which supports it at the closed end, the open end being plugged by the disc. The shaft is driven at about 250 r.p.m. The horizontal brushes, which move freely on the cross arms, press against the cylinder wall with only centrifugal force.

The fumed lint is put in the cylinder which, with the brushes in place, is slipped through the supporting opening and over the disc plug. The motor is started and run until lint dust ceases to fall. The outside of the cylinder is brushed or blown free of lint. A sheet of paper is placed below the cylinder, the latter is removed and dumped onto the paper, and the brushes freed of all foreign material, which is collected on the paper and all transferred to a container for weighing.

Machine brushing requires from 1 to 2 minutes against about 15 minutes for hand brushing.

---

# Thermal Properties of Fats and Oils

## IV. Some Observations on the Polymorphism and X-Ray Diffraction Characteristics of Tristearin and a Highly Hydrogenated Cottonseed Oil

**A. E. BAILEY, M. E. JEFFERSON, FLORENCE B. KREEGER, and S. T. BAUER**
**Southern Regional Research Laboratory,[1] New Orleans, Louisiana**

As a preliminary step in the calorimetric examination of certain highly saturated fats, it was considered necessary to investigate the polymorphic behavior of these materials under the conditions that obtain in the calorimeter. Saturated glycerides are known to be capable of existence in a multiplicity of polymorphic forms, and these presumably differ in their heat capacities and other thermal characteristics. For identification of the different polymorphic forms, melting point determinations were supplemented by x-ray diffraction measurements. The results point to the existence of hitherto unreported crystal structures in the lower-melting forms, and are otherwise of more than incidental interest; consequently, they are here made the subject of a separate communication. In the present literature there is virtually nothing dealing with the subject of triglyceride crystal structure beyond the publications of Malkin and coworkers (2,3,6,7).

### Preparation and Composition of the Samples

The samples examined consisted of cottonseed oil, hydrogenated in the laboratory almost to completeness with a nickel catalyst, and a highly purified sample of tristearin. The estimated fatty acid composition of the cottonseed oil, before hydrogenation, was recorded in a previous communication (8). According to the data of Hilditch and Maddison (5), cottonseed oil of this composition, when highly hydrogenated, should consist principally of β-palmitodistearin and tristearin, in the ratio of about 3 parts of the former to 1 of the latter. The hydrogenated oil had an iodine value of 0.85; hence it probably contained about 3 per cent of oleodisaturated glycerides. Its content of free fatty acids was 0.30 per cent.

Samples of tristearin were prepared by reacting stearoyl chloride in 10 per cent excess with glycerol and quinoline in chloroform solution, according to the method of Averill, Roche, and King (1), and repeatedly crystallizing the product from ether containing a small amount of alcohol. Stearic acid for preparation of the acid chloride was derived from a commercial product of about 90 per cent purity (Neofat No. 1-65) and was purified by treatment with sulfuric acid, followed by water washing to remove unsaturated products, fractional distillation in the form of the methyl ester, and multiple recrystallizations of the regenerated acid from acetone. This method is believed to yield saturated triglycerides of an exceptionally high degree of purity. For the production of a very pure material the step of sulfuric acid treatment of the fatty acids is considered important. By this means traces of unsaturated fatty acids in the product are sulfonated so that they may be subsequently removed by washing with water. Traces of unsaturated $C_{18}$ acids are difficult, if not impossible, to remove by either fractional crystallization or distillation.

TABLE I

Melting Points of Different Polymorphic Forms[1] of Tristearin, β-Palmitodistearin, and Highly Hydrogenated Cottonseed Oil (I.V. = 0.85)

| | M. P., °C., of form indicated | | | |
|---|---|---|---|---|
| | I | II | III | IV |
| Tristearin (Clarkson and Malkin) | 71.5 | 65.0 | 54.5 | ...... |
| Tristearin (present investigation, Sample 1) | 72.0 | 64.5 | 54.5 | ...... |
| Tristearin (present investigation, Sample 2) | 71.8 | 64.5 | 54.5 | ...... |
| β-Palmitodistearin (Malkin and Meara) | 68 | 64 | 56 | 50 |
| Hydrog. cottonseed oil (present investigation) | 62.3 | 61.0 | 58 5 | 50 5 |

