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

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ABSTRACT

cis- and *trans*-2-(2-Pentenyl)furans were synthesized and structures were confirmed by infrared, nuclear magnetic resonance and mass spectroscopy. Preliminary organoleptic evaluation of oil solutions of the compounds indicated that the *cis* isomer had a flavor threshold of ca. 0.25 ppm. with odor and flavor descriptions of beany, grassy and buttery at 0.50 ppm; and that the *trans* isomer had a flavor threshold of ca. 0.50 ppm with odor and flavor descriptions of beany, grassy and buttery at 1 ppm and strong painty and metallic at 4 ppm. These compounds, if found in soybean oil through the autoxidation of linolenate, may contribute to the characteristic reversion flavor.

INTRODUCTION

It was proposed in a recent publication (1) that linolenate may undergo the same autoxidation reactions as postulated by Chang et al. (2) for the formation of 2-pentyl furan from linoleate. The compounds which would form from linolenate via this mechanism are *cis*- and *trans*-2-(1-pentenyl)furan and 2-(2-pentenyl) furan. The synthesis and organoleptic characteristics of 2-(1-pentenyl)furan were reported in a previous publication (1). The present paper reports the synthesis and odor and flavor evaluation of *cis*- and *trans*-2-(2-pentenyl)furan.

EXPERIMENTAL PROCEDURE

Preparation of cis-2-Penten-1-ol

To 8.4 g (0.1 mole) or 2-pentyn-1-ol in 50 ml of hexane, 200 ml of 1 M diisobutylaluminum hydride (0.2 mole) in hexane was added dropwise. After addition, the mixture was refluxed overnight with stirring. To the reaction mixture, at room temperature, 100 ml of water was added. The mixture was filtered with suction, the aqueous layer extracted with ether, and the combined organic layers washed with water. The solution was dried over anhydrous sodium sulfate and the solvent removed with the use of a rotary evaporator. The yield was 5.4 g (60% of theory).

Preparation of cis-1-Bromo-2-Pentene

To 3.5 g of phosphorus tribromide (0.039 mole) in 5 ml of petroleum ether and one drop of dry pyridine, 3.2 g of ice-cold *cis*-2-penten-1-ol (0.037 mole) in 0.5 ml of dry pyridine and 5 ml of petroleum ether was added. The mixture was stirred in an ice bath during the addition, then at room temperature for one hour. The mixture was washed with a sodium bicarbonate-ice water solution, dried with anhydrous sodium sulfate, and the solvent removed by rotary evaporator. The yield was 3.5 g (67% of theory).

Preparation of cis-2-(2-Pentenyl)Furan

To 13.34 ml of 1.6 M solution of *n*-butyl lithium (0.021 mole) in 18 ml of tetrahydrofuran at -25 C, 1.33 g of furan (0.019 mole) was added dropwise. The mixture was stirred under nitrogen for 4 hr at -15 C. To the mixture, 2.9 g of *cis*-1-bromo-2-pentene (0.019 mole) in 2 ml of tetrahydrofuran was added. The solution was stirred for 1hr after addition, then at room temperature overnight. The mixture was poured over crushed ice, the layers separated, and the aqueous layer extracted with ether. The combined organic layers were dried with anhydrous sodium sulfate and the ether removed by rotary evaporator. The yield was 1.9 g (72% of theory).

Preparation of Trans-2-Penten-1-ol

To a -78 C, mechanically stirred solution of 4.6 g of sodium in 200 ml of anhydrous liquid ammonia, 4.2 g of 2-pentyn-1-ol (0.05 mole) was added gradually. After addition, stirring was continued for 4 hr then 15 g of ammonium chloride was added. The ammonia was removed and water and ether added to the residue. The organic extracts were washed with diluted sulfuric acid, sodium bicarbonate solution, and water. The solution was dried over anhydrous sodium sulfate, and the ether was removed by rotary evaporator. The yield was 3.9 g (90% of theory).

Preparation of Trans-1-Bromo-2-Pentene

trans-1-Bromo-2-pentene was prepared from *trans*-2-penten-1-ol employing the same procedures used for *cis*-1-bromo-2-pentene. The yield was 3.5 g (67% of theory).

