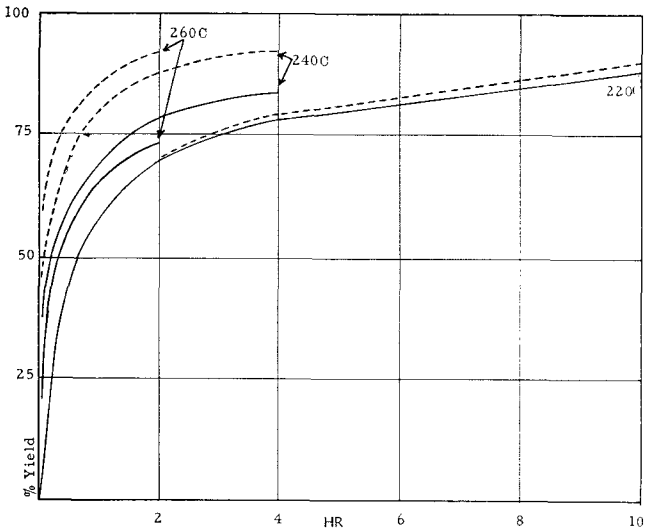

FIG. 1. Comparison of reaction rates at three temp. Mole ratio of stearic acid to methyl taurine is 1.5/1. Solid line indicates yield; broken line indicates methyl taurine used.

reaction becomes quite efficient.

The effect of temp is shown in Table III where three temp are compared at two mole ratios. It is difficult generally to consider temp independently of time and, in this case, separately from methyl taurine decomposition as well. The following conclusions can be drawn from the data in Table III: that higher temp speed up the reaction, as expected; that more methyl taurine is decomposed at higher temp; and (confirming), that higher mole ratios reduce the methyl taurine side reactions.

TABLE III

Effect of Temp at Mole Ratios of 1.5/1 and 2/1

Temp C	Time, hr	% Yield		% of used MeT not in acyl taurate	
		1.5/1	2/1	1.5/1	2/1
220	10	90	93.1	2	0
240	4	81	92.5	6	5
260	2	79	87.3	15	7.5

By analysis at intervals during the reaction period, data such as are plotted in Figure I are obtained. The rate of product formed (solid line) versus the methyl taurine used (broken line) is shown for three temp. Although the final amount of methyl taurine consumed is about the same in each of the three cases shown, the amount ending up as product varies. Products at the higher temp were increasingly darker. A plot of similar data for a mole ratio of 2/1 would show, as indicated in Table III, that the difference between methyl taurine consumed and product formed would be much less at the higher temp.

Considerable work has been done and is continuing in the application of these products in detergent bars. Characteristics such as hardness and other physical features of the bar, limesoap dispersing ability, and foaming may be varied depending on the fatty acid used. They are finding particular utility in combination bars. Amounts in the range of 15–20% have been found optimum for limesoap dispersing ability.

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[Received March 23, 1962]

• *Letters to the Editor*

Some Alleged Errors in the Azelaoglyceride Technique

IT HAS recently been alleged (1, 2) that acetone permanganate (Proc. I) (3) and acetic acid-acetone permanganate (Proc. II) (4a, 5) oxidation procedures for analysis of fats are liable to error due to production of incompletely oxidized products (I.O.P) stated to be ketohydroxy (acetoxy) derivatives which break down completely on saponification with alcoholic KOH to products giving water-soluble Mg. salts. The actual production of any ketoderivatives has not however been demonstrated by specific ketogroup reactions (quantitatively or qualitatively) in any instance. Further, some earlier results (6, 7) showed that no such compounds are produced in detectable amounts during either of these oxidation procedures. These results are as follows: (a) When known mixtures of methyl oleate and methyl stearate were oxidized by either of these procedures and the acidic products of oxidation were separated by washing in ether solution with aqueous carbonate, the same yields of neutral material (after correcting for residual iodine value) agreeing well with the known proportions of methyl stearate were obtained (6). The process used for isolation of neutral material cannot bring about the hydrolysis of I.O.P. and the results hence prove absence of production of I.O.P. in both procedures. (b) It was found that the higher saturated acid content of fats could be determined [in addition to the usual procedure of oxidizing the fat by Proc. I or II and submitting the oxidation products to Bertram separation after hydrolysis with alcoholic KOH (4a)], by oxidizing the mixed fatty acids by Proc. II and submitting the products of oxidation directly to Bertram separation (7). The new procedure avoids treatment of the oxidation products with alcoholic KOH and cannot produce breakdown of I.O.P. if any is formed. The yields of saturated acids for a number of representative fats by this new procedure were the same as by the usual procedure (7) confirming absence of production of I.O.P. in both oxidation procedures.

