Cyclic Fatty Acids: Separation From Straight-Chain Fatty Acids by Urea Adducting[1]

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Abstract

A mixture containing 37% cyclic and 63% straight-chain fatty acids, made by high-temperature treatment of linseed oil fatty acids with alkali, was separated by the urea adduct method to give unsaturated cyclic fatty acids (nonadduct) in 95% purity and 90–95% yield. Previous reports from this Laboratory describe a process for separating cyclic fatty acids from stearic acid by hydrogenation followed by crystallization at −40C. The urea adduct method avoids hydrogenation and low-temperature crystallization, and furthermore, unsaturated cyclic and unsaturated straight-chain products can be recovered as individual fractions. Then, by readducting the unsaturated straight-chain fatty acid fraction, the small amounts of palmitic and stearic acids are removed leaving an unsaturated fraction containing oleic, nonconjugated and conjugated linoleic and some unsaturated cyclic fatty acids.

Introduction

A PROCESS FOR MAKING SATURATED cyclic fatty acids from linseed oil was described in previous publications (2,3). It includes complete hydrogenation of monomeric fatty acids and separation of the resulting saturated cyclic fatty acids by crystallization of the saturated straight-chain fatty acids from a solvent solution at −40C. This method is satisfactory for producing saturated cyclic fatty acids, but it requires extremely low temperatures and substantial amounts of solvent for crystallization. During the process all the conjugated linoleic and oleic acids are converted to the less valuable stearic acid. The cyclic acids are recovered only in the saturated form and, generally, contain 2–3% palmitic acid. For certain uses it would be desirable to recover the cyclic fatty acids in the unsaturated form.

For these reasons, studies were conducted on urea adduction as a means of separating unsaturated cyclic acids from straight-chain fatty acids and on the optimum conditions for such a separation process. This procedure would replace the hydrogenation and low-temperature crystallization process. A second urea-adduct treatment of the recovered adduct fraction was investigated as a practical means of separating from the stearic and palmitic acids a fraction containing most of the alkali-conjugated linoleic acid. Flow diagrams of the hydrogenation-crystallization and urea adduct methods are shown in Fig. 1.

Experimental

The distilled fatty acid mixture used in the urea adduct studies contained 37% cyclic, 22% conjugated linoleic, 27% oleic, 8% palmitic, 4% stearic and 2% unconjugated linoleic fatty acids. It was prepared by heating linseed oil, sodium hydroxide and ethylene glycol at 295C for ½ hr. The amount of sodium hydroxide was 100% in excess of that required to saponify the linseed oil. The glycol:linseed oil ratio was 3:1 (w/w). The soaps resulting from the reaction were acidified with dilute hydrochloric acid, and the fatty acids were recovered and vacuum distilled to remove polymeric acids.

To prepare the adduct, various concentrations of urea and methanol were heated to 60C on a steam bath, and the distilled fatty acids were added with constant stirring. Distilled fatty acids were not added to the urea and methanol during the heat-up period because part of the fatty acids were found, by neutralization and saponification equivalent values, to esterify on prolonged contact with the methanol and urea. Some crystallization occurred immediately after addition of the distilled fatty acids. The heated mixture was immediately put into a refrigerator and cooled to a selected temperature (0 or 25C). The crystallized product was filtered with vacuum on a Büchner funnel fitted with a rubber dam to compress the cake. Adduct and nonadduct fractions were diluted with several volumes of water and the fatty acids washed twice with water to remove urea and methanol. To facilitate complete separation of fatty acids from the aqueous phase, about 1% sodium chloride was dissolved in the water and hexane was added to the fatty acids. The adduct fraction contained primarily straight-chain fatty acids, and the nonadduct fraction was rich in unsaturated cyclic fatty acids. Each fatty acid fraction was converted to its methyl esters (4), and the esters were analyzed with a 6 ft, ¼ in. gas-liquid chromatographic (GLC) column containing 20% diethylene glycol succinate (DEGS) on 80–100 mesh Gas-Chrom P. The fatty acid components of the adduct and nonadduct fractions were resolved, except for conjugated linoleic and unsaturated cyclic fatty acids (esters) that elute from the GLC column to give overlapping peaks. To analyze for cyclic fatty acids, a portion of each sample was completely hydrogenated to convert all C-18 straight-chain acids to stearic acid, and cyclic acids to saturated ones. This portion was then an-

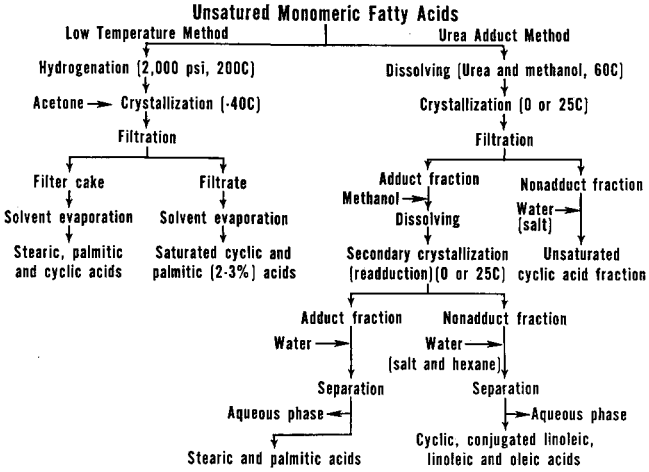

FIG. 1. Flow sheet of low temperature and urea adduct methods of separating cyclic from straight-chain fatty acids.

