Novel Furaldehydes from Oxidized Soy Phospholipids

A novel lipid oxidation product was isolated after HCl gas treatment of bitter-tasting soy phospholipids. It was identified by ultraviolet, infrared, proton nuclear magnetic resonance, and mass spectra as a 5-(pentenyl)-2-furaldehyde. Another furaldehyde, probably arising from decomposition of the pentenylfuraldehyde and subsequent reaction with HCl gas, was identified as chloromethylfuraldehyde. Although these furaldehydes possess a licorice odor, their contribution to flavor in soy has yet to be determined.

Lipids of green peas (*Pisum sativum*) and soybeans (*Glycine max*) have been extensively investigated because of their probable role in development of off-flavors during processing. Oxidized soy phosphatidylcholine (SPC) was shown to be a bitter principle in soybeans (Sessa et al., 1976). Most of the oxygenated fatty acids on the intact oxidized SPC have been identified (Sessa et al., 1977). Lovern (1952), and later Wagenknecht (1957) demonstrated the presence of plasmalogens, glycerophosphatides containing an acid-labile alkyl ether rather than the usual alkyl ester bond, in green peas and soybeans. This communication presents the identity of a novel aldehyde isolated from bitter-tasting SPC fraction when methods used for the isolation of bound fatty aldehydes were applied.

EXPERIMENTAL SECTION

Extraction and Isolation of Choline-Containing Phospholipids. Alcohol extracts (80% ethanol) of hexane-defatted soy flakes when chromatographed on a Sephadex LH-20 column yielded a crude phospholipid fraction (Sessa et al., 1976). Choline-containing phospholipids were isolated by column chromatography of this crude phospholipid fraction on acid-treated Florisil (Supelcosil ATF-061, Supelco Inc., Bellefonte, PA) (Sessa et al., 1974). Compounds eluting from this column with chloroform–methanol (1:1, v/v) and methanol were pooled and stripped of solvent on a rotary evaporator.

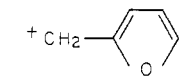
Isolation and Purification of Bound Fatty Aldehydes. Bound fatty aldehydes were released from the above fraction by HCl gas treatment (Ferrell et al., 1970). The reaction products dispersed in chloroform were chromatographed on acid-treated Florisil columns. Materials eluting with chloroform that possessed ultraviolet (UV) absorbance at 280 nm were pooled and stripped of solvent on a rotary evaporator. A purified aldehyde was obtained from these materials by preparative thin-layer chromatography (TLC) on 2-mm silica gel 60 F-254 plates (E. Merck, Darmstadt, Germany) developed with hexane–chloroform–methanol (73:25:2, v/v). The edge of the developed plate was sprayed with Purpald (Aldrich Chem. Co., Inc., Milwaukee, Wis.), the aldehyde-specific spray of Rahn and Schlenk (1973), to detect the aldehyde band. This band, extracted from silica gel with chloroform, filtered, and stripped of solvent was analyzed by UV, infrared (IR), high-resolution nuclear magnetic resonance (NMR), and gas–liquid chromatography–mass spectrometry (GC–MS) (Sessa et al., 1977).

RESULTS AND DISCUSSION

The components in the band obtained by preparative TLC possessed a single sharp UV maximum at 280 nm in chloroform with absorptivity of 69.3. IR spectrum in carbon tetrachloride had bands at 2750 and 2710 cm^{-1}, indicative of aromatic aldehyde CH stretch; 1692 cm^{-1} associated with conjugated carbonyl group; 1590, 1520, 1465 cm^{-1} for furan ring stretch; 1028 cm^{-1} for C–O–C symmetrical stretch; and 980 and 970 cm^{-1} for 2,5-disubstituted furan. When spectrum was rerun in carbon disulfide, bands at 805 and 765 cm^{-1} due to aromatic CH wag and at 770 and 725 cm^{-1} due to CH wag of C–Cl were noted.

Major NMR peaks of the aldehydic material and their respective assignments are: δ 4.61 (s, CH_2Cl), 6.59 (d, CH=C, J = 3.7 Hz), 7.20 (d, CH=C, J = 3.4 Hz), 9.65 (s, CHO). Absorption of olefinic protons and their coupling constants were indicative of a 5-substituted 2-furaldehyde. The presence of a second component was indicated by observation of minor absorption peaks at δ 0.88 (t, CH_3C), 1.26 (broad s, CH_2), and 2.33 (m, CH_2C=C), 5.36 (m, CH=CH), which signifies an unsaturated alkyl group.

Based on GC–MS analysis of the aldehydes, two separate peaks were noted. The major component (90%) is 5-chloromethyl-2-furaldehyde with molecular ion (M) at m/e 144 and 146 with ratio approximately 3 to 1, indicative of chlorine atom isomers; m/e 109 (M – 35), representing loss of chlorine atom; and m/e 80 for



The mass spectrum of a minor component (10%) illustrated in Figure 1 had a molecular ion (M) at m/e 164; m/e 135 (M – 29), representing loss of CHO; and m/e 107 (M – 57), representing a loss of CHOC=O analogous to that reported by Ho et al. (1978). The minor constituent, characterized as a 5-(pentenyl)-2-furaldehyde is consistent with GC–MS and NMR data. Definite location of the double bond on the pentenyl side chain has yet to be established.

