# Hydrogenation of a Fatty Acid Is Not Influenced by the Position It Occupies on a Triglyceride Molecule

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## Abstract

Randomly rearranged soybean oil (Iodine Value 128) was hydrogenated with samples being taken at decrements of 10 I.V. units. The composition of the fatty acids occupying the various positions of the triglyceride molecules of these fats was determined. The results demonstrate that the position an unsaturated fatty acid occupies on a triglyceride molecule does not influence its rate of hydrogenation.


## Introduction

Analysis with pancreatic lipase has unequivocally demonstrated that fatty acids of vegetable fats are not randomly distributed among the various positions of the triglyceride molecules. The 2-position of these triglycerides contains a larger portion of unsaturated fatty acids than does the 1- and 3-positions (1,2). This raises the question as to whether an unsaturated fatty acid occupying a certain position of a triglyceride molecule might be hydrogenated at a rate different from same type of fatty acid occupying another position on the triglyceride molecule.

Bushell and Hilditch (3) investigated the hydrogenation of several synthetic triglycerides containing oleic and palmitic or stearic acids. They concluded that the rate at which oleic acid was hydrogenated did not change regardless of whether the acid was esterified with the primary or secondary hydroxyl groups of glycerol. Since their study was limited to oleic acid, and since considerable acyl migration undoubtedly occurred during synthesis of the triglycerides, a re-evaluation of this matter is desirable. The lipase technique for studying fatty acid distribution in triglyceride molecules now affords a reliable method for following the hydrogenation of individual fatty acids.

## Experimental Procedures and Data

Soybean oil was the fat selected for this study because it contains the three unsaturated acids, oleic, linoleic, and linolenic, that are of general interest. This fat is typical of vegetable fats in that it contains a high proportion of unsaturated acids in the 2-position. It was realized that this unequal distribution of fatty acids would make interpretation of the results of the planned experiment difficult. Because of this, the soybean oil was randomly rearranged so there would be equal distribution of the fatty acids among all three positions of the triglyceride molecules. This rearranged oil was hydrogenated (165C, atmospheric pressure, 0.03% Ni) and samples were taken at 10 I.V. unit decrements.

The fatty acid composition of the various positions in the triglycerides of these fats was determined by hydrolysis with pancreatic lipase (4). Since under these conditions there is little or no hydrolysis of esters of secondary hydroxyl groups (5), the fatty acids of the monoglycerides isolated from the enzyme digest are those that were esterified at the 2-position of the triglyceride. The fatty acids of the triglycerides and of the monoglycerides resulting from the enzymatic digest were converted to methyl esters and their compositions determined by gas-liquid chromatography. The conditions used were: liquid phase, 12 wt % of ethylene glycol adipate polyester on 60–80 mesh, acid-washed and neutralized Chromosorb W; column length, 200 cm; temp, 200C; He flow rate, 50 ml per min, standard temp and pressure; sample size, 0.5 $\mu$l. Standard mixtures of pure fatty acid methyl esters were used as reference compounds.

I.V.'s were determined by the Wijs method (6). *Trans* double bond content was obtained by I.R. spectrometry (6).

## Results and Discussion

The fatty acid composition of the triglycerides and the composition of those acids esterified at the 2-position of the triglyceride molecules are given in Table I. Values from 1 to 5% have a maximal relative error of 10%; those above 5% have a maximal relative error of 5%. The last row for each fat is the percentage of that particular fatty acid of the triglyceride that is in the 2-position. The significance of this last group of numbers is dependent on the relative error in the values from which they are derived.

The unhydrogenated soybean oil used in these studies consisted of 84% of unsaturated acids, while the 2-position of these triglycerides (Sample 6) consisted of 98% of unsaturated acids; the specific distribution, which has been reported for this and other vegetable fats (1), is apparent. Rearrangement results in an equal distribution of all fatty acids among all three

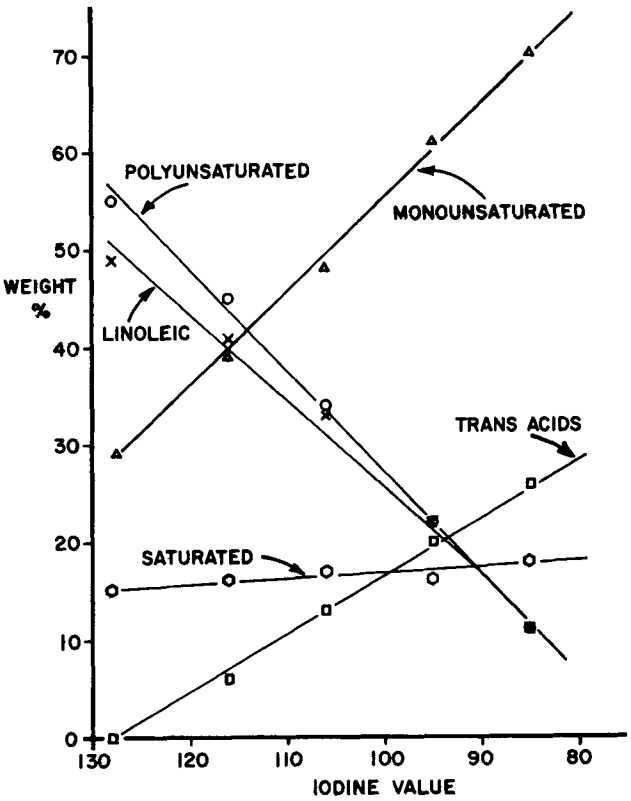


Fig. 1. Fatty acid composition of randomly rearranged soybean oil hydrogenated tto various iodine values (165C, atmospheric pressure, 0.03% Ni).