Preparation of Trans-2-(2-Pentenyl)Furan

trans-2-(2-Pentenyl)furan was synthesized by the same procedures described under *cis*-2-(2-pentenyl)furan. The yield was 2.0 g (76% of theory).

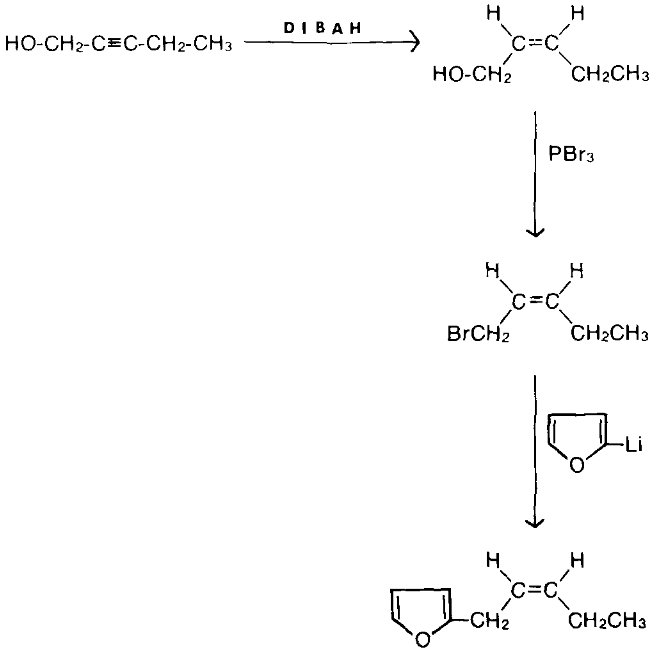

FIG. 1. Synthesis of *cis*-2-(2-Pentenyl)Furan.

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[1] Paper of the Journal Series, New Jersey Agricultural Experiment Station, Cook College, Rutgers, The State University of New Jersey.

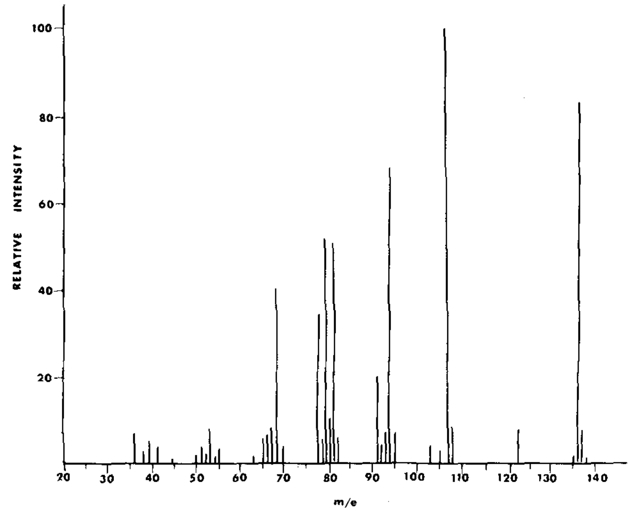

FIG. 2. Mass Spectrum of *cis*-2-(2-Pentenyl)Furan.

Purification of 2-(2-Pentenyl) Furans

The compound identified as *cis*-2-(2-pentenyl)furan was purified by gas chromatography on a ¼ in. x 10 ft. column packed with 10% SE-30 on 70/80 mesh Anakrom ABS at a temperature of 102 C with a helium flow rate of 72 ml/min. The retention time for *cis*-2-(2-pentenyl)furan was 11 min. In a similar manner, *trans*-2-(2-pentenyl)furan was purified on a 1/8 in. x 10 ft. column packed with 10% SE-30 on 70/80 mesh Anakrom ABS at a temperature of 87 C and a flow rate of 60 ml/min. Retention time was 6.5 min.

Identification of 2-(2-Pentenyl) Furan

The mass spectra were obtained on a DuPont 21-490 mass spectrometer. Nuclear magnetic resonance spectra were obtained on a Varian Associates Model T-60 NMR spectrometer. Infrared spectra were obtained on a Beckman Acculab 4 IR spectrometer using ultramicro sodium chloride cells of 0.1 mm light path.

