Occurrence, Detection, and Prevention of Cyclization During Hydrogenation of Fatty Oils

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Abstract

It has been shown that, under certain extreme conditions during catalytic hydrogenation of materials containing polyunsaturated fatty acids, o-substituted benzene monocarboxylic acids (aromatic fatty acids = AFA) can be formed. Pure AFA were isolated from isomerized linseed oil, and their structure was elucidated from spectroscopic data. Final confirmation of the structure was obtained by direct synthesis. Quantitative determinations involved IR and NMR measurements of the urea non-adduct forming fraction. In this way as little as 0.01% AFA can be detected. To provide a greater operational latitude in technical processing without formation of these compounds, a two-stage modified hydrogenation process has been worked out.

Introduction

As early as 1876 Cloëz (1) reported on the formation of monomeric cyclic fatty acids (CFA) by heat treatment of tung oil fatty acids. During recent years the influence of various experimental conditions (2–7) on the formation of CFA has been investigated. In the majority of cases the unsaturated material was heated in an inert atmosphere at temperatures exceeding 180C.

Only in few instances has identification of isolated CFA fractions been reported (8–10). In several cases the physiological effects of these cyclic compounds have been studied (2–7). The presence of alkali during heating was found to catalyze not only conjugation but also cyclization of polyunsaturated fatty acids (11,12).

The possibility of cyclization of fatty acids by heating them with supported palladium in an inert atmosphere was reported by Floyd et al. (13). In this case formation of fatty acids containing a benzene nucleus was demonstrated by UV and IR characteristics and by oxidative degradation to phthalic acid.

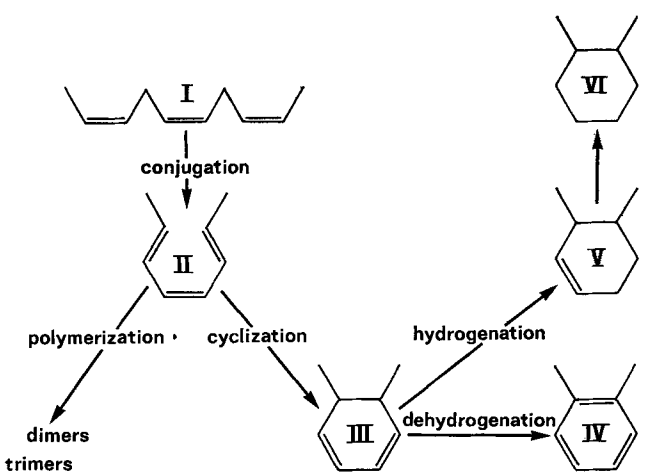

FIG. 1. Cyclization of trienoic acid.

Various authors (13–15) have commented on the possible mechanism for these cyclization reactions. A survey of their suggestions is presented in Figure 1, using a triene system as an example.

Formation of four types of CFA is possible. The relative amount of any specific product (III,IV,V,VI) will greatly depend on the reaction conditions applied. Polymer formation as a competitive reaction, involving intermolecular reactions, is clearly favored by high concentrations of unsaturated fatty acids. With increasing dilution the accent is shifted towards monomeric products.

In the catalytic hydrogenation of fatty oils the hydrogenation catalysts can also effect conjugation of double bonds in polyunsaturated systems. Since it is equally well known that hydrogenation catalysts have dehydrogenation activity, it was considered important to investigate whether in normal fat hydrogenation CFA can be formed.

In normal fat hydrogenation the ultimate concentration of CFA, if at all present, may be expected to be low. Because of their specific spectral properties, detection of benzene derivatives is much more sensitive than that of hydro-aromatic compounds. For this reason it was decided initially to concentrate on the detection and determination of type IV aromatic fatty acids (AFA).

Experimental

Preparation of Model C_{18}-AFA by Catalytic Cyclization of Linseed Oil (AFA_1)

Linseed oil was heated for 7 hr in CO_2 atmosphere at 140C in the presence of 1.2% Ni as a pyrophoric Ni-on-guhr catalyst, sulfurated with 3% sulfur (on nickel), according to Blekkingh (16).