TABLE I

Fatty Acid Composition of Whole Triglyceride and of Fatty Acids in 2-Position of Triglyceride and Proportion [a] of Each Fatty Acid in 2-Position

| | Iodine value | *Trans* acids | Weight % | | | | |
|---|---|---|---|---|---|---|---|
| | | | Palmitic | Stearic | Oleic | Linoleic | Linolenic |
| | | % | | | | | |
| Sample 1, rearranged SBO | | | | | | | |
| Triglyceride | 127.6 | 0 | 11.1 | 4.3 | 29.1 | 48.9 | 6.0 |
| 2-Position | ..... | 0 | 11.0 | 4.5 | 29.5 | 48.2 | 5.3 |
| Proportion | ..... | .... | 33.3 | 34.8 | 33.8 | 32.9 | 29.5 |
| Sample 2, hardened SBO | | | | | | | |
| Triglyceride | 116.2 | 6 | 11.2 | 4.7 | 38.8 | 41.4 | 3.4 |
| 2-Position | ..... | 7 | 10.8 | 4.4 | 37.5 | 42.8 | 3.7 |
| Proportion | ..... | 39 | 32.2 | 31.1 | 32.2 | 34.5 | 36.0 |
| Sample 3, hardened SBO | | | | | | | |
| Triglyceride | 106.2 | 13 | 11.8 | 4.9 | 48.4 | 32.8 | 1.5 |
| 2-Position | ..... | 10 | 11.3 | 4.7 | 50.2 | 31.9 | 1.5 |
| Proportion | ..... | 26 | 32.0 | 32.0 | 34.6 | 32.4 | 33.0 |
| Sample 4, hardened SBO | | | | | | | |
| Triglyceride | 95.3 | 20 | 11.4 | 5.0 | 61.2 | 21.8 | 0.4 |
| 2-Position | ..... | 20 | 10.8 | 4.8 | 58.7 | 24.5 | 0 |
| Proportion | ..... | 33 | 31.6 | 32.0 | 32.0 | 37.5 | .... |
| Sample 5, hardened SBO | | | | | | | |
| Triglyceride | 85.0 | 26 | 12.0 | 5.8 | 69.5 | 11.0 | 0 |
| 2-Position | ..... | 25 | 10.6 | 5.3 | 69.1 | 13.8 | 0 |
| Proportion | ..... | 32 | 29.5 | 30.5 | 33.1 | 41.8 | .... |
| Sample 6. original SBO | | | | | | | |
| Triglyceride | ..... | 0 | 11.3 | 4.3 | 29.1 | 49.5 | 5.8 |
| 2-Position | ..... | .... | 1.0 | 0.7 | 26.1 | 66.7 | 5.5 |
| Proportion | ..... | .... | 3.0 | 5.5 | 30.0 | 45.0 | 31.6 |

[a] 2-Position/(Triglyceride × 3) × 100 = Proportion, i.e., the percentage of that particular fatty acid that is in the 2-position.

positions of the triglycerides (Sample 1). Linolenic acid may appear to be an exception; however, considering the errors in the lipase method and the analytical methods the value of 29.5% cannot be considered as significantly different from the theoretical value of 33.3%.

The proportion values for each of the unsaturated acids remained at approximately 33% in the various hydrogenated fats. Thus the rates of hydrogenation of oleic, linoleic, and linolenic acids are not influenced by the position these fatty acids occupied on a triglyceride molecule. An exception to this is suggested by the values for linoleic acid in Sample 5. However, since all the other values, both for linoleic and the other acids, do not show any pattern digressing from randomness, this single deviation is considered to be experimental error.

Figure 1 is a graphic presentation of the fatty acid composition of the triglycerides of the randomly rearranged soybean oil and the hydrogenated fats prepared from it. These values are typical of those that have been reported for non-randomized soybean oil hydrogenated under these conditions (7). The similarity of the products of hydrogenation of randomized and non-randomized soybean oil further confirms that the position a fatty acid occupies on a triglyceride molecule does not influence its hydrogenation under these conditions.

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[Received December 15, 1961]

• *Letter to the Editor*

# Vinyl Ketones in Oxidized Fats

CROSSLEY, HEYES, AND HUDSON have reported the effect of heat on tricaprin and 2-oleo-dipalmitin both in the absence and in the presence of oxygen (1). Eighteen carbonyl compounds were isolated from 2-oleo-dipalmitin heated at 190C. in the presence of air. The two major components were unsaturated ketones and though not positively identified, were very closely related to n-heptylidene acetone and n-hexylidene acetone. After a discussion of degradative mechanisms Crossley et al. have suggested that the compounds might be vinyl n-heptyl and vinyl n-hexyl ketones.

We have recently identified a compound responsible for metallic flavor in oxidized dairy products and oxidized safflower oil as vinyl n-amyl ketone (oct-1-en-3-one) (2). This compound has a flavor threshold value of one part in $10^9$ in butterfat and one part in $10^{10}$ in water. We have also studied the $C_{4-9}$ vinyl n-alkyl ketones and found their flavors to be closely similar (3). Papers on their gas chromatographic behavior (4) and on the paper chromatography of their 2,4-dinitrophenylhydrazones (5) are being prepared for publication.

The gas chromatographic data for the two unknown compounds reported by Crossley et al. do not correspond to the behavior we have observed for the $C_{4-9}$ vinyl ketones, nor apparently do the light absorption or $R_f$ values for the 2,4-dinitrophenylhydrazones. The two unsaturated ketones reported by Crossley et al. may be alk-3-en-2-ones or di-unsaturated ketones such as alka-3,7-dien-2-ones whose properties will resemble closely the mono-unsaturated conjugated ketones. Neither type of compound has yet been isolated from fats or oils and the identification of either would be of considerable importance.

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(Received April 2, 1962)