kinetics of a higher order. Under 1 atmosphere but at a lower temperature (125°C., Figure 2), the rate of hydrogenation is of a higher order throughout. See also the data of Feuge *et al.* (4) containing many examples of over-all zero order kinetics.

A very important point must be made in relation to all these cases. Because of the slow, constant rate of diffusion of the hydrogen, the hydrogen coverage of the catalyst is very small and constant. But the Langmuir equilibrium is maintained in the case of the unsaturated compounds. In the case of methyl oleate equation 4 assumes, under zero order conditions, the simple form:

$$\phi = \text{GMA} \qquad (7)$$

since H has now become very small and term RH is negligible. Variation of A in the course of the reaction does not influence the rate simply because ϕ is so much larger than the constant hydrogen coverage. The case is analogous to that of a bimolecular homogeneous reaction where concentration of one reactant is much higher than the concentration of the other one and when, by some device, the latter is kept constant.

If several unsaturated species are present in the system, a relation such as 7 would apply to their respective coverages, and the small, constant hydrogen coverage available would be competitively shared by all adsorbed reactants proportionally to both their respective coverages and reactivities. This principle was postulated in a somewhat different form by Bailey and Fisher (2). Its successful application in interpreting the kinetics of the more complex systems constitutes the subject of the next article of the present series.

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Reaction of Methyl Alpha-Eleostearate with Mercuric Acetate

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THE ADDITION of mercuric salts at the ethylenic bonds of olefins has been investigated extensively (3), but little has been published on the reaction of these salts with long-chain unsaturated fatty acids and their esters. Early work by Leys (6) showed that mercuric acetate in acetic acid solution adds to oleic acid producing a mercurated compound reported to contain acetoxymercuri- (CH_3CO_2Hg-) groups. In the preparation of pure oleic acid Bertram (2) made a mercurated oleic acid which he separated from the unreacted saturated acids before regenerating the oleic acid by heating the mercurated product with hydrochloric acid. Ralston *et al.* (10) reacted mercuric acetate with ethyl oleate in boiling methanol and obtained a stable compound, readily soluble in kerosene, to which he attributed the structure, ethyl 9-acetoxymercuri-, 10-methoxy stearate. Patents (11) were obtained on the use of this and similar oxymercurated fatty materials for use as weed killers. Connor and Wright (4) found that methoxymercuration could be used as an analytical method for determining *cis-trans* ratios in certain fatty materials because oleic esters (*cis* form) reacted appreciably faster than elaidic esters (*trans* form).

A number of references to the use of mercury compounds to accelerate iodine value determinations were cited by Benham and Klee (1), who used mercuric acetate as a "catalyst" to cause complete saturation of conjugated double bond systems such as those in dehydrated castor oil and tung oil. Later it was observed in this laboratory that the order of adding mercuric acetate and halogenating solution affects the results of iodine value determinations on tung oils (9). More recently Inouye *et al.* (5) listed the R_F value of the addition compound obtained by reacting methyl beta-eleostearate with mercuric acetate in methanol but noted that the mercury content was "considerably lower than theoretical." This result is in accord with our results obtained on mercuration of methyl alpha-eleostearate and focuses attention on the fact that the reaction of mercuric acetate with fatty acids containing conjugated unsaturation has not previously been reported.

Preliminary experiments indicated that mercuric acetate adds readily at room temperature to tung oil or to purified methyl alpha-eleostearate in either methanol or acetic acid solution. The refluxing of a solution of mercuric acetate and methyl alpha-eleostearate in acetic acid gave a product with unexpectedly low mercury content (13%) and a copious precipitate of metallic mercury. This, together with the high acetoxyl content (25%), indicated that extensive addition followed by decomposition had occurred. Although reaction occurred readily at room temperature, giving products of increased mercury content, reaction at still lower temperatures (0 to 20°C.) afforded products of the highest mercury content, up to 27%. It was noted that the presence of inert solvents such as petroleum ether or ethyl ether retarded addition while exposure to light accelerated it.

