Countercurrent and Counter Double Current Distribution of 2-Methoxyethyl and 2-Chloroethyl Fatty Esters[1]

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Abstract

2-Methoxyethyl esters of linseed and safflower oils were made by a base-catalyzed transesterification and 2-chloroethyl esters by acid-catalyzed esterification of the free acids. Both esters were distilled in vacuum. Countercurrent distribution (CCD) of the two linseed esters with a hexane-acetonitrile solvent system indicated that partition coefficients for the individual esters are one half those of the corresponding methyl esters. These lower partition coefficients permit solvent ratios nearer to one to be used in both CCD and counter double current distribution (CDCD) and they also reduce loading and transferring errors. Selectivity of the system toward number of double bonds and carbon chain length is the same as when methyl esters are used. Conditions were determined for the CDCD preparations of 2-methoxyethyl and 2-chloroethyl linolenate and linoleate from linseed and safflower oils, respectively.

Introduction

The *n*-hexane-acetonitrile solvent system is used in countercurrent distribution (CCD) to separate fatty methyl esters that differ in chain length and degree of unsaturation (9). This solvent system has also been used in counter double current distribution (CDCD) to prepare methyl linolenate (4) and methyl linoleate (8). The low boiling points of both solvents facilitate sample recovery and, in CDCD, permit the continuous operation of steam heated stills for stripping solvent from the sample (4). Although selectivity of the system is high (9), for C-18 and longer chain length esters the partition coefficients are large and consequently, small solvent ratios (equilibrated upper layer volume/equilibrated lower layer volume) of one fourth or less are needed for separation. The small volume of upper layer associated with small solvent ratios increases transfer errors. This type of error is caused by the displacement of lower layer by the sample, which as it moves through the extraction train, leaves tubes short of lower layer. The upper layer is then left behind to make up the difference. In our experience with a CCD apparatus which has a lower layer volume of 40 ml, the amount of upper layer left behind can be 1 ml or more depending on the amount of sample in the apparatus. Since the upper layer left behind would be a larger proportion of a small volume, the transfer error associated with a small solvent ratio would be greater than for a larger solvent ratio. Concentration effects are also more pronounced when small upper layer volumes are used. For a given separation, solvent ratios which give an extraction coefficient (partition coefficient times solvent ratio) close to 1 are usually used in CCD. The results are that the upper layer volume will contain one half of the total sample in a tube. Thus, if the upper layer volume is small, the concentration of sample in it is much larger than that in the lower layer. If this concentration is high enough, the partition coefficient for a component will no longer be constant but will depend on the component's concentration and on the other components present. These effects might not be undesirable in all cases; however, they need to be avoided if predicted results are expected. Scholfield et al. (8) show these concentration effects for methyl esters. A superior solvent system having lower partition coefficients for C-18 esters while retaining high unsaturate selectivity and low boiling points is yet to be found.

Esters more polar than methyl esters would lower the partition coefficients of fatty acids in the *n*-hexane-acetonitrile solvent system and permit the use of solvent ratios closer to one. Two such polar type esters, 2-methoxyethyl and 2-chloroethyl, were used in CCD and in CDCD to prepare linolenate and linoleate.

Experimental Procedures

2-Methoxyethyl Esters

Linseed oil and safflower oil triglycerides were transesterified with a tenfold mole excess of 2-methoxyethanol and 0.5% sodium 2-methoxyethoxide as catalyst. The 2-methoxyethoxide was made by reacting the proper amount of Na with 2-methoxyethanol at room temperature. The triglycerides were then added and the mixture was heated at 110 C for 1 hr with constant stirring. The medium was then acidified with dilute hydrochloric acid and ice was added to cool and dilute the solution. 2-Methoxyethyl esters were extracted with petroleum ether (PE), washed with H_2O, dried with Na_2SO_4 and, after PE removal, distilled at 160–170/0.05 mm.

2-Chloroethyl Esters

Linseed and safflower fatty acids were esterified with a tenfold mole excess of 2-chloroethanol and 4% by weight H_2SO_4. After refluxing for 1 hr one half of the original volume of alcohol was removed by distillation. Ice was added to cool and dilute the mixture. The 2-chloroethyl esters were extracted with PE, washed with H_2O, dried with Na_2SO_4 and, after PE removal, distilled at 145–150/0.01 mm.

Countercurrent Distribution

Each tube of a 200 tube automatic CCD apparatus contained 40 ml of acetonitrile as lower layer and 20 ml of hexane as upper layer. Distributions were made according to the single withdrawal procedure (9) and a recording refractometer monitored the effluent hexane layer (2,3).

