

# Comparative Study of the Aromatic Profiles of Two Different Plum Species: *Prunus salicina* Lindl and *Prunus simonii* L

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**Abstract:** Volatile compounds of two plum species (*Prunus salicina* Lindl and *Prunus simonii* L) were analyzed by capillary gas chromatography-mass spectrometry using simultaneous vacuum distillation extraction. Aroma patterns were identified and quantified. A total of 60 compounds were identified, of which 23 were unique to *P. simonii*. The profile of *P. simonii*, as well as a study of the odor unit values of some identified compounds, indicated a much stronger aroma than *P. salicina*. Hexyl acetate, which produces a characteristic apple aroma, was present in *P. simonii* at levels 50-fold higher than in the studied cultivars of *P. salicina*.

**Key words:** *Prunus salicina*, *Prunus simonii*, volatile compounds, plum, fruit breeding, aroma.

## INTRODUCTION

The genus *Prunus* encompasses numerous tree crops: almond, apricot, cherry, nectarine, peach and plum. Within this genus, the plums represent one group having a wide range of genetic diversity from which traits of economic importance can be gleaned. Japanese plums (*P. salicina* Lindl) arrived in the US during the 1880s (Weinberger 1975). Hybridizations between Japanese and native American plums at many US locations have led to numerous cultivars being adapted to a wide range of environmental conditions.

The Agricultural Research Service (ARS) has had an active fruit breeding program in Fresno, California, for the past six decades. From this location, four Japanese plum cultivars—'La Roda', 'Nubiana', 'Queen Ann' and 'RedRoy'—were named and released by the ARS in 1954. Since these initial cultivar releases, seven other Japanese plums, including 'Blackamber' and 'Friar', have been made available to stone fruit growers. These two important cultivars account for over 17% of the bearing Japanese plum acreage currently planted in California (Tippett *et al* 1992). Current breeding objec-

tives include enhancing the flavor and aroma characteristics of selections already having large fruit size, high skin color and firm flesh.

Cultivars and plum species differ in appearance, aroma and flavor. The sensory properties are very important to consumers and can be a determining factor in the development and release of new fruit cultivars. To give plant breeders the information required for these sensory attributes, it is important to know their chemical nature.

Very little has been published on plum volatiles. The first report was carried out by Forrey and Flath (1974) in *P. salicina* var 'Santa Rosa'. It was determined that acetate esters predominated the volatile compounds of plums, but there were also appreciable quantities of the higher lactones. Based on the study of Williams and Ismail (1981), linalool and ethyl butanoate are very important in the aroma of European plums (*P. domestica*). The studies of Horvat *et al* (1992) with hybrids of *P. salicina* and *P. americana* demonstrated that, for most of the studied cultivars, (*E*)-2-hexenal, butyl acetate, butyl butanoate and  $\gamma$ -dodecalactone were the major constituents. Comparative studies of headspace volatiles between Japanese plum, apricot and interspecific hybrids between them using intact, tree-

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ripe fruit samples indicate that aromatic profiles of the studied cultivars 'Blackamber' and 'Friar' contained far fewer constituents than apricot or plum × apricot hybrids (Gómez and Ledbetter 1993).

In order to meet the objectives of developing plum cultivars with enhanced quality characteristics, it is necessary to evaluate new germplasm as it becomes available and incorporate genotypes having unique or enhanced fruit characteristics into the breeding program. Organoleptic analysis of fruit from a *P. simonii* clone during the 1992 fruit ripening season indicated a markedly more intense flavor when compared with commercial cultivars of Japanese plums. Personnel evaluating this clone reported a strong apple flavor. This clone is productive and fruit size averages 80–90 g. The flesh is firm, orange-colored and crisp.

This study reports on the volatile constituents present in *P. simonii* and a comparison with the profiles obtained from two *P. salicina* Lindl cultivars.

## EXPERIMENTAL

Clonal accessions of 'Blackamber' and 'Friar' Japanese plums and *P. simonii* were cultivated at the ARS Horticultural Crops Research Laboratory in Fresno, California. *P. simonii* (PI 91527) was obtained from the National Clonal Germplasm Repository in Davis, California. Trees were grown in a flood-irrigated orchard, and each clonal accession was grown on 'Nemaguard' rootstock.

Fresh, tree-ripened plums were collected and immediately stored at  $-18^{\circ}\text{C}$  until the analysis. All analyses were performed within one month of harvest. The volatile constituents were isolated using simultaneous vacuum distillation extraction.