The resulting isomerized oil was saponified, the unsaponifiable matter was extracted with ether from the soap solution, and the fatty acids were recovered in the usual manner. A urea crystallization was performed by dissolving 100 g of fatty acids in 1300 ml of dry methanol containing 400 g of urea. The mixture was heated to boiling, cooled to room temperature, and kept overnight. After filtration the adduct was washed twice with methanol saturated with urea, and the washing liquors were combined with the filtrate. From this solution the nonadducted fatty acids (NAFA) were recovered after dilution with water and acidification with dilute hydrochloric acid by extraction with ether and evaporation of the solvent.

Yield of NAFA on oil was 20.4%. These NAFA were esterified with methanol/sulfuric acid, and the methyl esters were subjected to a second urea crystallization (esters:methanol:urea = 1:4:4). Yield of the second NAFA was 7.1%, based on original oil. To remove residual unsaturated fatty acids, the second NAFA was oxidized with peroxy-formic acid. To this end 1 g NAFA was treated with a mixture of 14 ml glacial acetic acid, 1 ml formic acid (conc. >98%) and 1 ml 30% hydrogen peroxide. After standing overnight at room temperature and dilution with

water to a total volume of 50 ml, the mixture was extracted with petrol ether (40/60C). The resulting solution was washed free of water-soluble acids and evaporated to dryness, yielding 40.2% of residue, calculated on the second NAFA.

To eliminate oxidized material, the residue was chromatographed over silica (Mallinckrodt, dried for 1 hr at 120C). On elution with petrol ether:ethyl acetate (9:1) the middle fraction was found to be monomeric aromatic fatty acid (AFA) (methyl ester; $n_D^{25} = 1.4898$). Its purity was checked with paper chromatography according to Kaufmann and Nitsch (17). The C_{18}-AFA had the same Rf value as decanoic acid.

Preparation of Model C_{18}-AFA by Direct Synthesis (AFA_2)

As will be shown below, the spectroscopic data on the AFA formed in catalytic treatment of polyenoic fatty acids point, almost beyond doubt, to the structure $C_nH_{2n+1}C_6H_4C_mH_{2m}COOH$ (orthoposition of substituents). Furthermore it appears highly probable that, for the main component of the AFA derived from linolenic acid, the alkyl group is a propyl group ($n = 3$, $m = 8$). Therefore, as a final confirmation of the derived structure, the 9-(2′-propylphenyl)-nonanoic acid was synthesized by G. J. N. Egmond of the Vlaardingen laboratory as follows.

Pure o-bromopropylbenzene, $n_D^{20.5} = 1.5390$ (acc. to (18) $n_D^{20} = 1.5395$), was coupled with 8-methoxycarbonyl-octanoyl chloride, bp 157–157.5C/18 mm (acc. to (19) bp 139–141C/4.5 mm) analogous to the method of Ghosal (20) to obtain methyl 8-(2′-propylbenzoyl)-octanoate, bp 135C/0.04 mm, $n_D^{20} = 1.4990$, yield 39%. Purity (GLC) 98%. IR analysis showed bands at 760, 1495, and 1600 cm^{-1} (orthosubstituted aromatic compound), 1683 cm^{-1} (ketone), 1440 and 1738 cm^{-1} (methyl ester).

On reduction by the Wolff-Kishner method a crude acid was obtained, which was purified by fractionation of the methyl ester, bp 138C/0.01 mm, $n_D^{25} = 1.4895$, yield 75%. Purity (GLC on Celite-Apiezon L) >98%.

Characterization of AFA

a) *Ultraviolet spectrum.* Figure 2 shows the UV absorption spectra measured on a Cary UV spectrophotometer, Model 14, showing maxima at 264 and 272 mμ with molar specific extinction values in petrol ether of 310 and 290 respectively. The continuous line refers to the AFA prepared by catalytic treatment of linseed oil (AFA_1), the dotted line to the synthesized product (AFA_2). The two spectra are practically identical and show great similarity to the spectrum of o-xylene.

