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Chemical Reactions Involved in the Catalytic Hydrogenation of Oils. II. Identification of Some Volatile By-Products[1, 2]

A. SILVEIRA, JR.,[3] Y. MASUDA and S. S. CHANG, Department of Food Science, Rutgers, The State University, New Brunswick, New Jersey

Abstract

Gas chromatography of the volatile by-products produced during the catalytic hydrogenation of an autoxidized soybean oil with a peroxide number of 11.2 meq/kg yielded approx 41 peaks. Twenty-one of the gas chromatographic fractions were collected and rechromatographed, and their chemical identity studied with micro-IR and mass spectrophotometry. These volatile by-products, according to peak area of gas chromatogram, showed a predominance of hydrocarbons and alcohols.

The fractions which have been identified are *n*-octane, *n*-nonane, *n*-decane, *n*-heptadecane, *n*-hexanol, *n*-heptanol, *n*-decanol, *n*-hexanal, *n*-decanal and 3-nonanone. Among the gas chromatographic fractions collected, *n*-decanol has an odor most reminiscent of that of catalytic hydrogenation.

Introduction

THE IMPORTANCE OF THE chemical characterization of the volatile by-products of hydrogenation and the scarcity of literature in this field were discussed previously (1). The present paper reports an investigation of the isolation, fractionation and chemical identification of some volatile by-products which are produced during catalytic hydrogenation of a soybean oil with a peroxide value of 11.2 meq/kg.

Experimental

Volatile By-Products of Hydrogenation. The volatile by-products isolated from 9.5 gal of hydrogenated soybean oil as previously described (1), were used for the present investigation.

Gas Chromatography. The ether solution of the volatile by-products was fractionated with a Beckman GC-2A gas chromatograph. The temp was linearly programmed with a Thermotrac Temperature Programmer from 45–200C in 30 min and then maintained at 200C for the remainder of the chromatography. An 8-ft aluminum column, ¼ in. I.D. packed with 15% Ucon Polar 50HB 280X on 80/100 mesh Chromosorb W (Acid washed), was used at a helium flow rate of 80 ml/min.

Collection of Gas Chromatographic Fractions. The gas chromatographic fractions were collected with a fraction collector designed and built in our laboratories (2). This fraction collector can be used to collect 18 fractions from one run. The gas chromatography was repeated 10 times. Each fraction was accumulatively collected in one cold trap. In this investigation, two runs of collection were made. In the first, 10 fractions were collected; in the second, 18 fractions. Since some of the fractions collected were duplicate peaks, a total of only 21 different gas chromatographic fractions were collected and studied.

Identification of Gas Chromatographic Fractions. The gas chromatographic fractions were identified by their IR spectra with the use of Sadtler standard spectra. The identifications were then confirmed by comparison of retention times with known compounds. The IR spectra of the gas chromatographic fractions in carbon tetrachloride solution were determined with a Beckman IR-8 spectrophotometer using ultra-micro cavity cells of 0.1-mm path length and beam condenser (Connecticut Instrument Corp.). An attenuated grid and variable wedge cell (W-1, Connecticut Instrument Corp.) were used in the reference beam to compensate for the adsorption due to solvent. By this technique, an IR spectrum could be obtained from 0.2 mg of sample.

When IR spectrum alone was insufficient for the chemical characterization of a gas chromatographic fraction, its mass spectrum was determined with a Bendix time-of-flight mass spectrometer.

Results and Discussion

Gas chromatography of the volatile compounds which were produced from soybean oil (PV, 11.2 meq/kg) during catalytic hydrogenation at 180C with 0.125% nickel catalyst (1) yielded approx 41 peaks (Fig. 1). The gas chromatogram is considerably different from the one published in our previous paper because of temp programming and the use of a more concd solution. Carbowax 20M and Carbowax 1000 were also tried as the stationary phase but did not give as good resolution as Ucon Polar 50 HB 280X. As shown by the Arabic number on the chromatogram, 21 of these gas chromatographic fractions were collected. Each of the collected fractions was then rechromatographed under the original conditions to insure that it was not contaminated by its neighboring peaks. Each fraction yielded only one symmetrical peak.

