Characterization of odor-active compounds in three varieties of ciruela (Spondias purpurea L.) fruit

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ABSTRACT

The aroma-active compounds present in tree ripened fruits of ciruela (Spondias purpurea L.) cultivars Chi abal, Campech abal, and Ek abal were isolated by means of simultaneous distillation solvent extraction and solid-phase microextraction and analyzed by gas chromatography-mass spectrometry. Application of odor activity values (OAV) afforded 22 compounds in higher amounts than their threshold concentrations (OAVs >1). Results of the identification experiments in combination with the OAVs suggested that methyl 3-methylbutanoate, ethyl butanoate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, ethyl hexanoate, hexyl acetate, with fruity odor notes; (E)-2-hexenal, (Z)-3-hexen-1-ol, (E)-2-hexen-1-ol, 1-hexanol, and (Z)-3-hexenyl acetate, with grassy odor notes, and limonene (citrus-like) were the potentially important common odorants in all ciruela cultivars. Clear differences in the OAVs of some odorants between each of the cultivars suggested that they contributed to the unique sensory profiles of the individual cultivars.

ARTICLE HISTORY

Received 27 April 2017
Accepted 19 May 2018

KEYWORDS

Spondias purpurea; headspace solid-phase microextraction; simultaneous distillation-extraction; odor-active compounds

Introduction

The genus Spondias comprises 17 species, including 7 taxa in the Neotropics and 10 species in the Asian tropics.\textsuperscript{[1]} Spondias purpurea L., Anacardiaceae is one of three Spondias species native to Mexico and Central America.\textsuperscript{[2]} It is known as ciruela mexicana, jocote, siriguela, and red mombin.\textsuperscript{[2–6]} The fruits are highly variable in color and may be purple, dark- or bright-red, orange, yellow, or red-and-yellow. They vary from 1 to 2 inches in length and may be oblong, oval, obovoid, or pear-shaped. The skin is glossy and firm; the flesh aromatic, yellow, fibrous, very juicy, with a rich plum-like subacid to acid flavor. The ripe fruits are commonly eaten out-of-hand, but at home they are often stewed whole with sugar and consumed as a dessert. They can also be preserved simply by boiling and drying, which maintains them in good condition for several months. The strained juice of cooked fruits yields an excellent jelly and is also used for making wine and vinegar.\textsuperscript{[7]}

Ciruela has commercial value as fruit production, juices, jams, ice cream, and alcoholic beverages.\textsuperscript{[2]} Despite its wide acceptance in diverse regional markets and its great potential for commercialization as an exotic fruit, there is scarce information available regarding the volatile composition of this fruit. Simultaneous distillation-extraction (SDE) was employed to analyze the skin and pulp of fresh ciruela. Major compounds were 2-hexenal (~39%), hexadecanoic acid (18.5%), and hexanal (~7%).\textsuperscript{[8]} In an investigation using industrialized pulp, samples were subjected to solid-phase microextraction (SPME) utilizing several types of SPME fibers. The highest amounts extracted, evaluated from the sum of peak areas as well the number of identified compounds (119), were obtained using a CAR-PDMS fiber.\textsuperscript{[3]} Similar types of compounds were found in another study using SPME; although in this case, fresh
pulp was used as the sample. DVB-CAR-PDMS proved to be the more efficient qualitative and semi-quantitative fiber in trapping these compounds. A total of 27 volatiles were identified, especially ketones, alcohols, aldehydes, esters, and terpene hydrocarbons in the headspace. Quantitatively, the predominant were hexanal (10.6%), ethyl acetate (8.4%), 3-hexen-1-ol (6.8%), 2-hexen-1-ol (5%), (E)-2-hexenal (5%), and hexyl acetate (2%). The highest number of compounds (37) were obtained utilizing DVB/CAR/PDMS (50/30 μm) fibers. Hexanal, 3-hexen-1-ol, 2-hexen-1-ol, and ethyl acetate were the major identified compounds. However, neither of these studies attempted to evaluate the quantitative composition and aroma contribution of the volatile compounds.

The aim of the present work was to characterize the aroma of three varieties of ciruela cultivars utilizing simultaneous distillation-solvent extraction and solid-phase microextraction coupled with Gas Chromatography-Mass Spectrometry (GC-MS) and the use of odor activity values in order to identify volatile compounds with olfactive impact.