Organoleptic Evaluations

A panel of four experienced tasters was used for organoleptic evaluations. Three samples at 60 C were submitted to the panel at a time. One of the samples was a bland, freshly deodorized sunflower oil, and the others were the same oil with successively increasing amounts of 2-(2-pentenyl)-furan. The panel members were asked to pick out the sample containing 2-(2-pentenyl)furan, thus determining the threshold concentrations, and to describe the odor and flavor characteristics of the sample.

RESULTS AND DISCUSSION

Synthesis of Cis-2-(2-Pentenyl) Furan

The *cis* isomer of 2-(2-pentenyl)furan was synthesized according to the scheme shown in Fig. 1. 2-Pentyn-1-ol was reduced with two equivalents of diisobutylaluminum hydride (DIBAH) (3). One equivalent of DIBAH served as the protecting agent for the hydroxyl group while the other complexed stereospecifically with the triple bond. Hydrolysis yielded *cis*-2-penten-1-ol. This alcohol was then reacted with phosphorous tribromide to form *cis*-1-bromo-2-pentene (4). In the final reaction, furan was alkylated at the 2- position by the reaction of *cis*-1-bromo-2-pentene with the butyl lithium generated furyl anion to form *cis*-2-(2-pentenyl)furan (5,6).

The mass spectrum of *cis*-2-(2-pentenyl)furan is shown in Fig. 2. The molecular ion observed at m/e 136 agrees with the empirical formula $C_9H_{12}O$.

The infrared spectrum of *cis*-2-(2-pentenyl)furan (Fig. 3) indicated that it is an alkyl-substituted furan. The absorption bands at 3,030, 1,613, and 1,518 cm^{-1} are characteristic of a furan ring, while the strong C-H scissoring band at 1,471 cm^{-1} is indicative of alkyl substitution.

The NMR of *cis*-2-(2-pentenyl)furan, shown in Fig. 4, exhibits chemical shifts similar to those previously reported for *cis*-2-(1-pentenyl)furan (1).

Synthesis of Trans-2-(2-Pentenyl) Furan

In the synthesis of *trans*-2-(2-pentenyl)furan (Fig. 5), 2-pentyn-1-ol was reduced to *trans*-2-penten-1-ol by reduc-

