be obtained under average conditions prevailing in household service, with high foaming characteristics as desired for agitator-type machines, or with moderate, controllable foaming for cylinder machines.

Acknowledgment

The authors gratefully acknowledge the assistance of William J. Park, Rodney Blomfield, and Richard Thivierge, who performed the laboratory work reported.

REFERENCES

1. Harris, J. C., Oil & Soap, *23*, No. 4, 101 (1946).
2. Morrisroe and Newhall, Oronite Chemical Company, presentation before the Analytical Division, Pacific Industrial Conference, San Francisco, Oct. 21, 1947.
3. Borghetty, H. C., J. Am. Oil Chem. Soc., *26*, 319 (1949).
4. Borghetty, H. C., and Bergman, C. A., *ibid.*, *27*, 88 (1950).
5. Barker, G. E., *ibid.*, *26*, 304 (1949).
6. Flett, L. H., Morgan, O. M., and Hoyt, L. F., *ibid.*, *27*, 304 (1950).
7. Vaughn, Thomas H., and Suter, H. R., *ibid.*, *27*, 249 (1950).
8. ASTM Preprint No. 91, pp. 5-7 (1950).

[Received June 5, 1952]

Application of Urea Complexes in the Purification of Fatty Acids, Esters, and Alcohols. III.[1] Concentrates of Natural Linoleic and Linolenic Acids[2]

DANIEL SWERN and WINFRED E. PARKER, Eastern Regional Research Laboratory,[3]
Philadelphia, Pennsylvania

THE preparation of concentrates of polyunsaturated fatty acids (or methyl esters) which have the same configuration as that in the vegetable oils from which they are derived is an important and basic problem in fat chemistry. By far the bulk of fundamental research on these compounds in the past, particularly prior to 1945, was conducted on polyunsaturated substances prepared by bromination-debromination procedures since it was assumed that debromination products were essentially the same as the natural acids of the vegetable oils from which they were derived. Ultraviolet and infrared spectrophotometric methods for examining polyunsaturated materials however have been mainly responsible for showing that this assumption is not correct and that polyunsaturated materials prepared by bromination-debromination procedures, even though theoretical iodine numbers are obtained, may contain substantial amounts of isomers.

Natural linoleic acid (*cis,cis*-9,12-octadecadienoic acid) has apparently been isolated in pure form by Brown and coworkers (2, 3) by repeated low temperature fractional crystallization of the mixed acids from a number of vegetable oils. Natural linolenic acid (*cis,cis,cis*-9,12,15-octadecatrienoic acid), on the other hand, has not been obtained in the pure state by the same technique; the highest concentration reported is 88% (10). Riemenschneider and coworkers (4, 5, 8) however, employing adsorption fractionation on silicic acid, have recently prepared pure methyl esters of natural linoleic, linolenic, and other polyunsaturated acids.

Adsorption fractionation to prepare pure fatty acids is, at present, still limited to relatively small scale laboratory operations, it is time-consuming, and relatively large amounts of solvent are required. In this technique it is decidedly advantageous to employ mixtures which are as rich as possible in the component being sought so that the already limited adsorptive capacity of laboratory columns is not consumed in the removal of a large amount of unwanted components. Where the highest purity products are required, the urea complex separations to be described in this paper are an excellent preliminary concentration step.

As a logical extension of earlier investigations (12, 13), we have successfully applied urea complex precipitation technique to the preparation in good yield (50-90%) of concentrates of natural linoleic and linolenic acids (purity 66-95%) from oils rich in these acids, taking advantage of the preferential precipitation of the urea complexes of the saturated and monounsaturated acids from corn oil fatty acids, and the preferential precipitation of saturated, monounsaturated, and diunsaturated acids from linseed oil fatty acids or perilla oil fatty acids. The urea complex separation technique minimizes or obviates some of the disadvantages of the low-temperature crystallization or adsorption techniques discussed earlier in this paper. In the urea complex separation techniques described in this paper operations are usually conducted between room temperature and the boiling point of methanol, and occasionally at 0°C. Disadvantages of the urea complex separation technique have been discussed in our previous papers (12, 13).