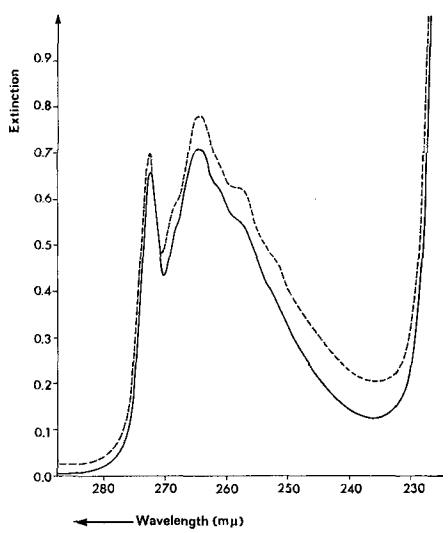

FIG. 2. UV spectra of C_{18}-AFA, solutions in petrol ether, 7.0 mg/10 ml, 1 cm.

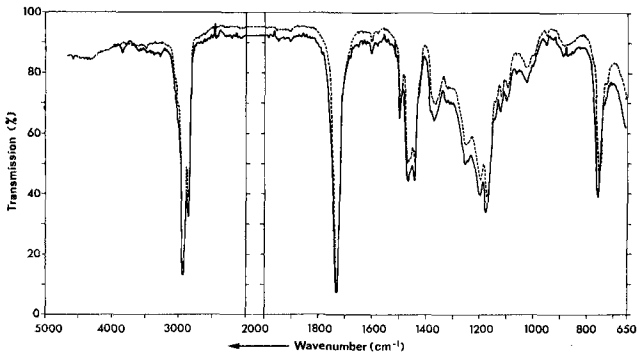

FIG. 3. IR absorption spectra of pure AFA methyl esters.

The low specific extinction values and the absorption in this spectral region by other possible components of hardened fats, such as conjugated trienes or oxidized material, make UV absorption measurements of little value for AFA detection in hardened fats.

b) *Infrared Spectrum.* Figure 3 shows the IR absorption spectra of the pure AFA methyl esters AFA_1 (continuous line) and AFA_2 (dotted line), measured on a Unicam SP 200 spectrometer (undiluted 7 μ film). The spectra are closely similar, showing pronounced bands at 1602 cm^{-1} (6.24 μ), 1498 cm^{-1} (6.7 μ), and 760 cm^{-1} (13.2 μ), which are characteristic of aromatic rings. The spectra are almost identical with the spectrum reported by Floyd et al. (13) for aromatized linoleic acid. The absorption at 13.2 μ characteristic of o-dialkylbenzene proved to be especially useful for the detection of small amounts of AFA and was used for quantitative determination as described below.

c) *Nuclear Magnetic Resonance Spectrum.* Figure 4 shows the proton magnetic resonance spectra of AFA_1 (continuous line) and AFA_2 (dotted line) in CCl_4-solution, run at 60 Mc (Varian A-60 spectrometer) with tetramethylsilane as internal reference ($\delta = 0$).

In the spectrum of AFA_1 the sharp absorption of the aromatic protons ($\delta = 7.03$, 4 protons compared with the methyl ester intensity of 3 protons as a standard) eliminates *meta*-substitution as well as a $COOCH_3$-group directly bonded to the ring; this is in accordance with the presence of two $-CH_2$-groups, directly attached to the ring ($\delta =$ ca 2.6, 4 protons).

The triplet at $\delta = 2.2$ (2 protons) originates from a methylene group *a* to the $COOCH_3$-group. Comparison of the terminal methyl pattern with the an-

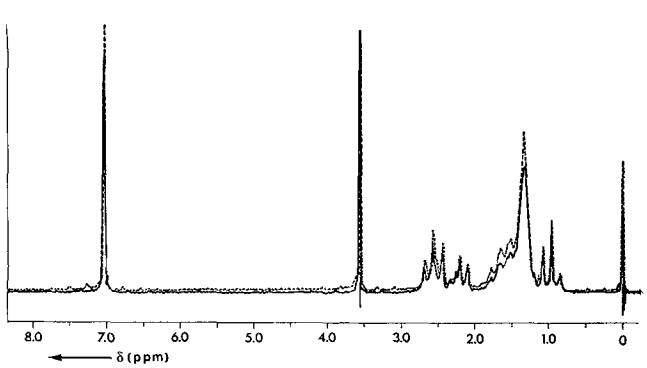

FIG. 4. Proton magnetic resonance spectra of C_{18}-AFA.

