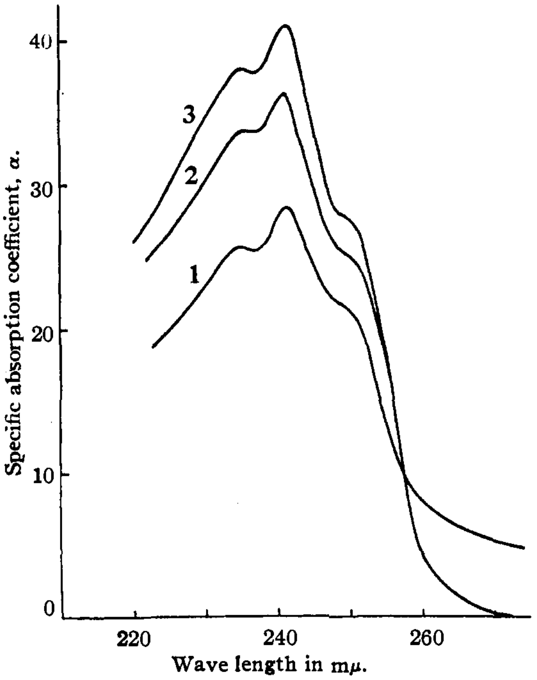

Fig. 4.—Ultraviolet absorption spectra: 1, N wood rosin; 2, rosin isomerized for half an hour; 3, rosin isomerized for one, two and three hours.

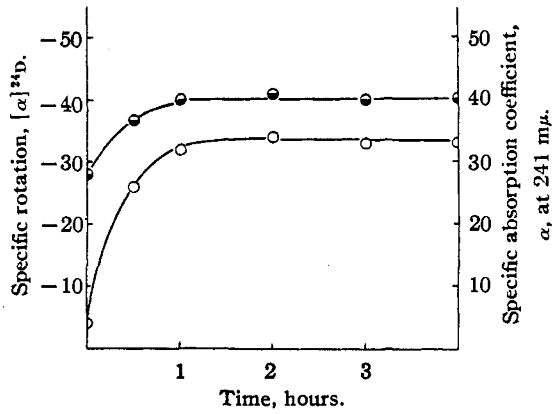

Fig. 5.—●, Rate of change of specific absorption coefficient of isomerized rosin: ○, rate of change of specific rotation of isomerized rosin.

The sample used was prepared in the following manner. To a hot solution of 250 g. of wood rosin (color grades N to X, acid number 166) in 740 cc. of 95% ethanol was added 42 cc. of concentrated hydrochloric acid and the resulting solution boiled under reflux for one and one-half hours. A stream of carbon dioxide was passed over the surface of the solution during the reflux period and when the solution was being cooled to avoid discoloration due to atmospheric oxidation. At the end of the reaction time, the alcohol and acid were steam distilled, the water decanted, and the residue dissolved in ether. The ether solution was washed free of acid with water, dried over sodium sulfate, and the ether evaporated. The last traces of solvent were removed by melting the rosin in an oil-bath at 180 to 200° under water-pump vacuum. The molten rosin, blanketed continuously with carbon dioxide, was poured into a paper boat for ease of handling, to obtain 245 g. of material with rotation $[\alpha]^{24}\mathrm{D}$ $-35°$.

Preparation and Purification of the Diamylamine Salt.—To a solution of the isomerized rosin (245 g.) in 375 cc. of acetone at incipient boiling was added 127 g. of diamylamine (Sharples Company, Philadelphia, Pennsylvania) slowly with vigorous agitation. On cooling to room temperature, crystals appeared in the form of rosets. The mass was agitated, cooled in ice and filtered to obtain a cake of salts that was washed with 150 cc. of acetone. The latter was dried in a vacuum oven at 50° to obtain material with rotation $[\alpha]^{24}\mathrm{D}$ $-18°$. After four crystallizations, using a sufficient amount of acetone (*ca.* 4 liters for 200 g. of salt) to obtain an almost clear solution and evaporating to incipient precipitation (*ca.* 2 liters of solution), 118 g. of the pure amine salt of abietic acid was obtained with rotation $[\alpha]^{24}\mathrm{D}$ $-60°$. On recovery and recrystallization of the back crops to material with rotation $[\alpha]^{24}\mathrm{D}$ $-60°$, an additional 29 g. of pure salt was obtained, making a total of 147 g. In obtaining the later crops of salt by concentration of the mother liquors, some amine is lost by evaporation that should be replaced by the addition of a few drops to the concentrated solution.