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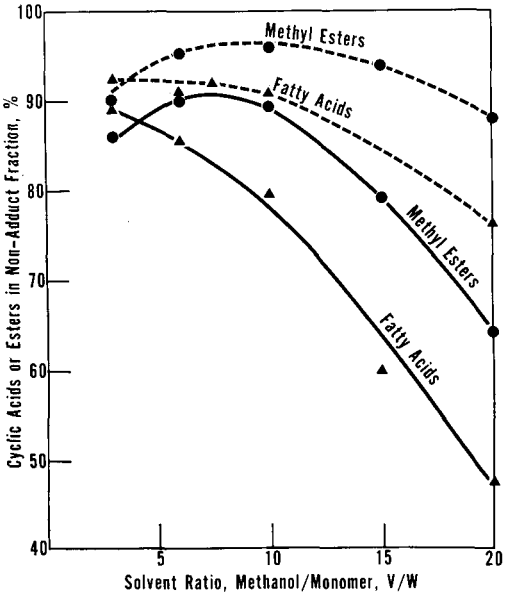

FIG. 2. Urea adduct separation of cyclic from monomeric fatty acids and esters: relation of crystallization temperature and solvent ratio to cyclic acid purity in nonadduct fraction.

alyzed by GLC and the true percentage of cyclic acids determined (1). The amount of conjugated linoleic acids was then calculated as the difference between the total percentage of unsaturated cyclic fatty acids and conjugated linoleic acids before hydrogenation, and the amount of cyclic fatty acids after hydrogenation. Several unsaturated fatty acid samples were analyzed for conjugated diene by UV absorption at 233 mμ to compare this method with that of determining conjugated linoleic acid content by GLC. There was close agreement between the two methods.

Results and Discussion

In this discussion, the methanol:fatty acid ratio will be called the solvent ratio, and the urea:fatty acid ratio will be referred to as the urea ratio.

The effects of solvent ratio and crystallization temperature on cyclic content of the nonadduct fractions from urea adduction of the distilled fatty acids and their methyl esters at a urea ratio of 3:1 are shown in Fig. 2. At comparable solvent ratios and

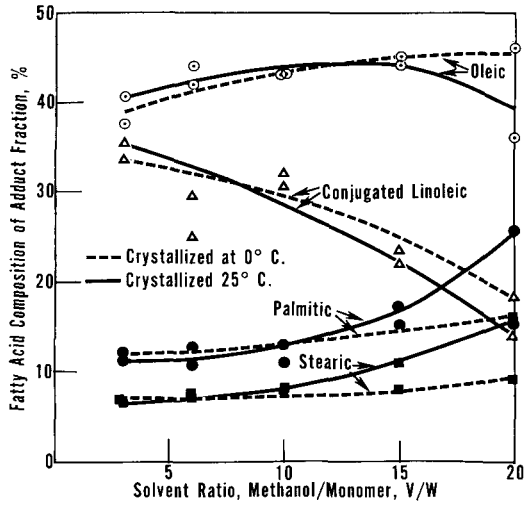

FIG. 3. Urea adduct separation of cyclic from straight-chain fatty acids: effects of solvent ratio and crystallization temperature on composition of adduct fraction.

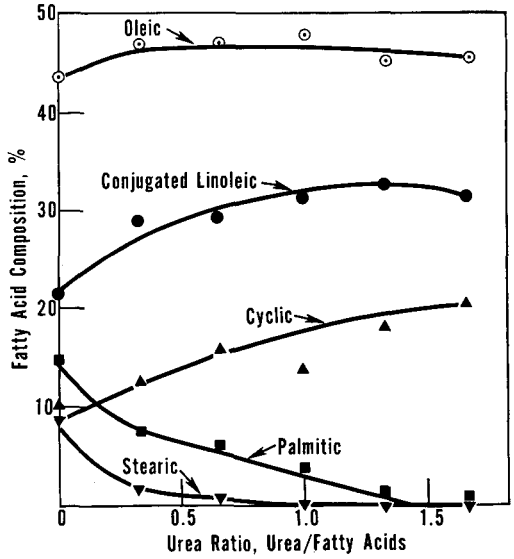

FIG. 4. Effect of urea:fatty acid ratio on composition of secondary nonadduct fraction.