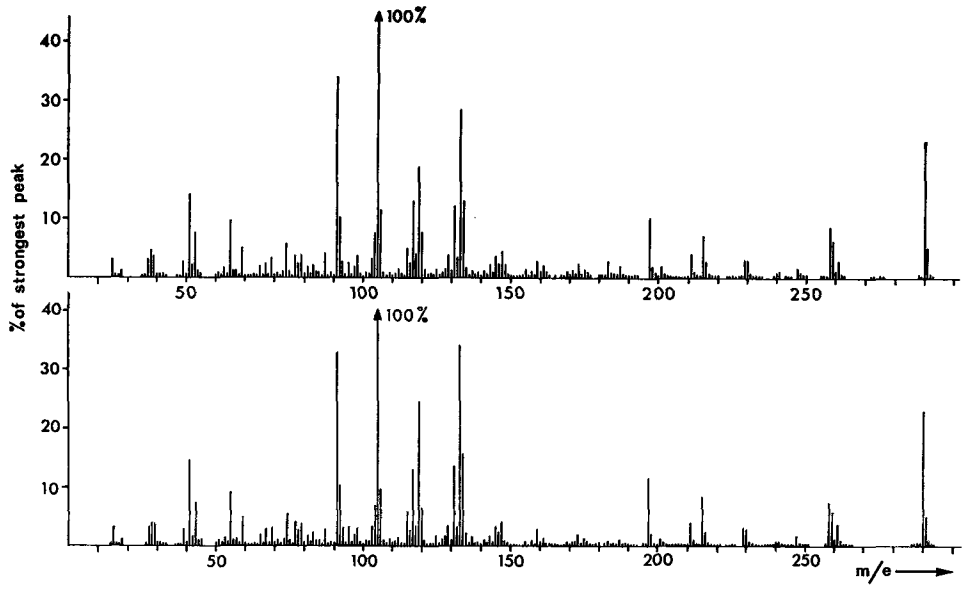

FIG. 5. Mass spectra of pure AFA methyl esters.

alogous absorption in alkyl chains, attached to an aromatic nucleus, strongly suggests the presence of a propyl group, bonded to the ring, because this triplet is rather sharp and appears at somewhat low field ($\delta = 0.95$, 3 protons). The alkyl chain is responsible for the remaining complex absorption (δ = ca 1.3, 14 protons).

Altogether the spectrum of AFA_1 largely confirms the assumed structure. The spectrum of the synthetic compound AFA_2 provides final confirmation. The NMR absorption of the aromatic protons proved to be extremely useful for determination of small amounts of AFA. From the spectra AFA-contents of 95% for AFA_1, 99% for AFA_2 can be calculated.

d) *Mass Spectrum.* Figure 5 shows the mass spectra of the pure AFA (AFA_1 top; AFA_2 bottom) as obtained on an AEI mass spectrometer, Type MS 2H. As expected, a parent peak at mass number 290 is found for AFA_1. The peaks at mass numbers 91, 105, 119, and 133 are strongly indicative of the presence of a substituted benzene nucleus. The spectrum may be said to be in accordance with the assumed structure. The close analogy of the spectra of AFA_1 and AFA_2 provides further confirmation.

From the above evidence it is certain that, when AFA is formed in catalytic treatment of polyenoic fatty acids, it has the structure $C_nH_{2n+1}C_6H_4C_mH_{2m}COOH$ (orthoposition of substituents). Furthermore it is highly probable that, for the AFA derived from linolenic acid, the alkyl group is a propyl group for the main component.

e) *Gas-liquid Partition Chromatography.* In Figure 6 the chromatograms of the pure AFA methyl esters (AFA_1 continuous line, AFA_2 dotted line) are shown. The chromatograms were obtained on a Carlo Erba P-AJD/2f chromatograph with flame ionization detection, using the following conditions: column: polyethylene glycol adipate, 5% on Diatoport S; temperature 197C; nitrogen flow rate: 11.4 ml/min.

