

[CONTRIBUTION FROM THE G & A LABORATORIES, INC., SAVANNAH, GEORGIA]

On Dihydrodibromoabietic Acid

BY TORSTEN HASSELSTROM AND JOHN D. MCPHERSON

It has been observed that when the abietic acids are reduced catalytically to the dihydro state, the dihydroabietic acids obtained vary greatly in melting points and optical rotations.¹ This evidently points out that mixtures of isomers are obtained. In previous communications we have described the presence of dihydroabietic acid in heat-treated rosin concluded by the fact that hydration of this product yields a lactone belonging to the tetrahydroabietic acid series.² More recently our findings were confirmed by Fleck and Palkin³ on heat-treated abietic acid. Though the lactone of the hydroxytetrahydroabietic acid is easily characterized, the isolation of the original dihydroabietic acids in the pyroabietic acid mixture has been difficult. Evidence has been obtained that isomeric dihydroabietic acids are produced by heat treatment of rosin or abietic acids.

Fleck and Palkin⁴ succeeded in isolating a dihydroabietic acid, m. p. 174–176°, $[\alpha]_D^{20} +108^\circ$, by means of fractional crystallization of heat-treated abietic acid. Ruzicka, *et al.*,⁵ isolated another dihydroabietic acid, m. p. 193–194°, $[\alpha]_D +9$, which apparently is similar to refined pseudopimaric acid, m. p. 195.5–198°, $[\alpha]_D +0.33$, prepared by us from heat-treated rosin and which has the composition of dihydroabietic acid.⁶ However, we could not regard our dihydroabietic acid (refined pseudopimaric acid) as a chemical indi-

vidual, since we did not succeed in obtaining an acid of constant melting point and constant rotation.

On reduction of dihydrodibromoabietic acid with sodium and absolute alcohol, we apparently have been able to synthesize another dihydroabietic acid of high purity (m. p. 217.5–218.5° corr., $[\alpha]_D -23$). The acid was characterized further by the preparation of the di-*n*-amylamine salt and methyl ester. Work is being continued to determine the nucleus of our dihydro acid since in the hydroaromatic series addition and splitting off of hydrogen halides not only causes shifting of the double bonds but also other types of intramolecular rearrangements.⁷ It seems unlikely that it should be the optical antipode of *d*-dihydropimaric acid because of the great differences in melting points of these acids and their methyl esters.⁸ However, until evidence to the contrary is obtained, we assume our dihydro acid obtained by reduction of dihydrodibromoabietic acid to be a new dihydroabietic acid.

The dihydrodibromoabietic acid was obtained according to Levy,⁹ using as starting material the abietic acid of Steele¹⁰ and of Palkin and Harris.¹¹ In the preparation of dihydrodibromoabietic acid we also attempted to isolate the monohydromonobromoabietic acid by using the method of Aschan,¹² employed for the synthesis of monohydromonobromopinabietic acid, but were unsuccessful inasmuch as apparently a mixture of abietic acid and monobromoabietic acid was obtained. In order to obtain a bromine free acid the mixture was refluxed with glacial acetic acid and then converted into the di-*n*-amylamine salt. The amounts of "abietic acid" recovered from the di-*n*-amylamine salt were too small to ascertain whether the product was an individual acid or a mixture of isomers. This investigation is being continued.

Experimental

Starting Material.—Rosin of WW grade was heated with glacial acetic acid¹⁰ and the separated crystalline

(1) (a) Johansson, *Arkiv. Kemi.*, **19**, 6 (1917); (b) Virtanen, *Ann.*, **424**, 150 (1920); (c) Aschan, *Nästenföreningar, Terpener och Kamferarter, Helsingfors*, 391 (1928); (d) Ruzicka and Meyer, *Helv. Chim. Acta*, **5**, 333 (1922); (e) Hasselstrom and Bogert, *THIS JOURNAL*, **57**, 2120 (1935).

(2) (a) Hasselstrom, Brennan and McPherson, *THIS JOURNAL*, **60**, 1267 (1938); (b) Hasselstrom and McPherson, *ibid.*, **60**, 2340 (1938); (c) Hasselstrom, U. S. Patent 2,121,032 (1938); (d) Hasselstrom, U. S. Patent 2,121,033 (1938).