crystallization temperatures, the nonadduct fractions of the esters had a higher cyclic content than the corresponding fraction of the distilled fatty acids. As the solvent ratio was decreased from 20:1 to 3:1 at a constant urea ratio, the nonadduct fraction from the distilled fatty acids increased in cyclic purity; however, with methyl esters the purity of the nonadduct fraction unexpectedly showed a maximum at a solvent ratio of 8:1. At comparable solvent ratios, greater cyclic acid purity resulted with either the acids or esters when they were crystallized at 0C than when samples were crystallized at 25C, although at low solvent ratios the difference was much less. When the distilled fatty acids were adducted at 0C, cyclic acid content of the nonadduct fraction was nearly constant at 91–93% with solvent ratios of 10:1 to 3:1. Unsaturated cyclic fatty acids of substantially 100% purity were obtained by readducting the 90–95% cyclic fatty acid fraction with a 3:1 solvent ratio and a 3:1 urea ratio.

Adduct fractions contained oleic, conjugated and nonconjugated linoleic, palmitic, stearic and unsaturated cyclic fatty acids.

Fig. 3 illustrates the composition of straight-chain fatty acids in the adduct fractions at various solvent ratios and a 3:1 urea ratio. Conjugated linoleic acid content of the adduct fraction decreased as the solvent ratio was increased from 3:1 to 20:1. The oleic acid content of the adduct fraction increased with increasing solvent ratio when the samples were crystallized at 0C; however, oleic content of samples that were crystallized at 25C also increased until a solvent ratio of 15:1 was reached and then sharply decreased. Crystallization temperature of 0 or 25C had little effect on the conjugated linoleic acid content of the adduct fraction. At low solvent ratios, the two stearic acid curves practically coincide for either crystallization temperature employed. At low ratios, curves for palmitic acid also reflect little effect of crystallization temperature. Above a 10:1 solvent ratio, the 25C crystallization curves indicate a more rapid increase in stearic and palmitic acid contents with solvent ratio than do those crystallized at 0C. Nonconjugated linoleic acid was not plotted on these curves because of the minor amount involved. Total adduct fraction decreased with increasing solvent ratio (Table I). Crystallization temperature

TABLE II

Composition of the Nonadduct Fraction After Readduction at a Solvent Ratio of 3.33:1

Urea ratio	Palmitic	Stearic	Oleic	Conjugated linoleic	Nonconjugated linoleic	Cyclic	Wt. % nonadduct fraction
Starting material	14.9	8.5	43.8	21.3	1.0	10.3	.....
0.33:1	7.6	1.9	46.8	29.7	1.7	12.3	85.5
0.67:1	8.6	1.5	46.9	30.0	2.0	12.8	79.2
1.00:1	4.8	0	47.9	31.2	2.5	13.6	65.8
1.33:1	1.6	0	45.1	32.3	2.4	18.1	52.4
1.67:1	0.9	0	45.4	30.9	1.9	20.9	40.2

began to make a difference in the weight of the adduct fraction at a solvent ratio of 10:1. Much greater weight differences were noted at higher solvent ratios.

Readduction of Straight-Chain Fatty Acid Fraction

Readduction studies were conducted on the initial straight-chain adduct fraction, which analyzed 43.8% oleic acid, 1% nonconjugated linoleic acid, 21.3% conjugated linoleic acid, 10.3% cyclic acid and 23.4% saturated acids. The object was to rid the fraction of palmitic and stearic fatty acids and thereby obtain an enriched conjugated linoleic fraction. Monomeric fatty acids were adducted with urea and methanol in a 3:1 urea ratio and a 3:1 solvent ratio.

TABLE I

Effect of Solvent Ratio on Fatty Acid Distribution of Adduct Fraction (wt. basis) at a 3:1 Urea Ratio and Crystallization Temperatures of 0 and 25C

Solvent ratio	Crystallization temp (C)	Wt. adduct fatty acid fraction (%)	Crystallization temp (C)	Wt. adduct fatty acid fraction (%)
3:1	25	60.0	0	60.6
6:1	25	52.7	0	52.0
10:1	25	48.0	0	50.6
15:1	25	34.7	0	46.7
20:1	25	18.0	0	41.3

After the adduct fraction was separated by vacuum filtration, the fatty acids were recovered. The effect of low urea ratio on the fatty acid composition of the secondary nonadduct fraction at a solvent ratio of 3.33:1 is shown in Table II and Fig. 4. Samples were crystallized at 0C. The weight percent of the nonadduct fractions at various urea ratios are also given in Table II. As the urea ratio was increased from 0.33:1 to 1.67:1, there was little change in the oleic acid composition of the nonadduct fraction; however, the conjugated linoleic composition was increased from 21.3 in the initial acids to 32.8% in the nonadduct acids at a urea ratio of 1.33:1. The palmitic and stearic acid contents were reduced from a total of 23.4% to less than 1% to give a fraction that is composed of 99+% unsaturated fatty acids, of which 80% are unsaturated straight-chain fatty acids.

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