The Synthesis of 2-(1-Pentenyl) Furan and Its Relationship to the Reversion Flavor of Soybean Oil[1]

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ABSTRACT

Cis and *trans*-2-(1-pentenyl) furan were postulated as possible contributors to the reversion flavor of soybean oil. These compounds were synthesized, and structures were confirmed by infrared, nuclear magnetic resonance, and mass spectroscopy. Organoleptic evaluation of them in oil suggested that they could contribute to the beany and grassy note of the reverted soybean oil. This approach to flavor problems of food was given a new name – reverse phase flavor chemistry.

INTRODUCTION

The development of a characteristic, objectionable, beany and grassy flavor in soybean oil, commonly known as reversion flavor, is an important classical problem of the food industry. Soybean oil tends to develop this objectionable flavor when its peroxide value is still as low as a few meq/kg while other vegetable oils, such as cottonseed, corn, and sunflower, do not.

The reversion flavor of soybean oil is not only a factor in depressing its market value but also makes it necessary to hydrogenate or hydrogenate and winterize it before it can be used as a good cooking oil or salad oil. Hydrogenation, of course, adds to the cost to the consumer of this major edible oil. In addition, it creates geometrical and positional isomers and decreases polyunsaturated fatty acid content, both of which have been claimed by researchers (1,2) as being undesirable to human health.

The search for the mechanism of the formation of reversion flavor in soybean oil, particularly the identification of the compound or compounds which are responsible for this objectionable flavor, has been conducted extensively (3-5). Smouse and Chang (6) systematically identified 71 compounds in the volatiles of a typical reverted-but-not-rancid soybean oil with a peroxide value of 4.3 meq/kg. They found that 2-n-pentyl furan significantly contributes to the beany and grassy flavor of soybean oil. The addition of 2 ppm of this compound to a freshly deodorized, bland oil of any kind will make it taste like reverted soybean oil.

Chang et al. postulated and later confirmed by laboratory experiments (6,7) that 2-n-pentyl furan can be formed from linoleate through autoxidation as shown in Figure 1. A linoleate could easily form a peroxide and then decompose to form the aldehyde according to Farmer's theory. It can then add a molecule of oxygen directly and then decompose to diradicals, according to Allen and Kummerow (8), which can then form the keto-aldehyde by the mechanism proposed by Bell (9). Enolization followed by dehydration will produce the 2-n-pentyl furan.

One obvious question concerning this hypothesis will immediately arise if one examines the fatty acid composition of soybean oil and other oils which have no reversion tendency (Table I). If indeed 2-n-pentyl furan is responsible for the reversion flavor, and, if indeed 2-n-pentyl furan is formed by the autoxidation of linoleate, then cottonseed, corn, and sunflower oils, with a high linoleic acid content, should also develop a beany and grassy flavor; but, they do not.

The fatty acid, which is present in soybean oil at 7%, but only in trace amounts in the nonreversion oils, is linolenic acid. It is, therefore, logical to think that the linolenate undergoes the same autoxidation reactions as linoleate to produce unsaturated pentyl furans, which then serve as the precursors of reversion flavor. This hypothesis appears quite attractive because linolenate is more prone to autoxidation. It has been reported (10) that the relative rate of oxidation of linolenate to linoleate is 100:42. Whether the presence of linoleate can retard the autoxidation of linolenate or the presence of linolenate can accelerate the autoxidation of linoleate has not been ascertained. However, it is known that oils containing a significant amount of linolenic acid are less stable. Therefore, linolenate may produce the unsatu-