The volatile by-products of hydrogenation according to peak area of gas chromatogram, showed a predominance of hydrocarbons and alcohols. As determined by the IR spectra of the 21 collected gas chromatographic fractions (Fig. 1), 10 were hydrocarbons (fractions 2,3,4,6,7,8,14,16,17 and 20), three were alcohols (fractions 10,13 and 18), two were aldehydes (fractions 5 and 15), one was a ketone (fraction 12), three were other carbonyl compounds (fractions 1,9

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[2] Paper of the Journal Series, N.J. Agricultural Exper. Sta., Rutgers, The State University of New Jersey, Dept. of Food Science, New Brunswick.

[3] Present address, Chemistry Dept., State University College, Oswego, N.Y.

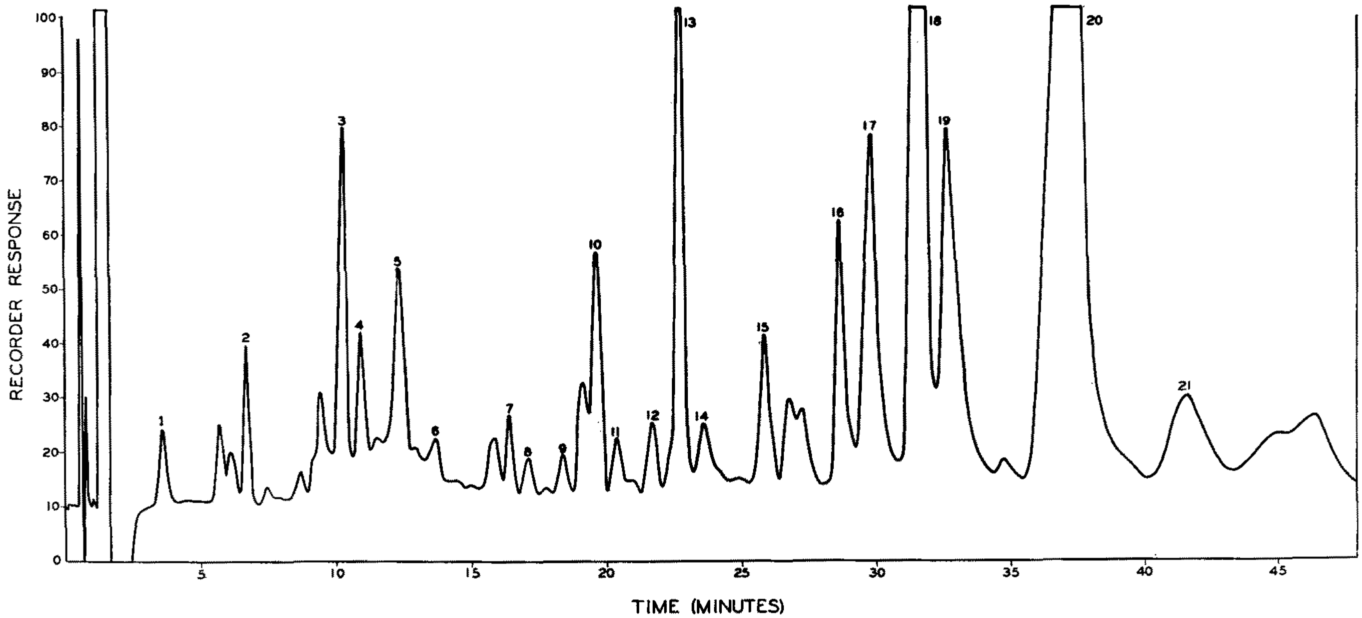


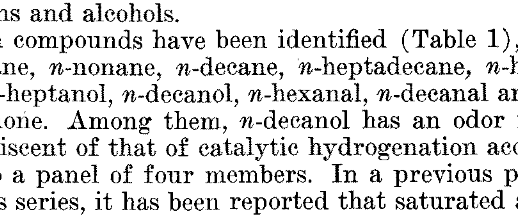
FIG. 1. Gas chromatogram of the volatile by-products evolved during hydrogenation of soybean oil.

and 11), and two could not be classified (fractions 19 and 21). These compounds are considerably different from the decomposition products of autoxidative degradation. The latter are predominantly carbonyl compounds while the former are predominantly hydrocarbons and alcohols.