The main peak corresponding to ca 76% of the AFA_1 shows a retention time corresponding to a carbon number of 21.85 (stearic acid methyl ester = 18). The minor peaks with carbon numbers of 21.28, 21.43, 21.62, 22.36, and 22.91 may result from isomeric AFA species which differ in the lengths of the substituents. The main peak, corresponding to ca 98% of AFA_2, has a retention time exactly corresponding to that of the main peak of AFA_1, which further confirms that the main constituent of AFA_1 is $o\text{-}C_3H_7C_6H_4C_8H_{16}COOCH_3$. For oils containing predominantly C_{18}-polyunsaturated fatty acids, this GLC-analysis may successfully be used for quantitative AFA determinations. Oils with more complicated polyunsaturated fatty acid composition, such as whale and fish oils, show, on cyclizing treatment, gas-liquid chromatograms of a large number of AFA homologues and isomers so that quantitative analysis is unlikely to be exact. However the peak distribution and heights may very well serve for identification purposes.

Quantitative Analysis of Hydrogenated Fats for AFA

For routine analysis of the AFA-content the following procedure proved satisfactory.

a) *Preparation of AFA-Concentrate.* Conversion of 20 to 50 g fat to methyl esters was done by transesterification with methanol and sodium methoxide. One-step urea crystallization (ratio ester:methanol: urea = 1:4:4) was carried out as previously described; for IR measurements the NAFA fraction is used as such. For NMR analysis, where CH_3-absorption is

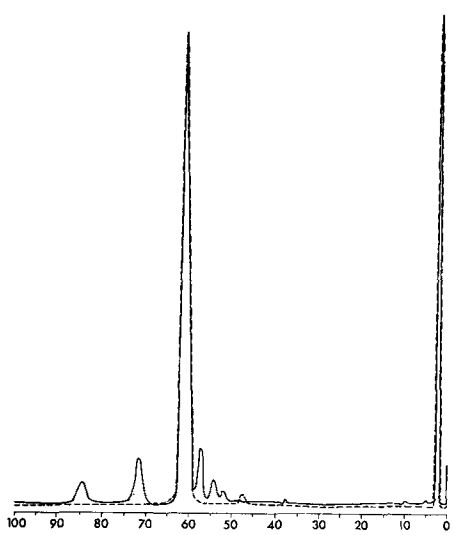

FIG. 6. Gas chromatograms of pure AFA methyl esters.

TABLE I
Comparative Determination of AFA Content by IR and NMR Measurements

Sample no.	1	2	3	4	5	6	7
% AFA by IR	3.5	2.0	0.10	0.19	0.17	0.06	<0.02
% AFA by NMR	2.7	1.7	0.11	0.18	0.18	0.06	<0.01

used as a reference, complete esterification is ensured by a subsequent treatment with diazomethane.

In both treatments the amount of NAFA is expressed as percentage of original fat. The NAFA content normally obtained is about 1 to 1.5% for vegetable fats and 2 to 3% for marine fats. The concentrate thus obtained from fats containing significant amounts of AFA shows the same spectral characteristics as the model AFA discussed above. IR or NMR measurements may now be used to determine the AFA content.

b) *IR Measurements.* IR measurements are carried out direct with the NAFA methyl ester. On a 25 μ film the absorption at 13.2 μ is used. For these quantitative determinations a spectrometer with linear wavelength scale (*e.g.*, Perkin Elmer Infracord) was found convenient in this wavelength region.

As aliphatic $(CH_2)_4$ chains absorb at 13.8 μ but also show a certain absorption (E) at 13.2 μ, the total E measured at 13.2 μ is not identical with the AFA absorption at 13.2 μ ($EA_{13.2}$) and therefore requires some correction. The true $EA_{13.2}$ was calculated from the partial absorptions of pure AFA and soybean oil methyl esters at 13.2 and 13.8 μ with the empirical formula:

$$EA_{13.2} = 1.19\ E_{13.2} - 0.44\ E_{13.8}$$

where $E_{13.2}$ and $E_{13.8}$ are the total absorptions.

The baseline for reading E was obtained by drawing a horizontal tangent at the absorption minimum near 12.5 μ. A calibration curve was finally obtained by plotting the true $EA_{13.2}$ of stepwise diluted solutions of AFA_1 in soybean oil methyl esters *versus* AFA concentration.

