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The Preparation of *l*-Abietic Acid (Schulz) and Properties of Some of its Salts[1]

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Abietic acid, one of the earliest rosin acids isolated, has received a great deal of study, mostly, however, in admixture with its isomers. Such mixtures have all too often been used without further purification in important investigations.

The term abietic acid, first used by Baup,[2] has been ascribed indiscriminately in the literature to various rosin acids thought to be individual compounds but consisting generally of mixtures of the *l*-abietic acid of Schulz[3] with varying proportions of isomeric acids isomorphous with it.[4]

Although its preparation has been greatly facilitated by the methods of Steele[5] and Dupont–Desalbres–Bernette,[6] its subsequent purification from the various isomers in order to obtain the pure Schulz acid (m. p. 171–173°, $[\alpha]_D$ about $-100°$) is ordinarily a laborious task requiring numerous crystallizations from acetic acid and alcohol.

As shown by Dupont,[7] nearly all the primary oleoresin acids undergo isomerization[8] readily by heat or treatment with mineral acids, with the formation of *l*-abietic acid. The course of isomerization is by no means simple or direct, there being formed isomerization products intermediate between the primary acids and *l*-abietic acid, and the latter, although relatively more stable, itself undergoes isomerization under appropriate conditions and there results, generally, a complex mixture of the various isomers. Since all of these are isomorphous with abietic acid, any process of separation depending upon fractional crystallization of the acids is rendered exceedingly laborious.

As was noted with the pimaric[9] acids, this isomorphous tendency was largely overcome by working with the salts. Progressive elimination of oxidation products is another advantage that follows the use of (sodium) salts for this purpose.

Although virtually it forms no crystalline neutral sodium salts, *l*-abietic acid[10] has been shown by Dupont and Desalbres[11] to form an acid sodium salt ($C_{19}H_{29}COONa \cdot 3C_{20}H_{30}O_2$) which crystallizes readily from alcohol. While this property is supposedly unique with *l*-abietic acid, it is apparently not limited to the pure acid, as mixtures with its isomers (*l*-abietic acid constituting the major portion) also form this acid sodium salt, from which the salt of the pure *l*-abietic acid may be obtained by fractional crystallization. As will be shown later (see Table I), the impression of the above-cited authors as to the homogeneity of the compound for which they report the properties $[\alpha]_J$ $-80°$ and m. p. 170–175° is apparently erroneous.

The advantage of using this compound as a medium for the gross removal of crude abietic acid from large quantities of rosin reaction mixtures over other methods such as distillation in high vacuum[12] or the frequently used Steele[5] method involving large volumes of glacial acetic acid, has, to some extent, been appreciated, but the practicability of preparing *l*-abietic acid free from its isomers by way of this acid salt has evidently been overlooked, since tedious crystallizations from acetic acid and alcohol (similar to the Steele method) have, for this purpose, been regarded as unavoidable.

As will be shown in the experimental part, an acid salt with a rotation of $[\alpha]_D$ $-95°$, and m. p. 205–208°, and from it an acid with a rotation of $[\alpha]_D$ $-102°$ and m. p. 170–174° can thus be speedily obtained.

Another even more effective means of purification is by way of its salts with organic bases, several of which have been prepared by Balas[14] and Dupont and Desalbres.[11] With the availability, recently, of some of these bases in commercial quantities, they too now afford a very practical laboratory method for the preparation of pure *l*-abietic acid in quantity, particularly for use in the later stages of purification.

(1) Presented before the Division of Agricultural and Food Chemistry, (Symposium on Naval Stores), St. Petersburg meeting of the American Chemical Society, March 25–30, 1934.

(2) Baup, *Ann. Chim. Phys.*, [2] **31**, 108 (1826).

(3) Schulz, *Chem. Z.*, **41**, 666 (1917).

(4) Schulz was the first to prepare this acid in anything like a pure state.

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

(6) Dupont, Desalbres and Bernette, *Bull. Inst. du Pin*, No. **22**, 349 (1926).

(7) Dupont, *Bull. soc. chim.*, [4] **29**, 718 (1921).

(8) Dextro pimaric acid does not isomerize.

(9) Palkin and Harris, THIS JOURNAL, **55**, 3677 (1933).

(10) Under special anhydrous conditions crystalline neutral salts have been obtained by Dupont, *et al.*[6] and Georgi.[13]

(11) Dupont and Desalbres, *Bull. Inst. du Pin*, No. 22, 352 (1926).

(12) Ruzicka and Schinz, *Helv. Chim. Acta*, **6**, 833 (1923).

(13) Georgi, *J. Chem. Ed.*, **10**, 415 (1933).

(14) Balas, *Casopis Ceskoslovenského Lékárnictva*, **7**, 320 (1927).

