Composition of Aqueous Essence and Essence Oil from *Citrus temple*

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Two volatile fractions prepared from *Citrus temple* juice distillate, aqueous essence and essence oil, were analyzed by gas chromatography and mass spectrometry. Twenty-eight components of aqueous essence and thirty-eight components of essence oil were identified. Two essence oil components, γ-cadinene and nootkatol, had not been reported earlier as citrus components. The influence of mandarin parentage in *Citrus temple* explained many differences in composition between aqueous essences and essence oils from this hybrid compared to those from orange varieties normally used in preparing orange juice products.

Aqueous orange essence and essence oil are two phases recovered by condensation of vapors from the first stage of an evaporator when juice is being concentrated (Nordby and Nagy, 1980). In recent years, the flavor of frozen concentrated orange juice (FCOJ) has been improved through the addition of one or both these fractions to the finished product. However, the flavor of FCOJ and other orange juice products still lacks the full aroma and taste of freshly squeezed orange juice. More information is needed on volatile components of fresh orange juice before the aroma and flavor of fresh juice can be duplicated in orange products.

Commercially produced aqueous orange essences and essence oils have been analyzed by several workers, and more than 140 components have been identified (Shaw, 1977a,b). These analytical results as well as taste panel studies on individual components and mixtures of components (Ahmed et al., 1978) have shown that orange flavor is the result of a complex mixture of components in the proper proportions.

Citrus temple (Hort. ex Y. Tanaka), commonly called Temple "orange", is believed to be a natural hybrid of orange and mandarin (Hodgson, 1967). Temple fruit bring a premium price on the fresh fruit market because of their rich aroma and flavor, but the juice is usually processed as a less than 10% blend with orange juices because the processed juice can develop off-flavors of unknown origin on storage. Thus, aqueous essences and essence oils from Temple fruit have rarely been collected and have not been analyzed for flavor components. The availability of these volatile fractions from a specially processed load of Temple fruit (Redd, 1981) enabled us to analyze these fractions from one of the most flavorful orange hybrids.

This study reports the identification of 28 components of aqueous essence and 38 components of essence oil from Temple fruit. The results are correlated with those from aqueous orange essences and essence oils.

EXPERIMENTAL SECTION

Aqueous essence and essence oil from *C. temple* fruit were obtained from a commercial plant producing essence by fractionation and condensation of vapors from the first stage of a juice evaporator. A 1400-mL sample of aqueous Temple essence was saturated with sodium sulfate and extracted with three 400-mL portions of methylene chloride (Wolford et al., 1962) which were combined and concentrated on a rotary evaporator under reduced pressure to produce the anhydrous essence analyzed below.

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Table I. *C. temple* Aqueous Essence Constituents

aldehydes	acetals
geranial	diethyl acetal
2-hexenal	esters
neral	ethyl acetate
octanal	ethyl butyrate
alcohols	ethyl 3-hydroxyhexanoate
1-butanol	ethyl propionate
ethanol	methyl butyrate
geraniol	hydrocarbons
hexanol	limonene
3-hexen-1-ol	ketones
linalool	carvone
2-methyl-1-butanol	oxides
3-methyl-1-butanol	*cis*-linalool oxide
2-methyl-3-butanol	*trans*-linalool oxide
2-methyl-1-propanol	
octanol	
1-pentanol[a]	
terpinen-4-ol	
α-terpineol	

[a] Tentative identification only.

Aqueous Essence Analysis. A Finnigan Model 4021 gas chromatograph–mass spectrometer (GC–MS) was used to separate and identify the constituents of aqueous essence listed in Table I. The GC was equipped with either a 0.02-mm i.d. by 50 m fused silica column coated with SP-2100 or with Carbowax 20M (Hewlett-Packard) with a flow rate of 1 mL/min and an injection port split ratio of 100:1. The initial oven temperature was held at 50 °C for 10 min and then programmed at 6 °C/min to 220 °C. Injection port, detector, transfer line, and jet separator were kept at 250 °C. Mass units were monitored from 40 to 300 at 70 eV. Mass spectral identifications were made by comparison of mass spectra and retention times with those of authentic compounds.

Essence Oil Analysis. Essence oil samples were also analyzed with the Finnigan GC–MS system described above. The SP-2100 GC column described above was used with a flow rate of 1 mL/min and an injection port split of 100:1. Initial oven temperature was held at 50 °C for 5 min and then temperature programmed at 3 °C/min to 225 °C.

