also shown in Table II. In a typical experiment, 692 g of Fraction 2 gave 448 g of pure MAZ, representing a recovery of 82.5%. The overall yield of MAZ depends on the ozonolysis procedure and subsequent treatment before distillation. In the laboratory we have realized yields of 88% C_9 aldehyde ester and acetal ester, corresponding to peak IV in Figure 2 and Table II, based on C_9 double bonds and assuming the absence of oleate positional isomers. Thus a 73% overall yield of pure MAZ from commercial methyl oleate is possible.

Commercial methyl oleate was ozonized, and the products were reductively decomposed in the pilot plant and will be reported elsewhere. The product was distilled through a Vigreux column to give Fraction 1, boiling range 28–94C at 3 mm, and Fraction 2, boiling range 65–118C at 0.5 mm. Fraction 2 (692 g, 79% MAZ) was added slowly with vigorous stirring to a saturated solution of sodium bisulfite: 576 g sodium metabisulfite dissolved in 1,000 ml of water to which 840 ml of absolute methanol was added (4). After stirring 3 hr at room temp, the addition compound was removed by filtration. The adduct was slurried with ether three times and filtered. MAZ was regenerated by shaking the bisulfite adduct with 1 liter each of ether and 10% NaOH solution. The ether removed the MAZ from the aqueous layer, displacing the equilibrium in the direction of the free aldehyde and minimizing possible saponification of the ester and condensation of the aldehyde functions. The basic solution was extracted several times to remove all the aldehyde ester. The combined ether extracts were washed with water until neutral and dried over anhydrous calcium sulfate. The solvent was then stripped off and the residue distilled through a 15-cm helix-packed column. The yield of MAZ was 448 g, 82.5% recovery, 99.8% purity by GLC analysis.

TABLE II
GLC Analyses of Methyl Azelaaldehydate Fractions

Peak	Compound	Product analyzed, wt %		
		Fraction 2	Regenerated MAZ	Distilled MAZ
I	Pelargonaldehyde	1.4	2.3	0.0
II, III	Unknowns	2.4	0.2	0.0
IV	MAZ	79.0[a]	90.3	99.8
V	Dimethyl azelate, C-10 aldehyde ester	4.4	1.5	0.2
VI	C-11 aldehyde ester	4.7	5.6	0.0
VII	Methyl myristate	6.9	0.0	0.0
VIII	C-13 aldehyde ester	0.3	0.0	0.0
IX	Methyl palmitate	1.0	0.0	0.0

[a] This figure includes MAZ dimethyl acetal.

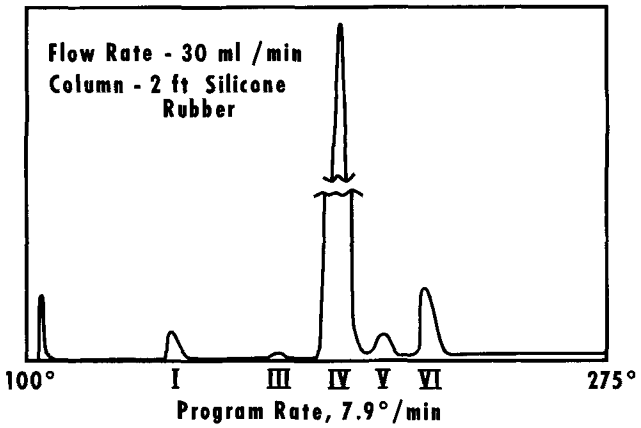

FIG. 2. GLC of regenerated methyl azelaaldehydate.

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[Received March 25, 1963—Accepted July 15, 1963]

Chemical Reactions Involved in the Catalytic Hydrogenation of Oils. I. Characteristics of the Volatile By-Products

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Abstract

The gas chromatogram of the isolated volatile by-products I, which were produced during catalytic hydrogenation of soybean oil is quite different from that of the isolated volatile by-products II, which were produced by a duplicate sample of the same oil subjected to the same conditions of hydrogenation with no nickel catalyst. Many of the peaks on these two gas chromatograms had different retention times. Furthermore, catalytic hydrogenation of I did not alter its gas chromatogram to equal that of II. The side reactions which may take place when an oil is treated under hydrogenation conditions are, therefore, affected by the presence of nickel catalyst.