On the basis of these preliminary observations methyl alpha-eleostearate was reacted with mercuric

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acetate in acetic acid solution at 10°, and the resulting products were examined.

The products obtained even at the lower temperatures proved to be relatively unstable, gradually decomposing to produce mercury or mercurous acetate or both even at room temperature. For this reason no pure compounds were isolated. The products obtained appeared to be more complex than was anticipated, and their stability and solubility (in hydrocarbons) were distinctly different from those reported for the reaction product of mercuric acetate with methyl oleate (2). Because of the instability of the products obtained, further investigation was discontinued. However it is believed worthwhile to report some of the more significant results obtained.

Experimental

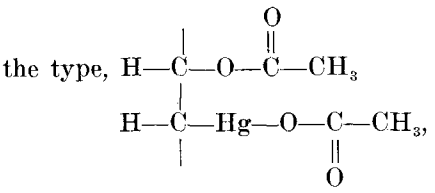
Preparation of Methyl Alpha-Eleostearate. Two kg. of domestic tung oil, screw-pressed from the seeds of *Aleurites fordii,* were added to 4 liters of boiling absolute methanol in which 6 g. of sodium had been dissolved. After refluxing for 1 hr., the solution was diluted with 4 liters of cold water and 1 liter of commercial hexane and acidified with an excess of hydrochloric acid. The mixture was transferred to a separatory funnel, and the upper layer was washed three times with 800-ml. portions of water. The solution of crude methyl esters thus obtained was dried over Na_2SO_4, filtered, and stripped with hydrogen under vacuum. The esters (1826 g.) were dissolved in 20 liters of acetone, cooled to —42°, held at that temperature for 1 hr. and filtered. The filtrate was cooled to —65°, held for 1 hr. and filtered again. The second precipitate (1,014 g.) was redissolved in 8 liters of acetone; the solution was cooled to —70° and held at that temperature for 1 hr. before being filtered. After stripping the precipitate with hydrogen under vacuum, 811 g. of a pale yellow oil were obtained. Ultraviolet absorption measurements on this product in cyclohexane by the method of O'Connor *et al.* (8) showed that no beta-eleostearate was present. The absorptivities were 140.2 and 160.0 at 269.0 and 271.5 mμ, respectively. Distillation under vacuum gave a colorless heart cut having absorptivities of 146.4 and 165.0 at the specified wavelengths, respectively. These absorptivities are somewhat higher than would be calculated for methyl alpha-eleostearate from the absorptivities reported for pure alpha-eleostearic acid even after correcting for the small amount (0.25%) of beta-eleostearate calculated by the binary method (8) to be present.

Preparation and Properties of Mercurated Methyl Alpha-Eleostearate. The mercury compounds which were studied most extensively were prepared by reacting methyl alpha-eleostearate (49 g.) with mercuric acetate (159 g.) dissolved in acetic acid (2.3 kg.) for several days at about 10°. After filtering off the precipitated mercurous acetate and diluting the filtrate with water, the crude mercurated products were removed by extraction with ether. Salts and acetic acid were washed out with water, and the ethereal solution was evaporated, leaving a pale yellow oil. Extraction of this oil five times with petroleum ether left a very viscous, nearly colorless material which hardened but did not crystallize on cooling. On standing at room temperature it developed a white cloudiness in a few hours. After one to two days' exposure at room temperature to daylight the mercurated product turned dark gray. These changes were due to decomposition of the original product with the formation of mercurous acetate and, later, metallic mercury.

One batch of material prepared from purified methyl alpha-eleostearate as described above analyzed as follows: Hg, 36.7% (by digestion with nitric acid followed by thiocyanate titration); C, 38.24%, H, 5.37%, O, 19.7% (by difference). The molecular weight, determined cryoscopically in dioxane, was 870. These data indicate that the mercurated material described is a mixture of two or more molecular species whose average composition (weight average) may be represented as $C_{27.9}H_{46.6}Hg_{1.6}O_{10.8}$.

