Aroma Components of Baelfruit (*Aegle marmelos* CORREA)[†]Yukiko TOKITOMO, Yūko SHIMONO, Akio KOBAYASHI
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The attractive and characteristically sweet aroma components of baelfruit—a tropical fruit—were investigated. The aroma concentrates possessing the sweet floral and somewhat terpene-like aroma were obtained from both the pulp and peel of fresh baelfruits by means of lyophilization and ether extraction, being analyzed mainly by GC-MS. A total of 39 components were identified. Among these components, terpene alcohols and β -ionone were considered to contribute to the aroma of baelfruit. At optimum ripeness, the fruit with excellent flavor contained a large quantity of an isomeric compound of 3,7-dimethyl-1,5,7-octatrien-3-ol. This compound couldn't be found in unripe fruit, and seems to be important in making the baelfruit flavor attractive.

Baelfruit (*Aegle marmelos* CORREA) is a tropical fruit native to Southeast Asia and belongs to Rutaceae family.

The peel of the fruit is a very hard shell and brown-green in color. The yellow edible pulp, which, in appearance, is like a boiled pumpkin, possesses a slightly sweet taste and a characteristic floral, terpene-like aroma. The pulp of the fruit is often used as a drink with the addition of water and sugar, and also used for making cream, sherbet and marmalade.

These studies were aimed to isolate and identify the contributory components of the floral and pleasant terpene-like aroma of baelfruit.

During the preparation of this report, the chemical investigation of baelfruit flavor was published¹⁾ by Macleod *et al.* They used both conventional Soxhlet apparatus and the Likens and Nickerson apparatus²⁾ to isolate the aroma components of the fruit. In our investigation, however, a lyophilization method without heating was used to obtain the aroma concentrates which possessed the fresh baelfruit-like aroma.

EXPERIMENTAL

Material. Fresh baelfruits for aroma identification were obtained from the market in Colombo, Sri Lanka in March 1980. A Ripe fruit on the tree was given by Dr. R. L. Wickremasinghe, National Institute of Plantation Management, Sri Lanka, for comparison between the aroma pattern of an excellently flavored, fully ripened fruit on the tree and an unripe one.

Preparation of aroma concentrates.

(1) *From pulp.* The pulp was removed from the fruits and 4.6 kg of pulp was extracted with 5 liters of methanol. The oleoresin from the methanol extract and the residual pulp after methanol extraction were lyophilized individually to obtain the aroma concentrates without heating according to the same procedure as described by Imagawa *et al.*³⁾ The yield of the oleoresin (presented as aroma concentrate I) and the residual pulp (presented as aroma concentrate II) were 2.3 mg% and 1.1 mg% of the original pulp respectively.

After lyophilization, the residual pulp was added to water and subjected to simultaneous distillation and extraction by a modified Likens and Nickerson's apparatus,⁴⁾ using diethyl ether as the solvent. The yield of the aroma concentrate (presented as aroma concentrate III) was 8.9 mg% of the original pulp weight.

Aroma concentrates I and II possessed a characteristic floral terpene-like aroma, while the aroma concentrate III was a sesquiterpene hydrocarbon-like woody aroma.

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(2) *From peel.* The peel (1.4 kg) was broken into small pieces and dipped in 1.8 liters of peroxide-free ether. The oleoresin from the diethyl ether extract was obtained in a yield of 490 mg% of the peel weight. It was separated into hydrocarbon and oxygenated fractions by silica-gel column chromatography using *n*-pentane and diethyl ether. The hydrocarbon fraction possessed a woody and terpene-like aroma, while the oxygenated fraction had a sweet and floral aroma. Yield of the former was 80 mg% and the latter was 100 mg% of the peel weight.

(3) *From ripe and unripe fruits.* To find out the aroma components contributing to the superior flavor at the stage of full ripeness, a fresh fruit (260 g) was divided into pulp (175 g) and peel (85 g). The pulp was extracted with diethyl ether and an oleoresin with an excellent fresh aroma was obtained.

On the other hand a oleoresin of less attractive odor was obtained by the same procedure from unripened green fruit.

Gas chromatography. A GLC analysis were carried out using a Shimadzu model GC-6A equipped with a flame ionization detector (FID). The column was a 30 m × 0.28 mm (i.d.), FFAP glass SCOT column and oven

temperature was programmed from 70 to 180°C at 2°C/min. The temperature of injection port was kept at 200°C with nitrogen as carrier gas at a flow rate of 1.2 ml/min.