The amount of AFA is read from the calibration curve. The lowest detectable amount of AFA in the NAFA is about 2%. Smaller amounts show no clearly recognizable absorption at 13.2 μ. Thus 0.02% to 0.04%, depending on the amount of NAFA obtained, of AFA in fat can still be determined.

c) *NMR Measurements.* Since the methyl ester absorption is used as an internal reference, AFA analysis by NMR on a methyl ester mixture is absolute. From the integrated intensities of the 7.03 and 3.57 ppm absorptions (aromatic protons and those of the ester CH_3-group respectively) the AFA content in mole percentage is readily obtained. The lowest detectable amount of AFA in the NAFA is 0.5%. Thus about 0.01% of AFA in fat can still be determined.

On a number of samples of different origin both IR and NMR determinations of AFA were performed. The results (Table I) demonstrate that the two methods agree satisfactorily, especially since, for the two series of determinations, separate concentration procedures were applied.

As a final check on the accuracy of the concentration and determination procedures two experiments were performed in which amounts of AFA_2 were added to an AFA-free hardened fat sample. The resulting mixtures were then subjected to the concentration procedure as described above, and the NAFA determined by NMR. The results given in Table II demonstrate the reliability of the method.

TABLE II
Recovery Efficiency of Analytical Concentration Method

Sample	% AFA_2 added	% AFA determined
1	0	<0.01
2	0.25	0.23
3	0.50	0.55

As mentioned before, the pure C_{18}-AFA (AFA_1) was used for calibration of the IR measurements. Theoretically this involves a small quantitative error in the determination of AFA homologues present in fish and whale oils with chain lengths between C_{16} and C_{24}. However, for comparative purposes as in the present studies, the amounts determined by IR are sufficiently exact and are expressed as C_{18}-AFA. In marine oils the actual amount may be about 1.1 times higher than indicated in the tables. The same correction applies to the NMR determination.

Influence of Hydrogenation Conditions on AFA Formation

In order to find hydrogenation conditions which ensure prevention of AFA formation, the effect of the most important conditions was studied.

Since it is evident that hydrogenation and cyclization are competing reactions, the influence of hydrogen supply was investigated. This influence is shown by the experimental results, summarized in Table III, from which also the large influence of the reaction temperature can be seen.

Also the type of raw material proved to be an important variable. In Table IV the results on seven different oils are represented. The experiments were performed with two different catalysts, one of low sulfur content and one with added sulfur, under conditions conducive to cyclization.

Discussion

The experimental results shown in Table III demonstrate clearly the great effect of temperature on AFA formation. For both series the results have been plotted against 1000/T in Figure 7. All experiments were continued to the same degree of hydrogenation, which, of course, was attained after different reaction times. If first order is assumed in concentration C_a of adsorbed unsaturated molecules for both the cyclization (c) and the hydrogenation (h) reaction and if it is considered that hydrogenation is first order in hydrogen, it may be stated that

$$\frac{\partial AFA}{\partial t} \sim A_c \cdot C_a \cdot e^{-E_c/RT} \qquad (1)$$

and

$$\frac{\partial \Delta I.V.}{\partial t} \sim A_h \cdot C_a \cdot C_{H_2} \cdot e^{-E_h/RT} \qquad (2)$$

TABLE III
Effect of Reaction Temperature and Hydrogen Supply on AFA Formation, Peruvian fish oil, pre-used Catalyst (2.5% S/Ni), High Stirring Intensity

Temperature C		130	140	150	160	180	190	200	210	225
Very little H_2	% AFA	<0.01	0.03	0.09	0.23	0.90				4.2
400 l H_2/hkg[a]	% AFA					<0.01	0.05	0.09	0.18	

[a] Liters of hydrogen per hour per kilogram.

in which C_{H_2} stands for concentration of hydrogen in its active form. Combining (1) and (2) gives

$$\frac{\partial AFA}{\partial \Delta I.V.} \sim \frac{A_c}{A_h C_{H_2}} : e^{-(E_c - E_H)/RT}$$

Since the degree of hydrogenation is equal for all experiments, it follows that

$$\ln AFA = B - (E_c - E_h)/RT - \ln C_{H_2} \quad (3)$$

Thus apparent activation energies, derived from Figure 7, are related to the differences of activation energies for cyclization and hydrogenation. Clearly the above treatment constitutes an oversimplification; in reality, the reaction system is far more complex and cannot be treated as two single parallel reactions.