Eshelman & Hammond (1) based their suggestion on an increase in ester groups in the oxidation products from methyl undecylenate, oleate and linoleate in Proc. II. This increase was probably due to some esterification of free carboxyl by ethanol generated from the di-ethyl ether during prolonged continuous extraction from an aqueous medium containing excess of strong mineral acid since the latter is known to produce splitting of ethers to alcohols (8). The larger increase for methyl linoleate was due to leaving out of consideration malonic acid from its oxidation products which will also get extracted and partially esterified. The lower than theoretical values in Proc. I was due to complete disruption of some of the oxidation products in this procedure as reported elsewhere (7).

Laxminarayana & Rebello (2) based their suggestion on the proportions of neutral derivatives (N.D.) obtained on passing di- and mono-saturated glycer-

ides, after oxidation by Proc. I or Proc. II, through basic alumina columns, their main data being isolation of 15% N.D. (of which 3% was original tristearin) from distearo-olein oxidized by Proc. II. If the non-tristearin material in N.D. were ketoacetoxy derivatives then the N.D. should show sap. val. 317 against 227 recorded and the oxidized concentrate should give, on Mg. salt separation (4a, 5), 93% insoluble azelaoglycerides (I.A.G.) of sap. val. 290 against 89.3% I.A.G. of sap. val. 279 recorded and 89.9% I.A.G. of sap. val. 281 required in the absence of production of I.O.P. Further, the acidic material removed by Bertram separation from the hydrolysis products of the N.D. showed sap. val. (calc.) 381 against 355 for nonoic acid 487 for an equimolecular mixture of nonoic and azelaic acids producible from I.O.P. by saponification with alcoholic KOH. The non-tristearin part of the N.D. from oxidized di- and mono-saturated glycerides show sap. vals. (calc.) of 230 and 234 against 221 and 264 required for distearo-nonoin and stearo-di-nonoin resly. and the N.D. is thus mainly composed of the above two triglycerides obviously formed by ester interchange on the basic alumina column.

It has further been suggested (2) that errors due to hydrolysis of azelaoglycerides occur during oxidation by Proc. II and also during Mg salt separation of the azelaoglycerides (4a, 5). Since theoretical yield of I.A.G. of theoretical sap. val. was obtained from disaturated glycerides (4a, 2) it is illogical to suggest any hydrolysis during oxidation by Proc. II. Proof that no hydrolysis of azelaoglycerides (and also formation of I.O.P.) need take place during normal analysis is provided by the example of the apricot kernel oil (4b) which showed only 0.2% monoazelains and fraction of peanut oil (most soluble fraction, low temp crystallization) which showed no I.A.G. at all (9) in spite of their containing 24 and 33% monosaturated glycerides resly. The Mg. salts of di-azelains are, however, much less stable towards alkali than those of the monoazelains and tend to undergo hydrolysis if during the Mg. salt separation there is too much excess of alkali, or rise in temp above 30C or again if the precipitated salts are not filtered off within a maximum of 20–30 min, and any actual hydrolysis produced will be due only to non-observance of the conditions specified for the separation.

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[Received March 12, 1962]

Analysis of Lipids and Oxidation Products by Partition Chromatography: Dimeric and Polymeric Products

UNDER the above title a chromatographic method was published (1) recently and was said to be useful for determining the extent to which an oil is oxidized before deodorization, and for following the various phases of oxidation, polymerization, and processing. Column chromatographic separation of the fatty acids obtained by saponification of deodorized oils, yielded three fractions, termed, respectively, unoxidized acids, "dimeric" or polymeric fatty acids, and highly polar compounds. The "dimeric" fatty acids fraction amounted to approximately 1 to 2% of the total fatty acids of the oils investigated.

We have applied the above method to soybean oil in its various stages of processing. According to graph No. 4 of FRANKEL et al. (1) deodorized soybean oil contains as much as 1.5% "dimers" at a peroxide value of zero. Therefore, we extracted soybean oil from selected whole beans in the laboratory. This crude oil was investigated by the chromatographic method in question and found to contain 1.7 to 2.2% of the "dimers." The same oil refined and deodorized had 1.3 to 2.1%. The values found during refining of a factory sample were: degummed oil 1.3 to 2.1%, neutralized oil 1.0 to 1.2%, bleached oil 0.7%, deodorized oil 0.8 to 1.8%.

From the above we may infer that the "dimers" are either already present in the non-extracted seed or are formed during saponification of the oil in the course of the analysis, although precautions were taken to avoid oxidation. Refining and deodorization of oils cannot explain the total amount of "dimers" as found by FRANKEL et al. Our data even suggest a decrease of "dimers" during refining.

This raises the question of the real nature of the "dimeric" acid fraction. It is generally known that there can exist two different kinds of polymers in fatty oils: thermal polymers, formed during thermal treatment in the absence of oxygen, and oxidative polymers, formed in oxidized oils. Determination of thermal polymers in normally refined, deodorized oils using a paper chromatographic method (2) showed that they do not normally contain more than 0.1% thermal polymers (3). The amount of oxidative polymers in normally refined, deodorized oils is not yet known with certainty. We intend to investigate this and to ascertain the structure of the constituents of the "dimeric" fraction.

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[Received: June 26, 1962]