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RACEMIC MONOCARBOXYLIC ACID RESOLUTION USING DEHYDROABIETYLAMINE

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U.S. Cl. 260—501.1 7 Claims

ABSTRACT OF THE DISCLOSURE

Dehydroabietylamine is a useful and novel resolving agent, particularly in the process of resolving a racemic organic monocarboxylic acid which comprises separating a mixture of the two diastereoisomeric salts of said acid with natural dehydroabietylamine by fractional crystallization and then converting said separated diastereoisomeric salts to the respective optical isomer of the carboxylic acid.

BACKGROUND OF THE INVENTION

Field of the invention

The resolution of racemic carboxylic acids is of substantial value as many resolved *d* or *l* isomers possess substantially different biological or potentiated activity.

Description of the prior art

The process of using dehydroabietylamine as a monocarboxylic acid resolving agent was heretofore unknown.

SUMMARY OF THE INVENTION

The invention embodies the process of resolving a racemic organic monocarboxylic acid which comprises forming a mixture of the two diastereoisomeric salts of said acid with natural dehydroabietylamine, separating said salts by fractional crystallization and converting said separated diastereoisomeric salts to the respective optical isomers of said carboxylic acid.

DETAILED DESCRIPTION

This invention relates to the use of dehydroabietylamine as a novel resolving agent and, more particularly, to the process of resolving a racemic organic monocarboxylic acid which comprises separating a mixture of the two diastereoisomeric salts of said acid with natural dehydroabietylamine by fractional crystallization and then converting said separated diastereoisomeric salts to the respective optical isomers of the carboxylic acid.

The resolution of racemic carboxylic acids has been commonly accomplished through the use of optically active bases such as certain alkaloids and a few synthetic amines such as dextroamphetamine. These optically active bases frequently do not give high yields of resolved acid, require large volumes of solvent and because of their cost necessitate the use of cumbersome procedures for the recovery of the resolving agent.

It is the objective of this invention to provide a process for the resolution of racemic organic acids which gives high yields of resolved acid, requires only small volumes of solvents, gives highly crystalline salts and utilizes a naturally occurring, optically active amine which is available commercially at such low cost as to make unnecessary its recovery for re-use.

These objectives have been achieved by the provision, according to the present invention, of the process of resolving a racemic organic monocarboxylic acid which comprises forming a mixture of the two diastereoisomeric salts of said acid with natural dehydroabietylamine, separating said salts by fractional crystallization and converting said separated diastereoisomeric salts to the respective optical isomers of said carboxylic acid, and, more particularly, of the process of resolving a racemic organic monocarboxylic acid which comprises the consecutive steps of

(1) mixing approximately equimolar weights of said racemic acid and natural dehydroabietylamine to form the unresolved dehydroabietylamine salt thereof;

(2) Isolating said salt;

(3) Recrystallizing said salt under conditions such that one diastereoisomer is substantially insoluble and the other diastereoisomer remains in solution in the mother liquor;

(4) Separating said insoluble diastereoisomeric salt;

(5) Mixing said insoluble diasteroisomeric salt with a metallic base to form dehydroabietylamine and the metal salt of the resolved acid;

(6) Separating said metallic salt of the resolved acid from said dehydroabietylamine;

(7) Acidifying said metallic salt of the resolved acid to produce the substantially pure resolved acid; and, if desired,

(8) Recovering the other isomer from said mother liquor in like fashion.

A preferred embodiment of the present invention is the process of resolving a racemic α-phenoxy(lower)-alkanoic acid which comprises the consecutive steps of

(1) Mixing approximately equimolar weights of said racemic acid and natural dehydroabietylamine in a minimal amount of a water-miscible, inert organic solvent to form a solution of the diastereoisomeric dehydroabietylamine salts of said acid;

(2) Diluting said solution with about the minimum amount of water sufficient to precipitate in partially purified form a major proportion of the isomeric dehydroabietylamine salt of the (+)-α-phenoxy(lower)alkanoic acid and no more than a minor proportion of the dehydroabietylamine salt of the (—)-α-phenoxy(lower)alkanoic acid, leaving the latter in the mother liquor, and isolating said partially purified isomeric salt;

(3) Recrystallizing said isomeric salt to about maximum melting point;

(4) Mixing said recrystallized isomeric salt with sufficient metallic alkali in a mixture of a water-immiscible organic solvent and water to liberate substantially all dehydroabiethylamine into the organic solvent and form an aqueous solution of the metallic salt of the (+)-α-phenoxy(lower)alkanoic acid;

(5) Separating the so-produced aqueous solution of the metallic salt of the (+)-α-phenoxy(lower)alkanoic acid from said organic solvent solution of dehydroabietylamine;

(6) Acidifying said aqueous solution to precipitate substantially pure (+)-α-phenoxy(lower)alkanoic acid;

(7) Recovering said substantially pure (+)-α-phenoxy-lower)-alkanoic acid; and, if desired,

(8) Recovernig the other isomer in like fashion from said mother liquor.