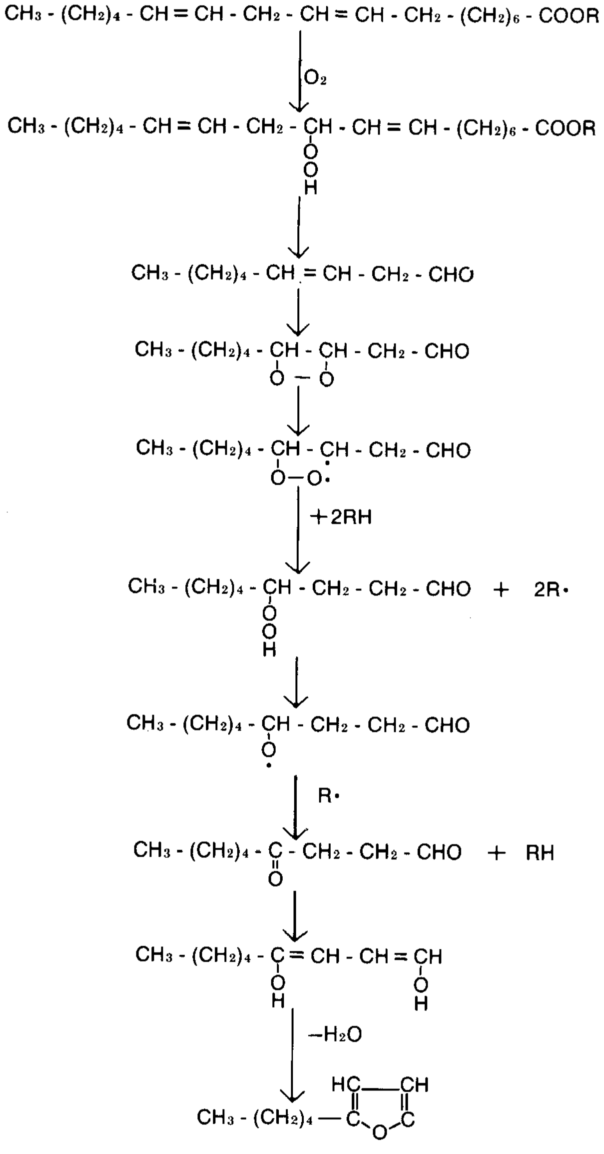

FIG. 1. Mechanism of the formation of 2-pentyl furan.

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TABLE I

Fatty Acid Composition of Common Vegetable Oils (%)

	Saturated	$C_{18,1=}$	$C_{18,2=}$	$C_{18,3=}$
Soybean oil	15	24	54	7
Cottonseed oil	26	22	52	Trace
Corn oil	15	29	56	Trace
Sunflower oil (southern)	10	37	52	Trace
Sunflower oil (northern)	10	19	70	Trace

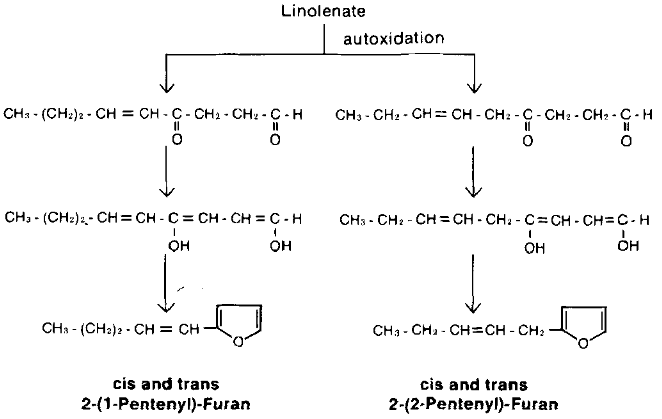

FIG. 2. Mechanisms of the formation of 2-(1-pentenyl) furan and 2-(2-pentenyl) furan.

