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Purification of Erucic Acid by Low-Temperature Crystallization

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Abstract

Purification of erucic acid for laboratory use by low-temperature crystallization from aqueous acetone, ethanol, and methanol has been investigated. Two crystallizations of technical grade commercial acid (76–86%) from acetone-water (5:1) provided products of 94–98% purity, depending on the original composition; residual impurities were primarily C_{20} monoene and C_{22} saturated acids.

A CONVENIENT laboratory procedure was desired for purification of erucic acid for other chemical studies. Low-temperature crystallization procedures employing aqueous systems in conjunction with other methods have been described previously (1–4). Work has also been reported in which nonaqueous solvents (5–7) were employed. One of these (7) in our hands gave results inferior to the procedures described here, which use as crystallization solvents, acetone, ethanol, and methanol, with varying amounts of water. Evaluation of product purities by gas-liquid chromatography (GLC) (8) provided more adequate characterization than that given by most previous investigators.

Table I shows the composition of the starting materials. The mixed acids from *Crambe abyssinica* seed oil were chosen for investigating application of our crystallization techniques to a natural erucic acid source of lesser erucic acid content than the technical product. *Crambe abyssinica* is a heavy-seeding annual of the Cruciferae family, having good crop potential and widespread adaptability for growth in the U. S., and its oil has the highest erucic acid content of any cruciferous seed oil analyzed (9). Tables II, III, and IV show results of the crystallization experiments. In each case the same solvent combination and temperature conditions were used throughout a particular run.

GLC was used for purity evaluations; there was no significant difference in iodine value between erucic acid and the less pure products from the filtrates.

Of the three solvent systems, acetone-water was the most effective under the test conditions. That solvent gave the most efficient removal of C_{18} polyunsaturated acids from erucic in the purification of mixed acids from *Crambe abyssinica* oil. The most persistent impurities were eicosenoic, behenic, and oleic acids. Optimum purification of erucic acid from sources such as *Crambe* oil was not achieved by this procedure alone. However when a commercial concentrate (86%) is used as the raw material source, the method conveniently provides working quantities of purified erucic acid with adequate recovery.

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Experimental

Materials. Ground seeds of *Crambe abyssinica* (270 g, air-equilibrated basis) were extracted overnight in a Soxhlet apparatus with petroleum ether (30–60C). Most of the solvent was evaporated on a steam bath at atmospheric pressure, and the remainder was removed *in vacuo*. The oil (102.1 g) was then refluxed with 1 l of 0.8 *N* ethanolic KOH under nitrogen for 3 hr. Water was added to the soap mixture and it was then extracted with ethyl ether to remove unsaponifiable matter (6.27 g), acidified with dilute HCl, and the free fatty acids were recovered (95.1 g) and used for the purification experiments.

Two batches of an erucic acid concentrate used in these experiments (76 and 86% pure by GLC) were purchased from the Archer-Daniels-Midland Co.

Crystallization Procedure. The erucic acid (10 g) was first dissolved in the organic solvent (20 ml). Measured amounts of water and the organic solvent were then added alternately to this solution in such a way that the resultant mixture became clear after slight warming on a steam bath. Once the proper solvent ratios were found (Tables II, III, and IV), this procedure was not repeated until a different solvent ratio was desired. The mixture was then cooled immediately and held for 1 hr at the crystallization temperature being investigated. The crystals were rapidly filtered, without washing with solvent, onto Whatman No. 1 filter paper, in an unchilled Buchner funnel, and then placed in a vacuum desiccator to remove last traces of solvent and water. After determining the weight and withdrawing a sample for methyl ester preparation, the second crystallization was done using the same conditions as the first.