Infrared spectra indicated that this product contained no epoxides and only traces of *trans* ethylenic linkages. Ultraviolet spectra indicated the presence of only trace amounts of conjugated unsaturation. The amount of unsaturation present could not be determined by the usual methods used in fat analysis. Catalytic hydrogenation with platinum or palladium-carbon was ineffective because of poisoning of the catalyst by mercury. Halogenation with Rosenmund-Kuhnhenn reagent (pyridine-sulfuric acid-bromine-acetic acid) and mercuric acetate (9) gave an apparent iodine value of 63. Corrections made on the assumption that each atom of mercury in the sample reacted with 2 atoms of bromine from the reagent reduced this to a calculated iodine value of 16.

Since mercuric acetate in acetic acid typically adds to ethylenic linkages to produce compounds of the type,



(3) the total acetoxyl content and that portion of the acetoxyl attached to mercury were determined separately. Total acetoxyl was determined as follows: a 100-mg. sample was saponified with 5 ml. of 0.6 N alcoholic KOH. The ethanol was evaporated, and the residue was acidified with 2 ml. of 2 N H_2SO_4. This product was mixed thoroughly with 3.3 g. of silicic acid and added to the top of a silicic acid column of the Marvel-Rands type (7), using the technique described by Roberts and Martin (12). The adsorbent used was Mallinckrodt silicic acid, 100-mesh, especially pre-prepared for chromatographic analysis.[2] Acids were eluted and determined according to the Marvel-Rands procedure. The acetic acid was collected in the 160-200 ml. effluent consistent with the peak effluent volume of 185 ml. for acetic acid reported by Marvel and Rands. The absence of other acids from the 160-200 ml. range was indicated by the fact that the weight of the total solids in the titrated solution was in excellent agreement with the weight of sodium acetate expected from the titration.

It was found that simple treatment of the mercurated product with dilute aqueous NaCl at room temperature sufficed to liberate acetate from acetoxymercuri-groups. Advantage was taken of this reaction to determine the acetoxymercuri-content of the mer-

[2] The use of trade names in this article is for identification and implies no endorsement of the manufacturer on his product.

curated product. This was done as follows. A 250-mg. sample dissolved in 5 ml. of methanol was added to 10 ml. of 0.5 N NaCl solution. After 1 hr. at room temperature the methanol was removed under vacuum; the aqueous portion was separated, evaporated to 0.5 ml., acidified with 1.5 ml. of 2 N H_2SO_4, and mixed with 3.3 g. of silicic acid. This was added to the top of a Marvel-Rands silicic acid column, and the acetic acid was determined in the manner described above.

In this way it was found that the mercurated methyl alpha-eleostearate contained 22.2% total acetoxyl and 10.3% acetoxyl attached to mercury. Acetoxyl attached to the carbon chain was therefore 11.9%. From these values it may be calculated that for each mercury atom in the mercurated methyl alpha-eleoestearate there were 2.06 acetoxyl groups, of which 0.96 were removed with aqueous NaCl, indicating attachment to mercury, and 1.10 not removed by this treatment, which may be presumed to be attached directly to the carbon chain. These data indicate that, when mercuric acetate in acetic acid is added to the olefinic linkages in methyl alpha-eleostearate, an equal number of acetoxymercuri- and acetoxy-groups are added to the carbon chain as previously reported for monolefinic materials. The indication that there are somewhat more acetoxyl groups attached to the carbon chain than to mercury atoms can be attributed to partial decomposition.

The analysis indicating 2.06 acetoxyl groups per mercury atom does not permit sufficient oxygen, after making due allowance for the oxygen originally present in the methyl ester to account for all of the oxygen found in the mercurated product (19.7%). Approximately one additional atom of oxygen per atom of mercury would be required to supply this amount of oxygen. This additional oxidation might well be expected from the fact that the formation of mercurous acetate was always observed whenever mercuration took place at or below room temperature. It is further indicated by the low iodine value of 16, corresponding to a little less than 0.3 double bonds per mercury atom or 0.4 double bonds per C_{18} chain and indicating additional disappearance of unsaturation.

