

Crystallization of Linseed Oil Fatty Acids from Acetonitrile

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In the fractionation of linseed oil fatty acids by crystallization, acetonitrile was used as the solvent. When the ratio of fatty acids to acetonitrile was 10:90 (w/w), concentrates containing 74.6 and 76 % linolenic acid were obtained in one crystallization at -20° and -40°C . The corresponding yields were 50 and 14 % of the starting amount. With acetonitrile:water (90:10 w/w) as the solvent the linolenic acid contents at -20° and -40°C were about 69 and 79 %, and the respective yields 72 and 20 %.

In the three-stage fractional crystallization the lowest temperature used was -40°C . The ratio of fatty acids to acetonitrile or to acetonitrile: water (90:10 w/w) in the starting solutions was 20:80 (w/w). The highest linolenic acid content, about 85 %, was obtained at -40°C with aqueous acetonitrile as the solvent, the yield being 15 % of the starting amount. With non-aqueous acetonitrile the corresponding values at -40°C were markedly lower. At -20°C fractions with about 72 and 75 % linolenic acid were obtained with good yields from non-aqueous and aqueous acetonitrile, respectively.

Of the large selection of fat solvents, those most commonly used in the fractionation of fatty acid mixtures by crystallization are hydrocarbons, alcohols, and ketones. Methanol and acetone are preferred in technical methods and low-temperature procedures. Of other solvents, acetonitrile has been suggested for the separation of saturated acids from oleic acid.^{3,8} This solvent has also proved selective in liquid-liquid extraction of unsaturated acids.¹

The outstanding property of acetonitrile is its limited capacity for dissolving fatty acids even the unsaturated ones at room temperature. According to Hoerr and Harwood,⁴ the respective solubilities of oleic and linoleic acids are 9.1 and 17.7 g per 100 g acetonitrile at $+20^{\circ}\text{C}$. Thus it would be possible to use acetonitrile as the solvent when separating unsaturated fatty acids by crystallization without using very low temperatures. This paper is concerned with the use of acetonitrile as the solvent in the fractionation of linseed oil acids by crystallization. The specific purpose of the work was to obtain information on whether fractions with high linolenic acid contents could be obtained without low working temperatures.

MATERIAL AND METHODS

Linseed oil fatty acids were prepared from commercial oil by the alkali saponification method described previously.⁷ The composition of the fatty acid mixture obtained, determined by gas chromatography,⁷ was the following: 6.6 % palmitic and palmitoleic acids, 5.4 % stearic, 12.1 % oleic, 15.8 % linoleic, and 53.1 % linolenic acid. The neutralization value was 182 and peroxide value 19.6.

Acetonitrile (Merck, zur Synthese) was used without further purification.

The solid and liquid fractions obtained in the crystallization procedures were separated by filtering at or above room temperature and by centrifuging (Christ Universal Junior refrigerated centrifuge) at lower temperatures.⁷

Gas chromatography was used for analyzing the fatty acid compositions.⁷

Dry weights of the fractions were determined by evaporating off the solvent in a rotating evaporator.

RESULTS

In order to determine the approximate solubility of linseed oil acids, a known amount of acetonitrile was saturated with linseed oil acids at constant temperatures. After an equilibrium time of 5 h the fatty acid concentration of the clear supernatant solution that had separated during this period of time was determined. At +20°C this saturated solution was found to contain 15.9 % (w/w) fatty acids and at +35°C, 32.6 % (w/w). It can be concluded from these solubility values that when crystallizing at lower temperatures, the fatty acid concentration of the starting solution has to be relatively low. For avoiding too large losses of the material, solutions containing 10 or 20 % (w/w) fatty acids in acetonitrile were used in the following crystallization experiments.

Single-stage crystallization. Acetonitrile and acetonitrile:water (90:10 w/w) were used as solvents. Linseed oil fatty acids were added to the solvents in the ratio of 10:90 (w/w). The solutions were allowed to crystallize in centrifuge filtration tubes over night at -20° and -40°C, after which the solid and liquid fractions were separated by centrifuge.⁷ The fatty acid compositions of the fractions (Table 1) indicate that crystallization from acetonitrile at -20°C already gave a concentrate with about 75 % linolenic acid, whereas the corresponding value with aqueous acetonitrile as the solvent was below 70 %. Lowering of the temperature to -40°C had no marked effect on the linolenic acid content when crystallizing from acetonitrile, but with aqueous acetonitrile as the solvent the linolenic acid content rose to 79 %. However, at this temperature the fatty acid yields in the liquid fractions were only 20 % or less. At both temperatures higher yields were obtained with aqueous than with non-aqueous acetonitrile.