Methyl Esters. The methyl esters for GLC an-

TABLE I

Composition of Starting Material by Gas-Liquid Chromatography[a]

Chain length	Commercial erucic acid		*Crambe abyssinica* seed oil acids
	86%	76%	56%
$C_{12}S$[b]	Trace	....	....
$C_{14}S$	....	....	Trace
$C_{16}S$	0.2	0.2	2.4
$C_{16}I$	....	....	0.4
$C_{18}S$	0.2	0.6	0.5
$C_{18}I$	1.9	}	18.0
$C_{18}II$	1.6	} 9.1	9.0
$C_{18}III$	0.1	}	6.7
$C_{20}S$	0.4	1.8	0.7
$C_{20}I$	7.2	9.9	4.2
$C_{20}II$	Trace	....	....
$C_{22}S$	1.8	2.9	0.8
$C_{22}I$	86.0	76.0	56.0
$C_{22}II$	0.2	....	....
$C_{24}I$	0.5	....	0.3
Other	....	....	0.3

[a] Area percentage of methyl ester peaks.
[b] I denotes the monoene; II, the diene; III, the triene; and S, the saturated fatty acids.

TABLE II
Purification of Erucic Acid with Aqueous Acetone

% Erucic acid in starting material	Solvent system			Erucic acid and major impurities[a]								Mp of erucic
	Acetone: H_2O (v/v)	Temp	Ml/g solute	Product	$C_{22}I$[b]	$C_{18}I$	$C_{20}S$	$C_{20}I$	$C_{22}S$	$C_{24}I$	Other	
		°C										°C
56	4:1	−11	5.0	1st	77(84)[c]	9.4	.....	2.5	1.6	.....	3.6 $C_{18}II$	25–32
				2nd	86(73)	4.3	.....	1.4	2.8	1.2	.....	28–31
				3rd	90(69)	1.3	1.4	.....	2.7	.....	.....	30–32
75	4:1	−11	5.0	1st	82(81)	2.1	.....	5.9	3.3	1.8	.....	27–31
				2nd	89(75)	.....	1.3	1.7	3.2	.....	1.2 $C_{24}S$	29–32
				3rd	90(73)	.....	1.4	1.4	3.2	1.6	.....	30–32
	5:1	−11	5.8	1st	91(80)	2.1	.....	3.3	2.4	.....	.....	28–31
				2nd	93(72)	0.9	.....	1.0	3.2	.....	.....	30–31.5
				3rd	90(60)	.....	1.0	0.9	3.7	.....	.....	30.5–32
85	5:1	−11	5.8	1st	94(89)	.....	.....	1.9	2.0	.....	.....	29–31.5
				2nd	98(84)	.....	.....	0.6	0.8	.....	.....	29–31
	5:1[d]	−11	5.8	1st	92(89)	.....	1.0	3.2	.....	1.1	.....	27.5–30
				2nd	99(78)	.....	.....	0.8	0.6	.....	.....	30–31.5
	5:1	−11	5.8	1st	94(87)	.....	.....	1.8	2.7	.....	.....	29–31
				2nd	98(79)	.....	.....	0.7	1.5	.....	.....	31–32
	5:1	+ 7	5.8	1st	91(75)	.....	.....	2.8	.....	.....	1.2 $C_{22}II$	28.5–30
				2nd	94(64)	.....	.....	1.8	2.7	.....	.....	30–31.5
	10:3	+10	6.3	1st	91(78)	2.2	.....	5.4	1.7	.....	.....	28.5–31
				2nd	96(64)	0.8	.....	2.0	0.7	.....	.....	29–30.5

[a] Area percentage of methyl ester peaks.
[b] I denotes the monoene, II the diene, and S the saturated fatty acids.
[c] Recovery based on the amount of erucic acid in starting material.
[d] Scale of operation 50 g starting material instead of 10 g.

