Urea Complexes of Technical Monoglycerides

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THE FORMATION of adducts between urea and various fatty acids or their methyl esters has proved of value in the purification of these compounds. Schlenk (9) stated that the procedure should also be applicable to the otherwise rather cumbersome separation of mono-, di-, and triglycerides although preliminary experiments by Roncero, Fiestas, Mazuelos, and Moreno (8) had not given satisfactory results.

Bradley, Mueller, and Shokal (3) and Roncero *et al.* (8) reported that urea forms complexes more easily with diglycerides than with monoglycerides. Contrary to this observation, Heckles and Dunlap (4) observed that the formation of a urea adduct with monoglycerides is easier than with the diglycerides and that urea fractionates on the basis of degree of esterification. However experiments in our laboratories with technical products of lauric acid and sesame oil show that the diglycerides have greater tendency to form urea adducts than the monoglycerides.

Aylward and Wood (2) made a stepwise crystallization of commercial monostearin with urea and found that distearin was preferentially precipitated. However, in later experiments (1), they found a discrepancy in the monoglyceride yield, which led to the conclusion that urea adduct formation may favor considerable methanolysis of glyceryl monostearate in 90% methanol.

In a previous study (5) monolaurin and the monoglycerides from sesame oil were fractionated at a ratio of 1:3:13.5 of monoglycerides:urea:methanol, followed by removal of part of the solvent. When the material balance for mono-, di-, and triglycerides was calculated, the results did not indicate methanolysis. Hence further experiments were undertaken to study the possibility of methanolysis during urea fractionation, under conditions similar to those given by Aylward and Wood (2).

Experimental

Lard monoglycerides (Myverol 18-40, Sap. No. 160–170, I.V. 45–55) and stearic acid monoglyceride (Myverol 18-05, Sap. No. 160–170, I.V. maximum 3) were obtained from Distillation Products Industries, Eastman Kodak Company, Rochester 3, N. Y. They were distilled esters containing a maximum of 1.5% glycerol and 1.5% (for lard monoglyceride) and 2.5% (for stearic acid monoglyceride) free fatty acids (as oleic acid). The physical and chemical characteristics reported herein were supplied by the manufacturers.

A weighed amount (15 g.) of the sample in a 500-ml. conical flask was dissolved in 30 ml. of methanol, 60 g. of urea were added and dissolved by warming. The mixture was cooled and kept over-night at room temperature (27–30°). The crystallized adduct was separated by filtration on a sintered glass funnel, using water suction. Warm acidulated distilled water was used to decompose the adduct. An emulsion was formed, and a saturated solution of salt was added to break the emulsion. The fatty portion was dissolved in chloroform. The contents were transferred to a separatory funnel and allowed to stand overnight to allow any emulsion to break completely. The chloroform layer was removed, dried over anhydrous sodium sulphate, and transferred to a weighed beaker; the chloroform was evaporated and the yield of the fatty portion was noted.

A second adduct fraction was separated after removing some methanol from the filtrate by distillation. The process was repeated to obtain further fractions. The fractions were analyzed for hydroxyl values by the pyridine acetic anhydride method (7) and monoglyceride content by the periodic oxidation method (6). Results are shown in Table I.

TABLE I
Urea Fractionation of Distilled Monoglycerides

Sample	Weight (g.)	Hydroxyl value	1-Monoglyceride[a] (%)	Diglyceride[b] (%)	1-Monoglyceride (g.)	Diglyceride (g.)
Lard monoglycerides[c]	15.03	....	88.0	....	13.23	....
Fraction I	10.40	....	84.4	....	8.78	....
Fraction II	3.70	....	95.9	....	3.55	....
Total	14.10	....	....	....	12.33	....
Loss	0.93	....	....	....	0.90	....
Stearic-acid monoglyceride[d]	15.13	320	88.6	10.0	13.42	1.51
Fraction I	5.01	283	83.6	16.4	4.19	0.82
Fraction II	8.10	307	94.3	5.7	7.64	0.46
Fraction III	1.52	313	96.7	3.3	13.30	1.33
Loss	0.50	....	....	....	0.12	0.28

[a] Experimental determination by periodic oxidation method.
[b] Calculated from theoretical hydroxyl value of monoglyceride as 318.6 and of diglyceride as 91.58.
[c] Myverol 18-40.
[d] Myverol 18-05.

Discussion

The present study of the fractionation of technical grade distilled monoglycerides by urea confirmed previous results (5) with monolaurin and monoglycerides from sesame oil. Losses in these fractionations were small, being about 6% for lard monoglycerides and 3.2% for monostearin. Material balances did not indicate any significant degree of methanolysis during urea adduct formation even though crystallizations required 18–20 hrs. Similarly Bradley *et al.* (3) observed no methanolysis or change in the equilibrium point during slow crystallization of the adducts.

