

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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[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

BY E. E. FLECK AND S. PALKIN

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-

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

(2) Ruzicka, Meier, Waldmann and Hösl, *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).

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°.

from the acid fractions of the sulfuric acid treated oleoresin and rosin was attended with considerable difficulty. However, by working through the acid sodium salt, *l*-abietic acid of relatively high purity ($[\alpha]^{20D} - 97^\circ$) was obtained in a yield of about 10%. While the yield of crude acid sodium salt of *l*-abietic was smaller from the cold sulfuric acid procedure than from the hot alcoholic hydrochloric acid treatment,⁶ the amount of pure *l*-abietic acid obtained was apparently the same in both cases. The purification of the acid sodium salt from the cold sulfuric acid process was accomplished with fewer recrystallizations than found necessary when alcoholic hydrochloric acid was the isomerizing medium.

Experimental evidence to prove that the sulfuric acid treatment itself did not produce the dihydroabietic acid was obtained by subjecting to the treatment with cold sulfuric acid, the pure acids of known identity.

When *l*-abietic acid, prepared by the method of Palkin and Harris,⁶ was subjected to the cold sulfuric acid treatment, no more than a trace of partially crystalline neutral material was obtained. The acidic portion was found to consist of apparently unaltered *l*-abietic acid, the specific rotation having been but slightly lowered, from -104 to -95° , by the procedure.

l-Pimaric acid subjected to the same treatment gave only a trace of partially crystalline neutral material, while the main reaction was the production of *l*-abietic acid in good yield and quality. By conversion into the acid sodium salt, characteristic of *l*-abietic acid, and recrystallization, followed by regeneration of the free acid, a product was obtained whose specific rotation, $[\alpha]^{20D} - 104^\circ$, remained constant on further preparation and recrystallization of the acid sodium salt. The fact that this acid was found to be identical with the *l*-abietic acid obtained by Palkin and Harris from rosin by treatment with alcoholic hydrochloric acid at reflux temperatures constitutes independent confirmation of the homogeneity of the *l*-abietic acid they obtained.

Treatment of *d*-pimaric acid with cold concentrated sulfuric acid yielded a mixture of approximately equal parts of a non-crystalline acid and non-crystalline neutral product, the nature of which will be considered in a later publication.

Hydrogenated rosin (commercial grade) subjected to the sulfuric acid treatment gave a good

yield of lactonized dihydroabietic acid, which was obtained readily in the pure state on recrystallization.

Experimental Part

Isolation of the Acid Fraction of Pine Oleoresin.—A 100-g. portion of pine oleoresin (collected in 1938) was dissolved in ether and filtered to remove "chips," dirt, etc. The filtrate was extracted with 0.25 *N* sodium hydroxide, the aqueous extract shaken four times with ether, and then acidified to congo red with dilute hydrochloric acid. The acids were extracted with ether and the ether solution was washed with water until the washings were neutral to congo red. The ether was distilled under reduced pressure from a bath not warmer than 30° . When concentrated to the point where excessive foaming took place the material was poured into drying pans and last traces of ether removed by evacuating in a desiccator at room temperature. The acids from *P. palustris* oleoresin had a rotation $[\alpha]^{20D} - 54^\circ$,⁷ and those from *P. caribaea*, $[\alpha]^{20D} - 32^\circ$.

Isolation of the Acid Fraction of Pine Rosin.—The procedure used was the same as that outlined for the pine oleoresin, with the exception that no attempt was made to hold the temperature below 30° . The rosins used were made from oleoresin collected in 1938. The final product was dried in vacuum at 80° .

Action of Sulfuric Acid on the Acids of Pine Oleoresin and Rosin.—Twenty grams of finely powdered rosin acids was added, in the course of ten minutes, to 100 cc. of concentrated sulfuric acid, cooled to -5 to -10° . Stirring and cooling was continued for forty-five minutes. The solution was then poured on 400 g. of ice and the precipitate that formed was collected and washed with ice water. The aqueous layer that separated when the filter cake was dissolved in ether was drawn off, the ether solution was extracted with 0.25 *N* sodium hydroxide, and then washed with water until neutral to phenolphthalein.

Lactone.—Distillation of the ether yielded a residue that crystallized when seeded with lactonized dihydroabietic acid. This crude product was recrystallized from 5 cc. of methyl alcohol.

NEUTRAL PRODUCT RESULTING FROM SULFURIC ACID TREATMENT

Calcd. for $C_{20}H_{32}O_2$: C, 78.88; H, 10.60.

Source of acids used	Crude, Re- g. cryst., g.		M. p., °C.	Analysis of lactonized dihydroabietic acid, m. p.	
				131-132° C	H
<i>P. palustris</i> oleoresin	1.7	0.7	124-129	78.67	10.69
<i>P. palustris</i> rosin	1.3	0.6	125-129	78.74	10.44
<i>P. caribaea</i> oleoresin	2.1	0.7	121-128	78.67	10.61
<i>P. caribaea</i> rosin	2.0	0.65	122-128	78.86	10.77

A second recrystallization from methyl alcohol yielded lactonized dihydroabietic acid, melting point $131-132^\circ$ from all fractions. These fractions all rotated $[\alpha]^{20D} - 4^\circ$, and showed no lowering of melting point when mixed with authentic lactonized dihydroabietic acid.