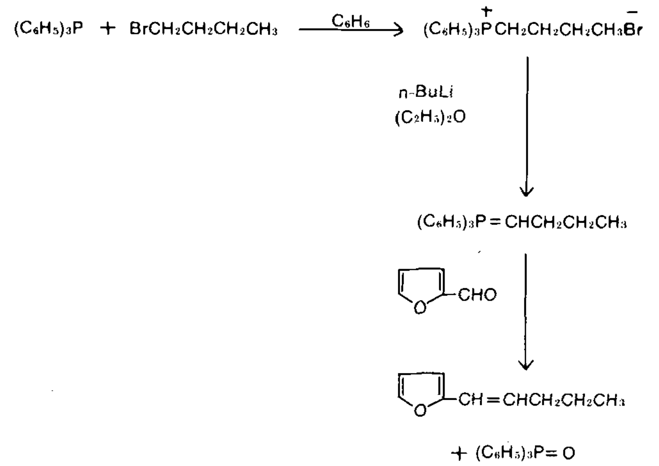

FIG. 3. Synthesis of 2-(1-pentenyl) furan.

rated pentyl furans at a faster rate than the formation of 2-n-pentyl furan from linoleate. Furthermore, the unsaturated pentyl furans may have lower odor and flavor thresholds than the saturated ones.

The present paper reports the synthesis of the *cis-* and *trans*-2-(1-pentenyl) furan and the study of their organoleptic properties.

EXPERIMENTAL PROCEDURE

Preparation of Triphenylbutylphosphonium Bromide

A mixture of 21.0 g (0.08 mol) of triphenylphosphine and 11.6 g (0.085 mol) of 1-bromobutane in 20 ml of dry benzene was refluxed with stirring for 2 days. The product was collected by suction filtration and dried in a vacuum oven at 100 C. Yield 32.0 g (quantitative).

Preparation of 2-(1-Pentenyl) Furan

To 35 ml of a cold solution of 1.6 M n-butyl lithium in hexane (0.056 mol) in 500 ml of anhydrous ether in a three-necked, round-bottomed flask equipped with a magnetic stirrer, a reflux condenser, a pressure equalizing dropping funnel, and a gas inlet tube, 18.0 g (0.045 mol) of triphenylbutylphosphonium bromide was added gradually. After 4 hr of stirring under nitrogen, 5.3 g (0.055 mol) of furfural in 50 ml of anhydrous ether was added dropwise. After refluxing overnight, the mixture was filtered by suction, the residue washed several times with 50-ml portions of water. The ethereal solution was dried over sodium sulfate, and the ether was removed by rotary evaporator. Yield 4.4 g of 2-(1-pentenyl) furan (71.1%).

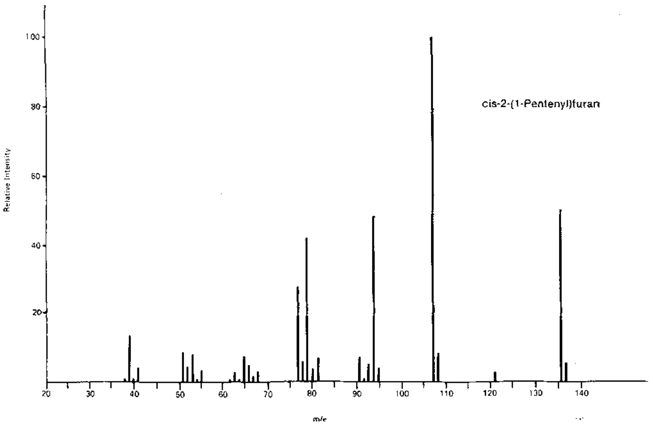

FIG. 4. Mass spectrum of *cis*-2-(1-pentenyl) furan.

Separation of *cis/trans* Isomers

The *cis/trans* isomers of the product were separated on an Aerograph A90P Gas Chromatograph using a 12 ft x ¼ in. preparative column of 10% SF96 on 70/80 mesh Anakrom ABS. The following conditions were employed:

Column temp	82 C
Detector temp	208 C
Injector temp	138 C
Flow rate (He)	30 ml/min

The retention times of the separated 5-μl samples were 42 min for *cis-* and 46 min for *trans*-2-(1-pentenyl) furan. The ratio of *cis:trans* isomers was 2.6:1.