Experimental Part

Isomerization and Neutralization.—While the procedure for the isomerization treatment and subsequent neutralization is in general as described by Dupont, Desalbres and Bernette,[6] the following precautions were necessary. The rosin (1200 g., grades K to W) dissolved in 2500 cc. of alcohol was refluxed with 21 cc. of concentrated hydrochloric acid for the isomerization. To the cooled solution only enough alkali (15.65 cc. of 16 *N* sodium hydroxide) was added directly to neutralize the mineral acid. To ensure against formation of a double layer, the additional alkali necessary to make the acid sodium salt, ascertained by titration of a 10 or 20 cc. portion, was diluted first with alcohol and then with rosin solution; 103 cc. of 8 *N* sodium hydroxide diluted with 150 cc. of alcohol and then with 100 cc. of rosin solution resulted in a clear homogeneous solution. This was added to the main rosin solution and the whole allowed to stand at room temperature for twenty-four hours. The crystalline mass which separated was filtered by suction, leached once with about 250 cc. of cold alcohol and filtered. It was then subjected to fractional crystallization, the successive steps of which are indicated in Diagram 1 of Fig. 1.

As the alcoholic concentration of the acid salt is an important factor in the fractionation, the recrystallizations were carried out in the following manner. The crop of crystals (rotation previously determined on a small sample) was dissolved in a slightly more than minimum of hot alcohol, and an aliquot (about 10 cc.) titrated with 0.5 *N* sodium hydroxide. From this the total resin acid equivalent was ascertained by multiplying the titration value by 1.33. (The concentrations indicated in the diagram are given on that basis.) The cooled solution was then allowed to stand at room temperature until the next day. The usual devices of scratching, seeding, etc., were found very helpful in the crystallizations.

Only the first crop in each step is indicated in the diagram. Additional crops, omitted in the diagram to conserve space, were combined where rotations warranted, and worked up in the usual manner. The numerical values of the respective experiment numbers represent approximate weights (moist) of each crop. The abietic acid (as in 120 H) was obtained from 420 F by neutralization with normal sulfuric acid in alcoholic solution a little more than the calculated quantity of the mineral acid (ascertained by titration of an aliquot of the alcoholic solution) being used and water being added very gradually to permit crystals to form. Melting point and rotations for either salt or free acid were determined on samples dried in vacuum at 50 to 60°. An alcoholic solution generally containing 1 g. per 100 cc. of solution was used for the rotations.

As will be noted in Diagram 1, rise in rotation to that of the Schulz acid is fairly rapid.

Diagram 1[a]

1210 C, $[\alpha]_D$ −60° —10[b]→ 910 D, $[\alpha]_D$ −78° —11→ 460 E, $[\alpha]_D$ −86.6° —15→ 420 F, $[\alpha]_D$ −95.3° —liberated→ Acid 120 H, $[\alpha]_D$ −100.5°, M. p. 171–173°

Diagram 2[a]

Abietic acid 380 A, $[\alpha]_D$ −83.1 —12[b]→ 230 B, $[\alpha]_D$ −57.1°(S)[c], $[\alpha]_D$ −93.5°(A) —10→ 130 C, $[\alpha]_D$ −60.6°(S), $[\alpha]_D$ −100.5°(A) —10→ 65 D[d], $[\alpha]_D$ −57°(S), $[\alpha]_D$ −104°(A), M. p. 172–7(A)

[a] Only the first crop in each step is indicated in order to conserve space. [b] Numbers on arrows indicate concentrations of the solutions in terms cc. per gram. Alcohol was the medium for the sodium acid salt and acetone for the diamylamine salt. [c] "S" = salt. "A" = acid. [d] This salt was recrystallized twice without change in properties.

Fig. 1.—Scheme for the preparation of pure *l*-abietic acid by way of the acid sodium salt (Diagram 1) and by way of the diamylamine salt (Diagram 2).

Abietic acid of higher purity was apparently obtained by recrystallization of the diamylamine salt (Diagram 2 of Fig. 1).

Salts with Organic Bases.—These were in general prepared by mixing molecular quantities of abietic acid and the appropriate base in acetone solution and, heating for a few moments on the steam-bath if necessary.

