Interesterification of Lard

E. S. LUTTON, M. F. MALLERY, and J. BURGERS, The Procter & Gamble Company
Miami Valley Laboratories, Cincinnati, Ohio

Abstract

The graininess, which develops at 27C(80F) in lard shortening which has not undergone interesterification, is due to large crystal aggregates of disaturated 2-palmitoyloleoylstearin (OPS) of intermediate melting level and existing in a β'-type form of triple-chain-length structure. This β'-3 phase exists in ordinary lard accompanied by the commonly reported β phase which is largely due to trisaturated glycerides. Random interesterification eliminates graininess, not by reducing the disaturated content which remains about the same, but by reducing OPS to its "random" proportion and producing a mixture of disaturated glycerides, which is substantially lower melting than the original OPS. The resulting product crystallizes typically in a β'-2 form, characteristic of hydrogenated vegetable oil shortenings. (Directed interesterification actually reduces disaturated content as well as graininess, while simultaneously creating trisaturated "hardstock.")

IN RECENT YEARS the quality of shortenings from animal sources, principally lard, has been brought to a level comparable to that of vegetable shortenings. There are several aspects to the improvement, but the main factors were improvement of keeping quality by addition of antioxidant, and improvement of consistency and texture by interesterification.

The effects of consistency and texture of the lard brought about by interesterification, random or directed, have been discussed in several places (1–10). It has been made clear that there are changes in crystallization tendency which involve changes in both crystal habit and polymorphic state. However, there has been no complete description of polymorphic state nor of its dependence on composition.

Ordinary lard is characterized by a translucence and a poor plastic range. Plasticizing, as by a scraped-wall cooling device, does not improve the situation and further introduces an unattractive rubberiness. Addition of sufficient hardstock overcomes these difficulties and produces an attractive fresh shortening of excellent performance. Unfortunately, aging under certain conditions introduces a distasteful graininess which is not overcome short of interesterification. The behavior described stems from the unique composition of lard.

Lard is a natural product of somewhat variable composition, which has typically about 2% trisaturated (S_3), 27% disaturated (S_2U), 47% monosaturated (SU_2), and about 24% triunsaturated (U_3) triglycerides (11,12). The important S_2U portion is substantially all OPS (12,13,14). This is the glyceride playing the principal role in consistency and in changes in consistency of lard from 10 to 38C over which range the Solid Content Index (SCI) (15) changes from about 26 to about 2. The polymorphism of OPS has been investigated (16) and found to involve sub α-2, α-2, sub β'-3 and β'-3 phases. Of these, the first two are highly unstable low-temperature phases, β'-3 is obtained only by solvent crystallization, while the similar sub β'-3 phase, melting at 37C, is obtained from melt and appears to be highly stable. Only the latter phase will be involved in the further discussion where it will be referred to as β'-3. It has a long spacing of about 69A and prominent short spacing lines corresponding to 4.08 and 3.75A.

Experimental

The following groups of observations were made: *Lard vs. Interesterified Lard Shortening.* Typical commercial lard with SCI of 20 at 21C (sample melted, 5 min 0°C, 30 min 33C, 5 min 0°C, read 21C) was interesterified by the following four procedures which proved to be equivalent:

1. With 0.3% $NaOCH_3$, 13 min at 85C, 47 min at 65C.
2. With 0.5% $NaOCH_3$, heated from 55 to 90C over 1 hr period.
3. With 0.5% $NaOCH_3$, 1 hr at 55C.
4. With 0.4% Sn $(OH)_2$, heated to 225C in 1 hr, then 1½ hr 225C.

   [The $Sn(OH)_2$ was prepared by neutralization of $SnCl_2 \cdot 2H_2O$ with NaOH and filtering off the precipitate.]

SCI values of 9.8 ± 0.4 at 21C were obtained on the interesterified samples.

Lard and the interesterified lards were plasticized by stirring down 2 lb samples in an ice-jacketed metal container until they were viscous, then held 24 hr at 24C. Plastic smears of all samples were examined by X-ray diffraction when fresh, and after successive periods of storage at 21 and 32C. Initially, flat films were taken at about 25C with a Norelco X-ray diffraction film unit employing CuK_α radiation, nickel-filtered, with 5 cm sample-to-film distance. Lard samples were a mixture of β and β' phases. The fresh samples of interesterified lard were β' and those stored at 21C were β' for the duration of observations—viz., 6 mo. The 32C samples of interesterified lard shortening transformed largely to β in 1 month storage. See Table I. Estimations of phase proportions (with accuracy of ± 10%) were made by comparison with a standard set of diffraction patterns of 10% mechanical mixes of hardstock in oil. The hardstock was itself a mechanical mixture of β (completely hydrogenated soybean oil) and B′ (completely hydrogenated palm oil). Estimation was based on the relative strengths of the 4.1–4.2A β' line and the 4.6A β line (17).