Identification of 2-(1-Pentenyl) Furan

The exact mass and mass spectra were measured by a Hitachi Perkin Elmer RMU-7 mass spectrometer. Nuclear magnetic resonance (NMR) spectra were obtained on a Varian Associates Model T-60 NMR spectrometer. Infrared (IR) spectra were obtained in chloroform solution on a Beckmann IR-8 spectrometer using ultramicro sodium chloride cells of 0.1 mm light path.

Organoleptic Evaluations

A panel of six experienced tasters was used for organoleptic evaluations. Three samples were submitted to the panel at a time. Two of the samples were bland, freshly deodorized sunflower oil, and the other was the same oil with successively decreasing amounts of 2-(1-pentenyl) furan added. The panel members were asked to pick out the sample containing 2-(1-pentenyl) furan and to describe the odor and flavor characteristics of the sample. After the optimal concentration of the 2-(1-pentenyl) furan in oil was decided, another three samples were submitted to the panel. Two of the samples were reverted soybean oil and the other the bland sunflower oil with optimal concentration of 2-(1-pentenyl) furan added. The panel members were asked to pick out the sunflower oil with 2-(1-pen-

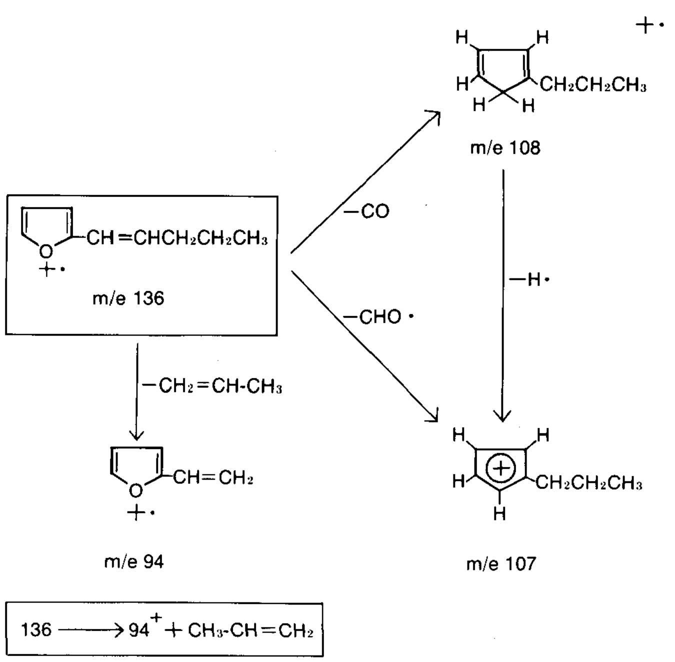

FIG. 5. Interpretation of the mass spectrum of *cis*-2-(1-pentenyl) furan.

tenyl) furan added and to describe the degree of resemblance of it from reverted soybean oil.

RESULTS AND DISCUSSIONS

Synthesis of 2-(1-Pentenyl) Furan

By the mechanisms proposed by Chang et al. for the formation of 2-n-pentyl furan, linolenate would produce four unsaturated pentyl furans as shown in Figure 2. They are the *cis* and *trans* forms of 2-(1-pentenyl) furan and 2-(2-pentenyl) furan.

The present paper reports the synthesis of *cis*- and *trans*-2-(1-pentenyl) furan and their relationships to reversion flavor. The study of *cis*- and *trans*- 2-(2-pentenyl) furan will be reported in a subsequent paper.

The 2-(1-pentenyl) furan was synthesized by Wittig reaction as shown in Figure 3. Triphenylphosphine was reacted with n-butyl bromide to form n-butyltriphenylphosphonium salts. Upon reaction with n-butyl lithium in ether solution, the salt released a proton to form an ylide (n-butylidenetriphenylphosphorane) which reacted with 2-furfural to form 2-(1-pentenyl) furan. The mixture was purified and fractionated by gas chromatography to yield pure *cis* and *trans* isomers.

Confirmation of Structures by Mass, IR, and NMR Spectra

The structures of the *cis*- and *trans*- isomers of 2-(1-pentenyl) furan were confirmed by Mass, IR, and NMR spectrometric analyses.