Isolation of Abietic Acid.—To a cooled solution of the amine salt of abietic acid (147 g.) in one liter of 95% ethanol was added 39 g. of glacial acetic acid at once with stirring and 900 cc. of water slowly at first with vigorous agitation to incipient precipitation and then more freely. The crystals were filtered at once and washed with a liter of water to free them of traces of acetic acid. The acid was recrystallized from 750 cc. of 95% ethanol by the slow addition of 600 cc. of water as above and dried in a vacuum desiccator at room temperature over sodium hydroxide in an oxygen-free atmosphere. Undue exposure to higher temperatures will result in isomerization, and contact with air will result in the oxidation of the material. In this manner, 98 g. (40% by weight of isomerized rosin; theoretical 47%) of abietic acid was obtained with rotation $[\alpha]^{24}\mathrm{D}$ −106°. For storage purposes, the acid should be kept in vials under good vacuum.

Absorption Spectra.—The absorption spectrum data were obtained from measurements made with a Beckman ultraviolet spectrophotometer. The formulas employed in making the calculations use the term α, specific absorption coefficient.

$$\alpha = \log_{10} I_0/I/cl$$

I_0 = intensity of radiation transmitted by the solvent (95% ethanol)
I = intensity of radiation transmitted by the solution
c = concentration of solute in grams per liter
l = length in centimeters of solution through which the radiation passes

Levopimaric Acid

Preparation and Purification of the Butanolamine Salt.—To a solution of 125 g. of "galipot" in 250 g. of acetone was added 37 g. of butanolamine (2-amino-2-methyl-1-propanol) in 37 g. of acetone.[22] The suspension was cooled, the salt filtered, and a second crop taken by concentrating the solution to half its volume. The salt was fractionally crystallized from methyl acetate to obtain 31 g. of material with rotation $[\alpha]^{24}\mathrm{D}$ −218°.

Isolation of Levopimaric Acid.—The decomposition of the amine salt of levopimaric acid was carried out with boric acid.[23] The salt was suspended in ether and shaken vigorously with a saturated boric acid solution until the amine salt crystals had disappeared. To assure complete decomposition of the salt, the ether solution was washed twice more with boric acid. The ether solution containing the resin acid was washed free of boric acid with water, dried and the ether evaporated.[22] The acid was crystallized by dissolving it in warm ethanol and adding water to incipient turbidity, to obtain, upon cooling to room temperature, 24 g. of levopimaric acid (20% of the "galipot") with rotation $[\alpha]^{24}\mathrm{D}$ −276°.

Isolation of Primary Resin Acids from Gum Oleoresin. When the oleoresin is to be used as the source of levopimaric acid, the resin acids are separated from the turpentine according to the following procedure and used as in the following section. To a solution of 200 g. of the gum oleoresin of *Pinus palustris* in 600 g. of narrow-range gasoline (boiling range 90–100°) at 40° was added 41 g. of cyclohexylamine (Monsanto Chemical Co.) in 41 g. of gasoline.[22] The mass of crystalline salts was agitated and the suspension cooled in ice before the salts were filtered and washed with 200 g. of fresh solvent.

The salts were first air-dried overnight to remove the solvent and then decomposed in the same manner as the butanolamine salts taking the usual precautions for complete decomposition and rise in temperature of the concentrated solutions. The last traces of ether were evaporated by puffing the residue to a powder under water-pump vacuum. In this way was obtained 124 g. of resin acids (62% of the total oleoresin) with acid number 185 and neutral equivalent 302.

Preparation and Purification of Amine Salt and Isolation of Levopimaric Acid.—The butanolamine salts of the resin acids fraction (124 g.) were prepared as in the case of "galipot" using the same ratio of amine and solvent. The decomposition of the salts was carried out with the same precautions and the regenerated acid crystallized from ethanol and water to obtain 18.6 g. of pure levopimaric acid (15% of the total oleoresin acids) with rotation $[\alpha]^{24}\mathrm{D}$ −276°.

Neoabietic Acid

Heat Isomerization of Abietic Acid; Isolation of Amine Salt of Neoabietic Acid.—A 50.0-g. sample of abietic acid, $[\alpha]^{24}\mathrm{D}$ −106°, prepared according to the method described in this paper, was heated at 300° for twenty minutes under a stream of carbon dioxide gas. At the end of this time the molten material was poured in a paper boat to cool, chipped and dissolved in 100 cc. of acetone. Diamylamine (27 g.) was added to precipitate the unreacted abietic acid as its insoluble salt. Two successive crops of salts were obtained, totalling 58.1 g. and corresponding to 76% of unaltered abietic acid. The mother liquor was diluted with 50 cc. of acetone and treated with 3.6 g. of butanolamine to form the butanolamine salts of the residual resin acids combined as diamylamine salts. A first crop with rotation $[\alpha]^{24}\mathrm{D}$ +24° was discarded, and the second, with rotation $[\alpha]^{24}$ +100°, obtained by concentrating the mother liquor to half the volume, was recrystallized from acetone to a constant rotation, $[\alpha]^{24}\mathrm{D}$ +102°.

