Essential Oils of Some Orange Peels

By Kazuyuki Maekawa, Masanobu Kodama, Mitsuo Kushii and Mitsutoshi Mitamura*

Department of Agricultural Chemistry, Faculty of Agriculture, Ehime University
Matsuyama, Japan

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The essential oils contained in the peels of Kabusu, Sudachi, Iyokan, Daidai and Natsudaidai orange were studied by gas-chromatography. The major components of each essential oil were d-limonene, β-pinene, camphene, 1,8-cineol, and caprylaldehyde. As minor components there were found 23 compounds in Kabusu, 14 in Sudachi, 9 in Iyokan, 14 in Natsudaidai, and 11 in Daidai oil.

The literature abounds with reports on the essential oils contained in various varieties of citrus fruit.1-21 Wolford et al. identified 35~40 components in the essential oil of Florida Valencia orange,3 by application of three different columns and by comparison with the components of other orange essences.4-6 Kugler et al.7 and Mukherjee et al.8 reported on mandarin oil. Nigan et al. carried out gas chromatographic analysis of citrus macrocarpa.9 DiGiacomo10 analysed Italian citrus oil by gas chromatography. There are reports on lime oil by Kovats,11 on Sicilian lemon oil by Slater.12 As for lemon oil, gas chromatographic results were presented by El-Deeb13 Ikeda,14 Bernhard,15a,b and Liberti.16 Recently, Hunter et al. described terpene and sesquiterpene hydrocarbons in various citrus essential oils, analyzing in a two-step procedure.17

* Present address: Kotegawa Soy Sauce Manufacturing Co., Oita.

2) W. B. Sinclair, "The Orange, its Biochemistry and Physiology" Univ. of Calif., Division of Agric. Sci., 1960, p. 287.
15a) R. A. Bernhard, Food Research, 23, 213 (1958).
For lack of the studies on the essential oils of Citrus Iyo, Citrus Daidai, Citrus Sudachi, Citrus Natsudaidai, and Citrus Aurantium Linn. form Kabusu, the authors have analysed the peel oil of those varieties.

Citrus Aurantium Linn. form Kabusu, which originated in the Himalayan region and are distributed in most parts of Japan, is not fit to be eaten raw because of its sour taste, but has been used as fruit vinegar in some parts of western Japan. Sudachi is also a sort of sour orange. It has been cultivated in Tokushima prefecture and has been used for seasoning because of its pleasant flavor. Citrus Iyokan, a kind of sweet orange, has been cultivated in most parts of Ehime prefecture and the flavor of its peel oil is unique and pleasant. Citrus Daidai is also distributed in western parts of Japan.

**EXPERIMENTAL**

**Materials**
- Citrus Iyo Hort. ex Tanaka
- Citrus Aurantium Linn. form Kabusu
- Citrus Aurantium Linn. subsp. amara, Engl.
- Citrus Natsudaidai Hayata
- Citrus Sudachi Hort. ex Shirai

**Methods of collecting essential oil**

a) Fresh orange peel was cut finely and extracted by soaking in methanol. The methanol solution was concentrated in vacuo and the residual oil was distilled with steam under reduced pressure.  

b) Finely cut peel was extracted with a severalfold volume of ether and then the solvent was removed by distillation.  
c) Peel was pressed by a presser in a cold room. The flavor of essential oil varied according to how it had been prepared.

The essential oil of Kabusu was prepared by method a. The cut peel of the Kabusu which was harvested between mid September and early October was soaked in methanol overnight. The extracted solution was concentrated by using Hempel’s fractionating column of 50 cm. Then the residual oil was distilled with steam under reduced pressure. The yield of essential oil was 0.5 per cent of the raw peel.

Sudachi oil could not be extracted by method a, for the obtained oil was quite different in flavor from the fresh material. But the oil of this orange obtained by method b retain most of its original flavor. The same quality of oil was also obtained by method c, but the stability of the oil was lower.

One hundred grams of finely cut peel of the Sudachi which was harvested about in mid September was dipped in 100 ml of ether overnight. The ether solution was concentrated in a water bath at 40°C by means of Hempel’s fractionating column of 30 cm. The residual oil was about 0.7 g.

The essential oils of Iyokan and Daidai were collected by pressing their peel and the separated upper layer was immediately used as sample for gas chromatography.

**Gas chromatography.** Gas chromatography of each of the essential oils mentioned above as carried out with Yanagimoto Gas chromatographic apparatus Type GCG-2 equipped with a thermal conductivity detector. The column used was 3 meters in length, 4 mm. in diameter, and packed with column material (60~80 mesh celite 545 coated with polyethylene glycol 6000, 30%). The operation was performed isothermally at 150°C, and at 160°C, the cell current being 150 mA, and the hydrogen flow rate was regulated at 40 and 64 ml per minute.