Some work has been published on the use of urea complexes in the preparation of concentrates of polyunsaturated acids and methyl esters from linseed and corn oils. Newey and coworkers (6) reported the concentration obtained by a single urea precipitation, based solely on iodine number, without demonstrating the practical limit of concentration which could be achieved by a repetition of the urea treatment. Furthermore the composition of the starting materials and the concentrates were not reported so that it is difficult to assess the efficiency of the separations. Schlenk and Holman (9) reported similar data and, in addition, stated that two preparations of methyl linoleate, iodine number 168 and 173, were obtained from corn oil methyl esters in 23% and 14% yields, respectively. Unfortunately operational details, such as the quantity of urea and methanol and the number of urea

---

[1] The preceding papers in this series are references 12 and 13.

[2] Presented at the Fall Meeting of the American Oil Chemists' Society, Cincinnati, O., Oct. 20-22, 1952.

[3] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

complex precipitations required, were not given. We have been unable to find any published work on the use of urea complexes in the preparation of linolenic acid concentrates from perilla oil.

Experimental

Materials Used. Urea and anhydrous methanol were the purest reagent grades. The fatty acids employed were prepared from corn oil (edible), linseed oil, and perilla oil by the rapid saponification technique already described (11). Yields of fatty acids from each oil were quantitative. All operations described in this paper were performed in a nitrogen atmosphere.

Linoleic Acid Concentrate from Corn Oil Fatty Acids. Corn oil fatty acids (1,800 g.) were rapidly distilled at 0.4 mm. in a Claisen flask; the initial 5% of distillate was discarded. (This distillation is optional.) The main fraction weighed 1,600 g. One thousand grams of the main fraction [straw-colored liquid; iodine number, 144.7; composition (1): 62% linoleic acid, 38% oleic and saturated acids] were added to a hot solution of 1,310 g. of urea in 3,270 ml. of methanol. A precipitate formed immediately, but the mixture was heated to effect complete solution, and then it was allowed to cool slowly to room temperature. The well-defined needles of urea complexes (1,200 g.; iodine number 30.6) were filtered with suction, and the filtrate was then evaporated at 50°C. until an additional precipitate formed at this temperature (filtrate volume about 2,500 ml.). Two hundred and sixty-five grams of urea were added and complete solution was effected by boiling. After the solution had cooled to room temperature, the urea complexes (630 g.; iodine number 33.8) were filtered off and the filtrate was again evaporated as described (filtrate volume about 1,500 ml.). Two hundred grams of urea were dissolved in the filtrate, and the precipitation of urea complexes at room temperature was repeated. The third crop of urea complexes weighed 431 g. (iodine number 45.8). The final filtrate was evaporated to dryness, warm water was added to the residue to dissolve the excess urea, and the oil layer was dissolved in petroleum naphtha (hexane fraction). The petroleum naphtha solution was washed several times with water to remove residual urea and the solvent was evaporated under vacuum. A yellow oil was obtained which weighed 390 g. and had an iodine number of 168.9. This was rapidly distilled from an alembic flask at low pressure and yielded the following fractions:

I, 17 g., b.p. 106-140°/0.04-0.10, n_D^{50} 1.4570, iodine number 173.9;

II, 328 g. b.p. 140°/0.03-0.05, n_D^{50} 1.4581, iodine number 176.2;

III, 11 g., b.p. 140°/0.06-0.09, n_D^{50} 1.4643, iodine number 171.4;

residue, dark brown viscous oil, 30 g. Fraction II was almost colorless and had the following composition (1): 95% linoleic acid, 5% oleic acid. The yield of linoleic acid recovered was 50%.

When only two urea precipitations were employed instead of three, 380 g. of linoleic acid concentrate, iodine number 173.6 (composition: 91% linoleic acid, 9% oleic acid) was obtained after distillation. The yield of linoleic acid recovered was 55%. A single urea precipitation yielded 520 g. of linoleic acid concentrate, iodine number 168.0 (composition: 85% linoleic acid, 15% oleic acid), after distillation. The yield of linoleic acid recovered was 72%.

