Iso-Linoleic Acids Responsible for the Formation of the Hardening Flavor[1]

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Abstract

The hardening flavor that develops in hydrogenated linseed oil and soybean oils during storage was recently identified as 6-nonenal. According to the theory of Farmer, certain *iso*-linoleic acids must be the precursors of this unsaturated aldehyde. By means of oxidation experiments on 9,15-, 8,15-, and 7,15-*iso*-linoleic acids, it was established that only the first two *iso*-acids are the precursors of this typical flavor.

Introduction

UNHARDENED SOYBEAN, LINSEED, AND MARINE OILS display to a greater or less extent a characteristic flavor deterioration that makes them less suitable for use in margarine, shortenings, or table oil. For this reason, and to obtain the consistency desired for edible fats, these oils are hardened. Yet it has been known for a long time that during the hydrogenation of linolenic acid-containing oils, such as soybean and linseed oils (1–6), as well as oils containing highly unsaturated fatty acids, certain flavoring components —hardening flavors—are formed which are not present in the unhardened products.

Hydrogenation under the influence of a nickel catalyst at normal hardening temperatures of 140–180C evokes in these products two distinct flavor types. One, the crude-hardened fat flavor, has not been further investigated since it can be completely and permanently removed by deodorization of the fat. The other flavor however is all the more unpleasant because it manifests itself rapidly even if the hardened fat is stored under normal conditions. A description of the isolation of this main hardening flavor (6-nonenal) was published earlier in this Journal (7).

Further investigation with different synthesized *iso*-linoleic acids has proved that only certain *iso*-acids, originating from linolenic acid which is present in unhardened fats, serve as precursors for this typical flavor.

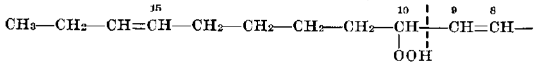
Procedure and Discussion

The methyl 9-*cis*,15-*cis*-, 8-*cis*,15-*cis*-, and 7-*cis*,15-*cis*-octadecadienoates were synthesized by Stroink and Sparreboom (15). Autoxidation experiments on these unsaturated esters were carried out as follows. Each sample of about 4 g was stirred under pure oxygen at 37C and atmospheric pressure for 12 hr. The oxidation products, which had peroxide values (PO-values) varying between 1.5 and 17.0, were first heated in a closed system under nitrogen at 100C for one hour to decompose the peroxides formed and were subsequently degassed (8) at 40C for five hours (pressure $< 10^{-5}$ mm Hg).

The volatile carbonyl decomposition products were converted into their 2,4-dinitrophenylhydrazones (DNPHs) (9). Analysis of these DNPHs by TLC (10–12) on 33.3% Carbowax 400, silica gel G, and 30% $AgNO_3$ impregnated silica gel G, showed that 6-*cis*-nonenal was formed in the experiments with 9-*cis*,15-*cis*- and 8-*cis*,15-*cis*-octadecadienoates.[2] The identity of the DNPH of this aldehyde was proved by the three Rf-values obtained which were identical with those of the model substance. With the 7-*cis*,15-*cis*-isomer, no 6-*cis*-nonenal could be detected although the detection limits of the chromatographic systems mentioned are extremely low (0.2–1 μg).

In the early stages of autoxidation the hardening flavor is formed, according to the theory of Farmer (13), from:

a) the hydroperoxide at C-atom 10 formed from 9,15-dienoic acid *with* allylic rearrangement:

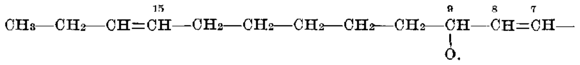


$$CH_3{-}CH_2{-}CH{=}\overset{15}{C}H{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\underset{\textstyle OOH}{\overset{10}{C}H}\,\vdots\,{-}\overset{9}{C}H{=}\overset{8}{C}H{-}$$

and

b) the hydroperoxide at C-atom 10 which was formed from 8,15-dienoic acid *without* allylic rearrangement. This hydroperoxide is identical with that from 9,15-dienoic acid mentioned under a).

Other possible autoxidations of the 8,15- and 9,15-dienoic acids do not lead to the formation of 6-nonenal as a primary decomposition product. The 6-nonenal is not formed directly from the 7,15-dienoic acid on hydroperoxide formation at C-atom 9, according to Farmer. From the alkoxy free radical



$$CH_3{-}CH_2{-}CH{=}\overset{15}{C}H{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\underset{\textstyle \dot{O}}{\overset{9}{C}H}{-}\overset{8}{C}H{=}\overset{7}{C}H{-}$$

an α,β-unsaturated aldehyde group and an alkyl free radical with 9 C-atoms, viz., $CH_3{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\dot{C}H_2$, are formed. This radical might be converted into 6-nonenal only by further oxidation. Since 6-nonenal was not found, in the early stage of autoxidation this mechanism is doubtful.

On semiquantitative determination of the primary carbonyl decomposition products from autoxidized 9-*trans*,15-*trans*-octadecadienoate (700 mg; PO-value 17.0) some 6% of 6-*trans*-nonenal was found in addition to the seven other aldehydes (four aldehydes from every double bond). These accompanying aldehydes may also contribute to the hardening flavor. However, after an investigation into the relationship between molecular structure and flavor perceptibility of aliphatic unsaturated aldehydes (14), it was established that an unsaturated aldehyde with a C_9-carbon chain and an isolated *trans* double bond at the terminal 3-position has the most intensive odor and taste. The threshold value of 6-*trans*-nonenal in paraffin oil for odor and taste are 0.005 and 0.0003 ppm respectively.

Moreover, in the analysis of these autoxidation products, only the DNPH of 6-nonenal displayed the typical hardening flavor. This is attributed to an

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[1] Part of paper presented by G. J. Henning, AOCS Meeting, Philadelphia, October 1966.

[2] The detailed analysis of the accompanying decomposition products will be published.

extremely slight spontaneous hydrolysis of the DNPH. The other DNPHs obtained in this way released hardly any flavor and certainly not one reminiscent of the hardening flavor.

On the basis of the oxidation experiments it can be concluded that 6-nonenal is formed as a primary decomposition product only from the oxidized 9,15- and 8,15-octadecadienoates and not from the 7,15-isomer. Only the first two *iso*-linoleic acids, formed on the hydrogenation of linolenic acid-containing oils, can be held responsible for the occurrence of the hardening flavor.

ACKNOWLEDGMENT

Experiments carried out by A. W. Schoenmakers, J. Th. de Goey, J. Bosma, G. A. Jongenotter, and Mrs A. Meyer-Broersen.

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[Received March 27, 1967]