Counter Double Current Distribution

Distributions were performed with a robot-operated 50 tube CDCD with hexane and acetonitrile as the immiscible solvent pair. The hexane volume was varied, whereas 50 ml of acetonitrile was used in all runs. About 300 mg of sample per transfer was fed into tube 26 of the train. Effluent samples and solvent were recovered by continuous operating stills

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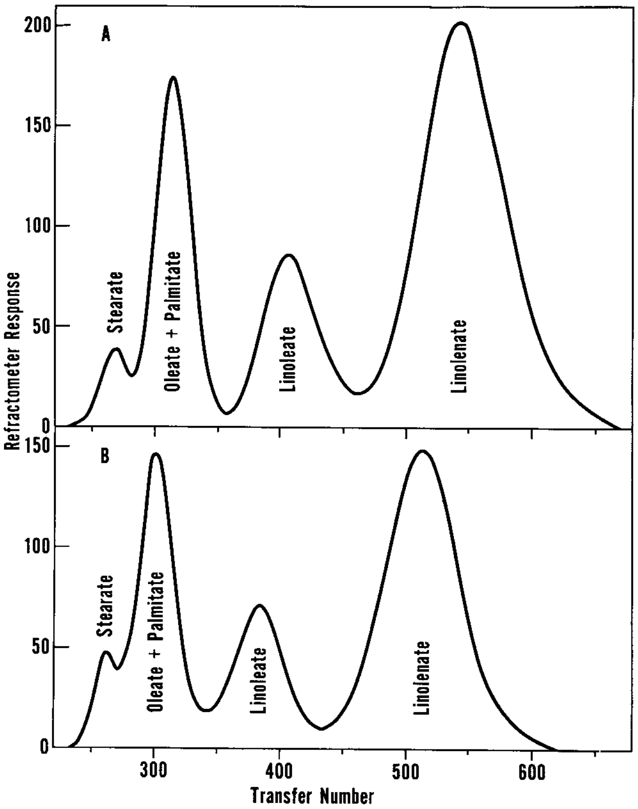

FIG. 1. Countercurrent distribution of (a) 2 methoxyethyl esters and (b) 2-chloroethyl esters of linseed oil. Solvent system: 20 ml *n*-hexane/40 ml acetonitrile.

as previously described (4). The contents of the odd number tubes and the feed tube were removed after 1000 transfers. Solvent was removed by vacuum and the remaining oil was weighed and then analyzed by GLC.

Gas Chromatographs

Chromatograms were run on a 1/8 in. × 5 ft stainless steel column packed with 25% stabilized DEGS on 60/80 Chromosorb. A flame ionization detector was used. The 2-chloroethyl esters were transesterified to methyl esters and run at 180 C. The 2-methoxyethyl esters were run at 215 C.

Results and Discussion

The 2-methoxyethyl esters were easily prepared by a base-catalyzed transesterification. These esters are readily vacuum distilled and are quite stable.

By contrast, the 2-chloroethyl esters were prepared by esterification of the free acids since transesterification of the triglycerides would not go to completion even when a tenfold mole excess of 2-chloroethanol was present. Both base and acid catalysts were tried for the transesterification; however, no better than about 70% conversion could be achieved. No problems were encountered with the esterification reaction. Other catalysts, such as HCl gas and BF_3, have been used for esterification in place of concentrated H_2SO_4 all with equal success (5–7). These esters are stable enough to be vacuum distilled but have a tendency to polymerize upon standing.

The distilled linseed esters of both types were put through the CCD apparatus to determine their partition coefficients. Figure 1b is the elution curve for the 2-chloroethyl esters and is quite similar to the elution curve for methyl esters; however, twice the volume of upper layer was used for the 2-chloroethyl esters. The CCD elution curve of the 2-methoxyethyl esters is shown in Figure 1a. This curve is similar to the 2-chloroethyl ester curve; however, the 2-methoxyethyl esters are retained longer, indicating that they are slightly more polar. Table I shows that the partition coefficients (determined from CCD) of 2-chloroethyl esters are more than one half those of methyl esters and that those of 2-methoxyethyl esters are less than one half those of methyl esters. It is important to note that even though the magnitudes of the partition coefficients are less, the ratios of partition coefficients between the fatty esters for a given alcohol moiety are the same for the three alcohols. Thus the selectivity of the solvent system for unsaturation in the fatty acid is not affected by these particular alcohol moieties and any observed separation for fatty methyl esters can be repeated with either 2-chloroethyl or 2-methoxyethyl esters as long as the solvent ratio is properly adjusted.