The carbonyl compounds in the volatile by-products which were formed during catalytic hydrogenation were converted into their 2,4-dinitrophenylhydrazones and then fractionated into dicarbonyls, saturated aldehydes, methyl ketones, 2-enals, and 2,4-dienals. Upon regeneration, the dicarbonyls, 2-enals, and 2,4-dienals did not yield the characteristic hydrogenation flavor, while the saturated aldehydes and methyl ketones did. The characteristic hydrogenation flavor would seem to be at least partially contributed by saturated aldehydes and methyl ketones.

Introduction

CATALYTIC HYDROGENATION is considered by many oil chemists as the most outstanding discovery in oil and fat processing during the past sixty years (1). It is estimated that 3 billion lb of hydrogenated fats are consumed in foods each year in the U.S. The main chemical reactions involved in hydrogenation, such as

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[1] Supported by a PHS research grant HE-06411 from the National Heart Institute, Public Health Service.

[2] Presented in part at the AOCS meeting, Toronto, 1962.

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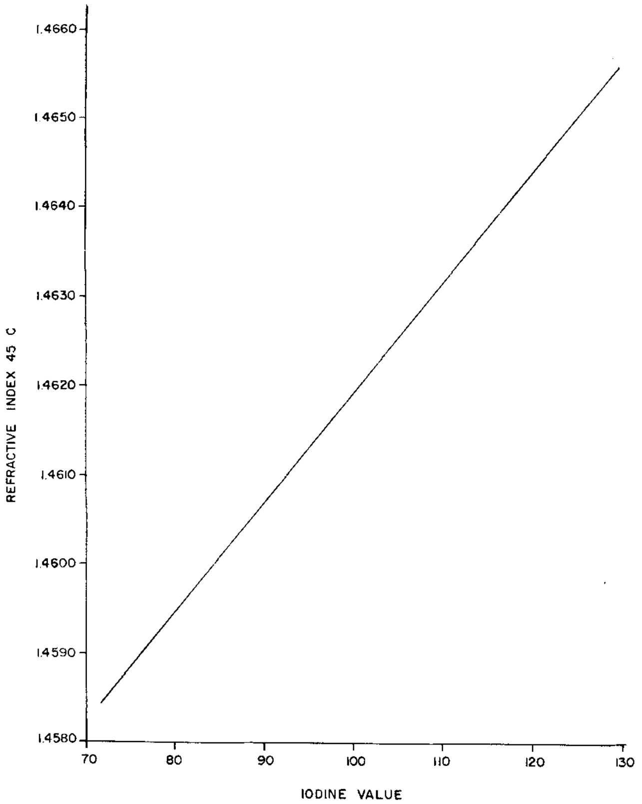

FIG. 1. Standard curve showing the relationship between Refractive Index and Iodine Value of Soybean Oil.

saturation and isomerization of double bonds and selectivity of catalyst, have been extensively studied. Side reactions accompanying the catalytic hydrogenation with the possible formation of cyclic, polymeric, hydroxy, keto, and other oxygenated compounds have, however, been almost completely neglected by oil chemists. There are at least two indications that such compounds of unknown structure may exist in the hydrogenated fats. One, the refined and bleached oils which are used for catalytic hydrogenation in the normal operations of oil refineries in the U.S. usually have a measurable peroxide number. In the case of soybean oil, the peroxide number is generally 5–10 meq/kg after open kettle bleaching, and 0.5–6 meq/kg when the oil is vacuum bleached. After hydrogenation, the peroxide number becomes nil. Whether the peroxide oxygen is decomposed, or is reduced, part of it may remain in the hydrogenated fat in unknown compounds. Two, a distinctive, characteristic, rather unpleasant odor and flavor, known as hydrogenation flavor, is developed during the catalytic hydrogenation. The chemical nature of this flavor has not yet been completely characterized. A literature search yielded only two references. Mielck speculated in 1930 that ethers and acetyl carbinols are responsible for the hydrogenation flavor (2). Tyutyurnikov and Grechishnikova reported that hydrocarbons, aldehydes, alcohols, and saturated, unsaturated, and hydroxy acids are present in the volatile by-products collected during the hydrogenation of sunflower seed oil (3). They did not report which of these compounds have the characteristic hydrogenation flavor.