[1] Following the scheme adopted by Daubert and Clarke (4) the different polymorphic forms are designated as I, II, etc., simply according to their melting points and without regard for the geometry of the crystal structure involved. Forms I, II, and III of tristearin correspond respectively to the β, α, and "vitreous" forms of Malkin and coworkers. The above tabulated forms of β-palmitodistearin are designated by Malkin and Meara as β, β′, α, and "vitreous" in decreasing order of melting point.

### Melting Points of the Samples

By application of the technique described by Clarkson and Malkin (3), wherein solidified samples in capillary tubes are plunged into constant-temperature water baths of different temperatures, it was possible to distinguish four different crystalline modifications in the hydrogenated oil. The melting points of the oils containing these modifications are listed in Table 1, together with the melting points reported by Clarkson and Malkin for tristearin, those found in the pres-

---

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

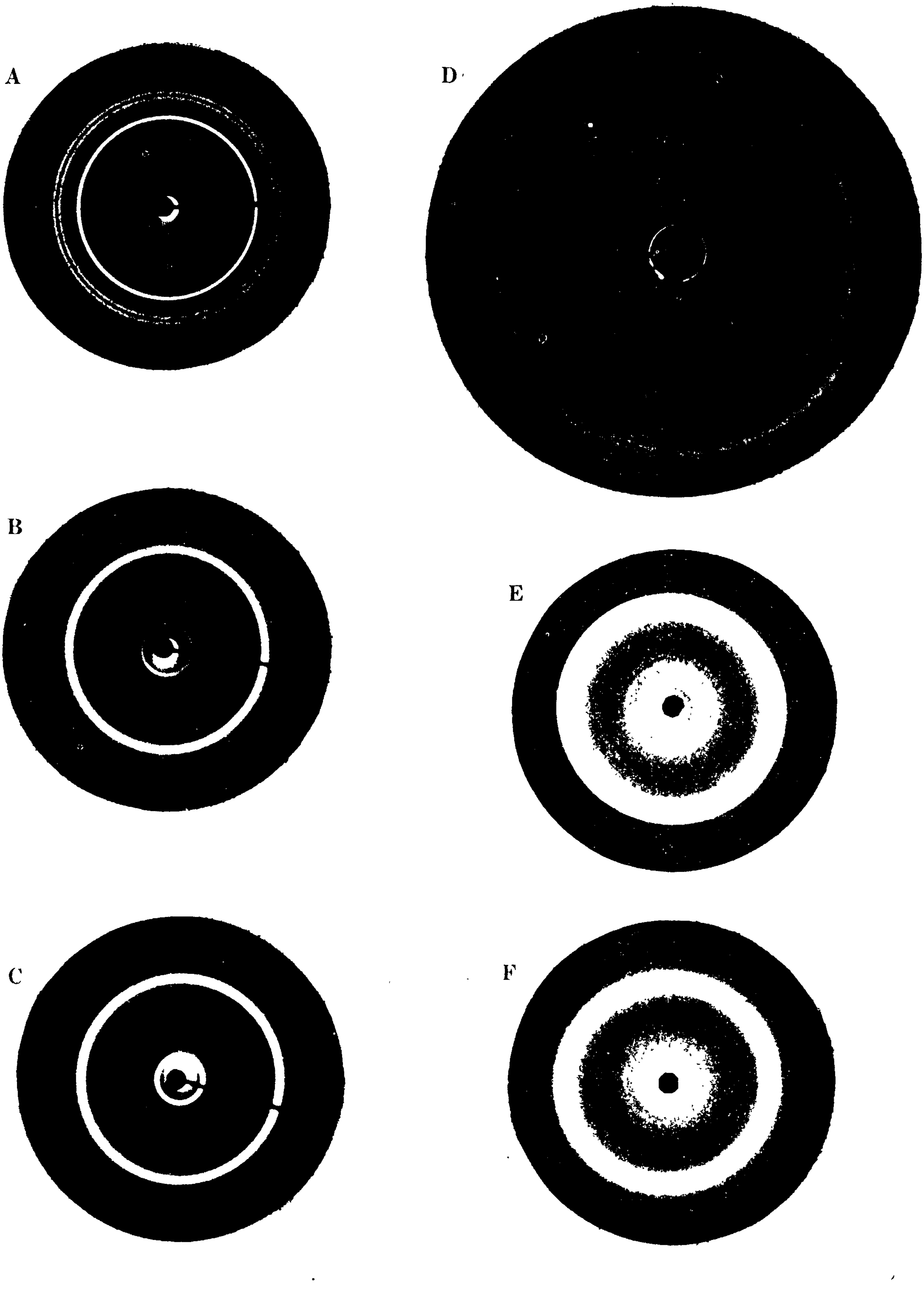

Fig. 1. X-ray diffraction photographs. Tristearin: (A) Form I; (B) Form II; (C) Form III; (D) Composite of the three forms. Hydrogenated cottonseed oil: (E) Form I; (F) Form IV. Film distance: for (D), 10 cm.; for all others, 5 cm.

ent investigation for tristearin, and those observed by Malkin and Meara (6) for *β*-palmitodistearin.

### X-Ray Examination of the Samples

X-RAY diffraction photographs were made by the pinhole method, with filtered CuK$\alpha$ radiation, on flat film, at film distances of 5 and 10 cm. As reference substances sodium chloride was employed for the short-spacing measurements, and muscovite for the measurements of long spacings.

Specimens of the fat were prepared for photographing in the form of flat sheets about 0.75 mm. thick, which were solidified in thin-walled copper cells provided with removable faces. In all cases the samples were first rapidly solidified in the lowest-melting form by immersing the cell containing the liquid fat in a cooling bath. When the material was desired in one of the higher-melting forms, this form