



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

Table I. Flavor Change Due to *trans,trans*-2,4-Decadienal in Single-Strength Orange Juice Using Paired Comparison Tests

decadienal level, ppb	correct judgments (24 presentations)	confidence level, %
15	15	NS ^a
16	18	95
18	19	99

^a NS, not significant.

was further separated into individual compounds and purified by gas chromatography.

Samples were analyzed by gas-liquid chromatography (GLC) on a Perkin-Elmer Model 900 gas chromatograph equipped with a thermal conductivity detector and on a 0.10 in. i.d. × 20 ft column packed with 10% UCW-98 on 60–80 mesh Gas-Chrom P. The following operating conditions were used: helium flow, 30 mL/min; injection port temperature, 250 °C; detector temperature, 275 °C; column temperature, 80–220 °C at 2 °C/min. Individual compounds were collected as they were eluted from the chromatograph and positively identified by comparison of infrared and mass spectra with those for authentic samples. Mass spectra were obtained on a DuPont Model 21-490 mass spectrometer at 70 eV and infrared spectra were obtained on a Perkin-Elmer Model 137A Infracord spectrophotometer as oil films.

Quantitative data were determined on oil samples obtained from Valencia and Pineapple oranges and from commercial tangerine oil. The carbonyl-rich fraction described above, which contained the *trans,trans*-2,4-decadienal, was used for quantitation by GLC. A Hewlett-Packard Model 3380A computing integrator was coupled to the gas chromatograph to determine the area of the peaks on GLC. Calculations of the amounts of each compound present in juice were based on a 0.0175% level of oil in juice.

RESULTS AND DISCUSSION

The highly flavor potent compound *trans,trans*-2,4-decadienal was isolated and identified for the first time as a citrus component from Valencia and Pineapple orange oils and from commercial tangerine oil. The sesquiterpene alcohol intermedeol was identified as a component of orange for the first time.

Estimation of the concentration of *trans,trans*-2,4-decadienal in each of the oils was based on the areas of GLC peaks (in percent) of fractions separated by liquid column chromatography from concentrated oils. Valencia cold-pressed oil was estimated to contain 255 ppm of *trans,trans*-2,4-decadienal. Thus, 45 ppb of this compound was estimated to be in single-strength processed juice. Cold-pressed Pineapple orange oil was estimated to contain 406 ppm of this compound and the processed juice, 71 ppb. Commercial tangerine oil and processed tangerine juice were estimated to contain 456 ppm and 80 ppb of *trans,trans*-2,4-decadienal, respectively.

Taste tests were conducted to determine the amount of *trans,trans*-2,4-decadienal necessary to significantly affect the flavor of single-strength orange juice (Table I). The taste threshold of this compound in water was reported to be 0.07 ppb (Buttery et al., 1971) but the concentration of *trans,trans*-2,4-decadienal necessary for flavor change in orange juice is considerably higher. An expert panel was able to determine, at the 99% confidence level, a flavor change in orange juice when 18 ppb of *trans,trans*-2,4-decadienal was added.

The *trans,trans*-2,4-decadienal in citrus oils could be produced by oxidative breakdown of the long chain fatty acids present in the oils (Nagy, 1977). If such fatty acid breakdown occurs, the level of *trans,trans*-2,4-decadienal should increase and the level present might be an indication of the storage history of the oil.

Intermedeol is a sesquiterpene alcohol isolated in trace quantities from a fraction of grapefruit oil rich in nootkatone by Sulser et al., (1971), who named it paradisiol. However, Huffman and Zalkow (1973) showed that the compound is identical with intermedeol. Intermedeol had not been identified previously in oils from the other major citrus varieties, although trace quantities of nootkatone had been found in all of them (MacLeod and Buigues, 1964). Sulser et al. (1971) pointed out that intermedeol is a possible precursor of the sesquiterpene valencene, which is found in the peel oil of oranges, but not of other major citrus varieties (Shaw, 1977). We found only trace quantities of intermedeol in orange peel oil; insufficient quantities were available for taste threshold determinations and the small amount prevented accurate estimation of the quantity present in orange oil.

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