This unidentified hydrogenation flavor is important in at least two respects. Commercially, hydrogenation flavor is objectionable. Nutritionally, the role of hydrogenation flavor is entirely unknown. Since the hydrogenation flavor can be at least partially removed by steam distillation under high vacuum, it may be assumed that it is caused by compounds which are formed by splitting off a relatively small fragment from triglyceride molecules. Such compounds of relatively low mol wt may be removed by deodorization during the processing. However, the portion of the triglyceride molecule after the splitting of the hydrogenation flavor may remain in the hydrogenated fat. The amount of such compounds may be small, nevertheless, they are present in major items of our daily diet. This paper is a preliminary study of the chemical characteristics of the volatile compounds which are by-products of catalytic hydrogenation.

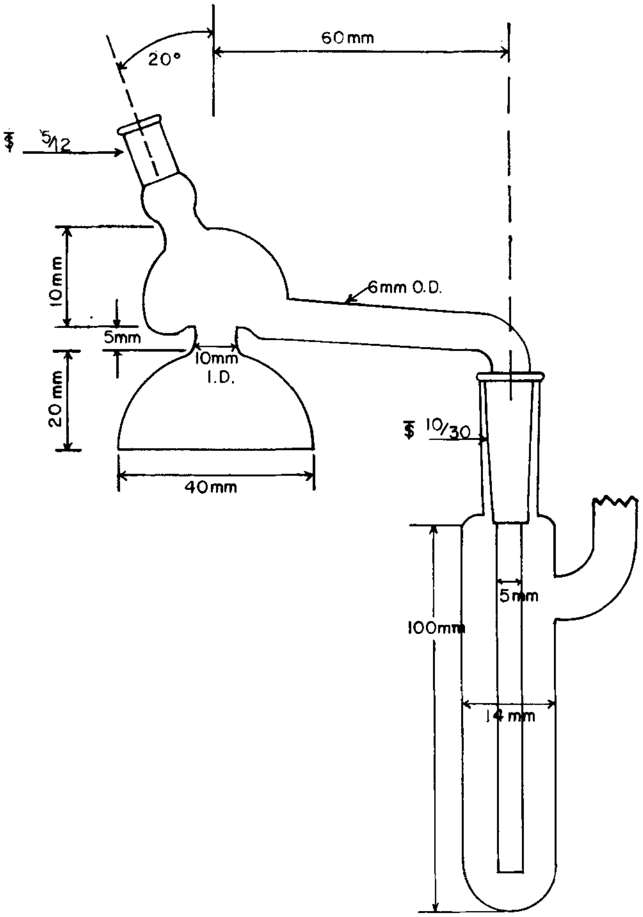

FIG. 2. Apparatus for vacuum distillation of concentrated ethyl ether solution of volatile by-products.

Experimental

Catalytic Hydrogenation. Soybean oil was hydrogenated in a Parr Pressure Reaction Apparatus of 2000 ml capacity, fitted with heating jacket and cooling coil (Series 4500, Parr Instrument Company, Moline, Illinois). The procedure used is typical of that practiced by the U.S. edible fats industry. Refined and bleached soybean oils, 1000 g per batch, were hydrogenated at 180C under 30 psig of hydrogen, with 0.125% nickel as catalyst. The reactants were stirred at 800 rpm. The catalyst was Rufert nickel flakes (Harshaw Chemical Co., Cleveland, Ohio), which contain 25% nickel in hydrogenated cottonseed oil. Progress of the hydrogenation was indicated by a flowmeter (Rotameter, Kontes Glass Co., Vineland, N. J.) connected between the hydrogen cylinder and the reactor. The decrease of iodine value (I.V.) of the oil was periodically measured by the refractive index of 5 ml samples withdrawn from the reactor. A standard curve, Figure 1, indicating the relationship of the R.I.