The ordinary analytical methods used to determine hydroxyl and carbonyl content could not be applied to the mercurated product because of interference by the acetoxymercuri-groups. Infrared spectra did not show the presence of free hydroxyl, but a band observed at 6.2 microns might indicate the presence of hydrogen bonding between hydroxyl and adjacent carbonyl. The presence of these groups may therefore be suspected.

This increased oxygen content was also indicated by the results obtained on treatment of the mercurated methyl alpha-eleostearate with either alkali or acid. Saponifications of the mercurated methyl alpha-eleostearate with alcoholic KOH and recovery of the water-insoluble acids by acidification and extraction with ether gave a dark brown viscous oil. Analytical data obtained on this material included: C, 66.94%; H, 9.94%; O, 23.12% (by difference); OH, 6.34%; neutral equivalent, 325; iodine value [modified Rosenmund-Kuhnhenn (9)], 132; iodine value (hydrogenation), 210; absorptivity (maximum at 233 mμ), 63. These data may be interpreted to indicate that the saponified product consists chiefly of C_{18} monocarboxylic acids containing, on the average, somewhat more than 1 hydroxyl group per mole, 1 additional oxygen atom per mole, and about 1.6 double bonds. The absorption maximum at 233 mμ would indicate about 65% of the molecules contain dienoic conjugation. The infrared spectrum showed a strong maximum at 10.1 microns, indicating that the dienoic conjugation was essentially all *trans-trans*, but no maximum indicative of isolated *trans* unsaturation at about 10.3 microns was observed. The difference in iodine value found by halogenation and by hydrogenation might result from the reduction of oxidized products during hydrogenation.

Treatment of the mercurated methyl alpha-eleostearate with dilute HCl resulted in complete removal of the acetoxymercuri-group. The product obtained gave a yellow, viscous oil and was found to contain C, 64.1%; H, 9.46%; O, 26.3% (by difference). There proportions are in good agreement with those calculated for a product containing an average of 1.5 acetoxyl groups and 1.5 additional atoms of oxygen per fatty acid chain and is in good agreement with previous indications that the mercurated methyl alpha-eleostearate contained about 1.5 acetoxyl groups (attached to carbon) and about 1.5 extra atoms of oxygen per fatty acid chain.

The acetoxyl group attached to mercury could readily be titrated at room temperature with aqueous alkali, using phenolphthalein as an indicator. This procedure can, in fact, be used as a simple method of determining the mercury content. Thus simple titration with aqueous alkali required 0.00185 meq. of base per gram of sample. This corresponds to 37.1% mercury in the mercurated methyl alpha-eleostearate compared to 36.7% mercury found by thiocyanate titration.

Summary

Methyl alpha-eleostearate has been reacted with mercuric acetate in acetic acid solution. Carrying out the reaction below room temperature gave products having the highest mercury content. Even these products were relatively unstable, gradually decomposing to produce mercury or mercurous acetate or both at room temperature. A typical product obtained at 10°C. is a viscous, pale yellow oil, insoluble in petroleum ether but soluble in alcohol, ether, and chloroform. Each C_{18} chain contained, on the average, 1.4 acetoxymercuri-groups (CH_3COOHg—), 1.5 acetoxyl groups attached directly to the carbon chain and 0.4 double bonds. For each mole of mercuric acetate added to the methyl eleostearate approximately one mole of mercuric acetate was reduced to mercurous acetate and a double bond in the ester chain was oxidized to an oxygen-containing group of undetermined structure. Treatment of the acetoxymercuri-, acetoxy-ester with aqueous chlorides or bases yielded the corresponding chloromercuri- or hydroxymercuri-derivative. Refluxing the acetoxymercuri-, acetoxy-ester in alcoholic potassium hydroxide saponified all the ester linkages and removed the acetoxymercuri-groups with the formation of an equal number of double bonds, most of which are present in conjugated *trans-trans* systems. The Marvel-Rands chromatographic procedure was modified to permit determination of total acetoxyl groups and of acetoxyl groups attached to mercury atoms. Ace-

toxyl groups of the latter kind can also be determined by direct titration with standard base.