(3) Fleck and Palkin, *THIS JOURNAL*, **61**, 247 (1939).

(4) Fleck and Palkin, *ibid.*, **60**, 8621 (1938).

(5) Ruzicka, Bacon, Sternbach and Waldmann, *Helv. Chim. Acta*, **21**, 59 (1938).

(6) Brennan, Cairncross, Hasselstrom and Hull, U. S. Patent 2,272,628 (1937). On fractional crystallization refined pseudopimaric acid shows the following melting points and optical rotations.

No. of cryst.	Solvent	M. p., °C.	$[\alpha]_D$
8	Acetone	187–192	+11.67
11	Acetone	191–194.5	+ 5.87
13	Abs. alc.	193–195	+ 3.52
16	Acetone	195.5–198	+ 0.33

Dihydroabietic acid (refined pseudopimaric acid), m. p. 195.5–198°, $[\alpha]_D^{20} +0.33$. *Anal.* Calcd. for $C_{20}H_{30}O_2$: C, 78.68; H, 10.60. Found: C, 79.17; H, 10.51.

(7) Hasselstrom, *Ann. Acad. Finn.*, **20**, 2 (1923).

(8) (a) Ruzicka and Frank, *Helv. Chim. Acta*, **15**, 1297 (1932);

(b) Hasselstrom and Hampton, *THIS JOURNAL*, **61**, 967 (1939).

(9) Levy, *Ber.*, **64**, 2441 (1931).

(10) Steele, *THIS JOURNAL*, **44**, 1333 (1922).

(11) Palkin and Harris, *ibid.*, **56**, 1935 (1934).

(12) Aschan, *Ann.*, **488**, 124 (1930).

material, m. p. 155–160° (corr.), $[\alpha]_D -46^\circ$ (ethanol), converted into sodium tetraabietate¹¹ which was recrystallized four times from methanol, $[\alpha]_D -99^\circ$ (ethanol). The abietic acid regenerated from this salt had the following constants, m. p. 171–174° (corr.), $[\alpha]_D -99^\circ$ (ethanol) $[\alpha]_D -31^\circ$ (in benzene).

Dihydrodibromoabietic Acid.—The procedure followed by Levy⁹ for the preparation of this compound was changed somewhat. Abietic acid (75 g.) was dissolved in 50 cc. of glacial acetic acid and allowed to cool slowly overnight to prevent crystallization. To this solution was added 300 g. of hydrogen bromide in glacial acetic acid (saturated at 0°). The mixture was shaken for six hours. After standing in the dark for two days, the precipitated solid was washed with glacial acetic acid and dried in vacuum at ordinary temperature. The yield of crude dihydrodibromoabietic acid was 164 g., m. p. 144–148° dec. (corr.). The purification was difficult due to the ease with which hydrogen bromide is split off. The crude compound was therefore covered with 600 cc. of dry ethyl acetate and shaken for two hours. After standing for twelve hours, the white crystalline dibromo acid was separated by filtration. This procedure was repeated three times; yield 20 g., m. p. 172–173°, dec. (corr.). The dihydrodibromoabietic acid was then recrystallized from anhydrous ether. The fine microscopic white crystals melted at 172–173°, dec. (corr.). Due to the insolubility of dihydrodibromoabietic acid and its changeability even on gentle heating, the optical rotation could not be determined with accuracy. In ethyl acetate solution the figures were $[\alpha]_D \approx 0$ to $[\alpha]_D +29.2^\circ$.

Anal. Calcd. for $C_{20}H_{32}Br_2O_2$: C, 51.71; H, 6.95. Found: C, 52.52; H, 6.84.¹³

The combined ethyl acetate solutions were filtered to remove traces of insoluble material. The ethyl acetate was evaporated in vacuum and the residue, 38 g., was recrystallized from acetone in the manner described by Aschan¹² for the preparation of monohydromonobromopinabietic acid. The crystalline material separating from the acetone solution was recrystallized from acetone, methanol and hexane. The acid obtained in the last fraction weighed 2.5 g. and melted at 173.5–174° (corr.), $[\alpha]_D -40$ (ethanol). The substance is intermediate in composition between a monobromo compound (Calcd.: C, 62.63; H, 8.15) and abietic acid (Found: C, 75.64; H, 9.85).