Isolation of the New Abietic-Type Acid, Neoabietic Acid.—The butanolamine salt was suspended in ether and decomposed with a saturated solution of boric acid in the usual manner.[23] The ether solution containing the resin acid was washed free of boric acid with water, dried over sodium sulfate, and the ether evaporated.[22] The residue was crystallized from alcohol and water to obtain the pure neoabietic acid with rotation $[\alpha]^{24}\mathrm{D}$ +159°, melting point 167–169°, neutral equivalent 302, calcd. 302, in about 1% yield.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.39; H, 10.00. Found: C, 79.46, 79.40; H, 9.97, 9.97.

Isolation of Neoabietic Acid from the Gum Oleoresin.—The resin acids of the gum oleoresin of *Pinus palustris* were separated from the turpentine according to the method described in the previous section on levopimaric acid and used in the following manner for the isolation of neoabietic acid.

To a solution of the total acids, 124 g., in 248 g. of acetone was added 37 g. of butanolamine in 37 g. of acetone. The first three crops of salt, with rotations $[\alpha]^{24}\mathrm{D}$ −218, −210 and −60°, highly concentrated with the salt of levopimaric acid, were isolated. Further concentration of the mother liquor, with intermittent addition of small amounts (2 g.) of butanolamine to replace that lost by evaporation, resulted in the isolation of the two dextrorotatory crops, with rotations $[\alpha]^{24}\mathrm{D}$ +12 and +15°. Since no further increase in dextrorotation could be realized, these salts were combined and decomposed with boric acid in the usual manner. The more specific diethylamine was used to prepare the salts of the regenerated acids. Four recrystallizations from acetone resulted in the isolation of salts with rotation $[\alpha]^{24}\mathrm{D}$ +70°, which again could not be increased by further fractionation. These salts were then decomposed with boric acid, the butanolamine salts prepared, and the latter recrystallized from acetone to the top rotation of $[\alpha]^{24}\mathrm{D}$ +102°.

The pure salt of neoabietic acid (8.2 g.) was decomposed with boric acid to obtain 6.1 g. (5% of the total oleoresin acids) of pure acid with rotation, $[\alpha]^{24}\mathrm{D}$ +159°.

Preparation of the Methyl Ester of Neoabietic Acid.—Five grams of neoabietic acid, $[\alpha]^{24}\mathrm{D}$ +159°, was dissolved in 50 cc. of ether; the resulting water-white solution was treated with an excess of an ether solution of diazomethane as evidenced by a permanent yellow coloration. After standing for twenty minutes, the solution was evaporated to dryness.[22] The seed crystal was obtained by cooling a methanol solution of one drop of liquid ester to −30° in an acetone–Dry Ice-bath. The ester, then, was readily crystallized from methanol with the aid of the seed crystal in excellent yield (5.0 g.) with a constant melting point, 61.5–62°.

Anal. Calcd. for $C_{21}H_{32}O_2$: C, 79.69; H, 10.19. Found: C, 79.70, 79.65; H, 10.07, 10.17.

The purity and homogeneity of neoabietic acid was established in the following manner. Material with rotation $[\alpha]^{24}\mathrm{D}$ +159° was used to prepare the butanol-

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(22) The formation of the amine salts is an exothermic reaction and great care must be taken that the temperature does not rise above 50° to alter the levopimaric acid (this applies to neoabietic acid as well) which is highly susceptible to isomerization by heat.

(23) Levopimaric acid (this applies to neoabietic acid as well) is highly susceptible to mineral acid and isomerizes almost completely to abietic acid in the presence of a trace of strong acid. Such precautions against acid isomerization must be taken in regenerating the resin acid from its amine salt. Boric acid, therefore, the weakest acid that can effect the decomposition of the amine salts, is always employed.

amine salt which was recrystallized several times to obtain the constant rotating salt (same as that from which the acid was isolated), $[\alpha]^{24}\mathrm{D}$ +102°. The resin acid was regenerated in the usual manner with the same rotation, $[\alpha]^{24}\mathrm{D}$ +159°, and the same ultraviolet absorption characteristics, particularly the height of the most intense band, 250 mμ, at $\alpha = 80.0$. The methyl ester, prepared with diazomethane as above, was obtained with the same constant melting point 61.5–62°. Saponification in alcoholic alkali with alkali in a sealed tube at 50° for ninety-six hours with subsequent acidification with carbon dioxide and boric acid resulted in the quantitative isolation of neoabietic acid with unchanged rotation, $[\alpha]^{24}\mathrm{D}$ +159°.