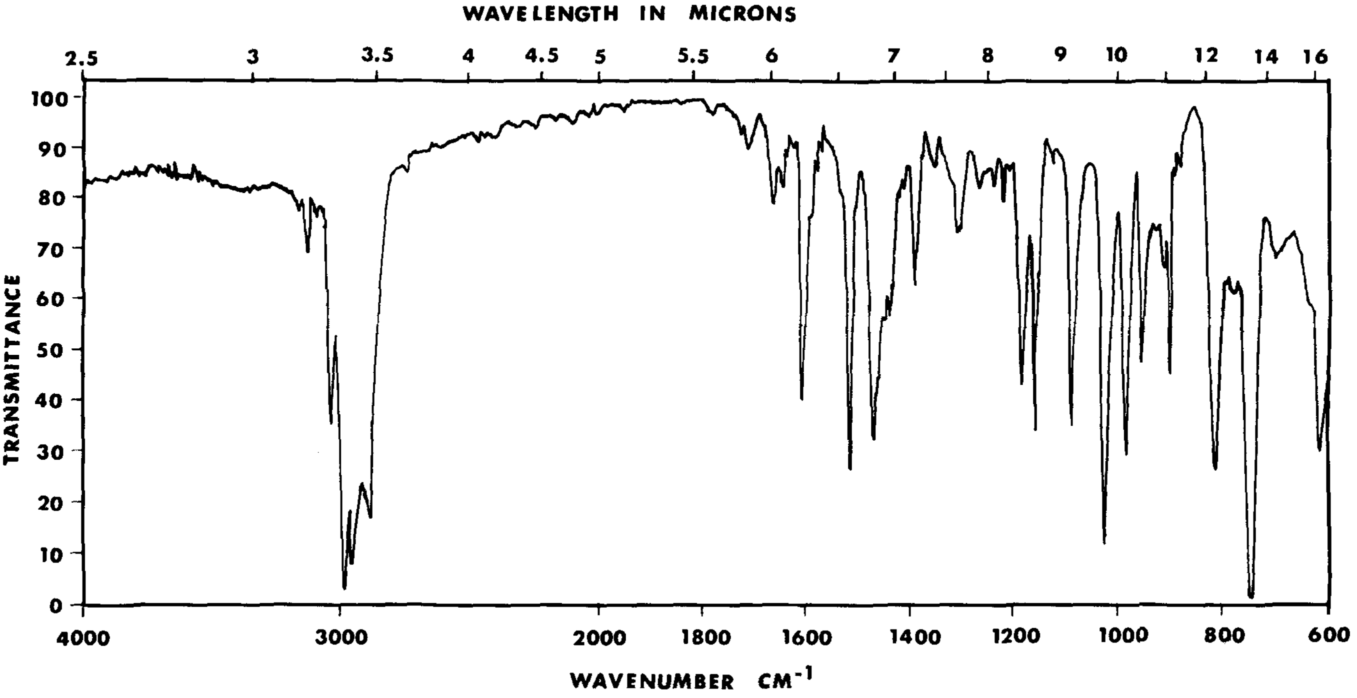

FIG. 3. Infrared Absorption Spectrum of *cis*-2-(2-Pentenyl)Furan.

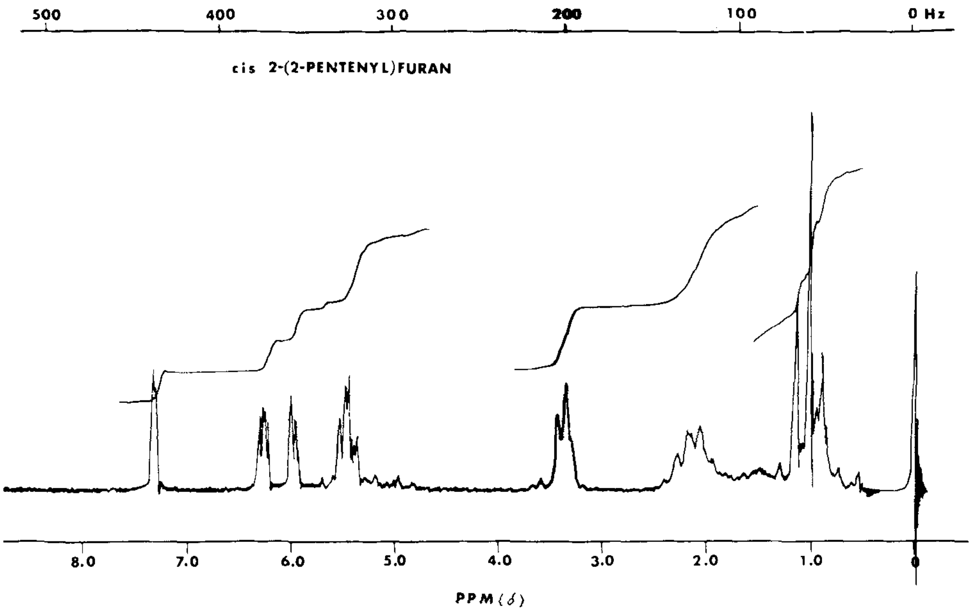

FIG. 4. Nuclear Magnetic Resonance Spectrum of *cis*-2-(2-Pentenyl)Furan.

tion with sodium in anhydrous liquid ammonia (4). The *trans* alcohol was brominated, as in the *cis* case, with phosphorus tribromide, and furan alkylated to form *trans*-2-(2-pentenyl)furan. The mass spectrum of *trans*-2-(2-pentenyl)furan (Fig. 6) resembles that of a *cis* isomer.

Figure 7 shows the infrared spectrum of *trans*-2-(2-pentenyl)furan. The strong absorption at 970 cm^{-1} indicates a *trans* olefinic structure.