The yield and purity of the recovered linoleic acid were slightly lower when the slurry method for preparing urea complexes was used (12, 13) instead of the solution method reported in this paper.

Linolenic Acid Concentrate from Perilla Oil Fatty Acids. One thousand grams of perilla oil fatty acids (iodine number 213.7; composition: 65% linolenic acid, 13% linoleic acid, 15% oleic acid, 7% saturated acids) were dissolved in a hot solution of 1,600 g. of urea in 4,000 ml. of methanol. The mixture was allowed to cool slowly to room temperature and the precipitate of urea complexes (1,331 g.; iodine number 39.6) was filtered with suction. The filtrate was evaporated to dryness, warm water was added to the residue to dissolve the excess urea, and the filtrate acids were isolated by solvent extraction as described in the preceding section under the separation of corn oil fatty acids. A brown oil was obtained which weighed 551 g. and had an iodine number of 244.4. This was rapidly distilled from an alembic flask and yielded the following fractions:

I, 31 g., b.p. 155°/0.2-0.5, n_D^{50} 1.4650, iodine number 246.0;

II, 455 g., b.p. 146°/0.05-0.08, n_D^{50} 1.4658, iodine number 252.8;

III, 13 g., b.p. 148°/0.08-0.10, n_D^{50} 1.4673, iodine number 249.1;

residue, dark brown viscous oil, 50 g., iodine number 172.5. Fraction II was pale yellow and had the following composition (1): 87% linolenic acid, 6% linoleic acid, 5% oleic acid, 2% saturated acids. The yield of linolenic acid recovered was 61%.

Reapplication of the urea complex precipitation procedure to Fraction II resulted in an increase in iodine number of only 3 units (linolenic acid content raised to 89%), but the overall yield of linolenic acid recovered was reduced to 55%.

Linolenic Acid Concentrate from Linseed Oil Fatty Acids. As described in the preceding section under separation of perilla oil fatty acids, 1,000 g. of linseed oil fatty acids [iodine number 183.1; composition (1): 47% linolenic acid, 17% linoleic acid, 27% oleic acid, 9% saturated acids] were processed with 880 g. of urea and 2,200 ml. of methanol, except that the solution was cooled to 0°C. The precipitate of urea complexes weighed 875 g. (iodine number 30.4) and the filtrate acids weighed 720 g. (iodine number 224.2). Distillation as described yielded the following fractions:

I, 13.5 g., b.p. 135-145°/0.08-0.1 n_D^{50} 1.4619, iodine number 219.5;

II, 648 g., b.p. 135°/0.03-0.07, n_D^{50} 1.4630, iodine number 228.0;

residue, dark brown oil, 47 g., iodine number 184.3. Fraction II was pale-yellow and had the following composition: 66% linolenic acid, 20% linoleic acid, 12% oleic acid, 2% saturated acids. The yield of linolenic acid recovered was 90%.

Reapplication of the urea complex precipitation at room temperature to Fraction II resulted in an increase in iodine number of 10 units (linolenic acid content 70%), and the overall yield of linolenic acid recovered was reduced to 87%.

Discussion

Concentrates of natural linoleic acid (linoleic acid content 85-95%) can be readily prepared in good yield (50-72%) from corn oil fatty acids by the use of the urea complex technique to precipitate saturated and monounsaturated acids preferentially. Whether one, two, or three precipitations is employed will depend on the relative importance of degree of concentration and yield. For some applications which we are investigating 85-90% natural linoleic acid is satisfactory, and only one or two urea complex precipitations are employed. For the most efficient application of the silicic acid adsorption technique to prepare pure natural linoleic acid, it may be desirable to conduct a third urea complex precipitation and start with the 95% linoleic acid.[4]

We have not studied more than three urea complex precipitations with corn oil acids because the maximum increase in iodine number (about 1 unit) to be anticipated for each additional precipitation would not justify the large reduction in yield. Furthermore the data suggest that a levelling-off will be encountered, and even if pure linoleic acid could be isolated, the yield would probably be quite low (9).