GC-MS. GC-MS spectra were recorded with a Hitachi RMU-6MG mass spectrometer combined with a Hitachi 063 gas chromatograph. The column was a 30 m × 0.28 mm (i.d.), Thermo 600T glass SCOT column and oven temperature was programmed from 60° to 220°C at 3°C/min. The ionizing energy was 20 eV. All peaks were identified by comparing their mass spectra and retention data from GLC with those of the authentic compounds.

RESULTS AND DISCUSSION

I. Identification of the aroma compounds

The gas chromatograms of aroma concentrates I, II, III from pulp are shown in Fig. 1. Twenty six components were characterized. Among these components, monoterpene and sesquiterpene hydrocarbons, linalool and its oxides were recognized as the main com-

FIG. 1. Gas chromatograms of Aroma Concentrates from Pulp.

Peak: A) ethanol; B) α -pinene; C) β -pinene; D) limonene; E) Δ^3 -carene; F) *p*-cymene; G) linalool oxides (furanoid); H) acetic acid; I) α -ylangene*; J) linalool; K) 3,7-dimethyl-1,5,7-octatrien-3-ol; L) caryophyllene; M) aromadendrene; N) α -humulene*; O) α -terpineol; P) β -copaene; Q) α -farnesene; R) benzyl acetate; S) linalool oxides (pyranoid); T) δ -cadinene*; U) a sesquiterpene hydrocarbon; V) benzyl alcohol; W) 2-phenylethanol; Y) β -ionone; X) unknown compound; Z) methyl cinnamate. (*Tentatively identified.)

FIG. 2. Gas Chromatograms of Aroma Concentrates from Peel of the Fresh Baelfruit Hydrocarbon Fraction (A) and Oxygenated Fraction (B).

Peak: 1) ethanol; 2) α -pinene; 3) 2-methyl-3-buten-2-ol; 4) limonene; 5) Δ^3 -carene; 6) *p*-cymene; 7) linalool oxides (furanoid); 8) linalool; 9) caryophyllene; 10) aromadendrene; 11) 3,7-dimethyl-1,5,7-octatrien-3-ol; 12) α -humulene*; 13) β -copaene*; 14) α -farnesene*; 15) δ -cadinene*; 16) linalool oxides (pyranoid); 17) ethyl dodecanoate; 18) guaiacol; 19) benzyl alcohol; 20) 2-phenylethanol; 21) 2-ethylhexanoic acid; 22) phenol; 23) ethyl myristate; 24) 4-methoxybenzaldehyde; 25) 4-ethyl-2-methoxyphenol; 26) eugenol + ethyl phenol*; 27) ethyl palmitate; 28) ethyl stearate; 29) vanillin. (*Tentatively identified.)

FIG. 3. Gas Chromatograms of Aroma Concentrates from a Fresh Fully Ripe Fruit (1) and Unripe Fruit (2).

Peak: a) α -pinene; b) β -pinene; c) limonene; d) Δ^3 -carene; e) a monoterpene hydrocarbon; f) *p*-cymene; g) linalool oxides (furanoid); h) linalool; i) 3,7-dimethyl-1,5,7-octatrien-3-ol; j) caryophyllene; k) α -humulene*; l) linalool oxides (pyranoid); m) β -copaene*; n) a sesquiterpene hydrocarbon; o) benzyl alcohol; p) 2-phenylethanol. (*Tentatively identified.)

ponents from their peak area. 3*S*-(+)-3,7-Dimethyl-1,5,7-octatrien-3-ol has a very sweet and floral aroma, which had been previously identified as one of the aroma constituents of black tea,⁵⁾ grape and wine.⁶⁾ β -Ionone has a sweet violet odor with a warm, woody and fruity undertone, with a threshold value as low as 0.007 ppb.⁷⁾ These compounds seem to be the constituents contributing to the baelfruit flavor.

The gas chromatograms of the hydrocarbon fraction and oxygenated fraction from peel are shown in Fig. 2. Besides the compounds found in the aroma of pulp, phenolic compounds such as phenol, an ethylphenol, guaiacol, 2-methoxy-4-ethylphenol, eugenol and vanillin were identified. These phenolic compounds, related to the lignin substances in peel, seem to contribute to the sweet and woody aroma of the oxygenated fraction.