The NMR spectrum of *trans*-2-(2-pentenyl)furan is shown in Fig. 8. The chemical shift of *cis*-2-(2-pentenyl)-furan (Fig. 4) exhibits a greater downfield shift from olefinic protons compared to that of the *trans* isomer. This is in agreement with anisotropic shielding concepts.

The Organoleptic Characteristics of 2-(2-Pentenyl)Furan

Both the *cis*- and *trans*-2-(2-pentenyl)furans have a strong odor and flavor and thus a low threshold. The *cis*-isomer has a flavor threshold in oil at 60 C. of ca. 0.25 ppm while the *trans* isomer has a threshold of ca. 0.5 ppm. If these compounds are, indeed, present in reverted soybean oil, then their low threshold concentration may explain why they have not been isolated and identified from reverted soybean oil.

At a concentration of 0.5 ppm in freshly deodorized sunflower oil, the odor and flavor of *cis*-2-(2-pentenyl)furan was described as beany, grassy and buttery, all of which have been used to describe reverted soybean oil. The *trans* isomer at a concentration of 1 ppm in oil had a similar odor and flavor. Upon increasing the concentrations of both samples to 4 ppm, differences were observed between the *cis* and *trans* isomers. At the higher concentrations, *cis*-2-(2-pentenyl)furan gave a grassy, buttery response, while the *trans* isomer yielded a strong, painty, metallic odor and flavor, reminiscent of that of a highly reverted soybean oil.

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

The isolation and identification of 2-pentenyl furans in a reverted soybean oil are now in progress.

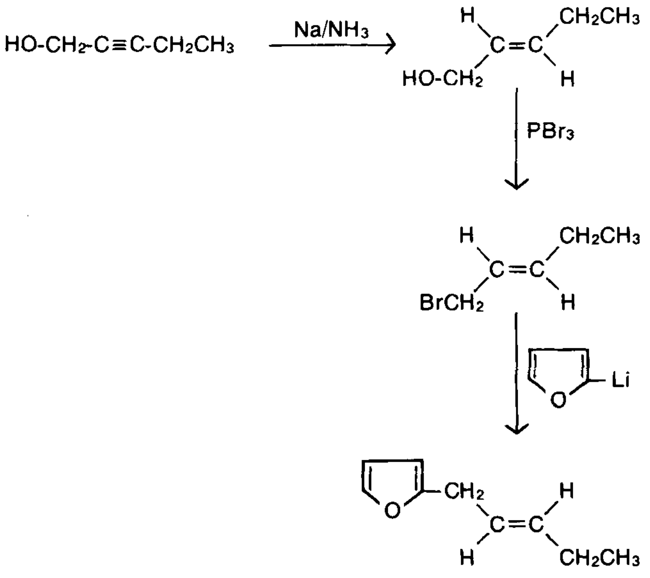

FIG. 5. Synthesis of *trans*-2-(2-Pentenyl)Furan.

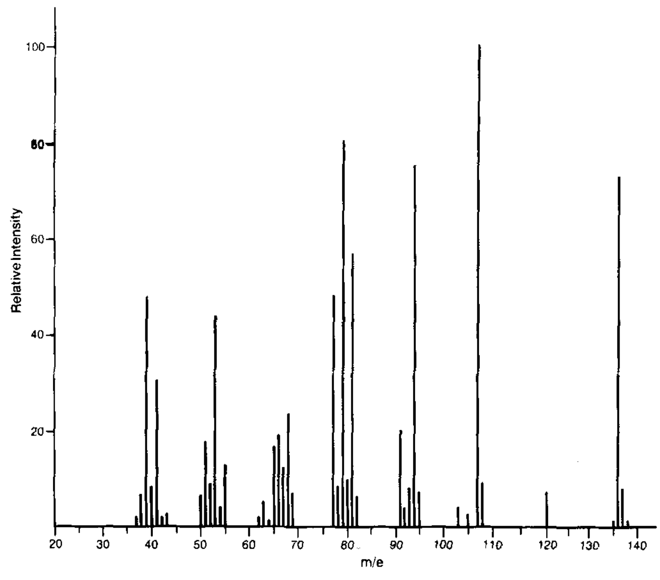

FIG. 6. Mass Spectrum of *trans*-2-(2-Pentenyl)Furan.