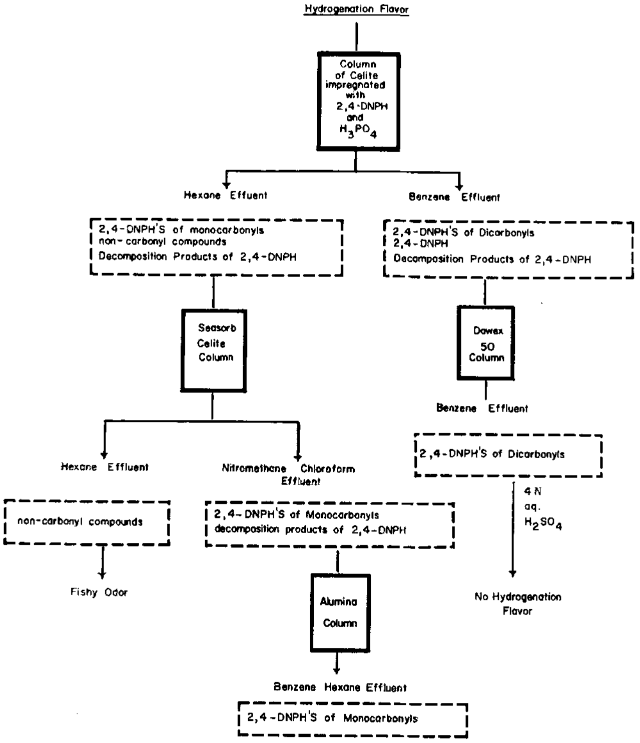

FIG. 3. Preparation of 2,4-dinitrophenylhydrazones of monocarbonyl compounds in the volatile by-products of hydrogenation.

and the I.V. was previously determined. The hydrogenated oil was freed from catalyst by stirring with 0.5% Tonsil Activated Clay, (L. A. Saloman & Brother, N. Y.) and then filtering through filter paper coated with Celite Filter Aid.

Isolation of the Volatile By-Products of Hydrogenation. Refined and bleached soybean oil (Wijs I.V. 134) was autoxidized at 60C to a peroxide number of 11.2 meq/kg and then hydrogenated to I.V. 71. The hydrogenated oil, 9.5 gal, was vacuum steam distilled partly by continuous process at 120C, as described by Chang (4), and partly by batch process at 160C for 1 hr under 0.01–0.03 mm Hg pressure, with 5% water. The deodorized oils from both continuous and batch processes had only a slight hydrogenation flavor. The steam distillates, collected in three traps connected in series and cooled with solid carbon dioxide, were combined and extracted with ethyl ether. The ethyl ether extract was concentrated with an Oldershaw column according to the method of Chang (4). In order to remove any oil which might be present in the concentrated ether solution from entrainment during the vacuum steam distillation, the solution was distilled as a thin film with a minimum of refluxing at 150C for 30 min under 0.01 mm Hg pressure in an apparatus. as shown in Figure 2. An ether solution I, 5 ml, of the volatile by-products formed during the hydrogenation of 9.5 gal of oil, was thus obtained.

Isolation of the Volatile By-Products of the Control. A sample of the same oil used in the hydrogenation process was heated, stirred, and treated in the Parr Pressure Reactor in exactly the same manner as the catalytic hydrogenation, except that no nickel was added. The treated oil was also stirred with Tonsil Activated Clay and filtered with Celite Filter Aid. The volatile by-products were isolated by the same procedure used for the hydrogenated oil. An ether solution II, 5 ml, of the volatile by-products formed by subjecting 5 gal of oil to the heating and processing conditions of hydrogenation, without actual hydrogenation, was thus obtained.

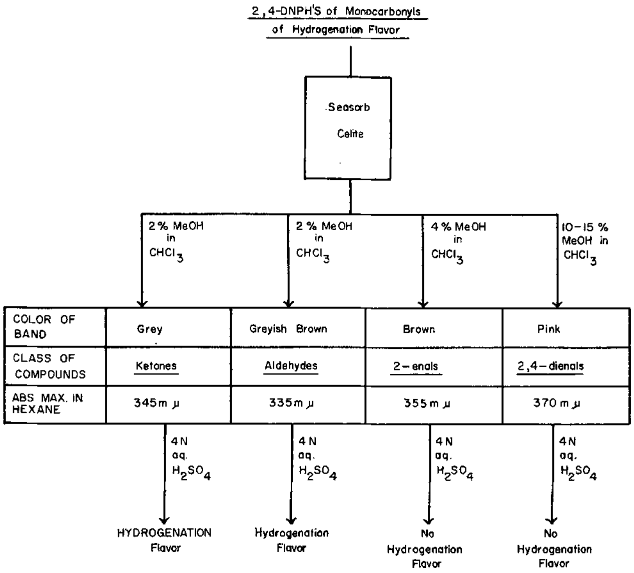

FIG. 4. Fractionation and regeneration of 2,4-dinitrophenylhydrazones of monocarbonyl compounds in volatile by-products of hydrogenation.