An important point which emerges is the influence of the hydrogen concentration. In accordance with (3), for the two series of experiments, more than an order of magnitude difference in AFA formation solely as a result of different amounts of hydrogen supplied is found. It is probable that the curvature of the plots of Figure 7 results from the temperature dependence of the effective hydrogen concentration (see below).

The results of Table IV show that the tendency toward formation of AFA increases with the degree of unsaturation of the raw material. The high content of polyunsaturated fatty acids of high IV oils will be primarily responsible for this effect. With oils of low sulfur content a sulfur-containing catalyst promotes cyclization; when the oil contains a significant amount of sulfur however, the catalyst takes up sulfur early in the course of the reaction and it may well be that, in this case, a more effective distribution of sulfur over the catalyst surface is obtained.

It has been seen that AFA formation is favored by a low hydrogen supply, a high temperature, and a high degree of unsaturation of the raw material. One author (21) has shown earlier that these conditions also induce a low concentration of hydrogen, dissolved in the oil and adsorbed on the catalyst, owing to the fact that hydrogen supply from the gas phase cannot keep pace with the hydrogen consumption on the catalyst. It has also been found that a high sulfur content in the catalyst tends to promote AFA formation.

Both low hydrogen concentration on the catalyst and the presence of sulfur on the catalyst promote conjugation of double bonds, which is probably an

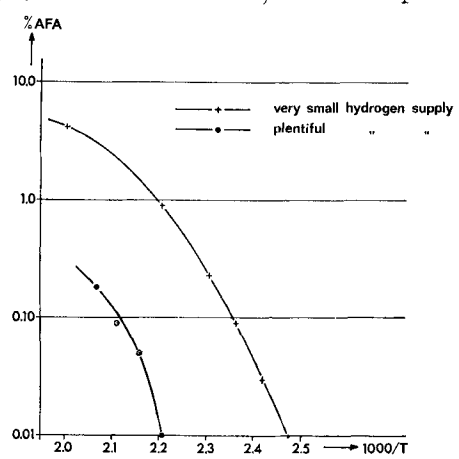

FIG. 7. Temperature dependence of AFA formation in hydrogenation of Peruvian fish oil.

TABLE IV

Influence of Type of Oil and Catalyst on AFA Formation, 200C, 300 lH₂/h kg, Low Stirring Intensity

Oil	IV	% AFA	
		Low sulfur catalyst	Sulfurated Catalyst 3% S/Ni
Peruvian fish oil	191	0.76	0.75
Linseed oil	185	0.51	1.00
Sunflower oil	130	0.06	0.21
Whale oil	125	0.20	0.16
Sesame oil	110	0.02	0.13
Rapeseed oil	100	0.14	0.09
Groundnut oil	90	0.01	0.01

intermediate step in cyclization (Figure 1). Hydrogenation, isomerization, and cyclization are competing reactions, and it is clear that conditions leading to low hydrogen concentration will favor reactions which do not consume hydrogen: isomerization and cyclization. It is well known however that, to some extent, selectivity and isomerization in oil hydrogenation go together so that there are good reasons to choose these conditions for obtaining selectively hydrogenated fats with steep dilatation lines. In the application of these selective conditions however some caution is desirable to prevent cyclization.

Once cyclization has occurred, probably yielding e.g. cyclohexadiene derivatives as primary products, low hydrogen concentrations will clearly favor dehydrogenation to AFA.

For oils containing fatty acids with more than three double bonds the possible formation of AFA with unsaturated side-chains must be considered. However it is normally found to be rather low, and even in the case of partial hydrogenations of fish oil (to IV 70–80) at least 80% of the AFA present does not contain olefinic unsaturation. These conclusions were derived by comparing the IR spectra of the NAFA before and after peroxy-acid oxidation and removal of the oxidation products over SiO_2.

From experiments shown in Tables III and IV not only the conditions favoring AFA formation can be derived but also those by which cyclization can be avoided.

