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SHORT COMMUNICATION

THE ORIGIN OF CITRUS FLAVOR COMPONENTS—IV.

THE TERPENES OF "VALENCIA" ORANGE LEAF, PEEL, AND BLOSSOM OILS*

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Abstract—The essential oils of "Valencia" orange peel and leaves were extracted at periodic intervals during the normal growing season, analyzed by gas–liquid chromatography, and qualitative variations noted. The major components of the peel oil from the very small immature fruit were linalool and sabinene, while at the end of the season (+)-limonene was the predominant compound in the mature fruit. The leaf oils did not show a pronounced seasonal variation. Analysis of the oils from petal, pistil, and stamen portions of the blossoms showed differences in their composition.

INTRODUCTION

THE PERCENTAGE variation in peel and leaf oil terpenes of three citrus cultivars, "Dancy" tangerine, "Hamlin" orange, and "Marsh" grapefruit, and the chemical composition of the petal, pistil, and stamen oils from these same three cultivars were reported by the authors.[1,2] The present paper extends this work to include comparable data from a fourth cultivar, the "Valencia" orange, which should be of particular interest because of its long cropping season and its reputation for desirable flavor and aroma. Whereas, the "Hamlin" orange[1] blooms in late February and is generally harvested before the next bloom; the "Valencia" orange also blooms in late February but does not become fully ripened for harvest until it has been on the tree for about 14 months. The normal "Valencia" picking season extends from approximately April to June of the year following the bloom. Consequently, "Valencia" trees normally bear blossoms, small immature fruit, and fully expanded fruit simultaneously during the spring months.

RESULTS

The percentages of nine components of "Valencia" peel oil which show significant seasonal variation, determined periodically from 12 April 1966 to 15 May 1967 are shown in Table 1. A similar analysis was made of the same sixteen major components of "Valencia"

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[1] J. A. ATTAWAY, A. P. PIERINGER and L. J. BARABAS, *Phytochem.* **6**, 25 (1967).
[2] J. A. ATTAWAY, A. P. PIERINGER and L. J. BARABAS, *Phytochem.* **5**, 1273 (1966).

leaf oil described in an earlier paper[1] but no great seasonal variation was found. Most of the hydrocarbon and the non-hydrocarbon components of the petal, pistil, and stamen oils

TABLE 1. PERCENTAGE COMPOSITION OF "VALENCIA" ORANGE PEEL OIL DURING 1966–67 SEASON

	Percentage composition on:																
	April			May			June		July	Aug.		Sept.	Dec.	Jan.		Feb.	May
Compound	12	18	25	2	16	31	13	27	12	8	22	19	19	5	24	6	15
β-Pinene+sabinene	32·1	32·4	22·0	10·1	10·3	5·3	2·4	2·4	2·2	2·2	1·6	1·5	1·1	1·2	1·1	0·9	0·9
α-Terpinene	0·9	0·1	0·6	0·2	0·1	0·1	0·1	—	—	—	—	—	—	—	—	—	—
(+)-Limonene	14·6	17·5	32·4	34·5	66·2	72·8	68·2	79·4	83·9	86·2	87·6	87·6	86·7	86·0	86·0	89·9	82·5
γ-Terpinene	2·2	0·3	2·2	0·9	0·5	0·5	0·6	0·3	0·2	0·2	0·2	0·1	—	0·1	0·2	0·2	0·1
Octanal	0·2	0·2	0·2	0·6	0·6	1·1	1·8	1·0	1·1	0·6	0·6	0·5	1·0	1·7	2·0	0·7	2·8
Terpinolene	0·5	0·1	0·5	0·2	0·1	0·2	0·1	0·1	—	—	—	—	0·1	—	—	—	—
Linalool	23·3	31·9	19·7	36·6	13·5	11·9	18·4	9·0	5·5	3·6	3·7	3·2	3·3	3·9	3·1	2·3	5·3
Terpinen-4-ol	4·5	3·8	5·9	4·5	0·6	0·4	1·1	0·3	0·2	0·1	0·1	0·1	0·1	0·1	0·1	0·1	0·2
α-Terpineol	1·5	1·9	1·1	2·8	0·7	0·8	1·4	0·7	0·5	0·3	0·3	0·3	0·3	0·4	0·4	0·2	0·5