TABLE III
Purification of Erucic Acid with Aqueous Ethanol

% Erucic acid in starting material	Solvent system			Erucic acid and major impurities[a]									Mp of erucic °C.
	EtOH: H_2O (v/v)	Temp	Ml/g solute	Product	$C_{22}I$[b]	$C_{16}S$	$C_{18}I$	$C_{18}II$	$C_{20}S$	$C_{20}I$	$C_{22}S$	$C_{24}I$	
		°C											
56	3:1	−11	4.0	1st	66(86)[c]	2.0	22	.....	.....	2.3	2.2	1.4	Liquid
				2nd	69(76)	1.6	17	2.1	.....	2.6	3.8	1.5	22–28
				3rd	76(66)	1.2	12	1.3	.....	1.8	4.2	1.5	25–30
	3:1	−11	5.8	1st	71(85)	1.6	18	.....	1.7	3.5	2.8	.....	Semisolid
				2nd	79(81)	1.2	12	.....	.....	1.8	3.5	.....	26–31
85	3:1	−11	5.8	1st	92(96)	.....	1.4	.....	.....	4.6	.....	1.0	27–30
				2nd	95(95)	.....	1.4	.....	.....	3.4	0.5	.....	28.5–30
				3rd	95(88)	.....	0.9	.....	.....	3.8	0.5	.....	28.5–30
	3:1	+ 7	5.8	1st	91(90)	.....	2.1	.....	.....	5.0	1.1	.....	26.5–30
				2nd	93(83)	.....	1.4	.....	.....	3.6	0.7	.....	28–31
	5:2	+11	6.8	1st	89(96)	.....	2.1	.....	.....	6.7	1.0	.....	26–29
				2nd	88(90)	.....	1.5	.....	.....	7.7	1.1	.....	28–30
	5:1	−11	5.9	1st	93(86)	.....	1.1	.....	1.0	4.4	0.6	.....	27.5–30
				2nd	96(78)	.....	0.7	.....	0.9	2.3	.....	.....	29.5–30.5

[a] Area percentage of methyl ester peaks.
[b] I denotes the monoene, II the diene, and S the saturated fatty acids.
[c] Recovery based on the amount of erucic acid in starting material.

TABLE IV
Purification of Erucic Acid with Aqueous Methanol

% Erucic acid in starting material	Solvent system			Product	Erucic acid and major impurities[a]									Mp of erucic
	MeOH: H_2O (v/v)	Temp	Ml/g solute		$C_{22}I$[b]	$C_{16}S$	$C_{18}S$	$C_{18}I$	$C_{18}II$	$C_{18}III$	$C_{20}S$	$C_{20}I$	$C_{22}S$	$C_{24}I$	
		°C													°C
56	6:1	−11	6.8	1st	63(99)[c]	1.7	1.6	22	2.4	....	....	3.7	2.1	2.3	Liquid
				2nd	66(91)	1.1	....	17	5.0	....	2.0	2.8	1.7	1.9	22–28
				3rd	72(91)	1.5	1.1	14	1.1	....	....	3.6	2.7	1.9	23–31
	8:1	−11	4.4	1st	66(95)	1.9	1.3	19	2.0	....	....	3.6	2.2	2.1	21–30
				2nd	73(92)	1.5	1.0	14	1.7	....	....	3.1	2.0	1.8	25–30
				3rd	78(88)	1.3	....	7.7	2.9	1.4	....	3.2	2.7	1.3	25–30
85	8:1	−11	4.4	1st	88(97)	....	....	....	....	....	0.9	5.1	1.4	2.0	27–30
				2nd	88(94)	....	....	....	....	....	0.9	5.4	1.3	1.6	27–30
				3rd	88(90)	....	....	....	....	....	1.0	5.1	1.7	2.0	28–30

[a] Area percentage of methyl ester peaks.
[b] I denotes the monoene, II the diene, and S the saturated fatty acids.
[c] Recovery based on the amount of erucic acid in starting material.

alysis were prepared by three different methods: by treatment with diazomethane, by refluxing with 1% sulfuric acid in methanol, and by treatment with 2,2-dimethoxypropane (10). No appreciable difference in composition was found among products prepared by any of the three methods.

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