The fruit was cut in half and the stones were removed and discarded. The skin and pulp (500 g) were blended with 1.5 liters of HPLC grade water for 30 s. 3-Nonanone was used as an internal standard. The mixture was added to a 5-liter round-bottomed flask.

A modified Likens–Nickerson distillation extraction head was used (Schultz *et al* 1977; Takeoka *et al* 1988). The fruit slurry was subjected to vacuum distillation extraction (60 mmHg) for 3 h with 60 ml of hexane.

Residual water was removed by freezing the sample at  $-40^{\circ}\text{C}$ . The hexane extract was then concentrated with a Vigreux column under reduced pressure (200 mmHg) to a final volume of 0.3–0.4 ml.

The concentrated extract was injected into a Hewlett-Packard 5890 gas chromatograph (Hewlett-Packard, Avondale, PA). Separations were performed using a DB-5 MS column (30 m × 0.25 mm, J & W Scientific Folsom, CA). The oven temperature was programmed from 50 to 250°C ( $4^{\circ}\text{C min}^{-1}$ ). Helium was used as a carrier gas and the average linear velocity was 60 cm  $\text{s}^{-1}$ . The injector was maintained at 200°C. The

temperature of the detector (Hewlett-Packard 5971A mass selective detector) was 170°C. The spectra were recorded at an ionization voltage of 70 eV, with a speed of 2.1 scan  $\text{s}^{-1}$  over a mass range of  $m/z^{-1}$  20–260. Data processing was performed with a Hewlett-Packard 5895 GC ChemStation.

Sample components were identified by mass spectrum matching with a mass spectral library collection. The mass spectrum identifications were verified by comparison of the component's experimental retention index with that of authentic reference standards in most of the cases, as indicated in Table 1.

## RESULTS AND DISCUSSION

Table 1 presents the volatile constituents identified and quantified in *P. simonii* and two cultivars of *P. salicina* ('Blackamber' and 'Friar'). The quantification of these compounds has to be considered approximate because the response factor of all compounds has not been calculated and all responses are considered the same as the internal standard, 3-nonanone.

In both species a total of 12 alcohols, 6 hydrocarbons, 10 aldehydes, 7 ketones, 21 esters and 4 lactones have been identified. Aldehydes and alcohols of six-carbon atoms were identified in both species. These compounds were hexanal, 2-hexenal, hexanol, 2-hexenol and 3-hexenol. The presence of these compounds was due to the lipoxygenase activity, action initialized by the disruption of the fruit tissues when it was blended (Frankel 1982). These  $\text{C}_6$  compounds are important to plum aroma (Ismail *et al* 1981) and contribute to the green note of the fruit (Guichard *et al* 1990).

Both *P. salicina* cultivars had very similar profiles that were quite different from *P. simonii*. In each of the volatile constituent classes, specific compounds were identified and quantified in *P. simonii* that were not present in either 'Blackamber' or 'Friar.' Of the seven identified ketones,  $\alpha$ -ionone appeared only in the profile of *P. simonii*. Among the alcohols, octanol, nonanol and geraniol only appeared in *P. simonii*. The number of hydrocarbons present in *P. simonii* was smaller than in *P. salicina*; however, esters were both qualitatively and quantitatively higher in *P. simonii*. Twelve of the 21 identified esters only appeared in *P. simonii*. Also, the concentration of lactones, important for the fruity aroma (Guichard *et al* 1990), was greater in *P. simonii*.

Esters are the main compounds responsible for the fruity aroma. Among the esters identified solely in *P. simonii*, butyl propanoate and 3-methyl-1-butyl acetate have a strong banana aroma and 2-methylpropyl butanoate and octyl acetate have a pleasant fruity aroma.

Some components were identified in both species but with great differences in their concentrations from one species to the other. These compounds were hexenal, hexanal and hexanol, the esters butyl acetate, hexyl