The acids recovered from the mother liquors, 5.5 g., had the following constants: m. p. 169–171° (corr.), $[\alpha]_D -60$ (ethanol) (Found: C, 76.34; H, 9.28).

Apparently the higher melting acid and the lower melting acid consist of an "abietic acid" and the monohydromonobromo acid in different proportions.

In order to obtain a bromine free acid, 8 g. of the acid mixture mentioned above was refluxed with 50 g. of glacial acetic acid for one-half hour. The acetic acid was then distilled off in vacuum and the viscous residue dissolved in ether. The ether solution was washed with water and dried with anhydrous sodium sulfate. After evaporating the ether, 4 g. of a slightly brownish resin was obtained. This was dissolved in about 50 cc. of acetone and to the boiling solution was added 4 g. of di-*n*-amylamine

(Eastman Kodak Co.) in 20 cc. of acetone. The mixture was refluxed for about fifteen minutes. On standing, the di-*n*-amylamine salt, 2.8 g., separated as slightly yellow needles which were subjected to recrystallization from acetone, m. p. 136–138.5° (corr.), $[\alpha]_D -44.5^\circ$ (ethanol).

Anal. Calcd. for $C_{30}H_{48}NO_2$: C, 78.35; H, 11.62. Found: C, 78.61; H, 11.76.

A solution of 0.7 g. of the diamylamine salt in 10 cc. of alcohol was made acid with a 5% solution of hydrochloric acid. The mixture was then poured into water and the separated solid extracted with ether. The ether solution was washed with water and dried with anhydrous sodium sulfate. After evaporating the ether, the remaining solid was recrystallized from methanol. The impure acid showed the m. p. 168–171° (corr.), and $[\alpha]_D -90.0^\circ$ (ethanol).

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.40; H, 10.05. Found: C, 78.67; H, 10.16.

Dihydroabietic Acid.—To 125 cc. of absolute alcohol was added 9 g. of sodium. After the sodium was in solution, 9 more grams of sodium was added alternately with 2.2 g. of dihydrodibromoabietic acid in small portions. After all sodium and bromide were dissolved, the mixture was refluxed, water added and the alcohol removed by distillation. The excess alkali solution was decanted from the semi-solid soapy sodium salt and the latter was dissolved in 3 liters of water. The salt solution was filtered and made acid with dilute hydrochloric acid. The white precipitate was washed thoroughly and crystallized from methanol, yielding 0.5 g. (34.7%) of transparent rectangular plates melting at 196–207°. After five recrystallizations from methanol and one from hexane, the melting point, which was constant after the third crystallization, was 217.5–218.5° (corr.), $[\alpha]_D -23^\circ$ (absolute ether). The acid mixture recovered from the mother liquors was not investigated at this time.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 78.88; H, 10.60; neut. equiv., 304.3. Found: C, 78.95; 78.75; H, 10.64, 10.70; neut. equiv., 305.

Di-*n*-amylamine Salt of the Dihydroabietic Acid.—A solution of 0.4 g. of material in 10 cc. of acetone was treated with 0.3 g. of di-*n*-amylamine in acetone. The solution was boiled for about ten minutes and filtered. On standing, 0.3 g. of di-*n*-amylamine salt was obtained, m. p. 114.5–118°. The compound was recrystallized five times from acetone and the melting point, constant after the second recrystallization, was 121.5–122° (corr.); $[\alpha]_D -24^\circ$ (absolute ether).

Anal. Calcd. for $C_{30}H_{48}O_2N$: C, 77.99; H, 12.01. Found: C, 77.70; H, 12.14.

The dihydroabietic acid recovered from the di-*n*-amylamine salt in the usual manner showed the following constants, m. p. 217.5–218.5° (corr.), $[\alpha]_D -24^\circ$ (absolute ether).

The Methyl Ester of Dihydroabietic Acid.—Dihydroabietic acid (0.2 g.) was dissolved in anhydrous ether and ethereal freshly prepared diazomethane was added until the yellow color persisted for thirty minutes. The ether and diazomethane were then distilled off, yield of ester, 0.2 g. It was recrystallized four times from methanol and the melting point remained constant after the second crys-

(13) Analysis by Mr. S. Gottlieb, Columbia University, New York City.

tallization, 131.5–132.5° (corr.), $[\alpha]_D -21.5^\circ$ (absolute ether).

