Organic Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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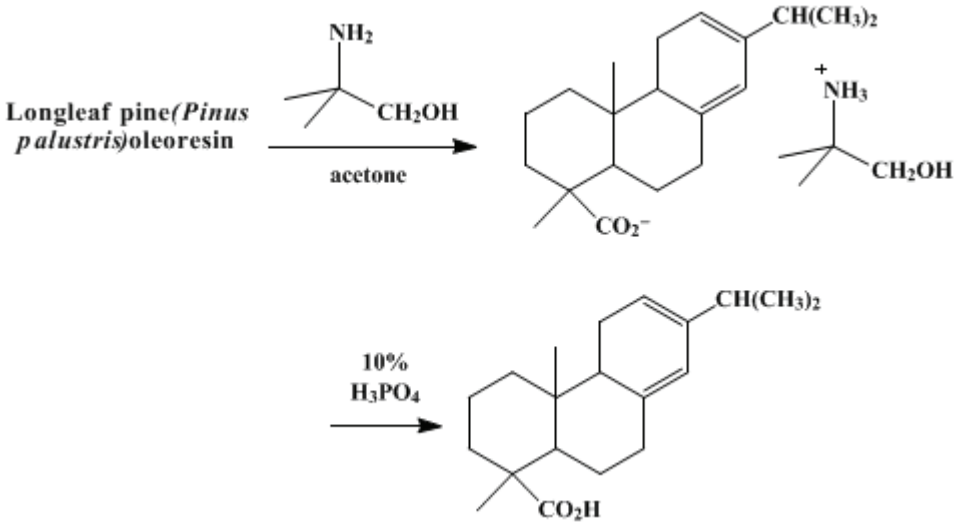
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.045.0064

Organic Syntheses, Coll. Vol. 5, p.699 (1973); Vol. 45, p.64 (1965).

LEVOPIMARIC ACID



Submitted by Winston D. Lloyd and Glen W. Hedrick[1].
Checked by William G. Dauben and Robert M. Coates.

1. Procedure

Pine oleoresin [1 kg. containing 260 g. (0.86 mole) of levopimaric acid] (Note 1) and (Note 2) is dissolved in 2 l. of acetone in a 4-l. beaker. A solution of 200 g. (2.2 moles) of 2-amino-2-methyl-1-propanol (Note 3) in 200 ml. of acetone is added as rapidly as possible with stirring. The pasty precipitate which forms almost immediately is collected by suction filtration and is pressed as dry as possible using a rubber dam (Note 4). The crude moist precipitate is returned to a 2-l. beaker and is dissolved in the minimum volume (~1 l.) of boiling methanol. The methanolic solution is cooled to 5° in a refrigerator and stirred occasionally to expedite crystallization. When the crystallization is completed, the solid is collected by suction filtration. The precipitate is redissolved in a minimum volume of boiling methanol (~1 l.) (Note 5), the solution concentrated to two-thirds its original volume (Note 6), cooled to 5°, and the amine salt allowed to crystallize. The solid is filtered by suction, and the filter cake is air-dried to yield 68–78 g. (20–23% of the available levopimaric acid) of the 2-amino-2-methyl-1-propanol salt of levopimaric acid, $[\alpha]^{25}D$ −202° (Note 7) and (Note 8). The recrystallization is repeated; approximately 0.8 l. of boiling methanol is used and then concentrated, the yield of amine salt is 41–46 g. (12–14% of the available levopimaric acid), $[\alpha]^{25}D$ −210° (Note 9).

In a 1-l. separatory funnel there are first placed 400 ml. of ether and 75 ml. of 10% phosphoric acid (Note 10), and then the above amine salt is added (Note 11). The mixture is shaken vigorously for a few minutes, an additional 50 ml. of 10% phosphoric acid added, and the vigorous shaking continued until all the solid has disappeared. The ether layer is separated, washed twice with 100-ml. portions of water, and dried over anhydrous sodium sulfate. The drying agent is separated by filtration, the ether is removed at room temperature under reduced pressure using a rotary evaporator, and the residue dissolved in 40–60 ml. of boiling ethanol. The levopimaric acid is collected by suction filtration, yield 26–31 g. (10–12%), m.p. 147–150°, $[\alpha]^{25}D$ −265° (Note 12), (Note 13), and (Note 14).