More detailed study of lard and interesterified lard was carried out with a Norelco diffractometer unit on samples stored 6 weeks at 21C. Results are shown

TABLE I
Phase Behavior of Lard and Interesterified Lards

Sample	% β				
	Fresh	1-Month storage		3-Month storage 21C	6-Month storage 21C
		21C	32C		
Lard	70	60	80	80	60
Interesterified lard 1	0	0	55	0	0
Interesterified lard 2	0	0	85	0	0
Interesterified lard 3	0	0	65	0	0
Interesterified lard 4	0	0	55	0	0

in Figure 1. Lard showed a double set of long spacings, 44.1A (1st and 3rd orders of the β-2 phase) and 70.2A [2nd and 5th orders of the β'-3 phase, the 1st being weak or absent (16)]; the interesterified lards each showed a single set of long spacings, approximately 44.9A (1st and 3rd orders of the β'-2 phase).

Lard Shortening. Shortening was made by mixing 88% slightly hydrogenated lard (5 I.V. drop) and 12% lard hydrogenated to 8 I.V. The latter is largely 2-palmitoyldistearin and is strongly β-tending. The fresh shortening plasticized in a typical scraped-wall cooling device was of good texture and was substantially in the β phase. On standing at 27C, it developed unsightly large grains. It was found by warming the grainy sample under the microscope that these grains were lower melting than the main crystalline matrix. Some were isolated and X-rayed and proved to be of β'-3 phase. From the known composition of lard (11,12,13), the melting level of the grains (<38C) and their existence in the β'-3 phase, it is clear that they are comprised of OPS.

S_3-Free Preparations of Lard and Modified Lard. As it was established that lard shortening grains were due to the intermediate melting disaturated portion and not the higher melting S_3, it seemed desirable to examine lard and some modified lards from which the S_3 was substantially eliminated. A comparison was made of 4 samples from typical but not identical lards: A) normal lard, B) slightly hydrogenated lard, C) interesterified lard, and D) interesterified lard, slightly hydrogenated. The four samples were dissolved in Skelly B (1 g sample:10 cc solvent) and crystallized at 0°C to precipitate S_3, which was removed by filtration. After evaporation of the solvent, the S_3-free samples were crystallized at 21C and X-rayed at that temperature for solid phase identification. Data on these samples appear in Table II. Inconsistencies in S_3 yield arise from variations in the lard sources. The higher I.V. of the precipitates from hydrogenated samples are due to a content of "isooleic glycerides" produced by hydrogenation.

TABLE II

Phase Tendency of S_3-Free Portion

Sample	I.V.	S_3 Yield %	I.V. of isolated S_3 portion	SCI (21C) for S_3-free portion	Phase of S_3-free portion (21C)
Lard	67.7	5.7	10.0*	16.0	β'-3
Interesterified lard	64.5	9.5	7.7	7.5	β'-3
Hydrogenated lard	60.3	5.3	22.5	15.0	β'-3
Interesterified lard hydrogenated	62.2	8.6	13.5	5.0	β'-2

*Approximate.