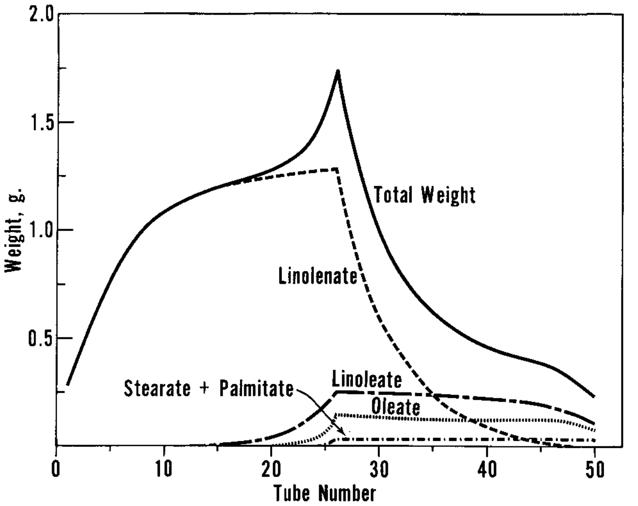

FIG. 2. Counter double current distribution of 2-methoxymethyl esters of linseed oil for the preparation of 2-methoxyethyl linolenate. Solvent system: 35 ml *n*-hexane/50 ml acetonitrile.

A solvent ratio of 0.32 is normal in preparing methyl linolenate in a 50 tube CDCD apparatus. It was determined that to prepare 2-chloroethyl linolenate requires a solvent ratio of 0.60; 2-methoxyethyl linolenate, 0.70. The steady state concentrations in the CDCD apparatus for the preparation of 2-methoxyethyl linolenate are plotted in Figure 2. It can be seen that 99+% linolenate is produced at 99+% of the rate at which linolenate is being fed as a part of the original oil. Since the weight in the feed tube (No. 26) is only 1.75 g and since the total solvent volume in each tube is 85 ml, a feed rate of almost one and a half times the 300 mg per transfer could be tolerated without exceeding the 2.5 g at which point the partition coefficients would change with concentration (8).

For the production of methyl linoleate by CDCD, a solvent ratio of 0.20 is used in the 50 tube apparatus-

TABLE I

Partition Coefficients for Various Fatty Acid Esters at 23 C

Ester	Methyl	2-Chloroethyl	2-Methoxyethyl
Stearate	12.0	6.67	5.65
Oleate	7.9	3.92	3.38
Linoleate	4.3	2.20	1.88
Linolenate	2.4	1.28	1.14

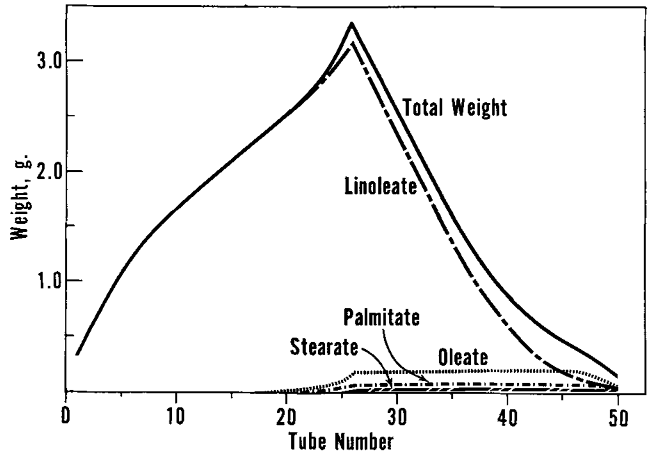

FIG. 3. Counter double current distribution of 2-methoxyethyl esters of safflower oil for the preparation of 2-methoxyethyl linoleate. Solvent system: 22 ml *n*-hexane/50 ml acetonitrile.

tus. This small ratio requires that only 10 ml of *n*-hexane be pumped for a 50-ml lower volume CDCD apparatus. Consequently, the amount of sample added per transfer has to be small because concentration limits are easily exceeded in the hexane layer. If 2-chloroethyl esters are used, the feed rate can be increased because the solvent ratio is 0.36. Figure 3 shows the steady state concentrations in the CDCD apparatus for the preparation of 2-methoxyethyl linoleate from safflower esters. The solvent ratio was 0.44. The feed rate of 0.300 mg per transfer was close to the allowable maximum since 3.20 g of oil are present in the feed tube. Linoleate of 99+% purity resulted at a recovery rate of 95+%.

Of the two ester types, the 2-methoxyethyl esters are preferable for CCD or CDCD for three reasons: they are easily made by a simple transesterification reaction; they are more stable and can be analyzed on GLC and they are slightly more polar and permit larger solvent ratios. 2-Methoxyethyl fatty esters should make the *n*-hexane-acetonitrile system more useful in that the high selectivity of the system is retained while solvent ratios are increased. The increased solvent ratio means that transfer errors will be lessened and that higher production rates can be attained. Esters of C_{20} and C_{22} chain length, which before the work reported here required solvent ratios of 0.125 (1,10) or less, can now be readily separated by CCD without recycling.

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