A specific, preferred embodiment of the present invention is the process of resolving racemic α-phenoxypropionic acid (and especially of preparing (+)-α-phenoxypropionic acid) which comprises the consecutive steps of

(1) Preparing a solution of the salt of natural dehydroabietylamine and racemic α-phenoxypropionic acid containing both diastereoisomers (e.g. by mixing approximately equivalent weights of said racemic α-phenoxypropionic acid and natural dehydroabietylamine) in a minimal amount of water-miscible solvent (e.g., a (lower) alkanol and preferably methanol);

(2) Diluting said solution with the minimum volume of water (e.g., 0.5 to 2.0 volumes per volume of solvent

and preferably about 0.7 volume of water) using, if desired, stirring and cooling (e.g., to about 10° C.) to precipitate a major proportion of the dehydroabietylamine salt of (+)-α-phenoxypropionic acid present and only at most a minor amount of the dehydroabietylamine salt of (—)-α-phenoxypropionic acid present and recovering said precipitated partially purified diastereoisomeric salt;

(3) Recrystallizing said partially purified diastereoisomeric salt to substantial purity (e.g. by dissolving it in a minimum volume of a water-soluble (lower)alkanol and particularly methanol as with warming and precipitating the purified diastereoisomeric salt by the addition of about the minimum necessary amount of water) to maximum melting point (i.e. as judged by the fact that further recrystallization fails to raise the melting point substantially);

(4) Mixing said purified recrystallized diastereoisomeric salt with sufficient metallic base of the alkali metal type (e.g. sodium carbonate, sodium hydroxide) in a mixture of water and a water-immiscible inert organic solvent (e.g. diethyl ether) to liberate substantially all the dehydroabietylamine as its free base into the solvent and at the same time form an aqueous solution of the metallic salt (e.g. sodium salt) of (+)-α-phenoxypropionic acid;

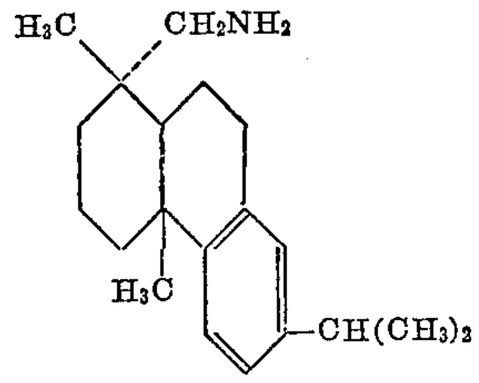
(5) Separating the so-produced aqueous solution of the metallic salt of (+)-α-phenoxypropionic acid from said organic solvent solution of dehydroabietylamine;

(6) Acidifying said aqueous solution to precipitate substantially pure (+)-α-phenoxypropionic acid; and

(7) Recovering said substantially pure (+)-α-phenoxypropionic acid.

As an optional step in this procedure the dehydroabietylamine salt of (—)-α-phenoxypropionic acid which remained in solution in the aqueous solvent (preferably aqueous methanol) used for the first crystallization is recovered after removal of substantially all the other isomer therein by customary procedures such as the addition of more water to precipitate it or by lyophilization of that mother liquor. From said purified dehydroabietylamine salt of (—)-α-phenoxypropionic acid there is recovered substantially pure (—)-α-phenoxypropionic acid by the same procedure used on the purified dehydroabietylamine salt of (+)-α-phenoxypropionic acid.

Dehydroabietylamine is commercially available in the form of a crude mixture from which it is isolated in high purity by the procedure described in U.S. Patent 2,787,637 issued to Lee C. Cheney. It is an optically active base which is inexpensive, relatively nontoxic and forms highly crystalline salts with organic acids. It has the formula



The process of the present invention is particularly applicable to racemic organic monocarboxylic acids which do not contain other functional groups, i.e. groups which would react with a primary amine such as dehydroabietylamine or with an alcohol such as may be used in the process of the present invention. α-Phenoxy(lower) alkanoic acids comprise leading examples of such racemic organic monocarboxylic acids containing no such reactive additional substituents provided, of course, that they are in fact racemic, i.e. contain one asymmetric carbon atom.