was obtained by appropriate heat treatment of the rapidly solidified fat (cf. Clarkson and Malkin) before it was removed from the cell. Samples of the lowest-melting form were easily obtained by rapid solidification of the fats within a wide range of temperatures; tristearin solidified in Form III at any temperature up to about 50° C., and at low temperatures could be obtained in this form in sheets as thick as 4 mm. Similarly, the highest-melting form of the fats (I) could be produced with certainty by tempering the samples for a few minutes at a temperature approaching their final melting points. Considerable care was required, however, to obtain forms of intermediate melting point. Tristearin could be obtained in Form II only by immersing samples of Form III in a bath held between 55° and 56° C. and allowing melting and resolidification to take place. Samples melted and resolidified at 57° and higher crystallized in Form I, as did samples solidified in Form III and slowly heated to 55° or higher.

X-ray exposures were in all cases made upon freshly prepared specimens, and melting points were checked before and after exposure, as assurance against the possible occurrence of polymorphic transformations before completion of the x-ray examination.

In Figure 1 are reproduced photographic prints made from representative negatives. These serve to indicate the characteristic x-ray diffraction patterns of the different forms, as determined by the more prominent spacings. In this figure the narrow ring near the center of each photograph corresponds to the third order of the long spacing of the material, while the outside rings indicate the side spacings. It was not possible to obtain distinctive photographs of Forms II and III of the hydrogenated oil, owing probably to the relative instability of the lower melting forms. Identical patterns were produced by the two samples of tristearin. The principal crystal spacings calculated from measurements made on the original negatives are listed in Table 2. In this table are also inserted, for comparison, the spacings reported for tristearin by Clarkson and Malkin (3), and for *β*-palmitodistearin by Malkin and Meara (6).