II. Comparison of the aroma pattern of ripe and unripe fruits

The gas chromatograms of the aroma concentrate from the pulp of a fresh fully ripened fruit which had the excellent aroma of baelfruit is shown in Fig. 3, compared with that of an early stage of ripeness green fruit. Peak X, whose peak area percentage was 24.7% in the chromatogram for the ripe fruit, was scarcely found in the unripe fruit.

Next, peak X, which was contained in the peel as shown in Fig. 2-(B), was trapped by preparative GLC for a spectrometric investigation. The aroma of the trap had a refreshing terpene and peppermint leaf-like aroma, and was thought to contribute to making the flavor of baelfruit more attractive. The MS was almost the same as that of 3*S*-(+)-3,7-dimethyl-1,5,7-octatrien-3-ol as shown in Fig. 4. From the IR and NMR spectra, the presence of the same partial structures (*i.e.*, terminal vinyl, tert-OH and substituted double bonds) as those of 3,7-dimethyl-1,5,7-octatrien-3-ol, were suggested. However, because of the limited amount of the sample, further information on the chemical structure was not obtained. The retention time on GC

FIG. 4. Mass Spectra of 3,7-Dimethyl-1,5,7-octatrien-3-ol (a) and an Unknown Compound X (b).

High resolution mass spectrum of X [m/z (element)] $\cdots$ 53.02932 (C_4H_5), 55.01964 (C_3H_3O), 67.05364 (C_5H_7), 68.05825 (C_5H_8), 70.04101 (C_4H_6O), 71.04797 (C_4H_7O), 72.05220 (C_4H_8O), 79.05302 (C_6H_7), 81.06777 (C_6H_9), 82.07671 (C_6H_{10}), 83.07861 (C_6H_{11}), 93.06833 (C_7H_9), 95.04570 (C_6H_7O), 95.08268 (C_7H_{11}), 119.08739 (C_9H_{11}), 125.09842 ($C_8H_{13}O$), 135.11488 ($C_{10}H_{15}$), 137.09597 ($C_9H_{13}O$).

was about twice as much as that of 3*S*-(+)-3,7-dimethyl-1,5,7-octatrien-3-ol, and therefore, peak X was presumed to be a steric isomer of 3*S*-(+)-3,7-dimethyl-1,5,7-octatrien-3-ol.

It is interesting that the major components of baelfruit flavor were monoterpenes and sesquiterpenes, similar to citrus fruits of the Rutaceae family, such as citrus unshiu^{8,9)} and *C. iyo*.¹⁰⁾ Although the appearance of the fruit is like wood apple or quince, the aroma components are quite different from those of wood apple¹¹⁾ and quince,¹²⁾ whose aroma consisted mainly of various esters.

III. Sensory test of the synthetic mixture of baelfruit flavor

Based on each peak area of gas chromatogram for the aroma concentrate from pulp obtained by lyophilization which is shown in Fig. 1-(I), the main compounds were mixed quantitatively as shown in Table I. The synthetic mixture in Table I was evaluated by five

TABLE I. SYNTHETIC MIXTURE COMPOSITION OF BAELFRUIT FLAVOR

Compound	Concentration (%)
Limonene	31.8
Δ^3 -Carene	5.7
<i>p</i> -Cymene	2.0
Linalool oxide I, II	19.2
Linalool	20.0
Benzyl acetate	5.2
Linalool oxide III, IV	10.8
Benzyl alcohol	1.5
2-Phenylethanol	1.5
β -Ionone	2.5

members of the Tea Research Institute, Sri Lanka, to have an odor similar to that of baelfruit. However, the aroma of the synthetic mixture lacked the refreshing floral and woody note when compared with that of best quality baelfruit.

We concluded that the compounds in Table I are important constituents to produce the basic or fundamental flavor quality of baelfruit, and 3,7-dimethyl-1,5,7-octatrien-3-ol and its isomer are responsible for making the aroma of this fruit more attractive.

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extracts from baelfruits and the odor judgement of synthetic aroma mixture of baelfruit, and Dr. R. L. Wickremasinghe of the National Institute of Plantation Management, Sri Lanka, for providing best quality ripe baelfruit.

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