[Contribution from the Naval Stores Research Section, U. S. Department of Agriculture]*

An Improved Procedure for the Isolation of Neoabietic Acid From Pine Oleoresin and Rosin

VIRGINIA M. LOEBLICH and RAY V. LAWRENCE

Received January 20, 1956

A method is described for isolating neoabietic acid from pine oleoresin or rosin in an 8–12% yield by recrystallization of the 2-amino-2-methyl-1,3-propanediol salt of the resin acids from methyl ethyl ketone.

Pine oleoresin and rosin contain a mixture of resin acids which, because of their closely related structures and tendency to form isomorphous mixtures, do not respond to conventional methods of isolation and purification. Two techniques have been successfully applied to the isolation of the pure resin acids—the fractional recrystallization of their sodium or amine salts, and chromatography.

Levopimaric and dextropimaric acids possess the property of forming crystalline sodium salts, a property which has served as a principal method for the isolation of these acids.[1,2,3] The recent method of selective recrystallization of the 2-amino-2-methyl-1-propanol salt of the resin acids in pine gum from a suitable solvent has greatly increased the yields and simplified the isolation of levopimaric acid in a high state of purity.[4,5] *l*-Abietic acid does not readily form a crystalline monosodium salt but does form the "quarter salt" ($C_{19}H_{29}COONa \cdot 3C_{20}H_{30}O_2$)[6] which can be prepared from acid-isomerized oleoresin or rosin and purified by recrystallization. The recrystallization of the diamyl amine salt[6,4] from acetone also affords a convenient means of isolating *l*-abietic acid.

In 1948, Harris reported the isolation of two new resin acids from pine oleoresin and rosin.[4,7] The first, iso-dextropimaric acid, was isolated by reacting the acid-isomerized, conjugated-diene acids with maleic anhydride and then separating the unreacted acids, iso-dextropimaric and dextropimaric acids, from the maleic anhydride adduct by precipitating them from aqueous alkaline solution at *p*H 6.2. The second, neoabietic acid, was isolated from the oleoresin in the following manner. The resin acids were precipitated from the gum as the cyclohexylamine salt and the levopimaric acid then was removed as the 2-amino-2-methyl-1-propanol salt. Salts of low dextrorotatory power from the mother liquor were converted to the diethylamine salt and were recrystallized from acetone. The final purification was effected by again converting the acids to the 2-amino-2-methyl-1-propanol salt. When rosin was used as the starting material, the neobietic acid was first concentrated as the diethylamine salt and was further purified as the 2-amino-2-methyl-1-propanol salt.

Recent composition studies in this laboratory revealed the presence of another abietic-type acid in pine oleoresin and rosin—namely, palustric acid.[8] This acid was isolated by means of partition chromatography.

The method described in this paper for the isolation of neoabietic acid is based on the selective recrystallization of the 2-amino-2-methyl-1,3-propanediol salt of the resin acids in pine oleoresin or rosin from methyl ethyl ketone. Two recrystallizations gave an 8% yield of the pure salt. The method is quite simple and can easily be adapted to a larger scale.

EXPERIMENTAL

Isolation of the 2-amino-2-methyl-1,3-propanediol salt of neoabietic acid from rosin. WW gum rosin[9] (acid no. 168) (400 g.) dissolved in 1400 ml. of methyl ethyl ketone[10] was placed in a 3-liter round-bottom flask equipped with a stirrer, thermometer, and condenser. The temperature was raised to 75° and 120 g. (mole/mole ratio of amine to resin acids based on the acid no. of the rosin) of 2-amino-2-methyl-1,3-propanediol was added with stirring. The heat was removed and the solution was allowed to cool slowly to room temperature overnight. The resulting amine salt then was recrystallized from methyl ethyl ketone, following a modi-

---

[*] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

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

(2) Ruzicka, Balas, and Vilim, *Helv. Chim. Acta*, **7,** 458 (1924).

(3) Palkin and Harris, *J. Am. Chem. Soc.*, **55,** 3677 (1933).

(4) Harris and Sanderson, *J. Am. Chem. Soc.*, **70,** 334 (1948).

(5) Loeblich, Baldwin, O'Connor, and Lawrence, *J. Am. Chem. Soc.*, **77,** 6311 (1955).

(6) Palkin and Harris, *J. Am. Chem. Soc.*, **56,** 1935 (1934).

(7) Harris and Sanderson, *J. Am. Chem. Soc.*, **70,** 2079 (1948).

(8) Loeblich, Baldwin and Lawrence, *J. Am. Chem. Soc.*, **77,** 2823 (1955).

(9) The same procedure can also be used with pine oleoresin as the starting material. The yield is usually slightly higher from rosin.

(10) Acetone may be substituted for methyl ethyl ketone as the solvent. Approximately the same yield is obtained using either solvent. Methyl ethyl ketone will completely dissolve the salt while the volume of acetone required for complete solution is so great that it is difficult to handle in the laboratory.