As illustrated below, the process of the present invention is also particularly applicable to the resolution of amino acids in the form of their N-benzyloxycarbonyl or N-formyl derivatives which are of course easily converted back to the amino acids themselves after resolution. The present invention thus includes as another preferred embodiment, the process of resolving a racemic amino acid of the monocarboxylic type which comprises separating a mixture of the two diastereoisomeric salts of the N-benzyloxycarbonyl or N-formyl derivatives of said amino acid with natural dehydroabietylamine by fractional crystallization; converting said separated diastereoisomeric salts to the respective optical isomers of the amino acid containing one of said blocking groups on its nitrogen and then converting, by the usual hydrogenolytic or hydrolytic procedure, said respective optical isomers to the corresponding substantially pure optical isomers of the amino acid itself.

The following examples will serve to illustrate this invention without limiting it thereto. Melting points are uncorrected and were obtained on Fisher-Johns apparatus. Optical rotations were measured on a Rudolph polarimeter. All temperatures are given in degrees centigrade.

EXAMPLE 1

Dehydroabietylamine acetate

To a solution of 2.85 kg. of crude dehydroabietylamine ("Amine D"; Hercules Powder Company) dissolved in 4.74 liters of toluene was added a solution of 654 g. (10.8 moles) of glacial acetic acid in 1.56 liters of toluene. The solution was stored at 10° for two hours. The crystalline salt was collected, washed with cold toluene and recrystallized from 4.23 liters of boiling toluene. The colorless crystals were collected, washed several times with n-pentane and air dried to obtain 1.365 kg. (78.5%) of pure dehydroabietylamine acetate with M.P. of 141–143.5°; $[\alpha]_D^{25}$ +30.2° (c.=5, methanol).

Analysis.—Calcd. for $C_{22}H_{35}NO_2$: C, 76.48; H, 10.21. Found: C, 76.70; H, 10.25.

Dehydroabietylamine

A mixture of 540 g. (1.57 moles) of pure dehydroabietylamine acetate was stirred with 2 liters of water on the steam-bath until the salt had dissolved. A total of 700 ml. of 10% sodium hydroxide was added, the mixture was chilled, and the amine was extracted with 2.5 liters of ether. The ether solution was washed with water and dried over anhydrous potassium carbonate. After evaporation of the ether, 440 g. (98%) of pure dehydroabietylamine was isolated as a pale yellow viscous oil which had a refractive index of n_D^{33} 1.5480 and crystallized after storage at room temperature for several days; M.P. 44–45°. Lit.[1] n_D^{30} 1.5498; M.P. 41°.

Dehydroabietylammonium (+)-α-phenoxypropionate

To a solution of 914 g. (3.2 moles) of pure dehydroabietylamine dissolved in 7 liters of methanol was added 537 g. (3.2 moles) of racemic α-phenoxypropionic acid. The stirred solution was slowly diluted with 5.5 liters of water and stored at 10° for five hours. The crystals of partially purified dehydroabietylammonium (+)-α-phenoxypropionate were collected and air-dried to obtain 850 g.; M.P. 168–170°. Recrystallization from a mixture of 8 liters of methanol and 3.5 liters of water during storage at 10° for seven hours gave 650 g. of salt, M.P. 173–177°. A final recrystallization was made from a mixture of 6 liters of methanol and 1.5 liters of water to yield 287 g. of colorless crystals of pure dehydroabietylammonium (+)-α-phenoxypropionate, M.P. 188–189.5°. Further recrystallization did not raise the melting point.

Analysis.—Calcd. for $C_{29}H_{41}NO_3$: C, 77.12; H, 9.15. Found: C, 77.03; H, 9.36. $[\alpha]_D^{23}$+27.7 (c.=1, methanol).

(+)-α-phenoxypropionic acid.