**Assignment of peak component.** Each of the peaks on the chromatograms was assigned in view of the relative retention volume and the aroma of the effluent gas, by comparison with authentic compounds. Compounds corresponding to some peaks on

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the chromatograms were trapped with potassium bromide powder and identified by infrared spectrometry.

RESULTS AND DISCUSSION

1) The chromatograms of the raw Kabusu oil (without treatment of fractional distillation) are shown in Fig. 1. As shown in Fig. 1a, five major components were recognized in the fresh material, but Fig. 1b shows that 1,8-cineol disappeared and caprylaldehyde was very prominent in the stored material. This fact may be due to the instability of the oil. As its main component was limonene, the Kabusu oil was distilled under a reduced pressure of about 20 mm Hg, and its volume

FIG. 2. Gas Chromatogram of Kabusu Oil.
P.E.G. 6000, 3 m. temp. 160°C, H2 64 ml/min.
Kc, low boiling fraction Kd, higher boiling fraction

FIG. 3. Gas Chromatogram of Sudachi Oil.
P.E.G. 6000, 3 m. Temp. 160°C, H2 64 ml/min.
Sb, low boiling fraction Sa, higher boiling fraction
was reduced to 1/20 by removing limonene and other low boiling compounds. The distillate (Kc), and the residual oil (Kd) were rechromatographed respectively. In the chromatogram of Kc-fraction, no different peak is found as compared with Fig. 1a, but in the chromatogram of Kd in Fig. 2, twenty peaks are now recognized. The observed retention volume and relative amount of different components are listed in Table I.

As shown in Fig. 3, at least twenty components were recognized in Sudachi oil, and 1,8-cineol is the most prominent component next to the limonene. This component seems to give Sudachi its characteristic flavor.

The gas chromatogram of Iyokan oil showed that 1,8-cineol and linalool were prominent components except for limonene (Fig. 4). The characteristic flavor of Iyokan oil may be attributable to linalool.

The chromatograms of Natsudaidai oil and Daidai oil presented in Fig. 5 and 6. Next to the limonene, 1,8-cineol is the most prominent component and gives Natsudaidai its characteristic flavor.

2) As the result of the experiment, it has been found that the five citrus varieties have much the same major components but that each has different minor components which seemed to be the cause of its characteristic
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TABLE I. OBSERVED RETENTION VOLUME AND RELATIVE AMOUNT OF COMPONENTS IN FIVE KIND OF ORANGE PEELS

<table>
<thead>
<tr>
<th>Peak number</th>
<th>Relative retention volume</th>
<th>Compound</th>
<th>Peak area percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Kabusu (%)</td>
</tr>
<tr>
<td>1</td>
<td>(air)</td>
<td></td>
<td>0.86</td>
</tr>
<tr>
<td>2</td>
<td>(ether)</td>
<td></td>
<td>0.86</td>
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<tr>
<td>3</td>
<td>0.34</td>
<td>water</td>
<td>10.90</td>
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<tr>
<td>4</td>
<td>0.46</td>
<td>camphene</td>
<td>73.82</td>
</tr>
<tr>
<td>5</td>
<td>0.54</td>
<td>1,8-cineol</td>
<td>5.70</td>
</tr>
<tr>
<td>6</td>
<td>0.73</td>
<td>caprylaldehyde</td>
<td>1.36</td>
</tr>
<tr>
<td>7</td>
<td>1.00</td>
<td>unidentif.</td>
<td>0.29</td>
</tr>
<tr>
<td>8</td>
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<td>1.27</td>
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<tr>
<td>11</td>
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<td>unidentif.</td>
<td>—</td>
</tr>
<tr>
<td>12</td>
<td>2.32</td>
<td>unidentif.</td>
<td>—</td>
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<td>13</td>
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<td>0.64</td>
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<td>0.32</td>
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<td>16</td>
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<tr>
<td>17</td>
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<tr>
<td>24</td>
<td>7.99</td>
<td>unidentif.</td>
<td>0.18</td>
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</table>

By mixing the identified compounds in the amounts estimated by gas chromatography, artificial flavors similar to those of fresh orange could be obtained, but they are far from the original. Some of the unidentified components still had orange-like aroma.

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flavor. Therefore, this compound may be the character-giving compound in the essential oil of that orange, according to Jennings's classification of aroma and flavor compounds.19

Generally, in the same species, the proper flavors of the individuals may be attributable to their minor components, while the major constituents seem to serve as contributory factors.