Isomerized Acids.—The alkaline extract of the sulfonation product was acidified with dilute hydrochloric acid

(7) The specific rotations recorded in this publication were all taken on 2% absolute alcoholic solutions.

(6) Palkin and Harris, *THIS JOURNAL*, **56**, 1935 (1934).

and then extracted with ether. After washing the ether extracts until the washings were neutral to congo red, the ether was distilled. The residue obtained was dissolved in four times its volume of alcohol. One-fourth of this solution was neutralized with 5% sodium hydroxide and then the remainder of the alcoholic solution was added. After standing for several days the crystalline acid sodium salt was filtered and recrystallized from 30 cc. of alcohol. The *l*-abietic acid was freed by addition of dilute hydrochloric acid and subsequent recrystallization from dilute alcohol.

Source of acids used	Yield of <i>l</i> -abietic acid, g.	$[\alpha]^{20D}$	M. p., °C.
<i>P. palustris</i> oleoresin	2.3	-99°	163-166
<i>P. palustris</i> rosin	2.4	-97°	164-167
<i>P. caribaea</i> oleoresin	2.0	-97°	164-167
<i>P. caribaea</i> rosin	2.1	-98°	167-169

No lowering of the melting point was produced when these samples of *l*-abietic acid were mixed with *l*-abietic acid prepared by the method of Palkin and Harris.⁶

The Action of Sulfuric Acid on *l*-Abietic Acid.—Fifteen grams of *l*-abietic acid,⁶ $[\alpha]^{20D} -104^\circ$, was added to cold concentrated sulfuric acid as outlined above. When separated into acid and neutral fractions, there was isolated only a trace of partially crystalline neutral material. The crude acid fraction was recrystallized from dilute alcohol and dried in vacuum at room temperature. The yield was 12.5 g. of material that melted at 169-172°, $[\alpha]^{20D} -95^\circ$, and showed no lowering of melting point when mixed with starting material.

Isomerization of *l*-Pimaric Acid with Concentrated Sulfuric Acid.—Four grams of powdered *l*-pimaric acid (m. p. 143-148°; $[\alpha]^{20D} -271^\circ$) was added during the course of ten minutes to 20 cc. of concentrated sulfuric acid, and cooled to -5 to -10°. Stirring and cooling was continued for forty-five minutes and then the light yellow colored solution was poured into 100 g. of ice. The precipitate was worked up as outlined above into neutral and acid fractions. There was only a trace of partially crystalline neutral material. Crystallization of the acid fraction from dilute alcohol gave 3.1 g. of material which

melted at 170-172°; $[\alpha]^{20D} -94^\circ$. This material was converted into the acid sodium salt, recrystallized from alcohol, and isolated as the free acid, as outlined above. The dried material rotated $[\alpha]^{20D} -104^\circ$. Further purification was attempted by reconversion into the acid sodium salt and recrystallizing the salt twice more from alcohol. When the free acid was regenerated and dried in high vacuum at room temperature, it melted at 169-172°, $[\alpha]^{20D} -104^\circ$. When mixed with *l*-abietic acid prepared by the method of Palkin and Harris,⁶ no lowering of the melting point took place. *Anal.* Calcd. for $C_{20}H_{30}O_2$: C, 79.41; H, 10.01. Found: C, 79.17; H, 10.18.

Lactonization of the Dihydroabietic Acid in Commercial Hydrogenated Rosin.—The acids were freed from neutral material, by extraction, as outlined above.

Twenty grams of the acids obtained from a commercial hydrogenated rosin was subjected to the action of cold concentrated sulfuric acid as outlined above. When separated into acid and neutral fractions, 7.7 g. of neutral crystalline material was obtained. After two recrystallizations from methyl alcohol, 3.2 g. of lactonized dihydroabietic acid, m. p. 131-132°, $[\alpha]^{20D} -4^\circ$, was obtained. This material showed no depression of melting point when mixed with authentic lactonized dihydroabietic acid.

Summary

Conversion to the isomeric lactone affords an excellent means for detecting dihydroabietic acid in the presence of large proportions of other resin acids.

By this means dihydroabietic acid has been shown to be present in the oleoresin and the rosin of *P. palustris* and *P. caribaea*.

Cold concentrated sulfuric acid has been shown to isomerize *l*-pimaric acid into *l*-abietic acid.

Lactonized dihydroabietic acid may readily be prepared from commercial hydrogenated rosin.

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Erythrina Alkaloids. III. Isolation and Characterization of a New Alkaloid, Erythramine

BY KARL FOLKERS AND FRANK KONIUSZY

From the studies which are being made in this Laboratory on species of *Erythrina*, a preliminary paper on twenty-six species showed that the principles of curare-like action were widely distributed in the genus, both geographically and in the various sections of the genus.¹ This wide distribution has been proven further by continued study of many additional species. The isolation of the first of several new physiologically active alka-

loids was announced² recently and the details as well as new data will be submitted for publication soon.

The present paper describes the isolation and characterizes another of the physiologically active alkaloids, which has been named erythramine. It was isolated from the seeds of *Erythrina sandwicensis* Deg. and *Erythrina subumbrans* (Hassk.) Merrill. The identity of the *Erythrina* seeds

(1) Folkers and Unna, *J. Am. Pharm. Assoc.*, **27**, 689 (1938).

(2) Folkers and Major, *This Journal*, **59**, 1580 (1937).