Fractional crystallization. The solvents used were acetonitrile and acetonitrile:water (90:10 w/w). The fatty acid concentration of the starting solution was 20 % (w/w). The fatty acid solution was first warmed until clear and then allowed to cool to room temperature (22°C) and filtered. The filtrate obtained was further crystallized in centrifuge filtration tubes according to the scheme seen in Fig. 1. The fatty acid compositions of the fractions and their yields are presented in Table 2. The highest linolenic acid content, about 85 %, was obtained at the lowest crystallization temperature, -40°C, with aqueous

Table 1. Single-stage crystallization of linseed oil fatty acids from acetonitrile and acetonitrile-water (90:10 w/w) at -20°C and -40°C. Fatty acid concentration of the solutions to be crystallized was 10% (w/w).

Temperature °C	Solvent	Fraction	Yield (%)	Fatty acid composition (%)						
				14:0	16:0	16:1	18:0	18:1	18:2	18:3
-20	Acetonitrile	Solid	50	+	11.4	+	9.3	29.0	14.7	35.6
		Liquid	50		0.9	+	+	7.6	16.9	74.6
	Acetonitrile:water	Solid	28	+	18.4	+	16.5	36.7	8.3	20.1
		Liquid	72		0.9	+	+	11.1	19.1	68.9
-40	Acetonitrile	Solid	86	+	7.1	(+)	6.0	20.1	16.3	50.2
		Liquid	14		0.8	+	+	11.3	11.9	76.0
	Acetonitrile:water	Solid	80	+	7.3	-	6.0	20.6	16.7	49.0
		Liquid	20		0.4	+	-	9.1	11.2	79.3

Table 2. Fatty acid compositions and the yields of the fractions, when crystallizing linseed oil fatty acids from acetonitrile and acetonitrile-water (90:10 w/w) according to the scheme in Fig. 1.

Solvent	Fraction	Yield (% of the starting amount)	Fatty acid composition (%)											
			14:0	16:0	16:1	18:0	18:1	18:2	18:3	X ₁	X ₂			
Acetonitrile	Solid +20°	18.0	+	10.4	+	16.6	24.6	13.2	35.2					
	Liquid +20°	82.0	+	6.3	+	2.7	19.0	16.3	55.7					
	Solid -20°	38.5	+	9.5	+	3.3	24.4	17.0	45.8					
	Liquid -20°	43.5	+	0.6	+	—	10.7	16.8	71.9					
	Solid -40°	34.0	0.3	0.9	+	—	10.0	19.1	69.7					
	Liquid -40°	9.5	0.4	0.5	0.4	—	7.9	10.8	80.0					
Acetonitrile:water	Solid +20°	5.5		10.7	0.2	38.3	18.1	6.5	23.4			2.1	0.6	
	Liquid +20°	94.5		5.6		2.9	20.1	17.5	53.9					
	Solid -20°	42.5		12.4	+	7.1	32.0	14.3	34.2					
	Liquid -20°	52.0		0.5		+	6.7	17.9	74.9					
	Solid -40°	37		0.6		+	9.7	20.3	69.5					
	Liquid -40°	15		+			6.6	8.7	84.7					