2. Notes

1. The longleaf pine (*Pinus palustris*) oleoresin used was analyzed by the method of Lloyd and Hedrick[2] and was found to contain a total resin acid content of 660 g. The oleoresin used by the checkers was obtained from Shelton Naval Stores Co., Valdosta, Georgia. The oleoresin can also be obtained from the following sources: K. S. Varn and Co., Hoboken, Georgia; The Langdale Co., Valdosta, Georgia; Vidalia Gum Turpentine Co., Vidalia, Georgia; Stallworth Pine Products Co., Mobile, Alabama;

Filtered Rosin Products Company, Baxley, Georgia; Taylor-Lowenstein and Co., Mobile, Alabama; and Nelio Chemicals, Inc., Jacksonville, Florida.
2. If any woody material remains undissolved, it should be removed by filtration of the acetone solution.
3. The 2-amino-2-methyl-1-propanol, m.p. 25–29°, N.E. 88.5–99.0, was obtained from the Commercial Solvents Corporation and was used without further purification. The checkers obtained their material from Matheson Coleman and Bell Co.
4. The use of a rubber dam is essential in this step to effect the separation of the residual acetone. It is also beneficial to use a rubber dam in the other suction filtrations in this process.
5. If a clear solution is not obtained, the undissolved material should be removed by filtration.
6. Concentration of the solution at this point gives a major improvement in yield. Crystallization does not occur during this concentration step unless the solution is seeded.
7. All rotations were taken with a 2% methanolic solution.
8. If the rotation is −210° or more negative, the next recrystallization may be omitted and the levopimaric acid generated directly.
9. The maximum observed rotation for the 2-amino-2-methyl-1-propanol salt of levopimaric acid is $[\alpha]^{24}D$ −218°.[3] Methanol and ethanol solutions give the same specific rotations, but methanol is the preferred solvent because the time required to effect solution in ethanol is longer. If pure levopimaric acid, m.p. 151–153°, $[\alpha]^{24}D$ −276° is desired, the salt with −210° rotation should be dissolved in 8 parts of boiling methanol, the solution concentrated to the point of incipient crystallization, cooled, and filtered. The yield in this recrystallization is about 70%.
10. The submitters find phosphoric acid more convenient than boric acid[3] or acetic acid.[4] Acid isomerization to abietic acid[3,5] did not occur under the conditions used here.
11. After an induction period of approximately 1 week, the amine salt begins to be oxidized by air and the salt should be converted to levopimaric acid as soon as possible after it has been isolated.
12. The checkers found that their material with $[\alpha]^{25}D$ −260° had a melting point at 125–150°. The melting point is very sensitive to impurities, and a few percent of impurities can lower it drastically.
13. The yields obtained using this procedure can vary with the source of the oleoresin; the submitters report a yield of 29–34% of levopimaric acid.
14. Using slash pine (*Pinus elliotti*) oleoresin containing approximately 16% of levopimaric acid,[6,7] the submitters found yields consistently less than their reported 29–34%. Pine "scrape," a material which crystallizes on the surface of the pine tree, has been used in a similar process[4] but gives highly variable yields and, owing to interference by oxidation products, may fail to give the desired material. To avoid the deleterious effects of oxidized materials, the use of fresh oleoresin is recommended.

3. Discussion

The described process of isolating levopimaric acid is based on the method of Summers, Lloyd, and Hedrick.[8] The procedure, a modification of the process devised by Harris and Sanderson[3] and Loeblich, Baldwin, O'Connor, and Lawrence,[4] is more convenient and gives improved yields.

4. Merits of the Preparation

In pine oleoresin, many resin acids occur. This procedure illustrates how, by the use of a specific amine, it is possible to get a specific precipitation of one resin acid from a mixture of acids.

References and Notes

1. Contribution of the Naval Stores Laboratory, Olustee, Florida, one of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.
2. W. D. Lloyd and G. W. Hedrick, *J. Org. Chem.*, **26**, 2029 (1961).
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8. H. B. Summers, Jr., W. D. Lloyd, and G. W. Hedrick, *Ind. Eng. Chem., Prod. Res. Develop.*, **2**, 143 (1963).

Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

LEVOPIMARIC ACID

2-amino-2-methyl-1-propanol salt of levopimaric acid

ethanol (64-17-5)

acetic acid (64-19-7)

methanol (67-56-1)

ether (60-29-7)

sodium sulfate (7757-82-6)

acetone (67-64-1)

phosphoric acid (7664-38-2)

boric acid (10043-35-3)

2-amino-2-methyl-1-propanol (124-68-5)

ABIETIC ACID (514-10-3)