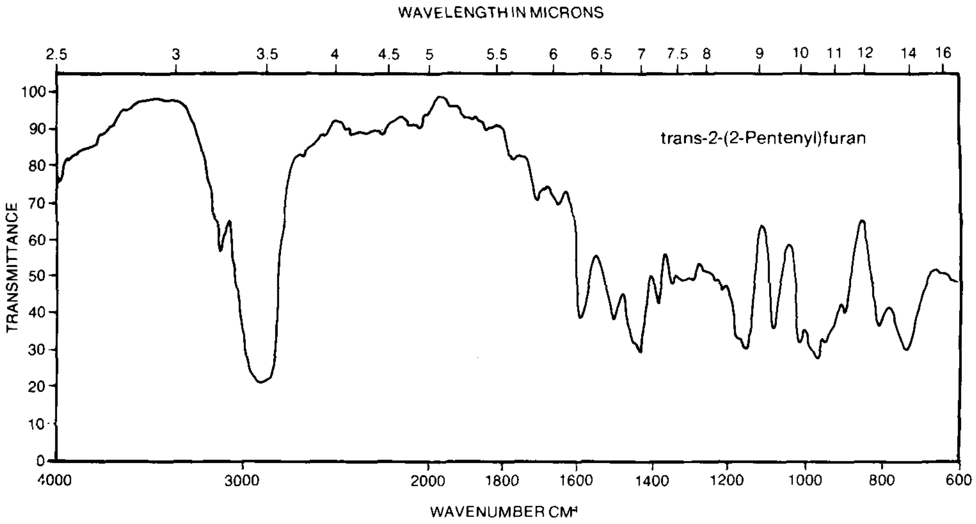

FIG. 7. Infrared Absorption Spectrum of *trans*-2-(2-Pentenyl)Furan.

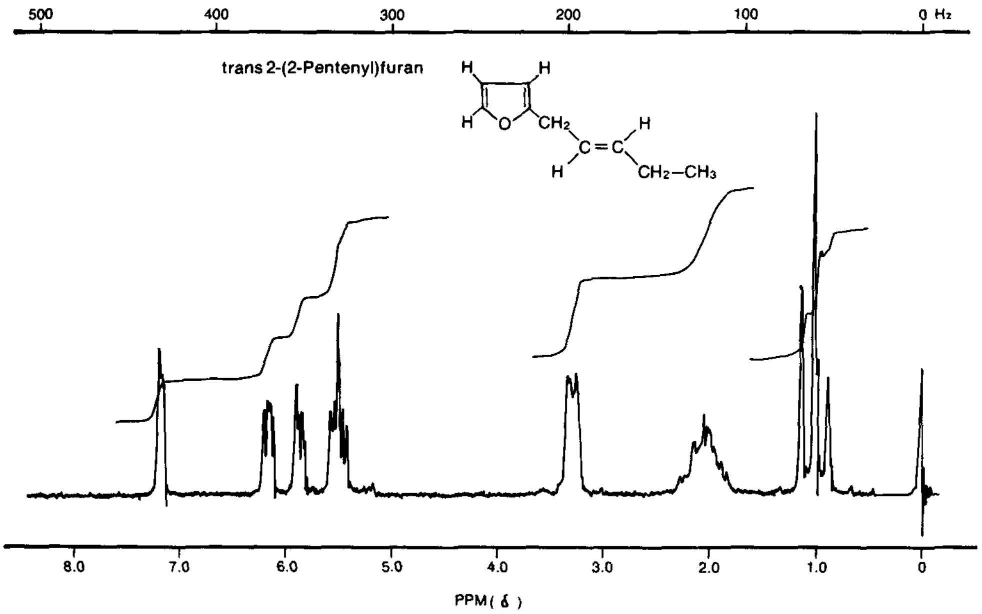

FIG. 8. Nuclear Magnetic Resonance Spectrum of *trans*-2-(2-Pentenyl)Furan.

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