TABLE 2. RELATIVE CONCENTRATIONS OF HYDROCARBONS FROM "VALENCIA" FLOWER PARTS*

Compound	Petal oil	Pistil oil	Stamen oil
α-Pinene	W	M	—
Unknown	—	VW	—
β-Pinene	W	W	—
Sabinene	VS	VS	VW
Myrcene	M	S	—
Car-3-ene	W-M	VW	VW
α-Terpinene	W	W-M	—
(+)-Limonene	S	VS	VW
β-Phellandrene	W	W-M	—
β-Ocimene	M	VS	—
γ-Terpinene	W-M	S	VW
p-Cymene	VW	W	—
Terpinolene	W	W-M	—
β-Caryophyllene	VW	W-M	VW
Valencene	VW	W-M	M

* — = not present in detectable quantities, VW = less than 5 per cent recorder scale deflection, W = 5–20 per cent recorder scale deflection, W-M = 20–50 per cent recorder scale deflection, M = 50–80 per cent recorder scale deflection, M-S = 80–100 per cent recorder scale deflection, S = off-scale peak returned to scale with one step of attenuation, and VS = off-scale peak requiring more than one step of attenuation to return to scale.

from "Valencia" blossoms are presented in Tables 2 and 3 respectively. These tables present data in the same form as was reported earlier.[1,2]

TABLE 3. RELATIVE CONCENTRATIONS OF NON-HYDROCARBONS FROM "VALENCIA" FLOWER PARTS*

Compound	Petal oil	Pistil oil	Stamen oil
Citronellal	VW	VW	—
Linalool	VS	VS	VS
Octanol	—	—	—
Unknown (21B)†	VW	VW	VW
Unknown (21C)	VW	VW	VW
Terpinen-4-ol	M	S	VW
Phenylacetaldehyde	W	VW	W
Neral	VW	VW	VW
α-Terpineol	W-M	W-M	W-M
Geranial	VW	VW	—
Citronellol	W	W	W
Nerol	VW	VW	—
Unknown (30A)	—	—	M
Geraniol	W	W	VW
Benzyl alcohol	W	W	—
Unknown (34A)	—	—	M
Phenylacetonitrile	VW	VW	—
cis-Nerolidol	W	—	W
Unknown (36A)	—	—	M
Unknown (36C)	—	—	VS
Unknown (38A)	—	—	M
Farnesol	S	W	—
Indole	VW	VW	W

* For explanation of —, VW, W, W-M, M, M-S, S, and VS see footnote on Table 2.

† Numbers of unknowns correspond to those assigned in an earlier paper.[2]

DISCUSSION

The distinguishing feature between the peel oils of "Valencia" orange and those of "Hamlin" orange, "Marsh" grapefruit, and "Dancy" tangerine described earlier[1] was the large concentration of the beta-pinene–sabinene mixture found in "Valencia" oils. In the earlier work it was shown that the greatest concentration of this mixture in "Hamlin" oranges was only 0·76 per cent on 26 April, while beta-pinene was not detected in "Marsh" grapefruit and "Dancy" tangerine. However, as shown in Table 1 the concentration of these components in peel oil from very immature "Valencias" was over 30 per cent of the total volatile oil. This difference was found to be largely at the expense of linalool which was only 20–30 per cent in immature "Valencias" compared to over 60 per cent in immature "Hamlins". However, in both varieties the (+)-limonene concentration rapidly increased with maturity until it became the dominant constituent, making up almost 90 per cent of the mature oil. By August the beta-pinene–sabinene peak had decreased to 2·2 per cent and the linalool peak to 3·6 per cent, while the (+)-limonene peak had increased to 86·2 per cent.

The leaf oils of the "Valencia" and "Hamlin" oranges were more alike qualitatively than were the respective peel oils. However, the "Valencia" leaves contained substantially less sabinene. "Hamlin" leaf oils consistently contained over 50 per cent sabinene throughout

the season while "Valencia" leaf oils ranged from 35–40 per cent of this terpene. "Hamlin" orange leaf oil contains a larger percentage of sabinene than any essential oil analyzed at this laboratory.

The oils from the "Valencia" blossoms were similar to those found from "Hamlin" blossoms. There were qualitative differences in some of the higher boiling unidentified compounds, and the concentrations of alpha-pinene, alpha-terpinene, terpinolene, and *cis*-nerolidol were substantially less in the "Valencia" petal oils than in the "Hamlin" petal oils.

EXPERIMENTAL

Preparation of Samples

Fruit, leaves, and blossoms were harvested and processed in the same manner reported earlier,[1,2] however, the "Valencias" were collected during a later harvesting season than the cultivars described earlier.

Oil Analysis by Gas–Liquid Chromatography

Gas chromatograms were prepared using the same instrumentation and techniques described in the earlier papers.[1,2]

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