To a 1-liter solution of saturated sodium carbonate was added 287 g. (0.635 mole) of the finely ground dehydroabietylammonium (+)-α - phenoxypropionate ob-

[1] A. Zvenjnieks, Svensk Kem. Tidskr., 66, 316 (1954) (In English); Chem. Abstr., 49, 15809e (1955).

tained above and one liter of ether. The mixture was shaken vigorously until all of the solid had dissolved. The ether layer was separated and the aqueous solution was washed twice with ether and acidified to pH 2 with concentrated hydrochloric acid. The mixture was cooled to 10° for two hours and the white crystals were collected to obtain 76 g. of pure (+)-α-phenoxypropionic acid with a M.P. of 88–89°. $[\alpha]_D^{23}$+40.0° (c.=1, absolute alcohol); Lit.[2] $[\alpha]_D^{20}$ +39.3°. A second crop of 22 g. was obtained from the mother liquor on further storage at 10° which had a M.P. of 88–89°; $[\alpha]_D^{23}$ +39.1° (c.=1, absolute alcohol).

EXAMPLE 2

Dehydroabietylammonium D(—)-α-benzyloxycarbonylaminophenylacetate

To a solution of 163 g. (0.57 mole) of α-benzyloxycarbonylaminophenylacetic acid dissolved in 3.7 liters of methanol there was added 163 g. (0.57 mole of pure dehydroabietylamine. The solution was diluted with 550 ml. of water and stored at 10° for three hours. The dehydroabietylammonium D(—) - α - benzyloxycarbonylaminophenylacetate was collected and dried to obtain 203 g.; M.P. 170–190°. Recrystallization from a mixture of 6 liters of methanol and 1.5 liters of water gave 103 g. of dry dehydroabietylammonium D(—) - α - benzyloxycarbonylaminophenylacetate. A final recrystallization from a mixture of 4 liters of methanol and 700 ml. of water afforded 75 g. of pure dehydroabietylammonium D(—)-α-benzyloxycarbonylaminophenylacetate as colorless crystals, M.P. 199–200°– $[\alpha]_D^{25}$ —93.2° (c.=0.8, alcohol).

D(—)-α-benzyloxycarbonylaminophenylacetic acid

The aforementioned diastereomeric salt D(—)-α-benzyloxycarbonylaminophenylacetic acid (75 g.; 0.131 mole) was treated with one liter of saturated sodium carbonate solution and two liters of ether as described for the isolation of (+)-α-phenoxypropionic acid. The acid was isolated by extraction of the aqueous layer at pH 2 with 3× 500 ml. of ether. The ether extracts were combined, washed with water and dried over anhydrous sodium sulfate. The ether was evaporated to ⅕ its original volume and one liter of "Skellysolve B" (petroleum ether, B.P. 60–71°) was added. The crystals of pure D(—)-α-benzyloxycarbonylaminophenylacetic acid weighed 30 g. after drying in vacuo over P_2O_5; M.P. 128–129°; $[\alpha]_D^{25}$ —116.5° (c.=1, absolute alcohol). Lit.[3] M.P. 130–130.5° $[\alpha]_D^{21}$ —119° (c.=4, alcohol).

EXAMPLE 3

Resolution of dl-α-aminothiophene-2-acetic acid and dl-α-aminothiophene-3-acetic acid using dehydroabietylamine

(A) 1-α-aminothiophene-2-acetic acid.—To 132.5 g. (0.843 mole of α-aminothiophene-2-acetic acid in 1.92 liters of 88% formic acid was added at 50° over a one hour period 640 ml. of acetic anhydride. The solution was stored overnight and the formic acid was evaporated off leaving behind a crystalline residue of dl-α-N-formylaminothiophene-2-acetic acid. That residue was dissolved in one liter of methanol and 120 g. (0.42 mole) of dehydroabietylamine was added. A total of 800 ml. of water was added and the salt slowly crystallized overnight at room temperature. The crystalline salt weighed 123.5 g., M.P. 167–170°. The salt was recrystallized from one liter of hot methanol to yield 45 g. of dehydroabietylamine salt of 1-α-N-formylaminothiophene-2-acetic acid; M.P. 176–178°. The salt (45 g.) was suspended in 500 ml. of methanol and saturated sodium carbonate was

[2] E. Fourneau and G. Sandulesco, Bull. Soc. Chem. 31–32, 988–993 (1922).
[3] F. P. Doyle, G. R. Fosker, J. H. C. Nayler and H. Smith, J. Chem. Soc. 1440 (1962).

added to pH 9. A total of one liter of water was added and the mixture was extracted twice with ether. The ether was removed and to remove the formyl group concentrated hydrochloric acid was added to pH 1 and the aqueous solution was heated for one hour on the steam bath. The solution was evaporated on a flash evaporator at reduced pressure to a volume of 150 ml. A solid precipitated which was 1-α-aminothiophene-2-acetic acid hydrochloride. This salt was dissolved in 50 ml. of water at pH 8.5 (with ammonium hydroxide) and adjusted to pH 6 with concentrated hydrochloric acid to precipitate 1-α-aminothiophene-2-acetic acid, which was collected, washed with acetone and found to weigh 3.5 g. after drying in vacuo over P_2O_5; $[\alpha]_D^{25}$ —78.0 (c., 0.423 water), M.P. 209–211° decomp.