TABLE I

PROPERTIES OF *l*-ABIETIC ACID (SCHULZ) AND ITS SALTS

No.	Base used	M. p., °C.	Salt[a] $(\alpha)_D$ (589.3 mμ)	Salt[a] $(\alpha)_I$ (578 mμ)	Index of refr.[g] n_α	Index of refr.[g] n_γ
1	(NaOH, 0.25 equiv.) $C_{19}H_{29}COONa \cdot 3C_{20}H_{30}O_2$	205–208	− 97	−102.5	1.555	1.595
		170–175[b]	− 80[b]		n_β = 1.575	
2	Diamylamine[c]	139–141	− 57	− 59.7		
3	Di-*n*-amylamine[d]	141–142	− 74.5		1.513	1.548
4	Diisoamylamine[d]	139–141	− 62.4		1.515	1.556
	Balas[e]	133	− 17.1			
5	Di-*n*-propylamine[d]	160–162	− 63.5	− 67.5	[f]	[f]
	Balas[e]	160				
6	Di-*n*-butylamine[d]	158–161	− 69.3		[f]	[f]
7	Quinine, cryst. from alcohol	185–187	−140.3		1.570	1.615
	Balas[e]	180				
8	*n*-Butylamine[d]	164–169 dec.	− 72.7		1.553	1.600

TABLE I (*Concluded*)

No.	M. p., °C.	Liberated acid $(\alpha)_D$ (579.3 mμ)	$(\alpha)_J$ (578 mμ)	Index of refraction n_α	$n\beta$	$n\gamma$
1	170–174	−102–105	−107–105			
2	171–177	−104	−110.5			
4				1.515	1.590	1.600
6	169–175	−103.9				
8	171–176					
Dupont[h]	172–173		−100			

[a] Rotations determined in alcohol solution, 1 g. per 100 cc. [b] Data reported by Dupont, Desalbres and Bernette, *Bull. inst. pin*, **22**, 349 (1926). [c] Sharples diamylamine (mixed isomers). [d] Eastman organic reagents. [e] Data reported by Balas, *Časopis Československého Lékárnictva*, **7**, 320 (1927). [f] Soluble in immersion liquids. [g] The crystallographic data were furnished by G. L. Keenan of the Food and Drug Administration. [h] Data reported by Dupont and Uzac, *Bull. soc. chim.*, **4**, 394 (1924).

CRYSTALLOGRAPHIC DATA

Sodium Acid Salt of Abietic Acid.—This substance crystallizes in colorless rods and needles. In parallel polarized light (crossed nicols), the extinction is straight and the sign of elongation −; the double refraction is strong; polarization colors of first order, usually white. The substance apparently crystallizes in the orthorhombic system.

Di-*n*-amylamine Salt of Abietic Acid.—This substance consists of colorless rods. In parallel polarized light (crossed nicols), the extinction is straight and the sign of elongation +; the double refraction is strong; polarization colors usually of first order. The substance apparently crystallizes in the orthorhombic system.

Diisoamylamine Salt of Abietic Acid.—This substance crystallizes in colorless rods showing straight extinction and positive elongation with crossed nicols. The double refraction is strong, $\gamma - \alpha = 0.041$.

Quinine Salt of Abietic Acid.—When examined in ordinary light, this substance is seen to consist of very fine, colorless needles. Most needles show n_α crosswise, and n_γ lengthwise. In parallel polarized light (crossed nicols), the extinction is straight and the sign of elongation is +.

***n*-Butylamine Salt of Abietic Acid.**—This substance crystallizes in colorless plates. In parallel polarized light (crossed nicols), the plates extinguish sharply and first order polarization colors usually shown; double refraction strong.

Abietic Acid.—This substance is colorless and consists of plates of irregular shape. The plates usually extinguish sharply with crossed nicols, and exhibit brilliant polarization colors. According to Groth [*Chem. Kryst.*, **3**, 766 (1910)] abietic acid crystallizes in the monoclinic system, optic sign, negative, $2E = 65°$.

The other salts were too soluble in the test liquids.

Diamylamine Salt (Mixed).—In the preparation of the diamylamine salt, 108 g. of diamylamine ("Sharples," mixture of di iso- and di-*n*-amines) in 100 cc. of acetone was added to an acetone solution (2400 cc.) containing 205 g. of abietic acid ($[\alpha]_D$ −83°). The resulting crystalline mass, filtered by suction, was subjected to fractional crystallization in acetone. The steps are indicated in Diagram 2, Fig. 1.

Since the base can be recovered in the usual manner without much difficulty, this procedure affords not only a very efficient, but a very practical means for procuring a pure *l*-abietic acid.

One of the particular advantages of organic bases is their antioxidant properties.

As will be noted in 65 D (Diagram 2), the abietic acid so obtained showed a higher rotation and melting point than heretofore recorded in the literature. These properties did not change on recrystallization from alcohol, acetic acid and acetone. Properties of the salt were not altered by recrystallization from acetone and alcohol.

Other salts of abietic acid were prepared as described for the diamylamine salt. Tabulated data on their properties are given in Table I.

The crystallographic data were furnished by G. L. Keenan of the Food and Drug Administration.

Summary

Improved methods of preparation for pure *l*-abietic acid (Schulz) are described and data on the properties of some of its salts are given.

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