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Beef Tallow in Shortening Preparations[1]

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IT IS WELL KNOWN that much edible grade tallow is diverted to inedible channels owing to lack of market in the edible field. It is also known that present meat merchandising practices cause much edible tallow to be lost as kitchen waste. In 1953 the production of edible tallow and oleo stock under Federal inspection was about 114 and 115 million pounds, respectively. In the same year there were about 17.6 million cattle slaughtered under federal inspection. At a conservative estimate of about 35 lbs. of fat available per animal, the total production of edible beef fat should have been over 600 million pounds. There is little doubt that the production of edible beef fat would be substantially increased if more of a market in shortening or margarine products could be created.

Blends of animal and vegetable fats for use as shortening or cooking fats have been on the market for three decades or more, with the principal objective of meeting the demand for low-price shortenings. In more recent years however it has been recognized that animal and vegetable fats are equal nutritionally, that with modern processing technology they should be interchangeable in the manufacture of the highest quality shortenings, and that they should command a comparable price.

Tallow, in general, has a poor plastic range and is too firm at room temperatures to meet the accepted requirements of a shortening. Hence the advantage of its admixture with vegetable oils or soft fats in the manufacture of shortenings appears obvious. The ratio of tallow to vegetable oil can also be adjusted to permit adequate control of extent of hydrogenation, thus facilitating the manufacture of a more uniform product. The application of ester interchange (rearrangement) in the manufacture of shortenings of this type has not been thoroughly investigated although the value of this process in effecting desirable changes in the physical properties of lard appears to be well established (1, 2, 3).

In addition to being too hard, tallow as such generally has an undesirable odor and flavor, and, even after deodorization, tends to develop "reverted" flavors. The limited use of tallow in shortenings has been attributed by some to its tendency to revert.

This paper describes a number of experimental shortenings made with tallow and cottonseed oil in an attempt to obtain a good plastic range and other desirable properties by varying the proportion of tallow and cottonseed oil and introducing some variations in processing treatments.

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Experimental

Materials. The materials used in this study were a typical edible beef tallow rendered in the laboratory from fresh beef fat tissue; a commercial edible grade cottonseed oil that had been refined and bleached; and commercial lard flakes with an iodine value of 4.2.

Hydrogenation. Hydrogenation was carried out in a stainless steel apparatus at 150°C. with 0.1% nickel catalyst and at a gage pressure of 50 lbs.

Rearrangement. The products were rearranged by a catalytic treatment with sodium methylate similar to the method of Vander Wal (2, 4).

Penetration data. Micropenetration data were obtained at 5° intervals from 20 to 35°C. by the procedure of Feuge and Bailey (5). Penetrations exceeding 375 mm./10 at a given temperature were considered as being too soft for a reading.

Dilatometric data. The dilatometers used were the type described by Schroeder (6), and the estimated percentages of solids were calculated according to Fulton *et al.* (7).

Carbonyl Values. The degree of reversion of the shortenings was measured by determining the amount of volatile carbonyl compounds formed by aging the oil under specified conditions, according to the procedure of Chang and Kummerow (8).

Cake Volume Tests. Baking tests were conducted with the experimental shortenings, using a pound-cake formula (2); the cake volume was determined by the seed-displacement method and was expressed as cc./100 g.

Consistency, or C Number. The C numbers of the shortenings were determined according to the method of Harrington *et al.* (9).

Preparation of Shortenings. Ten experimental shortenings were prepared as described below. All