Derivation of furaldehydes from lipids is unusual. They may arise from oxidation of decatrienal, a possible cleavage product arising from 9-hydroperoxylinolenic acid. Grosch and Schwencke (1969) identified 2,4-decadienal as an enzymatic decomposition product from action of soy lipoxygenase on linoleic acid. A furan ring may form via 1,4 addition of singlet oxygen on carbon atoms 2 and 5 of the decatrienal. Subsequent homolysis of the resulting cyclic peroxide and furan ring formation would follow the mechanism postulated by Turner and Herz (1977). Other routes of furan formation are via cyclodehydration of either diepoxy or diketo fatty acid (LieKenJie and Lam, 1977) or diols (Abbot et al., 1970). Chloromethylfuraldehyde may originate from HCl treatment of the pentenylfuraldehyde by a yet unknown mechanism. Location of double bond on the pentenyl furaldehyde and further study on the derivation of both isolated furaldehydes are currently being investigated.

Furanoid fatty acids have been isolated from fish lipids (Glass et al., 1975, 1977) and *Exocarpus* seed oil (Morris et al., 1966). Ho et al. (1978) reported on the synthesis of 2-(1-pentenyl)furan and suggested that this compound,

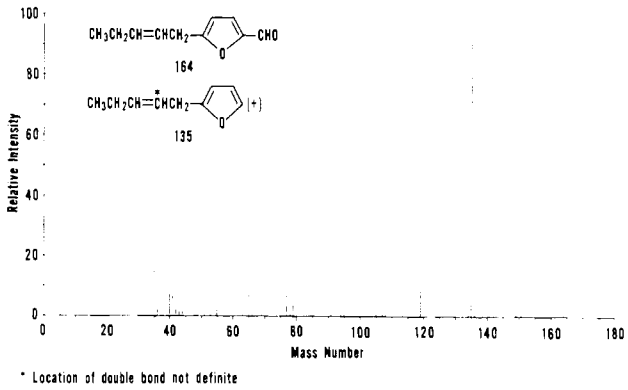


Figure 1. Mass spectrum of an isolated 5-substituted 2-furaldehyde.

possessing a licorice odor, contributes to the beany and grassy notes of reverted soybean oil. Although they have not isolated this compound from autoxidation of linolenic acid, they postulate its formation from a 10-hydroperoxide. 5-(Pentenyl)-2-furaldehyde, postulated to arise from a commonly occurring 9-hydroperoxide, likewise possesses a licorice-like odor. Its contribution to flavor in soy has yet to be determined.

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Isolation of *trans,trans*-2,4-Decadienal and Intermedeol from Cold-Pressed Citrus Oils

trans,trans-2,4-Decadienal has been isolated and identified as a citrus constituent for the first time from cold-pressed orange and tangerine oils. The sesquiterpene alcohol intermedeol has been identified as an orange oil constituent.

Citrus is the largest fruit crop in the United States, and maintaining high-quality citrus products is of economic importance to the citrus industry. In order to maintain high quality in citrus products, it is important to learn the identity of constituents responsible for flavors or off-flavors.

Comprehensive studies of individual flavor components in citrus oils have been reported by many researchers, and many other, as yet unidentified, constituents are known to be present (reviewed by Shaw, 1977). An aldehyde, *trans,trans*-2,4-decadienal, not previously reported in citrus fruit might make an important contribution to flavor because of its low flavor threshold in water. A sesquiterpene alcohol, intermedeol (eudesm-11-en-4-ol), reported as a trace constituent in grapefruit oil (Sulser et al., 1971) has not been found to date in any other citrus oil.

The present study reports the identification of *trans,trans*-2,4-decadienal in citrus oils and intermedeol in orange oil, as well as the minimum amount of the aldehyde needed to significantly alter the flavor of single-strength orange juice.

EXPERIMENTAL SECTION

Separation Procedure. Cold-pressed oil samples (300 mL each) from Hamlin, Pineapple, and Valencia oranges and from tangerines (commercial sample) were each placed in a rotary evaporator and distilled at 36 °C at a pressure of 1–2 mmHg until most of the terpene hydrocarbons (99% limonene) were removed. A 3-g sample of each residue was separated into two fractions on a 1 in. × 15 in. water-jacketed 9 °C column containing 100–200 mesh Florisil deactivated with 6% water (Lund and Coleman, 1977). Fractions were eluted with 300 mL of distilled hexane to remove the hydrocarbons and 300 mL of absolute ethanol to remove the oxygenated compounds. After the removal of solvent by vacuum distillation, the oxygenated fraction