The exact mass of *cis*-2-(1-pentenyl) furan was determined to be 136.0884, while the exact mass of *trans*-2-(1-pentenyl) furan was found to be 136.0875. The empirical formula of the compound was, therefore, determined to be $C_9H_{12}O$ within 0.5 mmu error of the calculated mass, 136.0888.

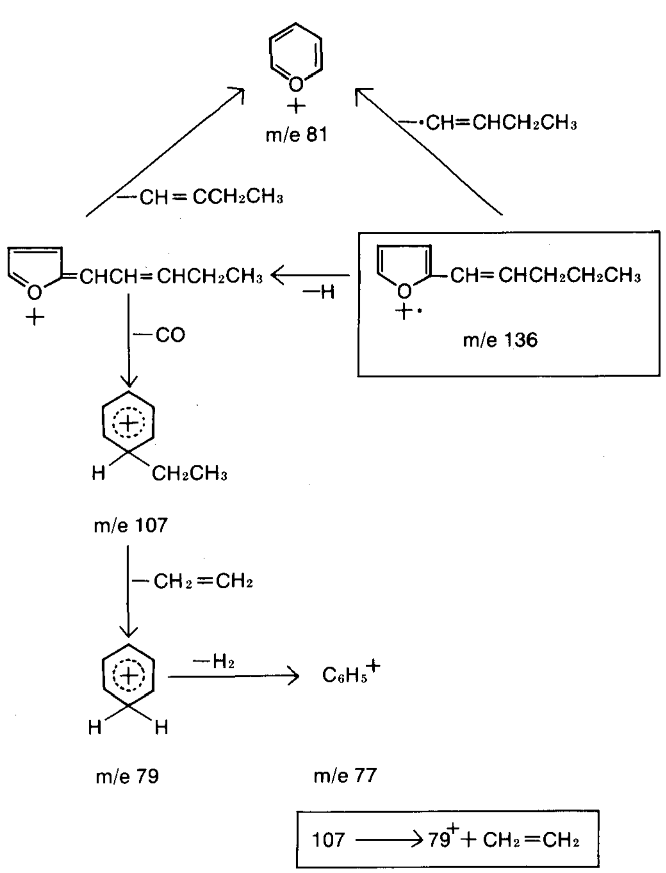

FIG. 6. Interpretation of the mass spectrum of *cis*-2-(1-pentenyl) furan.

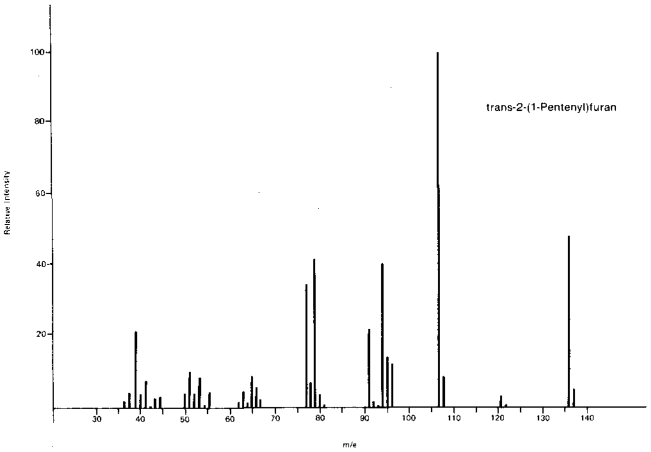

FIG. 7. Mass spectrum of *trans*-2-(1-pentenyl) furan.