Individual essence oil constituents were separated for infrared spectral analysis by using a Perkin-Elmer Model 900 gas chromatograph equipped with a thermal conductivity detector and a 0.10-in. i.d. by 20 ft stainless steel column packed with either 10% Carbowax 20M or with 10% UCW-98 on 60–80-mesh Gas-Chrom P. For all runs the injection port temperature was 275 °C and detector temperature was 290 °C. The oven temperature was programmed from 80 to 210 °C at 2 °C/min and the he-

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Table II. *C. temple* Essence Oil Constituents

aldehydes	esters
citronellal	citronellyl acetate
decanal	ethyl acetate
dodecanal	geranyl acetate[a]
geranial	1,8-*p*-menthadien-9-yl acetate
neral	neryl acetate[a]
octanal	octyl acetate
perillaldehyde	alcohols
α-sinensal	elemol
hydrocarbons	ethanol
γ-cadinene[a]	intermedeol
β-caryophyllene	linalool
α-copaene	nerol
β-copaene	nootkatol[a]
β-cubebene	octanol
β-elemene	terpinen-4-ol[a]
limonene	α-terpineol
nootkatene	thymol[a,b]
α-pinene	ketones
β-pinene	carvone
epi-α-selinene	nootkatone
valencene	

[a] Not reported earlier as a component of aqueous orange essence or essence oil. [b] Tentative identification only.

lium flow was 30 mL/min. Individual components were collected as they were eluted from the GC.

Positive identifications of constituents from Temple essence oil were made by comparison of their infrared spectra, mass spectra, and retention times with those of authentic samples (Table II). The one component that was only tentatively identified (thymol) was identified by GC retention time and by enrichment of a sample of essence oil with an authentic sample injected onto the 0.02 mm by 50 m SP-2100 column described above.

RESULTS AND DISCUSSION

Two commercially prepared volatile fractions from *C. temple* juice, aqueous essence and essence oil, were analyzed and the identified components are listed in Tables I and II. All of the 28 identified components of aqueous Temple essence (Table I) had been reported earlier as components of aqueous orange essence (Shaw, 1977b).

The 38 identified components of Temple essence oil are listed in Table II. Six components found in Temple essence oil had not been reported earlier as constituents of aqueous orange essence or essence oil or of Temple peel oil (Hunter and Brogden, 1965; Braddock and Kesterson, 1976). However, three of them as well as many ofthe other identified components had been identified as constituents of cold-pressed orange peel oil (Shaw, 1977a). Some peel oil is present in freshly extracted citrus juice as well as some oil of slightly different composition that is naturally present in the juice (juice oil). During the distillation, these two oils are in equilibrium in the juice. After condensation, the aqueous essence and essence oil are in equilibrium in the oil separator. Thus, it is not surprising to find unknown components of juice, peel oil, and juice oil in either aqueous essence or essence oil.

The three essence oil components not identified earlier as constituents of orange were γ-cadinene, nootkatol, and thymol. γ-Cadinene is a sesquiterpene hydrocarbon and nootkatol is a sesquiterpene alcohol not reported earlier as components of citrus (Shaw, 1977a,b). The latter compound had been synthesized at our laboratory from the citrus oil component, nootkatone (Wilson and Shaw, 1978). These two components would be expected to contribute to the heavier oily flavor in juice rather than the rich flavor bouquet that distinguishes fresh Temple juice.

The third new component, thymol, is a component of tangerine aqueous essence and essence oil (Moshonas and Shaw, 1972; Coleman and Shaw, 1972) and of mandarin peel oil (Kugler and Kovats, 1963), and it is believed important to the aroma and flavor of mandarin (Kugler and Kovats, 1963). Its importance to mandarin flavor has been studied (Wilson and Shaw, 1981), but its contribution to the flavor of Temple fruit is not known.

Some qualitative and quantitative differences were noted when the gas chromatographic data for Temple aqueous essence and essence oil were compared with similar data for commercial orange essence and essence oil previously reported from this laboratory (Moshonas et al., 1972; Lund and Bryan, 1977; Coleman et al., 1969; Coleman and Shaw, 1971; Moshonas and Shaw, 1979). Aqueous essence from Temple fruit contained less ethyl 3-hydroxyhexanoate than did the commercial essence samples.

Temple essence oil contained a large amount of β-pinene, a compound that had not been detected in commercial orange essence oil (Shaw, 1977a; Moshonas and Shaw, 1979). These data support the belief that the Temple hybrid probably contains mandarin parentage (Hodgson, 1967). Thus, tangerine aqueous essence also contains a much lower amount of ethyl 3-hydroxyhexanoate than does commercial orange essence (Moshonas and Shaw, 1972), and tangerine essence oil contains β-pinene, while orange essence oil does not (Coleman and Shaw, 1972; Moshonas and Shaw, 1979).

The results of this study on Temple volatile fractions increase our basic knowledge of citrus flavor chemistry. However, more information is needed on volatile constituents of orange, including identification of trace volatile components yet unidentified, before the full, rich flavor of fresh orange juice can be understood and duplicated in citrus products.