Isolation of Neoabietic Acid from Gum Rosin.—A 200-g. sample of gum rosin was dissolved in 400 g. of acetone and treated, at 50°, with 45 g. of diethylamine in an equal weight of acetone. The complete precipitation of salts was allowed to take place over a long period of time (twenty-four hours) at room temperature. No attempt was made to hasten the crystallization by cooling because the necessary fractionation was not obtained in this manner. The salts were fractionated from acetone to a rotation $[\alpha]^{24}\mathrm{D}$ +70° and converted to the butanolamine salts by dissolving in acetone and adding the necessary amount of butanolamine. The latter were, in turn, crystallized to a rotation $[\alpha]^{24}\mathrm{D}$ +102° and the pure neoabietic acid isolated in 5% yield (10.0 g.) with rotation $[\alpha]^{24}\mathrm{D}$ +159°.

Summary

1. An improved method, based on the amine salt technique, for the isolation of abietic acid from acid-isomerized wood rosin and levopimaric acid from the gum oleoresin of *Pinus palustris* is described.

2. The isolation of a new, abietic-type acid, termed neoabietic acid, from heat-isomerized abietic acid, the gum oleoresin of *Pinus palustris* and gum rosin is described.

3. The ultraviolet absorption spectra, utilizing specific absorption coefficients, α, have been determined for each of the three abietic-type acids.

WILMINGTON, DELAWARE RECEIVED[24] AUGUST 12, 1947

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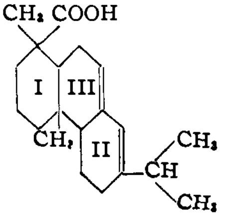
[24] Original manuscript received August 9, 1946.

[CONTRIBUTION FROM THE HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

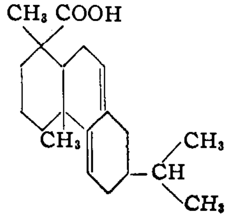
Resin Acids. II. The Structure of Neoabietic Acid

BY GEORGE C. HARRIS AND THOMAS F. SANDERSON

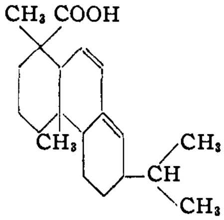
Neoabietic acid[1] has been isolated from the oleoresin and rosin of *Pinus palustris.* It has now been proved that this acid is an abietic-type acid since upon dehydrogenation with palladium–carbon catalyst retene, 1-methyl-7-isopropylphenanthrene, was isolated. The presence of two double bonds was shown by catalytic hydrogenation to the tetrahydro acids and by absorption in the ultraviolet region.[2] The intense band (Fig. 1, Curve 1) at 250 mμ, indicated also that the two double bonds are conjugated between two rings or that one is exocyclic with respect to the other in analogy with the absorption of abietic acid at 241 mμ and in contrast with that of levopimaric acid at 272 mμ. With this information, the structures I–V came into consideration.



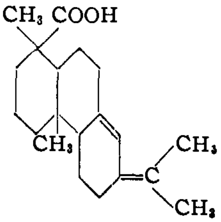
242 mμ
I



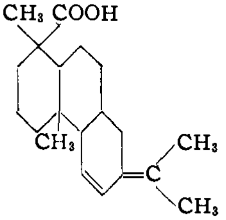
247 mμ
II



237 mμ
III



252 mμ
IV



242 mμ
V

From the work of R. B. Woodward[3] predictions can be made concerning the wave length of the most intense band of absorption of this type of conjugated system. These predictions are based on the degree of substitution of the double-bond carbon atoms; they are given below each formula. Since neoabietic acid demonstrates its most intense band at 250 mμ and since the predicted value for abietic acid, I, was so close to that found, 241 mμ, formula IV was at once suspected as that for neoabietic acid.

If formula IV were that for neoabietic acid, ozonization and decomposition of the ozonide with water would result in the formation of acetone, as one of the products. The experiment was carried out and acetone was isolated as its 2,4-

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

[2] The ultraviolet absorption data were determined by Dr. Evelyn V. Cook of this Laboratory.

[3] R. B. Woodward, THIS JOURNAL, 64, 72 (1942).