Summary

Technical monoglycerides have been fractionated with urea in methyl alcohol. Complexes were formed more easily with diglycerides than with monoglycerides as shown by Bradley, Mueller, and Shokal and contrary to the observation of Heckles and Dunlap. Further, in stepwise crystallization of commercial monoglycerides, there was no methanolysis of the monoglycerides as observed by Aylward and Wood.

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Letter to Editor

A Note on Glyceride Structure: Specific, Random, and Restricted-Random Distribution

KARTHA (1) has advanced the theory that the fatty acyl groups in all natural fats are distributed at random among the triglyceride molecules unless the quantity of GS_3 so produced exceeds that which can exist in a fluid state *in vivo*. In this event the excess of saturated acids is distributed at random among the remaining glyceride types, GS_2U, GSU_2, and GU_3. This form of dispersion is known as "restricted-random distribution." He assumes that the acyl groups are all equally reactive and in dynamic equilibrium among all the triglyceride molecules that are in a fluid state and that all positions in the molecules are equivalent.

The theoretical proportions of GS_2U, GSU_2, and GU_3 present in a fat which is in restricted random distribution can be calculated from the proportions of GS_3 and the saturated acids found by analysis. The molar percentages of the four glyceride types found in cacao butter by Hilditch and Stainsby (2) and those for GS_2U, GSU_2, and GU_3 calculated by Kartha (1) from their data in accord with the restricted-random distribution theory are presented in the table. Included are the results of analyses by Meara (3) and Amberger and Bauch (4), as reinterpreted by Lewkowitsch (5).

The Glyceride Type Composition of Cacao Butter

	GS_3	GS_2U	GSU_2	GU_3
Hilditch and Stainsby (experimental)	2	77	21	....
Kartha (calculated)	2	80	17	1
Meara (experimental)	2.5	83	13.5	1
Amberger and Bauch (experimental)	....	80	20	....

Examination of the table shows clearly that the results of the calculations by Kartha based on the restricted-random distribution theory agree with the experimental results of the others.

Calculations from other data from various sources on other fats give similar results. The glyceride-type composition of lard, which does not agree with the theory (6), would do so if the latter were amended to permit, in some instances, restriction in the formation of GS_2U as well as that of GS_3. In this event the excess of acyl groups must perforce appear in the GSU_2 fraction.

Kartha has determined the proportions of the glyceride types in several natural fats of various kinds, the S content of which varied from 8 to 99 mol per cent, by direct analysis. The results are in close agreement with those calculated in accord with the restricted-random distribution theory.

The evidence points to the conclusion that the proportions of the glyceride types in many fats are, at least approximately, in agreement with the theoretical values based on the restricted-random distribution theory. Included are those in which the glyceride types are present in the proportions in which they would occur if fatty acid distribution were at random (1, 6, 9, 10, 11).

STRICT ADHERENCE to Kartha's theories would require that the fatty acids constituting individual mixed triglycerides be distributed among the three positions at random. It is likely however that in some or all fats the fatty acids are not distributed within the individual mixed glyceride molecules at random. In lard, for instance, saturated acids appear to occupy predominantly the 2-position in the mixed glycerides. In cacao butter, on the other hand, the 2-position is said to be occupied almost exclusively by unsaturated acids. The earlier work has been reviewed by Hilditch (7), and more evidence has appeared recently from several sources (8). It has been suggested by Lutton (8) that triglycerides of specific constitution are characteristic of natural fats rather than triglycerides formed by random fatty acid distribution.

Kartha's data do not disagree with this view. In his calculations and analyses he dealt with saturated and/or unsaturated acyl groups combined in groups of three as triglycerides. He made no attempt to show by experiment that these acyl groups were distributed at random within the triglyceride molecules. His analyses and the calculations based on chance by which his results could have been predicted do appear to show that, in several fats at least, the three saturated and/or unsaturated long chain acyl groups constituting each triglyceride molecule become parts thereof by chance. Under some circumstances this chance association results in random distribution of the glyceride types. Under other circumstances, chance association results in a certain kind of nonrandom, or "restricted random," distribution of the glyceride types.

Perhaps, in many natural fats, long-chain saturated and/or unsaturated groups become associated by chance in those triglyceride molecules formed but are not distributed within each molecule at random. These may prove to be facts related to the mechanics by which triglycerides in general are synthesized *in vivo*. They may provide clues to the nature of these mechanisms. They also may be related to the processes by which fatty acids are synthesized *in vivo*.

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