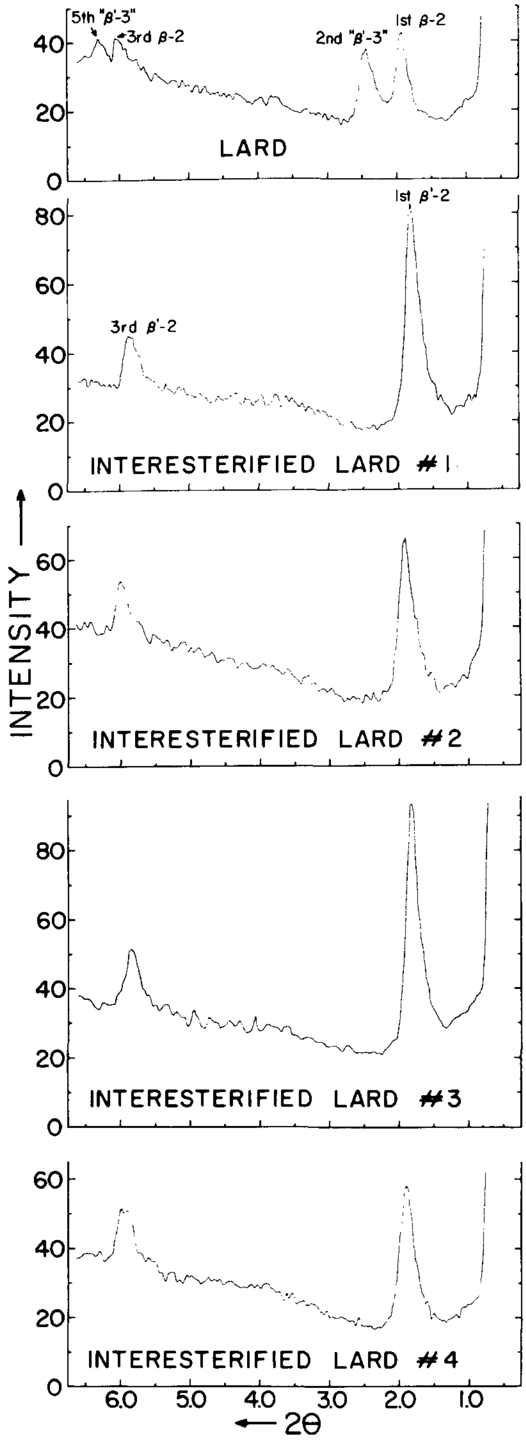

FIG. 1. Tracings of diffractometer patterns of lard and interesterified lard after 6 weeks 21C.

Discussion. When natural lard is plasticized, it typically forms a mixture of liquid and two solid phases, a higher melting S_3-rich β-2 phase and an intermediate-melting OPS-rich β'-3 phase. Since there is some tendency for S_3 and OPS to form solid solutions, some OPS will be in the S_3-rich phase. This is particularly true for lard shortenings made with added hardstock. In any case, as the temperature is raised above room temperature, more and more of the OPS will leave the solid state and be largely in the liquid state at 32C. Graininess does not develop at 32C; it is not associated with the S_3 portion of the shortening. Neither does graininess develop after cooling to 21C, probably because OPS crystallizes rapidly with many nuclei. At 27C, however, OPS is just a little below the upper limit of existence in an OPS-rich phase; this is just the situation for growth of large crystals on a few nuclei and for digestion of many small crystals into a few large ones. Grain development in lard shortenings is the formation of large aggregates of β'-3 crystals of OPS (not β crystals of POS as has been suggested). It is this β'-3-forming OPS that needs to be altered.

The dilatometric data mentioned earlier show that random interesterification halves the solid content of lard. This reduction is not due to reduction of disaturated (or trisaturated) glycerides, however, but rather due to increased solubility (lower melting level) of the disaturated mixture which replaces the original OPS. Typical lard with 2% S_3, 27% S_2U, 47% SU_2, 24% U_3 (11,12) on random interesterification has 4.5% S_3, 25% S_2U, 44% SU_2, 26.5% U_3

(molar basis). That the data in Table II do not correspond quite closely with such S_3 figures is largely a result of variation in natural lards. It is evident from Table II that, in those S_3-free test samples, slight hydrogenation itself or interesterification itself does not destroy the β'-3-tendency of lard, but combined hydrogenation and interesterification do. Hydrogenation presumably plays a role, though a small one, in reducing β'-3-tendency of modified lard, hence probably in reducing graininess potential.

The greater β'-2 tendency of the interesterified lards of Table I than that in Table II is believed to be due to the S_3 content in those of Table I, rather than to difference in crystallizing conditions.

Broadly speaking, the elimination of graininess in lard shortening results from a change in the disaturated glycerides which comprise ¼ of the lard, natural or interesterified. The β'-3-tending disaturated OPS is exchanged for a mixture of disaturated glycerides, lower melting, i.e. more soluble, and tending to crystallize in the more familiar β'-2 form which is the typical form of hydrogenated vegetable oil shortenings.

Directed interesterification of lard (3,4,5,8,9) results in production of S_3 or hardstock *in situ* and a consequent reduction in the "random mixture" of β'-2-tending disaturated glycerides. There results both an improvement in plastic range and reduced graininess potential.