(B) 1-α-aminothiophene-3-acetic acid.—The formylation of the racemic acid was carried out as described above. The N-formyl acid was resolved by using 67 g. (0.36 mole) of racemic α-N-formylaminothiophene-3-acetic acid and 51.5 g. (0.18 mole) of dehydroabietylamine in one liter of methanol and 500 ml. of water. A total of 70 g. was collected; M.P. 193° decomp. This was recrystallized from 1.5 liters of methanol to yield 24.3 g. of dehydroabietylamine salt of 1-α-N-formylaminothiophene-3-acetic acid; M.P. 216–217° decomp. This salt was then treated with 75 ml. of saturated sodium carbonate solution and 100 ml. of methanol. After a slurry was made 300 ml. of water was added and the mixture was extracted with ether twice. The aqueous layer was separated and acidified to pH 5 with concentrated hydrochloric acid. Another 25 ml. of concentrated hydrochloric acid was added and the solution was heated for one hour on the steam bath to remove the formyl group. That solution was evaporated to 75 ml. under reduced pressure and the aminoacid hydrochloride which precipitated was collected. This was dissolved in 20 ml. of water and made basic to pH 7 with ammonium hydroxide to precipitate 1-α-aminothiophene-3-acetic acid which was collected, washed with acetone and found to weigh 6 g.; $[\alpha]_D^{27}$ —132° (c., 1; 1 NHCl).

While in the foregoing specification various embodiments of this invention have been set forth in specific detail and elaborated for the purpose of illustration, it will be apparent to those skilled in the art that this invention is suceptible to other embodiments and that many of the details can be varied widely without departing from the basic concept and the spirit and scope of the invention.

I claim:

1. The process of resolving a racemic α-phenoxy(lower)alkanoic acid which comprises the consecutive steps of

(1) mixing approximately equimolar weights of said racemic acid and natural dehydroabietylamine in a water-miscible, inert organic solvent to form a solution of the diastereoisomeric dehydroabiethylamine salts of said acid;

(2) diluting said solution with about the minimum amount of water sufficient to precipitate in partially purified form a major proportion of the isomeric dehydroabietylamine salt of the (+)-α-phenoxy(lower)alkanoic acid and no more than a minor proportion of the dehydroabietylamine salt of the (—)-α-phenoxy(lower)alkanoic acid and isolating said partially purified isomeric salt;

(3) recrystallizing said isomeric salt to maximum melting point;

(4) mixing said isomeric salt with sufficient metallic alkali in a mixture of a water-immiscible organic solvent and water to liberate all dehydroabietylamine into the organic solvent and form an aqueous solution of the metallic salt of the (+)-α-phenoxy(lower)alkanoic acid;

(5) separating the so-produced aqueous solution of the metallic salt of the (+)-α-phenoxy(lower)alkanoic acid from said organic solvent solution of dehydroabietylamine;

(6) acidifying said aqueous solution to precipitate substantially pure (+)-α-phenoxy(lower)alkanoic acid; and

(7) recovering said substantially pure (+)-α-phenoxy-(lower)alkanoic acid.

2. The process of preparing (+)-α-phenoxypropionic acid from racemic α-phenoxypropionic acid which comprises the consecutive steps of

(1) mixing approximately equimolar weights of said racemic α-phenoxypropionic acid and natural dehydroabietylamine in a minimum volume of a water-miscible alcohol to form a solution of the dehydroabietylamine salt of said acid;

(2) diluting said solution with sufficient water to precipitate in partially purified form a major proportion of the isomeric salt dehydroabietylammonium (+)-α-phenoxypropionate and only a minor amount of dehydroabietylammonium (−)-α-phenoxypropionate and recovering said partially purified isomeric salt;

(3) recrystallizing said partially purified isomeric salt from aqueous alcohol to maximum melting point;

(4) mixing said recrystallized isomeric salt with sufficient metallic base of the alkali metal type in a mixture of a water-immiscible organic solvent and water to liberate all dehydroabietylamine into the organic solvent and form an aqueous solution of the metallic salt of (+)-α-phenoxypropionic acid;

(5) separating the so-produced aqueous solution of the metallic salt of (+)-α-phenoxypropionic acid from said organic solvent solution of dehydroabietylamine;

(6) acidifying said aqueous solution to precipitate substantially pure (+)-α-phenoxypropionic acid; and

(7) recovering said substantially pure (+)-α-phenoxypropionic acid.