**TABLE 1**  
Concentration of the volatile compounds identified in the two plum species ( $\mu\text{g kg}^{-1}$ )

Constituent	Blackamber	Friar	<i>P. simonii</i>	Identification <sup>a</sup>	KI <sup>b</sup>
<i>Ketones</i>					
2,2,6-Trimethyl-cyclohexanone <sup>c</sup>	— <sup>d</sup>	—	0.7 <sup>e</sup>	MS	1036
Isophorone	—	1.0	0.8	KI, MS	1059
Acetophenone	1.7	—	—	KI, MS	1065
$\alpha$ -Ionone	—	—	4.4	MS	1422
Dihydro- $\beta$ -ionone	—	0.4	—	KI, MS	1433
Geranylacetone	4.6	0.6	5.0	KI, MS	1449
$\beta$ -Ionone	8.3	3.1	18.2	KI, MS	1482
<i>Alcohols</i>					
( <i>Z</i> )-3-Hexen-1-ol	6.4	12.8	19.5	KI, MS	849
( <i>E</i> )-2-Hexen-1-ol	2.5	5.0	—	KI, MS	858
Hexanol	32.9	12.3	357.5	KI, MS	862
4-Methylpentanol	—	—	8.9	MS	874
2-Ethylhexanol	3.7	0.6	—	MS	1028
Octanol	—	—	39.5	KI, MS	1068
Linalool	18.0	7.6	21.1	KI, MS	1104
Nonanol	—	—	8.4	KI, MS	1178
$\alpha$ -Terpineol	—	1.4	3.5	KI, MS	1199
Geraniol	—	—	3.0	KI, MS	1221
Nerol	1.0	—	—	KI, MS	1251
Nerolidol	—	0.7	—	MS	1562
<i>Aldehydes</i>					
Hexanal	19.5	5.9	93.3	KI, MS	802
( <i>E</i> )-2-Hexenal	—	11.9	43.5	KI, MS	848
Heptanal	2.5	1.4	2.0	KI, MS	898
( <i>E</i> )-2-Heptenal	—	0.4	0.8	MS	953
( <i>E,E</i> )-2,4-Heptadienal	3.3	—	—	MS	998
Phenylacetaldehyde	28.2	1.3	11.7	KI, MS	1045
Nonanal	51.1	13.8	39.1	KI, MS	1105
$\beta$ -Cyclocitral	—	1.2	4.2	KI, MS	1219
( <i>E,Z</i> )-2,4-Decadienal	—	—	4.1	KI, MS	1295
( <i>E,E</i> )-2,4-Decadienal	—	—	4.2	MS	1319
<i>Esters</i>					
Butyl acetate	1.2	0.2	904.5	KI, MS	813
3-Methylbutyl acetate	—	—	30.9	KI, MS	864
Butyl propanoate	—	—	2.3	KI, MS	910
3-Methyl-2-buten-1-ol-acetate	—	—	4.6	MS	923
2-Methylpropyl butanoate	—	—	23.6	MS	945
( <i>Z</i> )-3-Hexenyl acetate	16.1	2.8	55.3	KI, MS	1005
Hexyl acetate	42.7	2.3	2121.5	KI, MS	1010
( <i>E</i> )-2-Hexenyl acetate	6.4	0.7	—	KI, MS	1014
Heptyl acetate	—	—	14.1	KI, MS	1110
( <i>Z</i> )-3-Hexenyl butanoate	—	0.6	0.4	KI, MS	1183
( <i>E</i> )-2-Hexenyl butanoate	—	—	14.7	KI, MS	1191
Ethyl octanoate	4.7	—	—	KI, MS	1196
Octyl acetate	—	—	100.9	KI, MS	1200
( <i>Z,E</i> )-3-Hexenyl 2-hexenoate	—	1.2	—	MS	1228
Bornyl acetate	6.0	0.4	5.9	KI, MS	1287
Pentyl hexanoate	—	—	3.3	MS	1289
Nonyl acetate	—	—	3.4	KI, MS	1308
2-Ethyl-3-hydroxyhexyl 2-methylpropanoate	—	—	0.8	MS	1373
Geranyl acetate	—	—	5.2	KI, MS	1377
( <i>Z</i> )-3-Hexenyl hexanoate	13.8	9.4	9.5	KI, MS	1376
Dodecyl acetate	—	—	3.2	MS	1406

TABLE 1—Continued

Constituent	Blackamber	Friar	<i>P. simonii</i>	Identification <sup>a</sup>	KI <sup>b</sup>
<i>Lactones</i>					
$\gamma$ -Octalactone	—	—	3.8	KI, MS	1255
$\gamma$ -Decalactone	3.1	—	106.0	KI, MS	1476
$\gamma$ -Undecalactone	—	—	1.2	KI, MS	1656
$\gamma$ -Dodecalactone	16.1	4.8	297.8	KI, MS	1681
<i>Hydrocarbons</i>					
1,4-Dimethylbenzene	2.1	0.6	—	MS	865
1,2,3-Trimethylbenzene	2.5	1.7	—	KI, MS	966
Limonene	5.9	1.3	3.8	KI, MS	1031
Naphthalene	4.9	0.9	0.8	KI, MS	1186
2-Ethyl-1,4-dimethylbenzene	—	—	1.8	MS	1141
Diethylphthalate	4.2	1.1	—	MS	1585

<sup>a</sup> Compound identified by mass spectrum (MS) and/or Kovats indices (KI).