The mass spectrum of *cis*-2-(1-pentenyl) furan is shown in Figure 4. The interpretation of the mass spectrum is shown in Figures 5 and 6. The base ion observed at m/e 107 may be produced by the loss of CO from the parent ion with recyclization to form the cyclopentadiene radical ion which further loses a hydrogen atom forming the stable cyclopentadienyl ion (m/e 107). Alternatively, loss of CHO from the parent ion also leads to the cyclopentadienyl ion. The metastable ion observed at m/e 84.2 confirms that the m/e 107 ion is the daughter ion of m/e 136. The fragmentation mechanism for the formation of m/e 94, 81, 79, 77 is interpreted in those figures. The observation of metastable peaks at 65 and 58.3 confirms the following transitions:

$$136^+ \rightarrow 94^+ + CH_3 - CH = CH_2$$

and

$$107^+ \rightarrow 79^+ + CH_2 = CH_2.$$

The mass spectrum of *trans*-2-(1-pentenyl) furan shown in Figure 7 closely resembles that of its *cis* isomer.

The infrared spectrum of *cis*-2-(1-pentenyl) furan shown in Figure 8 indicated that it is an alkyl-substituted furan

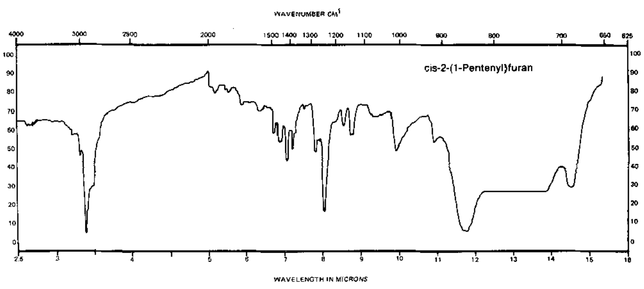

FIG. 8. Infrared absorption spectrum of *cis*-2-(1-pentenyl) furan.

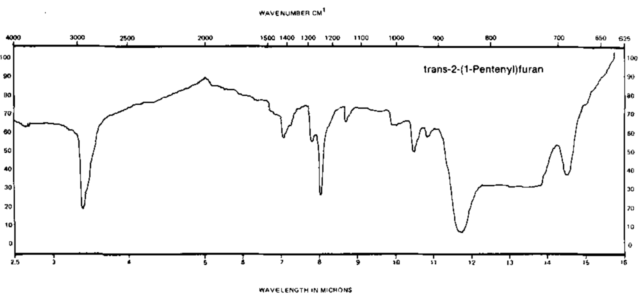

FIG. 9. Infrared absorption spectrum of *trans*-2-(1-pentenyl) furan.

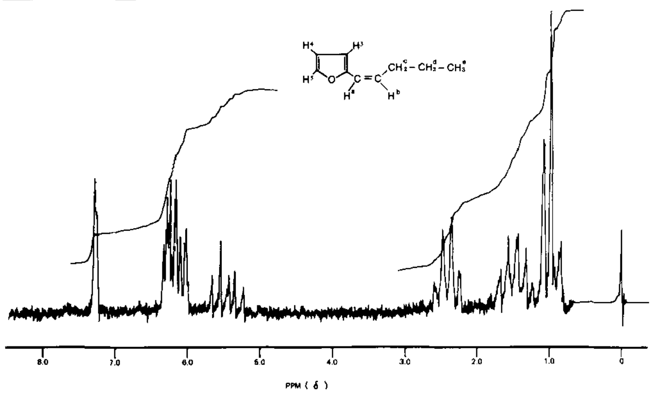

FIG. 10. Nuclear magentic resonance spectrum of *cis*-2-(1-pentenyl) furan.

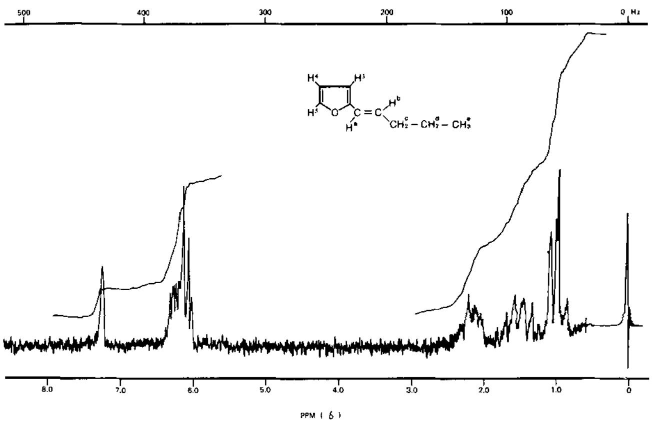

FIG. 11. Nuclear magnetic resonance spectrum of *trans*-2-(1-pentenyl) furan.

compound. The absorption bands at 3.3, 6.35, and 6.7μ were characteristic of a furan ring (7).