Registry No. Geranial, 141-27-5; 2-hexenal, 505-57-7; neral, 106-26-3; octanal, 124-13-0; 1-butanol, 71-36-3; ethanol, 64-17-5; geraniol, 106-24-1; hexanol, 25917-35-5; 3-hexen-1-ol, 544-12-7; linalool, 78-70-6; 2-methyl-1-butanol, 137-32-6; 3-methyl-1-butanol, 123-51-3; 2-methyl-3-butanol, 598-75-4; 2-methyl-1-propanol, 78-83-1; octanol, 29063-28-3; 1-pentanol, 71-41-0; terpinen-4-ol, 562-74-3; α-terpineol, 98-55-5; diethyl acetal, 105-57-7; ethyl acetate, 141-78-6; ethyl butyrate, 105-54-4; ethyl 3-hydroxyhexanoate, 2305-25-1; ethyl propionate, 105-37-3; methyl butyrate, 623-42-7; limonene, 138-86-3; carvone, 99-49-0; *cis*-linalool oxide, 5989-33-3; *trans*-linalool oxide, 34995-77-2; citronellal, 106-23-0; decanal, 112-31-2; dodecanal, 112-54-9; perillaldehyde, 2111-75-3; α-sinensal, 17909-77-2; elemol, 639-99-6; intermedeol, 6168-59-8; nerol, 106-25-2; nootkatol, 50763-67-2; thymol, 89-83-8; citronellyl acetate, 150-84-5; geranyl acetate, 105-87-3; 1,8-*p*-menthadien-9-yl acetate, 15593-88-1; neryl acetate, 141-12-8; octyl acetate, 103-09-3; γ-cadinene, 39029-41-9; β-caryophyllene, 87-44-5; α-copaene, 3856-25-5; β-copaene, 18252-44-3; β-cubebene, 13744-15-5; β-elemene, 515-13-9; nootkatene, 5090-61-9; α-pinene, 80-56-8; β-pinene, 127-91-3; *epi*-α-selinene, 35387-23-6; valencene, 4630-07-3; nootkatone, 4674-50-4.

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Isolation and Identification of Volatile Flavor Compounds in Fried Bacon

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Volatile flavor compounds were isolated from 120 lb of fried bacon by a specially designed apparatus. The isolated volatile flavor compounds were subjected to extensive gas chromatographic fractionation, and the pure fractions obtained were identified by infrared and mass spectrometry. A total of 135 compounds were identified. The compounds identified in the volatiles of fried bacon included hydrocarbons, alcohols, ketones, aldehydes, acids, esters, ethers, phenols, pyrazines, furans, thiazoles, oxazoles, oxazolines, pyrroles, pyridines, and miscellaneous compounds. Two interesting halogenated pyrroles, *N*-acetyl-2-chloropyrrole and *N*-acetyl-2-bromopyrrole, were synthesized to confirm the identification.

There have been a limited number of reports concerning the flavor constituents of cured pork and its related products. These reports (Cross and Ziegler, 1965; Langer et al., 1970; Lillard and Ayres, 1969; Ockerman et al., 1964) dealt exclusively with ham and sausage flavor constituents and resulted in the identification of a number of acids, alcohols, sulfur compounds, and, particularly, carbonyl compounds. On the other hand, extensive literature (Baltes et al., 1981; Fiddler et al., 1970a,b; Hamid and Saffle, 1965; Hruza et al., 1974; Kim et al., 1974; Kornreich and Issenberg, 1972; Lustre and Issenberg, 1969; Porter et al., 1965) exists on the comparison of sawdust smoke and liquid smoke (natural) flavors. Lustre and Issenberg (1970) studied the uptake of phenols from wood smoke in smoked pork belly. Knowles et al. (1975) reported the identification of 13 phenols, furfuryl alcohol, and cyclotene in the phenolic fraction of traditional kiln-smoked bacon. Most recently, Shu et al. (1980) identified 2,4,5-trimethyl-3(2*H*)-furanone from the phenolic fraction of the volatile flavor isolate of cooked Oscar Mayer bacon. However, literature on the systematic analysis of volatile flavor constituents of cooked bacon is nonexistent.

The present paper reports the isolation and systematic characterization of the volatile flavor constituents of fried bacon.

EXPERIMENTAL SECTION

Isolation of the Volatile Compounds from Fried Bacon. The bacon used for this study was Oscar Mayer bacon ($^1/_8$ in. thick slices, 1 lb/package) purchased from a local supermarket.

Bacon was pan fried at 350 °C for 5 min to a golden yellow color. The volatile flavor compounds of fried bacon were isolated by the apparatus previously described by Chang et al. (1977). Nitrogen gas was used to remove the volatile compounds from the fried bacon. The samples and nitrogen gas were kept at 65 °C during the isolation period. Twenty pounds of fried bacon was used for each isolation which lasted 48 h. A total of six isolations were run. The total volatile isolate collected in traps cooled with dry ice and acetone was treated in a manner similar to that described by Herz and Chang (1966). The condensate was saturated with NaCl and extracted with anhydrous ethyl ether. The ether extract was dried with anhydrous sodium sulfate and then concentrated down to a final volume of 3 mL with the use of 30-plate Oldershaw column and a 200-plate spinning band still.

Fractionation of the Flavor Isolate. The fried bacon flavor isolate was fractionated in a manner similar to that described by Coleman et al. (1981). The initial preparative chomatography of the fried bacon flavor isolated was performed on a Beckman GC-5 gas chromatograph equipped with a thermal conductivity detector, fitted with

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