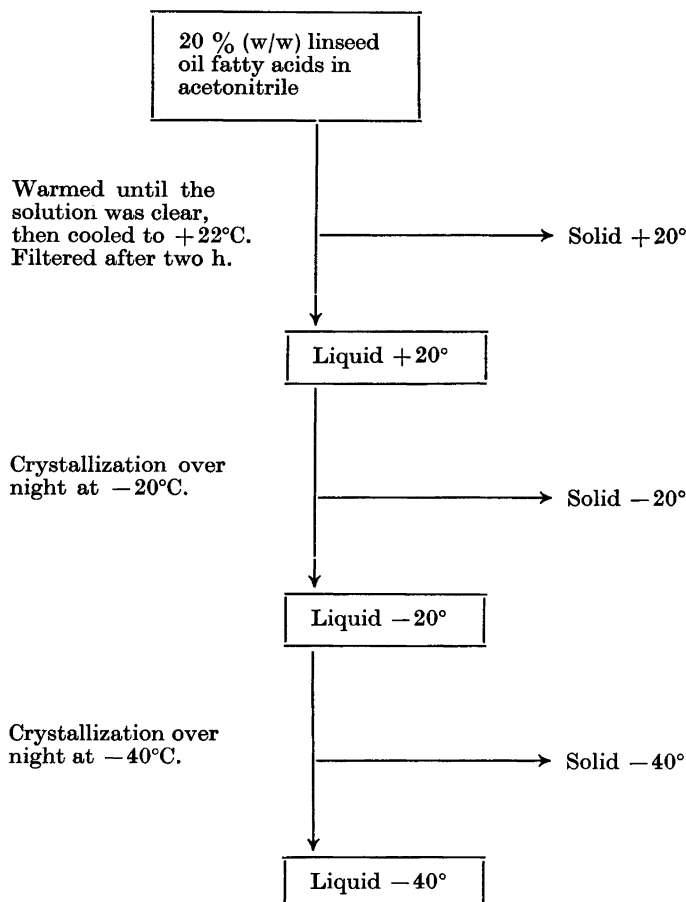


Fig. 1. Fractional crystallization of linseed oil fatty acids from acetonitrile and acetonitrile:water (90:10 w/w).

acetonitrile as the solvent. The yield of this fraction was, however, only 15 % of the starting amount. The purity of the linolenic acid concentrate obtained at the same temperature from non-aqueous acetonitrile was markedly lower, and the yield was only about 10 %.

DISCUSSION

Low-temperature crystallization as a practical laboratory method for separating linolenic acid has met with no success. Even in the best cases only small amounts of linolenic acid in the purity of 91–92 % have been obtained at a temperature of -75°C .² Crystallization as urea complex is often an excellent

method for preparing fatty acids in high purity (99–100 %), but pure linolenic acid cannot be obtained by this method from its natural sources. Thus, for instance, the purity of linolenic acid obtained by urea fractionation from linseed oil⁵ was only 86 % and that from perilla oil⁶ 89 %.

In our earlier work with linseed oil fatty acids it has become evident that the separability of unsaturated C₁₈ fatty acids is very poor when crystallized from absolute or aqueous methanol.⁸ "Acid" soaps instead of free acids gave better results, but as low temperatures as –40°C were required to produce small amounts of linolenic acid in the purity of 76–80 %.

Hoerr³ suggests addition of 3–5 % water to acetonitrile, which greatly increases the solubility of oleic acid without increasing that of stearic and palmitic acids. This affords a ready separation of oleic acid from the saturated acids. In the present work, addition of 10 % water to acetonitrile was found to increase the yields of the liquid fractions rich in unsaturated acids. When crystallizing at –40°C, the selectivity toward linolenic acid also increased simultaneously. At –20°C single-stage crystallization of 10 % solutions was less effective in aqueous than in non-aqueous acetonitrile. However, with a 20 % starting solution (see fractional crystallization) the selectivity of aqueous acetonitrile for linolenic acid was higher than that of non-aqueous even at –20°C.

In the fractionation of unsaturated C₁₈ fatty acids by crystallization, acetonitrile has some advantages over other solvents. First it does not require quite as low temperatures as many other solvents. The accumulation of strongly colored compounds in the solid fraction also indicates that at least part of the oxidized material has separated from the unoxidized during crystallization. In addition, the solvent is easily regenerated by distillation because of its low boiling temperature (81.6°C). A disadvantage of acetonitrile is its relatively low dissolving capacity for fatty acids, and thus quite large volumes of the solvent are needed in crystallization procedures.

The information obtained in the present work is not sufficient for evaluating the actual use of acetonitrile in large-scale separation procedures of fatty acids. Still it is interesting to note that it offers a way to avoid low crystallization temperatures when a purity of about 70 % of linolenic acid is sufficient.

Acknowledgement. The authors wish to thank the United States Department of Agriculture, Agricultural Research Service, which partly financed this research.

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Received March 9, 1966.