2-*trans*-Nonenal, the Hardened Flavor Present in Hydrogenated Peanut Oil[1]

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Abstract

Oils belonging to linoleic-oleic acid group may have a characteristic hardening flavor after hardening and refining. This flavor was isolated from hardened peanut oil by degassing and preparative gaschromatography. An investigation into the structure of this flavor showed it to be 2-*trans*-nonenal. The structure was confirmed by comparison with an authentic synthesized product. 10-Octadecenoic and 11-octadecenoic acid which are formed during the hardening process (isomerization) of linoleic and oleic acids, are proposed as precursors of the hardening flavor.

Introduction

For some years, we have been working on the isolation and identification of certain hardening flavors. We have already published the identification of 6-nonenal, the carrier of the hardening flavor present in linseed and soyabean oils. Its precursors have been shown to be the 8,15- and 9,15-isolinoleic acids (1–2). In the course of our investigations in this field, we have also observed that, depending upon the quality of the starting oil, linoleic and oleic acid-containing oils, e.g., peanut, cottonseed and sunflowerseed, may likewise develop a typical flavor reminiscent of unused linen after hardening and refining. To our knowledge, this hardening flavor has not yet been mentioned in the literature. The identification of this flavor is of interest since its development in fairly expensive oils may be a disadvantage.

Procedure of Isolation and Identification

Starting Oil

Fully refined peanut oil was hardened under the following conditions to develop the hardening flavor: catalyst, fresh Ni/guhr (0.05% Ni); temperature, 180–185 C; hardening pressure, 2–3 atm gauge; and final melting point, 36–38 C.

Concentration of the Volatile Decomposition Products

The primary volatile decomposition products present in 500 g refined hardened peanut oil (peroxide value 2) were obtained by a degassing technique developed by de Bruyn and Schogt (3) at 80 C/10^{-6} mm Hg residual pressure.

The volatiles were trapped in a U-tube, cooled by liquid nitrogen, and then dissolved in optically pure light petroleum. The characteristic hardening flavor was easily perceptible.

Isolation of Hardening Flavor Carrier by Gas Liquid Chromatography

After carefully removing the solvent by distillation under vacuum and cooling, the volatiles were analysed on a temperature-programmed (60–180 C) gas liquid chromatography (GLC) apparatus (column diameter, 4 mm; immobile phase: 10% PEGA on Gaschrom. Q) fitted with stream splitter and flame-ionization detector. The eluting peaks were then assessed for odor. The peak with the odor resembling the flavor of the original hardened peanut oil was trapped in a condenser, cooled with liquid nitrogen, and subsequently taken up in carbonyl-free hexane. The characteristic odor of the hardened peanut oil was easily perceptible in the hexane solution.

Investigation Into the Carbonyl Function

A portion of the concentrated compounds was converted into their DNPHs according to Schwartz et al. (4), after which procedure the smell had disappeared but was observed again after hydrolysis of a small amount of the DNPHs. This indicates the hardening flavor has a carbonyl group.

Chromatography of DNPH Derivative

The rest of the DNPHs was chromatographed on Silica Gel G plates impregnated with 30% $AgNO_3$ (5). The DNPHs gave only one band. The UV maximum at a wavelength of 374 nm, measured in chloroform, showed that the hardening flavor was a 2-enal. IR measurements showed characteristic absorptions at 990 and 1640 cm^{-1}, indicating the presence of a 2-*trans*-alkenal DNPH.

Ozonolysis

To collect more data on the chain length of the aldehyde, part of the DNPH, dissolved in carbonyl-free pentane, was treated with ozone at −70 C. The ozonide formed was reduced with triphenylphosphine and the carbonyls formed were analyzed by GLC, the conditions of which were equal to those mentioned above.

The chromatogram showed that mainly heptanal had been formed.

Comparison with Model Substance

From the above investigation of the chemical structure, the following indications have been obtained: UV analysis, aldehyde with a double bond at the 2 position; IR analysis, 2 *trans*-alkenal; and ozonolysis, presence of a straight saturated chain with 7 C atoms in the molecule.

These data suggest that the hardening flavor is 2 *trans*-nonenal.

For a further identification, various properties of the isolated hardening flavor were compared with those of synthetic 2-*trans*-nonenal purified by gas chromatography. Several characteristics of this commercial 2-*trans*-nonenal have been determined.

Flavor of the Aldehyde

The flavor of the synthetic compound appeared to be identical with that of the isolated carrier.

Retention Time on GLC Columns

The retention time of synthetic 2-*trans*-nonenal as well as that of the hardening flavor carrier was determined by GLC using silicone oil and PEGA as immobile phases. On both columns, the carbon numbers of 2-*trans*-nonenal appeared to be 9.6 and 10.6 respectively, which are in agreement with those of the isolated flavor.

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[1] Presented at the ISF-AOCS World Congress, Chicago, 1970.

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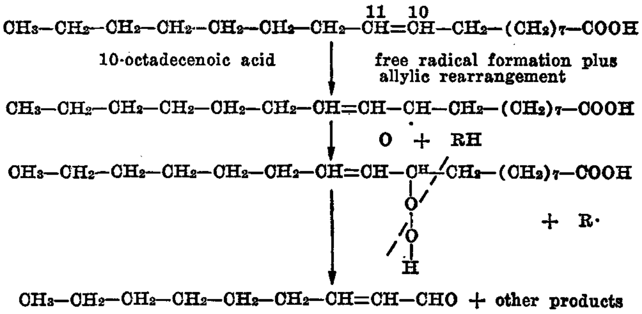
Chromatographic Behavior on Different TLC Plates

The chromatographic behavior of 2-*trans*-nonenal-DNPH prepared from the purified commercial compound were compared with the DNPH of the hardening flavor carrier using kieselguhr G plates impregnated with 33.3% Carbowax 400 as well as on Silica Gel G plates impregnated with 30% $AgNO_3$ (5). On both plates, the Rf values of the DNPH of the hardening flavor carrier and that of 2-*trans*-nonenal DNPH were identical.

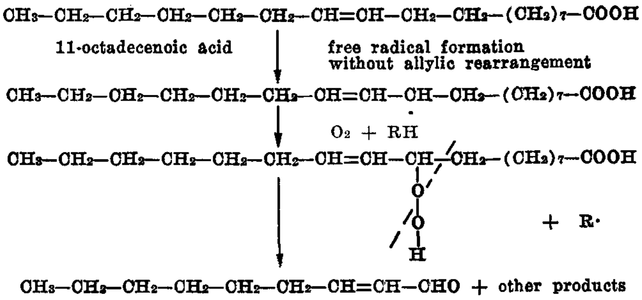
The conclusion may therefore be drawn that the aldehyde which was isolated as carrier of the hardening flavor is identical with 2-*trans*-nonenal.

Precursors of the Hardening Flavor

On hardening linoleic or oleic acid, or both, iso-oleic acids are formed. Allen and Kiess (6,7) found that, on hydrogenation of linoleic or oleic acid, both 10-*trans*-octadecenoic- and 11-*trans*-octadecenoic acid are formed. From the theory of autoxidation proposed by Farmer (8), these two iso-oleic acids could be precursors to the hardening flavor as is illustrated by the following mechanism:



and:



Additional evidence was obtained by using the analytical procedure of Hoffmann and Meijboom (9) by which we could indeed establish the presence of 2-*trans*-nonenal among the primary decomposition products of 11-octadecenoic acid (vaccenic acid).

The influence of the quality of the starting oil on the development of the hardening flavor may enhance the positional and geometrical isomerization of fatty acids via poisoning of the catalyst by oxidation products present in the oil.

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[Received December 2, 1970]