Analysis of Flavor Constituents from Lemon and Lime Essence

Manuel G. Moshonas* and Philip E. Shaw

Aqueous lemon and lime juice essences were analyzed and 27 volatile compounds were identified from lemon essence, including 13 alcohols, four aldehydes, four ketones, three hydrocarbons, two ethers, and one ester. Twenty-five of these are newly found lemon juice constituents. Thirty-four volatile compounds were identified from lime essence, including 18 alcohols, six aldehydes, two ketones, three hydrocarbons, two esters, and three oxides, all of which are newly found lime juice constituents. The essences were extracted with methylene chloride and ether. Gas chromatography was used for separation and purification, and compound identifications were made by mass spectrometry and infrared spectroscopy.

Two commercially available citrus essences, lemon and lime, have not been analyzed extensively. The importance of aqueous orange essence as a flavor enhancing material for orange products has led to a number of investigations of the flavor constituents in this essence by Kirchner and Miller (1957), Wolford *et al.* (1962), Wolford and Attaway (1967), Schultz *et al.* (1964, 1967), Moshonas *et al.* (1972), and Moshonas and Shaw (1972). At our laboratory, the compositional analyses of both grapefruit essence (Moshonas and Shaw, 1971) and tangerine essence (Moshonas and Shaw, 1972) have recently been studied.

Lemon and lime aqueous essences have pleasant aromas characteristic of the fruit, but neither has been widely used to enhance citrus product flavor or aroma. Increasing interest in the commercially available lemon and lime essences for use in citrus, household, and cosmetic products indicates the need for information on flavor constituents in these two essences. The only report to date on volatile lemon juice constituents was that of Di Giacomo and Rispoli (1962), and there have been no previous studies on the volatile constituents of lime uice. This paper reports the separation and identification of 27 lemon essence and 34 lime essence constituents.

EXPERIMENTAL

Aqueous lemon and lime essences were obtained from a commercial plant producing essence by fractionation and condensation of vapors from the first stage of the juice evaporator (Redd Laboratories, Inc., Lakeland, Fla.). Anhydrous lemon and lime essences were prepared by the methylene chloride extraction method of Wolford *et al.* (1962). This method does not extract the major organic component, ethanol, which might interfere with subsequent glc analysis of minor components. A 1400-ml sample of lemon or lime aqueous essence was saturated with sodium sulfate and extracted with three 400-ml portions of methylene chloride, and the combined extracts were concentrated under reduced pressure to produce anhydrous essence. Then three 400-ml portions of diethyl ether were used to extract the ethanol and a few minor organic components from the residual water solution. The ether extract was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The methylene chloride and ether extracts were each analyzed by gas chromatography.

The glc analyses were made on an F&M Model 810 gas chromatograph using a thermal conductivity detector and equipped with a $^1/_4$ in. × 20 ft column packed with 20% Carbowax 20M on 60–80 mesh Gas Chrom P. The oven temperature was programmed from 80 to 225° at 1° per min, with a helium flow of 60 ml per min. When separation of individual components was not complete, the mixture was collected and rechromatographed on a $^1/_4$ in. × 20 ft column packed with 10% of the nonpolar liquid phase UCW-98 (Applied Science Lab., Inc., State College, Pa.) on 60–80 mesh Gas Chrom P. The injection temperature was 250° and the detector temperature was 280°. Injection volume was 25 μl. Fractions were collected in short capillary tubes for infrared and mass spectral analysis. Mass spectra were obtained on a Bendix Model 3012 (TOF) mass spectrometer and infrared spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer.

Acetaldehyde, acetone, 1,1-ethoxymethoxyethane, and ethyl acetate were identified by comparing the mass spectra and retention times with those of known compounds. The remaining constituents were identified by comparison of infrared spectra, mass spectra, and retention times of known compounds.

RESULTS AND DISCUSSION

Constituents separated and identified from the methylene chloride extraction of lemon essence are shown in Table I and those from lime essence are in Table II. Twenty-five of the compounds identified from lemon and all of those from lime are being reported for the first time as components of lemon and lime juice, respectively. Spectral and gas chromatographic analysis of the ether extract showed this fraction from both lemon and lime essences to be mostly ethanol. In this extract, small quantities of methanol and acetaldehyde were also isolated.