REFERENCES

1. Bailey, A. E., "Industrial Oil and Fat Products" Interscience Publishers, Inc., New York (1945), p. 682.
2. Norris, F. A., and K. F. Mattil, JAOCS, *24*, 274 (1947).
3. Hawley, H. K., and G. W. Holman, *Ibid.*, *33*, 29 (1956).
4. Placek, C., and G. W. Holman, Ind. Eng. Chem., *49*, 162 (1957).
5. Eckey, E. W., U. S. Patent 2,442,532 (1948).
6. Vander Wal, R. J., and L. A. Van Akkeren, U. S. Patent 2,571,315 (1951).
7. Mattil, K. F., and F. A. Norris, U. S. Patent 2,625,478 (1953).
8. Holman, G. W., and L. H. Going, U. S. Patent 2,875,066 (1959).
9. Holman, G. W., and L. H. Going, U. S. Patent 2,875,067 (1959).
10. Hoerr, C. W., and D. F. Waugh, JAOCS, *32*, 37 (1955).
11. Quimby, O. T., R. L. Wille, and E. S. Lutton, *Ibid.*, *30*, 186 (1953).
12. Riemenschneider, R. W., F. E. Luddy, M. L. Schwain, and W. C. Ault, *Ibid.*, *23*, 276 (1946).
13. Hilditch, T. P., and W. J. Stainsby, Biochem., *25*, 1954 (1931).
14. Mattson, F. H., and E. S. Lutton, J. Biol. Chem., *233*, 868 (1958).
15. Fulton, N. D., E. S. Lutton, and R. L. Wille, JAOCS, *31*, 98 (1954).
16. Lutton, E. S., J. Am. Chem. Soc., *73*, 5595 (1951).
17. Lutton, E. S., JAOCS, *27*, 276 (1950).

[Received March 20, 1961]

Studies in Soap Crystallization Processes. Part III. Acid Soap Crystallization in the Segregation of Tall Oil Fatty Acids

EDWIN M. MEADE, The Meade Laboratory & Process Company, Unionville, Ontario, Canada

Abstract

Tall oil fatty acids have been fractionated into 80–90% oleic acid, and 60–80% linoleic acid fractions, by precipitation of the oleic acid as acid soap from polar solvents. Sodium and potassium acid soaps are equally effective, but ammonium acid soaps require lower operating temperatures. The choice of solvent is not critical as regards degree of separation, but technically attractive filtration rates have been obtained only with methanol and acetone. Acidulation gives colorless oleic acid of very low rosin acid and unsaponifiable content, but with 5–10% of conjugated linoleic acid.

TALL OIL is a mixture of approximately equal parts of rosin acids and fatty acids, the latter being themselves a 50:50 mixture of oleic and linoleic acids. The "oil" is in steady supply as a by-product of the kraft paper industry, and there is ample fractionating capacity for separation into rosin and fatty acids. If the fatty acids could be further separated into high linoleic and high oleic fractions, then there would be available new tonnage sources of high drying value acids for the alkyd industry, and of oleic acid, independent of its usual tallow source, and with a nonfluctuating supply background suitable for its proper consideration as a heavy organic chemical intermediate. Tall oil fatty acids are accordingly an attractive substrate for the investigation of oleic/linoleic separations.

Oleic and linoleic acids have been separated completely by elution chromatography, using hexane and silicic acid; by gas phase chromatography, using polyester stationary phases; and by countercurrent distribution, using hexane and acetonitrile in a Craig machine. A high degree of separation has been achieved by vacuum fractionation, using high reflux ratios in high efficiency columns, and lesser degrees by crystallization from solvents, by urea complexing, and by thermal diffusion. Preceding most of these methods, Freeman's (1) separation by countercurrent distribution between furfural and hexane was carried through to a large pilot plant scale by Gloyer in 1948 (2).

Difficulties in the above methods are various: chromatographic methods have yet to emerge from the laboratory scale; vacuum distillation demands an uneconomic reflux ratio and column design; cold crystallization is complicated by the very wet low temperature filter cakes, 20% solids appearing "dry" at −30C; and thermal diffusion calls for a heat flux of some 100,000 BTU per lb of product treated. The Gloyer method is straighforward, and is the only one so far to merit the term "process."

Crystallization of soaps has been of little value so far in this field; the lithium soap method for oleic acid is the only reasonably successful application, but work in progress on the crystallization of soaps of substituted fatty acids indicated that acid soaps were capable of giving useful degrees of separation in rather unexpected cases; promising results were obtained as soon as the method was applied to tall oil fatty acids. The acid soaps referred to are well authenticated substances in the saturated fatty acid field having the composition R–COOH.R–COO(Na, K, or NH_4); they are appreciably less soluble in alcohols than the corresponding neutral soaps, and have the added advantage of a good crystal habit. In the unsaturated fatty acids, however, only a single acid soap has been described, potassium hydrogen dioleate having been prepared by McBain and Stewart as far back as 1927 (3). Ralston (4), without source reference, gives solubilities of 4.3% (1.34M) for neutral potassium oleate, and 6.5% (1.30M) for the acid soap, fig-