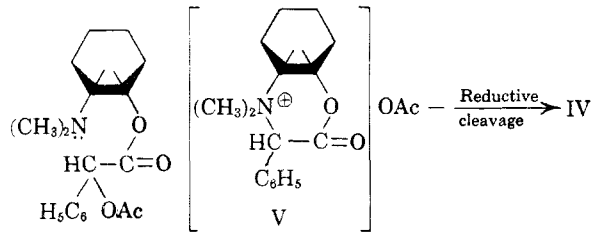
yield, has a curious feature in the reductive loss of the —OAc group leading to IV. One possible explanation for this facet of the reaction draws on the special geometry resulting from the *cis*-relationship of functional groups in I, permitting a nucleophilic attack of the basic $(CH_3)_2N$- group (*i.e.*, that small fraction present in equilibrium with the protonated form) on the mandelic carbon displacing acetate ion;



Such a process eliminating acetate ion and yielding the intermediate quaternary cycle V would have to be paired with a reductive cleavage step leading to the observed product IV. The most likely hydrogen donor in this step under these reaction conditions would be the excess amino alcohol I present, with the reductive cleavage being accompanied by its concomitant oxidation to amino ketone.

EXPERIMENTAL[5]

The *acetate of mandelyl chloride* (II) was prepared from purified mandelic acid, m.p. 118–119°, in standard fashion by successive reactions with acetic anhydride and thionyl chloride; b.p. 150° (14 mm.), reported[6] 142° (18 mm.). The product solidified in the receiver on standing; yellow solid, m.p. 34–36°. The *cis*-aminoalcohol I was prepared from the corresponding aminoketone by reduction with Pt and H_2 in ethanol solution as in the previous work.[4]

After preliminary studies indicating that reflux of I and II in chloroform for extended intervals gave only starting materials, toluene was incorporated into the reaction mixture to give a higher reflux temperature. In a typical esterification run, 10 g. (0.047 mole) of the acid chloride II and 6.78 g. (0.047 mole) of the solid amino alcohol I were dissolved in 50 ml. of chloroform and this solution diluted with 50 ml. of toluene. The mixture was brought to reflux and sufficient chloroform stripped off to bring the reflux temperature to about 105°, at which point it was held for 50 hr. The cooled solution was then saturated with HCl gas, resulting in separation of an oil that was found to consist largely of I as its hydrochloride. The supernatant solution was then stripped of solvent and the residual oil subjected to crystallization from chloroform-ether mixture. There was obtained 1.0 g. (7.1%) of crystals of the hydrochloride IV, white rosettes of needles, m.p. after repeated recrystallization 152.5–153.5° (Fisher-Johns).

Anal. Calcd. for $C_{16}H_{24}NO_2Cl$ (the phenylacetic ester): C, 64.52; H, 8.12; N, 4.70; Cl, 11.91. Found: C, 64.37; H, 7.96; N, 4.71; Cl, 11.94.

For comparison purposes, an authentic sample of IV was prepared by prolonged reflux of equimolar portions of I and phenylacetyl chloride, in chloroform-toluene mixture, followed by several recrystallizations of the product from chloroform and ether. M.p. 152.5–153.5°, mixed m.p. with the product from the acid chloride II, 152.5–153.5° (Fisher-Johns).

The compound prepared in reaction (1) was subjected to an *O*-acetyl determination essentially according to the procedure of Clark,[7] with the results described in the discussion section above.

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(5) Analyses by courtesy of the Microanalytical Laboratory, National Institute of Arthritis and Metabolic Diseases. Infrared spectra were obtained by Mr. W. M. Jones.

(6) R. Anschutz and R. Bocker, *Ann.*, **368**, 59 (1909).

(7) E. P. Clark, *Semimicro Quantitative Organic Analysis*, Academic Press, 1943, p. 73.

[CONTRIBUTION FROM THE NAVAL STORES RESEARCH SECTION, U. S. DEPARTMENT OF AGRICULTURE]

A New Method for Isolating Isodextropimaric Acid from Pine Oleoresin and Rosin

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A method is described for isolating isodextropimaric acid from pine oleoresin and gum rosin. The piperidine salt of the resin acids is precipitated from *n*-heptane solution, recrystallized from ethanol, and converted to the acid in acetone with hydrochloric acid. The yield of pure isodextropimaric acid varies from 3% to 5% depending on the species of oleoresin or rosin used. A new derivative, isodextropimarinol, was prepared and characterized.

In 1948 Harris and Sanderson[2] reported the presence of isodextropimaric acid in *Pinus palustris* oleoresin, wood rosin, and gum rosin. It was isolated by reacting the acid-isomerized, conjugated-diene acids with maleic anhydride and then separating the unreacted acids, isodextropimaric and dextropimaric acids, from the maleic anhydride adduct by precipitating them from aqueous alkaline solution at *p*H 6.2. Further fractionation of the mixture by recrystallization of the 2-amino-2-methyl-1-propanol salt yielded isodextropimaric acid.

The method described in this paper is based on the precipitation of the piperidine salt of the resin acids from *n*-heptane solution of pine oleoresin or rosin followed by selective recrystallization of the

(1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) G. C. Harris and T. F. Sanderson, *J. Am. Chem. Soc.*, **70**, 2079 (1948).

salt from 95% ethanol. The yield of isodextropimaric acid varies with the species of oleoresin or rosin used—5% for *Pinus elliotti* (slash pine) and 3% for *Pinus palustris* (longleaf pine).