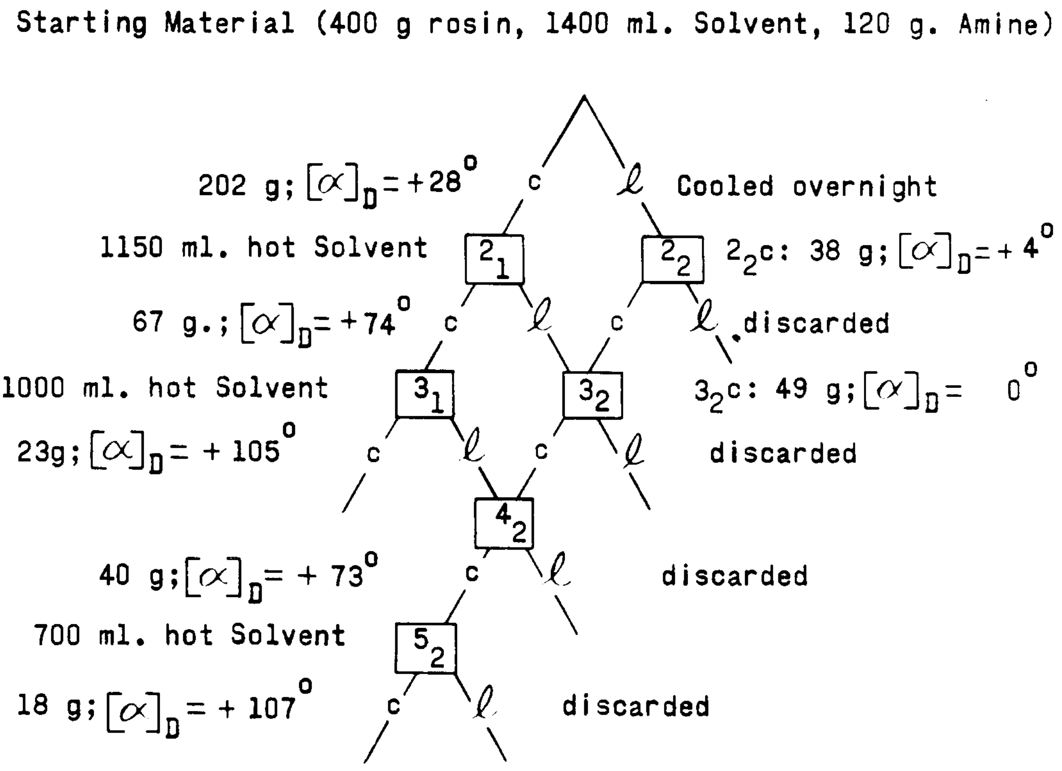

FIG. 1. SCHEME OF RECRYSTALLIZATION OF THE 2-AMINO-2-METHYL-1,3-PROPANEDIOL SALT OF NEOABIETIC ACID FROM ROSIN.

fied scheme of triangular recrystallization[11] diagrammed in Figure 1. Combination of fractions 3_1c and 5_2c gave 41 g. of salt with $[\alpha]_D$ +106° (2% soln. in 95% EtOH).[12] This weight of amine salt represents an 8.3% yield of neoabietic acid based on the acid no. of the rosin.

Conversion of the amine salt to the acid. The amine salt was converted to the free acid by suspending combined fractions 3_1c and 5_2c in 250 ml. of acetone and adding a slight excess of 2 *N* acetic acid to the suspension. The amine salt dissolved as it was converted to the free acid. The acid was precipitated by adding water until the solution was quite turbid and neoabietic acid began to crystallize. It was filtered and recrystallized from 180 ml. of acetone to give Crop 1; wt., 18.5 g., $[\alpha]_D$ +156°, m.p. 164–169°. Crop 2 was obtained by the evaporation of the mother liquor of Crop 1 to one-third its volume; wt., 5.5 g., $[\alpha]_D$ +157°. Crops 1 and 2 were combined and recrystallized from the minimum amount of boiling acetone. There was obtained 21 g. of neoabietic acid with an $[\alpha]_D$ +159.8°, m.p. 166.5–169° and maximum ultraviolet absorption at 252 mμ, $\alpha = 80.0$. On conversion of the salt to the acid, the yield of pure neoabietic acid was 70%. This figure can be raised by further evaporation of the acetone mother liquor.

Large scale isolation of the 2-amino-2-methyl-1,3-propanediol salt of neoabietic acid from rosin. The procedure described above was converted to a larger scale with excellent results. Two runs were made using 5 lbs. of rosin for each run. The first 5 lbs. of rosin was dissolved in 2.1 gal. of methyl ethyl ketone and 3 lbs. of amine was added. As shown in Figure 1, the scheme of recrystallization was followed on the left side of the triangle through 3_1c using proportionally larger amounts of solvent for the recrystallizations. This crop contained 145 g. of salt with an $[\alpha]_D$ of +102° and represented a 5.2% yield. The mother liquor from the original precipitation of the salt, 1_1, was discarded. A second 5 lbs. of rosin was dissolved in the mother liquor from the first recrystallization of run 1 (2_1l) and 3 lbs. of amine was added. The resulting crystals, 3_2c, were recrystallized from 3_1l to yield 4_2c. This crop was then recrystallized from the necessary amount of methyl ethyl ketone. Crop 5_2c contained 337 g. of salt with an $[\alpha]_D$ of +96°, representing a 12.1% yield. Hence, the advantage of using the mother liquors from a previous preparation is exemplified by the yields of 5.2% for run 1 as compared with 12.1% for run 2.

OLUSTEE, FLORIDA

---

(11) Tipson, in *Technique of Organic Chemistry*, A. Weissberger, Ed., Interscience Pub., New York, 1950, Vol. 3, pp. 424–426.

(12) Although the specific rotation for the pure 2-amino-2-methyl-1,3-propanediol salt of neoabietic acid is +118° (2% soln. in 95% EtOH), it has been found that recrystallization of the salt to obtain an $[\alpha]_D$ above +100° is not necessary. The remaining impurities can be removed by one or two recrystallizations of the acid from acetone.