### Rate of Transition Between the Different Polymorphic Forms

At room temperature tristearin appeared to be stable in any one of its three different polymorphic forms. However, in the hydrogenated cottonseed oil transformations occurred with comparative readiness. Exposure for 24 hours to room temperature was sufficient to increase the melting point of rapidly solidified samples from *ca.* 50° to *ca.* 60° C. and to cause a disappearance of the characteristic Form IV x-ray pattern. Samples of hydrogenated cottonseed oil quickly solidified and heated rapidly during the course of conventional capillary-tube melting-point determinations did not melt at 50.5°, but merely became slightly less opaque. Tristearin, similarly treated, melted completely at *ca.* 54.5°

TABLE 2

Summary of X-ray Data

| Observer | Long Spacing, Å | Short Spacings, Å |
|---|---|---|
| | Tristearin—Form I | |
| Clarkson & Malkin | 45 | 5.3, 4.6, 3.9, 3 7 |
| Present work | 45.3 | 5.39(w), 5.20(w), 4 79(vw) 4.55(s), 3.97(vw), 3.81(m) 3.65(m), 3.52(vw), 3.41(vw) 3.25(vw), 3.12(vw) 2.54(vw) |
| | Tristearin—Form II | |
| Clarkson & Malkin | 50.6 | 4.2(diffuse) |
| Present work | 46 4 | 4.19(s), 3.79(w) |
| | Tristearin—Form III | |
| Clarkson & Malkin | none | 4.2(very diffuse) |
| Present work | 50.7 | 4.1(s) |
| | Hydrog. C.S O —Form I | |
| Present work | 45.3 | 5.61(vw), 4.13(s), 3 73(m), 3.19(vw), 2.51(vw), 2.22(vw) |
| | Hydrog. C.S.O —Form IV | |
| Present work | 49.3 | 4 04(s) |
| | *β*-Palmitodistearin—Form I | |
| Malkin & Meara | 44 2 | 5.34, 4 61, 3.86, 3 68 |
| | *β*-Palmitodistearin—Form III | |
| Malkin & Meara | 50 5 | 4 19 |

*Note.* In reference to intensity of short spacing lines above: s=strong, m=medium, w=weak, vw=very weak.

### Discussion of the Results

THERE are marked discrepancies between the present x-ray data for tristearin and those reported previously by Clarkson and Malkin (3). Whereas Malkin and coworkers ascribed to Form III of tristearin and other saturated triglycerides the characteristics of a glass, the present evidence indicates a very definite crystal structure. Although a variety of conditions were employed in chilling the samples, in some instances liquid nitrogen being employed as a cooling bath, to accomplish the most rapid solidification possible, the quickly solidified specimens invariably yielded strong and sharp lines indicating a long spacing of *ca.* 51 Å and a single short spacing of 4.1 Å. Photographs made by the authors, with use of the "melted-layer" technique of Malkin and coworkers on samples chilled with solid carbon dioxide after melting, showed a single diffuse ring corresponding to a spacing of *ca.* 4.2 Å, and one or two orders ($n = 1, 3$) of a long spacing of *ca.* 50 Å. The sharp, coherent melting of the material appears to rule out the possibility of the existence of mixtures of Forms II and III. The present Form III pattern thus appears to correspond to the Form II or $\alpha$-pattern reported by Clarkson and Malkin.

The present pattern of Form II is entirely different from that recorded by Clarkson and Malkin. It differs markedly from Forms I and III in short spacings and relative intensity distribution (Table 2). The difference in long spacings between Forms I and II appears to be outside the experimental error. In the case of Form I, the present data agree almost exactly with those of Clarkson and Malkin.

The technique employed in the present investigation apparently permits the observation of reflections not recorded by previous workers. The data of Clarkson and Malkin were obtained by an oscillating-sample method with pressed or melted layers which enhanced reflections for the long spacings. Control of the cooling rate was depended upon to produce the particular crystal form desired in the melted layers. It is noteworthy that in a later investigation of monoglycerides Malkin and el Shurbagy (7) concluded that the Clarkson-Malkin technique produced layers unfavorably oriented for the observation of side spacings and in subsequent work abandoned it in favor of a method which employed specimens solidified in the form of thin rods.