The infrared spectrum of *trans*-2-(1-pentenyl) furan (Fig. 9) and the absorption band at 10.46μ clearly indicate the *trans* olefinic structure.

In the NMR spectrum of *cis*-2-(1-pentenyl) furan, (Fig. 10), the doublet of triplet splitting at δ5.47 was due to olefinic proton H^b. The spin-spin coupling constant J_{ab} = 12 cps and J_{bc} = 6.8 cps suggested that it is *cis* olefin. The methylene protons adjacent to the double bond showed a quartet at δ2.43, while the methylene protons adjacent to methyl groups showed a sextet at δ1.25. The methyl protons had a triplet pattern with spin-spin coupling constant J_{de} = 6.8 cps. The three protons on the furan ring and the olefinic proton adjacent to the furan ring showed a singlet at δ7.29 and a multiplet between δ6.03 and δ6.43.

The NMR spectrum of *trans*-2-(1-Pentenyl) furan (Fig. 11) was different from its *cis* isomer in that the olefinic proton, H^b was no longer separated from the furan ring protons and the olefinic proton H^a.

The Organoleptic Characteristics of 2-(1-Pentenyl) Furans

The *cis*- and *trans* 2-(1-pentenyl) furans in concentrated form both have a licorice odor. This is interesting because this term is sometimes used by oil chemists to describe reversion flavor. It should be noted, however, that in concentrated form, these two compounds imparted no beany and grassy odor to the organoleptic panel members.

The flavor threshold of *cis*-2-(1-pentenyl) furan in oil at room temperature is ca. 6 ppm, while the *trans*-2-(1-pentenyl) furan has a flavor threshold of only 1 ppm. This was determined by submitting samples of various concentrations to an organoleptic panel.

At a concentration of 8 ppm, the *cis* isomer in a freshly deodorized sunflower oil had a characteristic odor and flavor slightly reminiscent of that of reverted soybean oil. The *trans* isomer at a concentration of 2 ppm in oil had an odor and flavor moderately suggestive of those of reverted soybean oil.

The organoleptic results, therefore, suggest that the *cis*- and *trans*-2-(1-pentenyl) furans could contribute to the reversion flavor of soybean oil if they are formed by the autoxidation of linolenate.

Reverse Phase Flavor Chemistry

We are giving the method we are using in this study a new name – Reverse Phase Flavor Chemistry – which we think is an alternate approach to solving flavor problems of food.

In the normal steps of flavor identification, the volatile compounds responsible for the aroma must first be isolated from the food. The isolated flavor is then fractionated into pure components by gas chromatography. The pure fractions are identified by IR, mass and NMR spectroscopy. The identification of these spectra is confirmed by comparison with those of authentic compounds. Finally, the identified components are evaluated organoleptically to determine their odor and flavor characteristics.

The flavor of a food is usually a very complex mixture of compounds. With the advancement of gas chromatography with glass capillary columns, hundreds of peaks may be obtained. The identification of the key compounds which contribute predominantly to the characteristic odor and flavor of food becomes extremely difficult. Therefore, the reverse phase flavor chemistry as described in this paper might serve as an alternate approach to flavor chemistry.

In this method, the chemical structures of possible flavor compounds are postulated from known constituents of the food with established mechanisms. The postulated compounds are then synthesized, and their structures are confirmed. The organoleptic properties of these authentic compounds can then be characterized by an organoleptic panel to determine whether they are important to the flavor in question. If they are, then their presence in the food can be easily established because their retention times are already known.

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