Catalytic Hydrogenation of the Isolated Volatile By-Products. An aliquot, 1 ml, of II was hydrogenated by stirring with 0.1 g palladium catalyst (Engelhard Industries, Inc., Newark, N. J., 5% of palladium oxide on activated carbon) 45 min under 6 psig hydrogen at room temp. This process had been previously checked with a known conjugated unsaturated aldehyde, crotonaldehyde. The progress of the hydrogenation of the crotonaldehyde was followed by the disappearance of the absorption maximum at 218 mμ using absolute ethanol as solvent.

Gas Chromatography. The ethyl ether solutions of I, II, and the hydrogenated II, were gas chromatographed at 130 and 160C with a Beckman GC-2A gas chromatograph with thermal conductivity detector. A 6 ft stainless steel column, ¼ in. inside diam, packed with 15% Ucon Polar on 80/100 mesh Chromosorb, was used at a helium flow rate of 46 ml per min.

Preparation and Fractionation of the 2,4-dinitrophenylhydrazones of the Carbonyl compounds in the Volatile By-Products of Hydrogenation. The procedure of Mookherjee and Chang (5) was used. A 1 ml aliquot of the ethyl ether solution of the volatile by-products of hydrogenation was mixed with 100 ml of carbonyl-free hexane. This solution was passed through a column packed with celite, which was homogeneously impregnated with 2,4-dinitrophenylhydrazine and phosphoric acid in order to convert all the carbonyl compounds into their 2,4-dinitrophenylhydrazones (Fig. 3). The hexane effluent was further purified by chromatography with a Seasorb Celite column and then with an Alumina column. This yielded the pure 2,4-dinitrophenylhydrazones of the monocarbonyl compounds. The benzene effluent was further purified with a Dowex 50 ion exchange resin column to yield the 2,4-dinitrophenylhydrazones of the dicarbonyl compounds.

The 2,4-dinitrophenylhydrazones of the monocarbonyl compounds were fractionated by chromatography, Figure 4, into the 2,4-dinitrophenylhydrazones of four classes of carbonyl compounds, viz., methyl ketones, saturated aldehydes, 2-enals, and 2,4-dienals.

Regeneration of the Carbonyl Compounds from

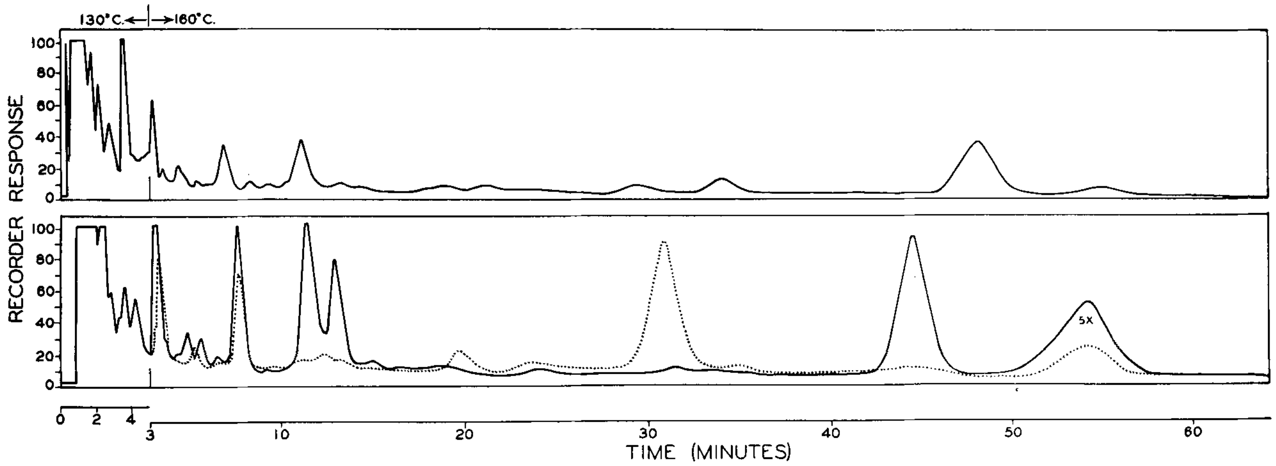

FIG. 5. Gas chromatograms of volatile by-products. Upper curve, I isolated from hydrogenated soybean oil; lower solid curve, II isolated from soybean oil treated under conditions of hydrogeneration with no catalyst; lower dotted curve, II after catalytic hydrogenation.