Of the 25 compounds being reported for the first time from lemon juice essence, 12 have been reported as constituents of lemon oil (Di Giacomo and Calvarano, 1970) and 15 which are noted in Table I have not been previously found in any study of lemon. Two major anhydrous essence constituents characteristic of lemon aroma are geranial and neral (Ikeda *et al.*, 1962). Other components which have distinct aromas and are found in relatively large quantity in lemon essence as indicated by the glc analysis are: ethyl acetate, 2-methyl-3-buten-2-ol, 4-methyl-2-pentanone, limonene, γ-terpinene, linalool, terpinen-4-ol, α-terpineol, carvone, methanol, ethanol, and perillaldehyde. Three compounds identified in lemon essence which have never been previously found in any citrus fruit are *cis*-*p*-2-menthen-1-ol, 3-methyl-2-buten-1-ol, and 1,4-dioxane. The latter is possibly a contaminant.

Citrus and Subtropical Products Laboratory, Southeastern Marketing and Nutrition Research Division, Agricultural Research Service, U.S. Department of Agriculture, Winter Haven, Florida.

Table I. Compounds Identified in Lemon Essence

Alcohols	Esters
Butyl alcohol[a]	Ethyl acetate[a]
Ethyl alcohol[a]	**Ethers**
trans-Carveol[a]	1,4-Dioxane[b]
Hexanol	1,1-Ethoxymethoxyethane[a]
cis-3-Hexen-1-ol	**Hydrocarbons**
Linalool	Limonene
Methyl alcohol[a]	Myrcene
cis-p-2-Menthen-1-ol[b]	γ-Terpinene
2-Methyl-3-buten-2-ol[a]	**Ketones**
3-Methyl-2-buten-1-ol[b]	Acetone[a]
Nerol	Carvone
Terpinen-4-ol	4-Methyl-2-pentanone[a]
α-Terpineol	Piperitenone[a]
Aldehydes	
Acetaldehyde[a]	
Geranial	
Neral	
Perillaldehyde[a]	

[a] Newly found lemon constituents. [b] Newly found citrus constituents.

Table II. Compounds Identified in Lime Essence

Alcohols	Esters
Borneol	Ethyl acetate[a]
p-Cymene-8-ol[a]	Neryl acetate
Ethyl alcohol[a]	**Hydrocarbons**
Geraniol	*p*-Cymene
cis-3-Hexen-1-ol[a]	Limonene
Isoamyl alcohol[a]	γ-Terpinene
Isopropyl alcohol[a]	**Ketones**
Linalool	Acetone[a]
cis-p-2-Menthen-1-ol[b]	Piperitenone[a]
Methyl alcohol[a]	**Oxides**
2-Methyl-2-butanol[b]	1,8-Cineol
2-Methyl-3-buten-2-ol[a]	*cis*-Linalool oxide[a]
3-Methyl-2-buten-1-ol[b]	*trans*-Linalool oxide[a]
Nerol	
Aldehydes	
Acetaldehyde[a]	
Geranial	
Hexanal[a]	
2-Hexenal[a]	
Neral	
Perillaldehyde[a]	

[a] Newly found lime constituents. [b] Newly found citrus constituents.

All 34 compounds isolated and identified in aqueous lime essence are being reported for the first time as lime juice constituents. Fourteen of these have previously been reported as lime oil constituents (Di Giacomo and Calvarano, 1970). The 20 remaining compounds not previously reported in any lime study are noted in Table II. As in the lemon essence study, geranial and neral are major anhydrous essence constituents. The other major constituents are 2-methyl-3-buten-2-ol, limonene, 2-hexenal, 1,8-cineol, linalool, terpinen-4-ol, α-terpineol, borneol, isopropyl alcohol, methanol, and ethanol. Along with the 3-methyl-2-buten-1-ol and *cis-p*-2-menthen-1-ol found in both lemon and lime essence, another compound new to citrus, 2-methyl-2-butanol, was identified from lime essence.

The similarity of a number of constituents in lemon and lime essence was expected, but there were considerable differences in the qualitative composition of the two essences. Compounds found only in the lemon essence were: 1,1-ethoxymethoxyethane, 4-methyl-2-pentanone, butyl alcohol, myrcene, hexanal, carvone, and *trans*-carveol. Those constituents found only in the lime essence were: 2-hexenal, 1,8-cineol, *cis*- and *trans*-linalool oxides, borneol, geraniol, *p*-cymene-8-ol, thymol, isopropyl alcohol, 2-methyl-2-butanol, hexanol, isoamyl alcohol, 1-penten-3-ol, and neryl acetate. Thus, the differences in lemon and lime essence aroma are clearly reflected by the compositional differences seen in this study.

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