In the light of the present results it appears probable that both the "vitreous" and "$a$"-patterns of Clarkson and Malkin corresponded actually to Form III, and that differences between the two arose simply from conditions that were in one case favorable and in the other case unfavorable for the crystal orientation requisite for the observation of well-defined spacings.

As would be expected in a mixed material, the crystal spacings for the more complex Form I of the hydrogenated cottonseed oil did not conform to those of corresponding forms of either of the major components of the oil, namely tristearin and $\beta$-palmitodistearin. However, the pattern of the simpler Form IV was very similar to those of the pure components, although not in exact agreement with either.

## Summary

1. Melting points and x-ray diffraction patterns have been determined for cottonseed oil hydrogenated to an iodine value of less than 1, and for a very pure sample of tristearin.

2. Contrary to the observations of previous investigators, the x-ray patterns indicate a well-defined crystal structure with a sharp long spacing and a single sharp short spacing in the lowest-melting form of tristearin. A new pattern, with two short spacings and a long spacing, was observed in tristearin of intermediate melting point.

3. Four polymorphic forms of the hydrogenated cottonseed oil were detected. The x-ray pattern of the lowest-melting form of the hydrogenated oil was similar to that of the correspopnding form of tristearin. The pattern of the highest-melting form of the hydrogenated oil differed from that of either tristearin or $\beta$-palmitodistearin, the major components of the oil. Distinctive patterns for the intermediate forms of the hydrogenated oil could not be obtained, presumably because of the instability of the lower melting forms at room temperature.

### LITERATURE CITED

1. Averill, H. P., Roche, J. N., and King, C. G., J. Am. Chem. Soc. *51*, 866-72 (1929).
2. Carter, M. G. R., and Malkin, T., J. Chem. Soc. *1939*, 577-81, 1518-21.
3. Clarkson, C. E., and Malkin, T., J Chem. Soc. *1934*, 666-71.
4. Daubert, B. F., and Clarke, T. H , J. Am. Chem. Soc. *66*, 690-91 (1944).
5. Hilditch, T. P., and Maddison, L., J. Soc. Chem. Ind. *59*, 162-68 (1940).
6. Malkin, T., and Meara, M. L., J. Chem. Soc. *1939*, 103-08, 1141-44.
7. Malkin, T., and el Shurbagy, M. R., J. Chem. Soc. *1936*, 1628-34.
8. Oliver, G. D., Singleton, W. S., Todd, S. S., and Bailey, A. E., Oil and Soap *21*, 297-300 (1944).

---

# Evaluation of Color Quality of Crude Soybean Oil — Some Data and Difficulties Incident to Developing a Suitable Test for Off Grades[1]

## An Elaboration of Some Aspects of the Bleach Test Committee Report and of Other Unpublished Recent Technical Committee Work

**EGBERT FREYER**
**Spencer Kellogg and Sons, Inc., Buffalo, New York**

IT SHOULD hardly be necessary to remind our oil chemists and technologists of the distressing consequences stemming from the occurrence of an early severe frost throughout most of the soybean-growing States in the Fall of 1942. Most of us lived with and struggled with those consequences during the succeeding twelve months, and many of us no doubt kept our fingers crossed during the frost-susceptible weeks in the Fall of 1943, while the new crop was maturing. In this there was added anxiety in the circumstance that heavy rains and floods in important sections of the most concentrated bean-growing areas had caused deferring of planting or replanting weeks beyond normal planting time.

This arresting of the maturation process in a very large proportion of the beans grown that year could hardly have occurred at a worse time from the standpoint of those in the industry — whether farmer, processor, or refiner. Consider these things: the crop had expanded to roughly double the previous record size, and the oil production was to go well over the billion-pound mark, exceeding cottonseed oil tonnage for the first time. We were at war and could ill afford to lose any degree of quality and especially any reduction in yield. Then, there emerged a realization in the trade of a need for revising trading rules for the settlement of crude soybean oil transactions, rules which

---

[1] Paper presented at the Spring meeting of the A. O. C. S. at New Orleans, May, 1944. Opinions expressed in this paper do not necessarily represent those of the Bleach Test Committee.