Perilla oil is an excellent source of natural linolenic acid. Concentrates of linolenic acid (linolenic acid content, 87%) can be readily prepared in about 60% yield from mixed perilla oil fatty acids by a single preferential precipitation at room temperature of the urea complexes of the saturated, monounsaturated, and diunsaturated fatty acids, followed by distillation of the non-complexed (filtrate) acids. Repetition of the urea precipitation procedure results in only a slight increase in purity to about 89%. The failure of the urea complex precipitation technique to raise the purity of the linolenic acid above about 89% parallels the experience with low temperature crystallization of linolenic acid-rich fatty acids, in which a maximum linolenic acid content of about 88% is also obtained (10). The inability to obtain a more complete separation of linoleic from linolenic acid is undoubtedly related to the ratio of their equilibrium constants for the formation of urea complexes (7), coupled with the ratio of linoleic to linolenic acid in the fatty acid mixture.

Application of the urea complex precipitation technique to linseed oil fatty acids does not yield concentrates as high in linolenic acid as are obtained from perilla oil fatty acids, but the yield of linolenic acid recovered is excellent. Considering the ready availability and low price of linseed oil, it is probably the best starting material in the preparation of 70% linolenic acid by the urea complex precipitation technique.

Summary

Concentrates of natural linoleic acid (linoleic acid content, 85-95%) have been prepared in 50-72% yields from corn oil fatty acids by preferential precipitation of the saturated and monounsaturated fatty acids at room temperature as their urea complexes.

By a similar procedure, concentrates of natural linolenic acid (linolenic acid content, 87-89%) have been prepared in 55-61% yields from perilla oil fatty acids by preferential precipitation of the saturated, monounsaturated, and diunsaturated fatty acids. Although concentrates of natural linolenic acid containing only 66-70% linolenic acid were obtained from linseed oil fatty acids, yields were 87-90%.

A levelling-off effect has been observed in the use of the preferential precipitation technique in raising the purity of concentrates of linoleic and linolenic acid. This parallels the experience in the purification of these acids by low-temperature crystallization.

REFERENCES

1. Brice, B. A., Swain, M. L., Herb, S. F., Nichols, P. L. Jr., and Riemenschneider, R. W., J. Am. Oil Chem. Soc., *29*, 279-287 (1952).

2. Frankel, J., and Brown, J. B., J. Am. Chem. Soc., *63*, 1483-1484 (1941).

3. Frankel, J. S., Stoneburner, W., and Brown, J. B., J. Am. Chem. Soc., *65*, 259-262 (1943).

4. Herb, S. F., Riemenschneider, R. W., and Donaldson, J., J. Am. Oil Chem. Soc., *28*, 55-58 (1951).

5. Herb, S. F., Witnauer, L. P., and Riemenschneider, R. W., J. Am. Oil Chem. Soc., *28*, 505-507 (1951).

6. Newey, H. A., Shokal, E. C., Mueller, A. C., Bradley, T. F., and Fetterly, L. C., Ind. Eng. Chem., *42*, 2538-2541 (1950).

7. Redlich, O., Gable, C. M., Dunlop, A. K., and Millar, R. W., J. Am. Chem. Soc., *72*, 4153-4160 (1950).

8. Riemenschneider, R. W., Herb, S. F., and Nichols, P. L. Jr., J. Am. Oil Chem. Soc., *26*, 371-374 (1949).

9. Schlenk, H., and Holman, R. T., J. Am. Chem. Soc., *72*, 5001-5004 (1950).

10. Shinowara, G. Y., and Brown, J. B., J. Am. Chem. Soc., *60*, 2734-2738 (1938).

11. Swern, Daniel, Knight, H. B., Scanlan, J. T., and Ault, W. C., Oil and Soap, *22*, 302-304 (1945).

12. Swern, Daniel, and Parker, W. E., J. Am. Oil Chem. Soc., *29*, 431-434 (1952).

13. Swern, Daniel, and Parker, W. E., J. Am. Oil Chem. Soc., *29*, 614-615 (1952).

[Received April 23, 1952]

---

[4] Safflower seed oil (iodine number, 146.3; fatty acid composition: 78% linoleic, 12% oleic, 9% saturated) was found to be an excellent source of natural linoleic acid. One urea complex precipitation gave a 75% yield of 93% linoleic acid.