3. The process of preparing (+)-α-phenoxypropionic acid from racemic α-phenoxypropionic acid which comprises the consecutive steps of

(1) mixing approximately equimolar weights of said racemic α-phenoxypropionic acid and natural dehydroabietylamine in methanol to form a solution of the dehydroabietylamine salt of said acid;

(2) diluting said solution with the minimum volume of water needed to precipitate in partially purified form a major proportion of the isomeric salt dehydroabietylammonium (+)-α-phenoxypropionate and only a minor amount of dehydroabietylammonium (−)-α-phenoxypropionate and recovering said partially purified isomeric salt;

(3) recrystallizing said partially purified isomeric salt from aqueous methanol to maximum melting point;

(4) mixing said recrystallized isomeric salt with sufficient metallic base of the alkali metal type in ether and water to liberate all dehydroabietylamine into the ether and form an aqueous solution of the metallic salt of (+)-α-phenoxypropionic acid;

(5) separating the so-produced aqueous solution of the metallic salt of (+)-α-phenoxypropionic acid from said ethereal solution of dehydroabietylamine;

(6) acidfying said aqueous solution to precipitate substantially pure (+)-α-phenoxypropionic acid; and

(7) recovering said substantially pure (+)-α-phenoxypropionic acid.

4. The process of preparing (+)-α-phenoxypropionic acid from racemic α-phenoxypropionic acid which comprises the consecutive steps of

(1) mixing approximately equimolar weights of said racemic α-phenoxypropionic acid and natural dehydroabietylamine in about the minimum volume of methanol sufficient to form a solution of the dehydroabietylamine salt of said acid;

(2) diluting said solution with slightly less than one volume of water in the cold to precipitate the isomeric salt dehydroabietylammonium (+)-α-phenoxypropionate in partially purified form and recovering said partially purified isomeric salt;

(3) recrystallizing said partially purified isomeric salt from aqueous methanol to maximum melting point;

(4) mixing said recrystallized isomeric salt with sufficient sodium carbonate in ether and water to liberate all dehydroabietylamine into the ether and form an aqueous solution of the sodium salt of (+)-α-phenoxypropionic acid;

(5) separating the so-produced aqueous solution of sodium (+)-α-phenoxypropionate from said ethereal solution of dehydroabietylamine;

(6) acidifying said aqueous solution to precipitate substantially pure (+)-α-phenoxypropionic acid; and

(7) recovering said substantially pure (+)-α-phenoxypropionic acid.

5. The process of resolving racemic α-phenoxypropionic acid which comprises the consecutive steps of

(1) mixing approximately equimolar weights of said racemic acid and natural dehydroabietylamine in a water-miscible, inert organic solvent to form a solution of the diastereoisomeric dehydroabietylamine salts of said acid;

(2) diluting said solution with about the minimum amount of water sufficient to precipitate in partially purified form a major proportion of the isomeric dehydroabietylamine salt of the (+)-α-phenoxypropionic acid and no more than a minor proportion of the dehydroabietylamine salt of the (−)-α-phenoxypropionic acid and isolating said partially purified isomeric salt;

(3) recrystallizing said isomeric salt to a maximum melting point;

(4) mixing said isomeric salt with sufficient metallic alkali in a mixture of a water-immiscible organic solvent and water to liberate all dehydroabietylamine into the organic solvent and form an aqueous solution of the metallic salt of the (+)-α-phenoxypropionic acid;

(5) separating the so-produced aqueous solution of the metallic salt of the (+)-α-phenoxypropionic acid from said organic solvent solution of dehydroabietylamine;

(6) acidifying said aqueous solution to precipitate substantially pure (+)-α-phenoxypropionic acid; and

(7) recovering said substantially pure (+)-α-phenoxypropionic acid.

6. Dehydroabietylammonium (+) - α - phenoxypropionate.

7. Dehydroabietylammonium (−) - α - phenoxypropionate.

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