A new derivative, isodextropimarinol, was prepared in essentially quantitative yields by reduction of isodextropimaric acid in an ether suspension of lithium aluminum hydride. Since the specific rotations of the resin acids and their derivatives differ in various solvents,[3,4] the specific rotation of a 1% solution of isodextropimarinol and isodextropimaric acid was determined in the more common organic solvents.

EXPERIMENTAL

Isolation of the piperidine salt of isodextropimaric acid from rosin. A solution of 400 g. of commercial WW gum rosin[5] (90% slash pine, acid No. 168) in 800 ml. of *n*-heptane was filtered and 102 g. of piperidine (mole/mole ratio of amine to resin acids based on the acid No. of the rosin) were added. A slight rise in temperature was observed. The solution was allowed to cool to room temperature and then placed in the refrigerator for 2 hr. Frequent stirring and scratching while the solution warmed to room temperature produced a haze; whereupon the mixture was placed in the refrigerator overnight. The resulting amine salt (wt. 43 g., $[\alpha]_D$ −3.3°, α at 241 mμ = 8.8) was recrystallized from 95% ethanol following a triangular scheme of recrystallization (Fig. 1).

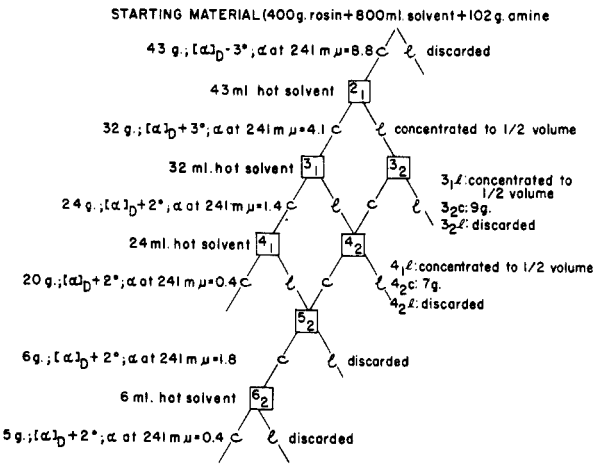

FIG. 1. SCHEME OF RECRYSTALLIZATION OF THE PIPERIDINE SALT OF ISODEXTROPIMARIC ACID FROM ROSIN.

A few drops of piperidine were added each time the salt was recrystallized or the mother liquor concentrated to compensate for loss by dissociation and evaporation.

Combination of fractions 4_1C and 6_2C gave 25 g. of amine salt representing a 5.4% yield of isodextropimaric 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 4_1C and 6_2C in 150 ml. acetone and adding 30 ml. of 3*N* hydrochloric acid. The acid was completely precipitated by adding 200 ml. of water. It was filtered, redissolved in 150 ml. of acetone, and again precipitated by the addition of water. One recrystallization of the acid from the minimum amount of boiling acetone gave 17 g. of isodextropimaric acid having an $[\alpha]_D$ 0° (2% solution in 95% EtOH), m.p. 162–164°, and no characteristic ultraviolet absorption in the region 220–320 mμ. This yield of pure isodextropimaric acid was 4.7% based on the acid No. of the rosin.

The specific rotation of isodextropimaric acid in the more common organic solvents was determined (Table I).

TABLE I

SPECIFIC ROTATIONS OF ISODEXTROPIMARIC ACID AND ISODEXTROPIMARINOL IN VARIOUS SOLVENTS

Solvent	$[\alpha]_D$ Isodextropimaric Acid (1% Solution)	$[\alpha]_D$ Isodextropimarinol (1% Solution)
Ethanol	0	−18.6°
Methanol	+ 4.4°	−13.6°
Benzene[a]	+26.1°	−26.8°
Isooctane	+ 4.8°	−20.5°
Heptane	+ 8.9°	−21.0°
Cyclohexane	+ 1.9°	−22.0°
Chloroform	− 1.3°	−24.6°
Ether	− 6.8°	−15.7°
Acetone	+ 3.8°	− 9.8°
Acetic acid	+ 6.1°	−10.0°
Acetonitrile	+10.5°	− 2.0°

[a] The $[\alpha]_D$ of a 10% benzene solution of isodextropimaric acid was +26.2°.

Isolation of the piperidine salt of isodextropimaric acid from longleaf oleoresin. A solution of 400 g. of longleaf oleoresin (acid no. 128) in 800 ml. *n*-heptane was filtered and 78 g. of piperidine was added. The procedure was identical to the one described using rosin as the starting material. The yield of pure salt was 3.2% based on the acid No. of the oleoresin.

Preparation of isodextropimarinol. Five grams of isodextropimaric acid was dissolved in 100 ml. of anhydrous ether and this solution was added to a suspension of 1.8 g. of lithium aluminum hydride in 60 ml. of ether. The mixture was refluxed for 4 hr. The excess lithium aluminum hydride was destroyed with water, and the mixture was acidified with 3*N* acetic acid, washed until neutral, dried over sodium sulfate, and evaporated to dryness. A quantitative yield of crystalline isodextropimarinol, m.p. 85–86°, was obtained by recrystallization from ethanol and water.

Anal. Calcd. for $C_{20}H_{32}O$: C, 83.27; H, 11.18, Found: C, 83.56, 83.30; H, 11.10, 11.16.

The specific rotation of a 1% solution of isodextropimarinol in various solvents is listed in Table I.

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(3) D. E. Baldwin, V. M. Loeblich, and R. V. Lawrence, *J. Am. Chem. Soc.*, **78**, 2015 (1956).

(4) V. M. Loeblich and R. V. Lawrence, *J. Am. Chem. Soc.*, **79**, 1497 (1957).

(5) The same procedure can also be used with slash pine oleoresin as the starting material. Based on the acid No. of the oleoresin, the yield of pure salt is 5%.