As noticed in Table III, a reduction of the temperature leads to a marked decrease of AFA content. At temperatures below 140C, AFA are below the detection limit (0.01% AFA/oil) even if drastic hydrogen shortage occurs. Although, with a generous hydrogen supply, cyclization sets in only above 180C (Table III), a wider safety margin is provided by choosing lower temperatures (*e.g.*, 150C or lower) for factory processing.

These low-temperature conditions need only be applied as long as the danger of cyclization exists. As soon as the majority of conjugatable polyunsaturated fatty acids are eliminated, especially those with three or more double bonds, the temperature may be raised to ensure selectivity also in this later stage. Thus products, similar to the normal one-stage products with respect to melting behavior and flavor stability, can be obtained. For this second stage temperatures more than 200C should be avoided in any case, but a temperature of e.g. 180C is advisable.

Various authors have reported toxic effects of cyclic fatty acids in animal experiments (2–7). Owing to the cyclization method (heat treatment and alkali isomerization) applied in the reported cases, the cyclic material probably consisted predominantly of cyclohexene- and cyclohexadiene-derivatives. In the present experiments these components could not be detected. This may be because of the intrinsic stability of the

benzene nucleus, which leads to preferential formation of AFA in the presence of a hydrogenation catalyst in the case of hydrogen shortage, which is the only condition under which cyclization can occur.

In these experiments the biological aspects of these aromatic fatty acids have been studied by Gottenbos and Thomasson, and the results obtained so far were recently reported (22). They justify the standpoint that the toxic action of the aromatic fatty acids, present in properly hardened fats, is insignificant for human nutrition because biological effects in animals could only be demonstrated if the dose administered were at least one thousand times the amount consumed by man.

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REFERENCES

1. Cloëz, M. S., Compt. Rend. *83*, 943–945 (1876).
2. Crampton, E. W., R. H. Common, F. A. Farmer, A. F. Wells and D. Crawford, J. Nutr. *49*, 333–347 (1953).
3. Crampton, E. W., R. H. Common, E. T. Pritchard and F. A. Farmer, J. Nutr. *60*, 13–24 (1956).
4. Common, R. H., E. W. Crampton, F. A. Farmer and A. S. W. DeFreitas, J. Nutr. *62*, 341–347 (1957).
5. Matsuo, N., J. Chem. Soc. Japan, Pure Chem. Sect. *81*, 469 (1960).
6. Friedman, L., W. Horwitz, G. M. Shue and D. Firestone, J. Nutr. *73*, 85–93 (1961).
7. Firestone, D., W. Horwitz, L. Friedman and G. M. Shue, JAOCS *38*, 418–422 (1961).
8. Roszmann, E., Fettchem. Umschau *40*, 117–123 (1933).
9. McInnes, A. G., Can. J. Chem. *39*, 1906–14 (1961).
10. Hutchison, R. B., and J. C. Alexander, J. Org. Chem. *28*, 2522–2526 (1963).
11. Waterman, H. I., J. P. Cordia and B. Pennekamp, Research (London) *2*, 483–485 (1949).
12. Eisenhauer, R. A., R. E. Beal and E. L. Griffin, JAOCS *40*, 129–131 (1963).
13. Floyd, D. E., R. F. Paschke, D. H. Wheeler and W. S. Baldwin, JAOCS *33*, 609–614 (1956).
14. Paschke, R. F., and D. H. Wheeler, JAOCS *32*, 473–478 (1955).
15. Scholfield, C. R., and J. C. Cowan, JAOCS *36*, 631–635 (1959).
16. Blekkingh, J. J. A., German Pat. 883,892.
17. Kaufmann, H. P., and W. H. Nitsch, Fette und Seifen *56*, 154–158 (1954).
18. Lamneck, J. H., J. Am. Chem. Soc. *76*, 1106–1107 (1954).
19. Cason, J., J. Am. Chem. Soc. *64*, 1106–1110 (1942).
20. Chosal, M., B. Shinka and P. Bagchi, J. Org. Chem. *23*, 584–586 (1958).
21. Coenen, J. W. E., Proc. Intern. Congr. Catalysis, Paris (1960), p. 2705–2731.
22. Gottenbos, J. J., and H. J. Thomasson, lecture before the Group of European Nutritionists, Wageningen, May 11–13, 1964; Nutr. Dieta *7*, 110–129 (1965).

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