Their 2,4-Dinitrophenylhydrazones. The 2,4-dinitrophenylhydrazines of the dicarbonyls, methyl ketones, saturated aldehydes, 2-enals, and 2,4-dienals were heated, respectively, for 30 min with 5 ml 4*N* aqueous solution of sulfuric acid in a 10 ml pear-shaped flask, which was heated in a glycerol bath at 110C. The flask was connected to a trap by means of a tube extended to the trap's bottom. This trap, which contained 1 ml hexane, was cooled with ice water. The distillate from the flask containing the regenerated carbonyl compounds was condensed in the trap and extracted by the hexane.

Results and Discussion

This investigation indicated that the side reactions which may take place when an oil is treated under the conditions of hydrogenation are affected by the presence of nickel catalyst. The gas chromatogram of the volatile by-products I, which were produced by soybean oil during catalytic hydrogenation at 180C with 0.125% nickel catalyst, is quite different from the gas chromatogram of the volatile by-products II, which were produced by a duplicate sample of the same oil subjected to conditions identical to those of hydrogenation except that no nickel catalyst was present (Fig. 5).

Retention times of most of the peaks on the chromatogram of I were different from most of the peaks of II. This indicated that they are composed of many different chemical compounds. To ascertain whether or not the difference is due to the hydrogenation of II after they were produced by the conditions used in hydrogenation, II was hydrogenated with a palladium catalyst. The gas chromatogram of the hydrogenated II was again different from that of I (Fig. 5). This seems to prove that the side reactions which may take place when soybean oil is treated under the conditions of hydrogenation are changed by the presence of nickel catalyst. One explanation is that in the presence of nickel catalyst, a portion of the hydroperoxide groups in the oil may be reacted to form more stable oxygenated functional groups, such as hydroxy or keto groups, before they are decomposed by the thermal treatment under the conditions of hydrogenation. On the other hand, in the absence of nickel catalyst, all peroxide groups are decomposed by heat. Furthermore, if dihydroperoxide molecules are present in the oil, the reation of one of them into other functional groups will certainly affect their pattern of decomposition.

Organoleptically, the isolated volatile by-products I, had a distinctive, characteristic, unpleasant odor which is usually associated with the hydrogenation process. The isolated volatile by-products II, on the other hand, had a fishy, beany, and rancid odor. When II was catalytically hydrogenated, it developed an odor reminiscent of but not identical with that of I.

The carbonyl compounds were shown to play an important role in the characteristic hydrogenation flavor. After the hexane solution of the isolated volatile by-products of hydrogenation was passed through a celite column impregnated with 2,4-dinitrophenylhydrazine and phosphoric acid (Fig. 3) and after the 2,4-dinitrophenylhydrazones thus formed were removed with a Seasorb Celite column, the hexane solution had no hydrogenation flavor but a weak fishy odor (6). This is not positive proof that all compounds with characteristic hydrogenation flavor are carbonyl compounds. It is quite possible that trace amounts of chemical compounds may be absorbed or may even react chemically on these two chromatograph columns. When the carbonyl compounds were regenerated from each of the five classes of their 2,4-dinitrophenylhydrazones by refluxing with 4*N* aqueous sulfuric acid, only the saturated aldehydes and methyl ketones had odors reminiscent of the characteristic hydrogenation odor (Figs. 3, 4). Again, this is not positive proof that the characteristic hydrogenation flavor is not contributed by 2-enals, 2,4-dienals or dicarbonyls. It is known that the regeneration of carbonyl compounds from their 2,4-dinitrophenylhydrazones is often incomplete and has many side reactions. It is, however, positive proof that the characteristic hydrogenation flavor is at least partly due to saturated aldehydes and methyl ketones.

ACKNOWLEDGMENTS

Soybean oils contributed by Archer-Daniel-Midland Co. and A. E. Staley Manufacturing Co.

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[Received January 28, 1963—Accepted July 15, 1963]