Ten compounds have been identified (Table 1), viz. *n*-octane, *n*-nonane, *n*-decane, *n*-heptadecane, *n*-hexanol, *n*-heptanol, *n*-decanol, *n*-hexanal, *n*-decanal and 3-nonanone. Among them, *n*-decanol has an odor most reminiscent of that of catalytic hydrogenation according to a panel of four members. In a previous paper of this series, it has been reported that saturated aldehydes and ketones may also contribute to the characteristic hydrogenation flavor (1).

The mechanism for the formation of by-products by catalytic hydrogenation is difficult to postulate because many variables, such as temp, pressure, catalyst and oil may each affect the reactions involved. Since the refined and bleached oils used for this experiment have a peroxide number of 11.2 meq/kg, a likely source of the volatile by-products could be hydroperoxides.

The generally accepted mechanism for the formation of carbonyl compounds by decomposition of hydroperoxides of unsaturated fatty esters is based upon Farmer's theory (3,4) which involves a homolytic abstraction of a hydrogen atom to give the alkoxyl radical [1] which undergoes carbon-to-carbon fission to form the carbonyl compound:



$$\underset{\substack{|\\O\\O\\H}}{R_2\text{—}CH\text{—}R_1} \longrightarrow \underset{\substack{|\\O\\\cdot}}{R_2\text{—}CH\text{—}R_1}\text{—}\begin{cases}\xrightarrow{A} R_2CHO + R_1\cdot \\ \xrightarrow{B} R_1CHO + R_2\cdot\end{cases}$$

[1] [2]

R_1 = ester end
R_2 = hydrocarbon end

The formation of *n*-hexanal and *n*-decanal could occur by a type A cleavage. The formation of alcohols and hydrocarbons could be explained by a type B cleavage. For example, a type B cleavage from the 8-hydroperoxide of reduced oleate could lead to *n*-decanol or *n*-decane by combining the alkyl radical with hydroxyl or hydrogen radicals respectively. Since it is well known that peroxides are readily reduced to alcohols, if the above scheme is applicable, one would have to assume that the thermal decomposition of the hydroperoxide occurs more rapidly than reduction.

TABLE I
Gas Chromatographic Fractions Identified

Fraction number	Identified as
1	Acetone (tentative)
2	*n*-octane
3	*n*-nonane
5	*n*-hexanal
6	*n*-decane
10	*n*-hexanol
12	3-nonanone (by mass spectrum)
13	*n*-heptanol
15	*n*-decanal
18	*n*-decanol
20	*n*-heptadecane (by mass spectrum)

The formation of 3-nonanone could be predicted by the mechanism as suggested by Smouse and Chang (5) through the reaction of a carbonyl free radical originated from an aldehyde and a free ethyl radical. It is also possible that 3-nonanone is produced by catalytic hydrogenation of vinyl hexyl ketone. Fross (6) has reported that vinyl amyl ketone can originate from the autoxidation of linoleate. The *n*-heptadecane may be formed through decarboxylation of a free fatty acid under the conditions of hydrogenation.

The present investigation indicates that a major predominant by-product of catalytic hydrogenation is hydrocarbon. Its formation may also yield relatively high mol wt carbonyl esters as shown by [2], where R in this formula could conceivably be a triglyceride group. Difunctional compounds of this type would not be expected to be volatile under conditions of deodorization and would therefore remain in the hydrogenated oil. Studies on the nonvolatile constituents remaining in the oil are currently in progress.

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