Anal. Calcd. for $C_{21}H_{34}O_2$: C, 79.18; H, 10.76.
Found: C, 79.05; H, 10.87.

Summary

1. An apparently new dihydroabiatic acid of

high melting point and purity was obtained from dihydrodibromoabiatic acid on reduction with sodium and absolute ethyl alcohol.

2. The dihydro acid was characterized through its di-*n*-amylamine salt and methyl ester.

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RECEIVED MARCH 22, 1939

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

The Presence of Dihydroabiatic Acid in Pine Oleoresin and Rosin

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As shown previously, dihydroabiatic acid is readily converted to its isomeric lactone with either hydrobromic acid¹ or concentrated sulfuric acid.²

The high stability of the lactone, not only as compared with its isomeric dihydroabiatic acid, but with the completely saturated tetrahydrohydroxyabiatic acid saponification product,² is evidenced both by the drastic saponification conditions required to form the tetrahydrohydroxy acid, and by the ease with which the latter splits off water and reverts to the lactone. This takes place readily when the tetrahydrohydroxyabiatic acid is kept at the melting temperature (165°) for a few minutes.²

The ease with which the lactone is formed, its high stability toward alkali, and good crystallizing properties render this compound an excellent medium for the qualitative and approximately quantitative determination of dihydroabiatic acid in mixtures of resin and rosin acids. It has thus been possible to establish the presence of small quantities of dihydroabiatic acid in pine oleoresin, rosin, and other complex mixtures containing large proportions of other resin and rosin acids, hitherto impossible of accomplishment by any of the known methods.

Earlier investigators have shown the presence of dextropimaric, levopimaric³ and proabiatic acids⁴ in pine oleoresin, but the presence of dihydroabiatic acid in either oleoresin or rosin has not been recorded.

The oleoresin or rosin to be tested for dihydro-

abiatic acid was first freed from neutral material, such as resenes and turpentine, by dissolving in ether and extracting with alkali. These neutrals were discarded. The acids, regenerated from the soaps, were dried below isomerization temperatures and then dissolved in cold concentrated sulfuric acid. The precipitate formed by pouring the solution on ice was separated into acid and neutral fractions by extraction of an ether solution with dilute alkali. Lactonized dihydroabiatic acid is not saponified by the alkali, and was therefore present in the neutral fraction. The pure material was obtained by recrystallization from methyl alcohol.

The oleoresin and rosin of *P. palustris* and *P. caribaea* subjected to this treatment yielded 3 to 4% of lactonized dihydroabiatic acid. As the amount obtained from rosin was about the same as that from the oleoresin, the formation of dihydroabiatic acid as a secondary product due to disproportionation⁵ of hydrogen during normal processing of oleoresin, would seem highly improbable, and the presence of dihydro acid as an original constituent, both in the original oleoresin and rosin, would seem to be proved. In the case of the acids isolated from pine oleoresin, the temperature was not allowed to rise above 30° at any time during the operation.

An interesting finding in connection with the treatment of the oleoresin and rosin with concentrated sulfuric acid is that *l*-abiatic acid is formed very rapidly by low temperature isomerization. The latter is complicated, however, by the formation of a small amount of ill-defined sulfonated products, so that the isolation of pure compounds

(5) The temperature required for the disproportionation reaction was shown to be about 250° [Fleck and Palkin, *THIS JOURNAL*, **61**, 247 (1939)]. In normal processing of oleoresin for rosin, the temperature does not exceed 165°.

(1) Ruzicka and Meyer, *Helv. Chim. Acta*, **5**, 332 (1922).

(2) Ruzicka, Meier, Waldmann and Hösli, *ibid.*, **16**, 178 (1933); Hasselstrom, Brennan and McPherson, *THIS JOURNAL*, **60**, 1267 (1938); Fleck and Palkin, *ibid.*, **60**, 2621 (1938).

(3) Cailliot, *Bull. soc. chim.*, [2] **21**, 387 (1874); Vesterberg, *Ber.*, **18**, 3331 (1885); **20**, 3248 (1887).

(4) Kraft, *Ann.*, **524**, 1 (1936).