<sup>b</sup> Experimental Kovats indices for DB-5 column.

<sup>c</sup> Mass spectra were consistent with those of reference standards.

<sup>d</sup> Not found.

<sup>e</sup> Approximate concentration since percent recovery and response factors were not determined for each compound (assuming all had a response factor of 1). The concentration values are the average of two extractions.

acetate and (*Z*)-3-hexenyl acetate, as well as  $\gamma$ -decalactone and  $\gamma$ -dodecalactone. These esters and lactones, together with hexanal, contribute to the plum-like aroma and the characteristic fruity flavor of *P. simonii*.

The relative contribution of various constituents to the blended plum aroma was determined by calculating the number of odor units (Uo). The odor unit was defined by Guadagni *et al* (1966) as the concentration of

the compound divided by its odor threshold. This value gives an indication of the significance each volatile contributes to the plum aroma. Table 2 list the odor units of some plum constituents calculated from their concentrations and odor threshold (Takeoka *et al* 1990). The most important compounds of *P. salicina* are  $\beta$ -ionone (despite its low concentration, this compound has a very low odor threshold) and nonanal, as well as hexyl acetate in 'Blackamber'. In *P. simonii*, hexyl acetate and

TABLE 2

Detection odor thresholds in water (Tc) and odor units in the *P. salicina* cultivars 'Blackamber' (Ub) and 'Friar' (Uf) and in *P. simonii* (Up) for some of the identified compounds

Constituent	Tc (H <sub>2</sub> O, $\mu\text{g liter}^{-1}$ )	Ub	Uf	Up
( <i>E</i> )-2-Hexenal	17	—	0.7	2.5
Hexanal	5	3.9	1.2	18.7
( <i>Z</i> )-3-Hexen-1-ol	70	0.1	0.2	0.3
( <i>E</i> )-2-Hexen-1-ol	400	0.006	0.01	—
Hexanol	2500	0.01	0.004	0.14
Hexyl acetate	2	21.3	1.6	1060.7
2,2,6-Trimethyl-cyclohexanone	2	—	—	0.3
Phenylacetaldehyde	4	7.0	0.3	2.9
Linalool	6	3.0	1.3	3.5
Nonanal	1	51.1	13.8	39.1
Nonanol	50	—	—	0.2
$\alpha$ -Terpineol	330	—	0.004	0.2
Geraniol	40	—	—	0.07
$\gamma$ -Octalactone	7	—	—	0.5
( <i>E,E</i> )-2,4-Decadienal	0.07	—	—	58.6
$\gamma$ -Decalactone	11	0.3	—	9.6
$\beta$ -Ionone	0.007	1185.0	442.8	2600.0
$\gamma$ -Dodecalactone	7	2.3	0.7	42.5

$\beta$ -ionone are the most important compounds, with the odor unit of hexyl acetate being 1060.7. This ester is present at a high concentration in apples (Willaert *et al* 1983), and is responsible for the characteristic apple-like aroma found in this species. But there are other compounds with a high odor unit value such as hexanal, described, when diluted as a plum-like aroma (Williams and Ismail 1981); nonanal, a characteristic constituent of plums skin waxes, with a fragrant woody-like aroma; (*E,E*)-2,4-decadienal and the lactones  $\gamma$ -decalactone and  $\gamma$ -dodecalactone, which are described as being responsible for the fruity, peach and coconuts background aromas of fruit (Takeoka *et al* 1990).

Contrasting the aromatic profiles of *P. simonii* with both 'Blackamber' and 'Friar', it appears that *P. simonii* could be a useful parental accession in a plum breeding program for its unique aromatic constituents and quantitatively important aroma compounds. Of the 60 quantified compounds identified in this study, 23 are only present in *P. simonii*. Twelve of these unique compounds are esters; taken collectively, they probably contribute to the intense fruity aroma of *P. simonii*. Hybridizations between *P. salicina* cultivars and *P. simonii* are planned, with the objective of selecting of high levels of these important aromatic compounds in fruit of the progeny.

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