Materials and methods

Chemicals and reagents

Fresh, healthy, ripe ciruela fruits were harvested at a commercial orchard in the central part of the Yucatan peninsula, Mexico. Three cultivars were collected: Campech abal, Ek abal, and Chi abal. Basic juice chemistry for samples is reported in Table 1 (soluble solids, titratable acidity, and brix/acid ratio).

Standards used for identifications were supplied by Aldrich (Steinheim, Germany) and Fluka (Buchs, Switzerland). Some standards were provided by Dallant (Barcelona, Spain). An n-alkane solution (C₈–C₃₂) from Sigma-Aldrich (St. Louis, MO) was utilized to calculate the linear retention index (RI) of each analyte. Dichloromethane, n-pentane, n-hexane, and n-heptane were procured from Merck (Darmstadt, Germany) and were redistilled and checked for purity.

Soluble chemical analysis

Soluble solids and total acidity (as anhydrous citric acid) were determined in the fruit pulp according to standard methods.

Isolation of volatile compounds by SDE

Volatile compounds were isolated according to a previously reported method. A sample of 250 g of fresh fruit homogenate was blended with 1000 mL of distilled water; 0.5 mL of methyl nonanoate standard solution (3.5 mg/mL) was added as an internal standard. The volatile compounds were isolated by means of a SDE apparatus using 40 mL of dichloromethane for 1 h. The extract was dried over anhydrous Na₂SO₄ and concentrated to 0.6 mL in a Kuderna-Danish evaporator with a Vigreux column and further concentrated to 0.2 mL with a gentle nitrogen stream. The concentrated extract was stored in a glass screw-top vial at −20°C until analyzed. Each sample was analyzed in triplicate.

Table 1. Basic juice chemistry for ciruela varieties.

| Variety   | Soluble solids (Brix) | Titratable acidity (g/kg as citric acid) | Brix/acid |
|-----------|-----------------------|-----------------------------------------|-----------|
| Campech abal | 11.38                 | 0.71                                    | 16.03     |
| Ek abal   | 9.41                  | 1.19                                    | 7.91      |
| Chi abal  | 13.59                 | 0.82                                    | 16.57     |
Isolation of volatile compounds by solid-phase microextraction (HS-SPME)

Volatile compounds from fresh fruit homogenate headspace were extracted using 50/30 µm DVB/CAR/PDMS (Supelco, Park, Bellefonte, PA). The fiber was conditioned before use and cleaned between analyses by inserting them into the GC injector and were maintained at the recommended temperature to prevent contamination and utilized immediately following conditioning. Headspace Solid-Phase Microextraction (HS-SPME) extraction was performed at 30°C on 6 g of stirred homogenate in a 15-mL vial sealed with a polytetrafluoroethylene-lined screw cap with constant magnetic stirring (600 rpm). A pre-extraction time of 30 min and an additional extraction time of 30 min were applied. The sampling conditions were chosen after preliminary Gas Chromatography-Flame Ionization Detector (GC-FID) analyses and were similar to those reported in other fruit studies. [12,13] Each sample was analyzed in triplicate.

GC-FID and GC-MS analysis

A Perkin-Elmer Autosystem XL (Shelton, CT, USA), equipped with a 30-m × 0.25-mm × 0.25-µm film thickness AT-5 ms (Alltech, Deerfield, IL, USA) fused-silica capillary column and with a flame ionization detector, was used. Oven temperature was held at 50°C for 2 min and then raised to 280°C at 4°C/min and held for 10 min. Carrier gas (helium) flow rate was 1 mL/min. The injection and detector temperatures were 240°C and 250°C, respectively. For the SDE extracts 1 µL was injected in 1:10 split mode and for SPME extracts splitless mode (2 min) was applied. The retention times of a series of straight-chain alkanes (C_5–C_32) was used to calculate the retention indices for all identified compounds and for reference standards. Estimated concentrations for all compounds were made by GC peak area comparisons of the SDE extract components with the peak area of a known quantity of internal standard. Concentrations were expressed as mg methyl nonanoate equivalents/kg of fresh weight, response factors being taken as 1.0 for all compounds with reference to the internal standard, and a recovery factor of 80% was considered.

GC-MS analyses were performed on a Perkin-Elmer Clarus 500 gas chromatograph with a similar fused capillary column as in GC-FID. The temperature program and carrier gas flow rate were the same, as in GC-FID. MS analysis was performed on EI mode, electron energy was 70 eV, and both ion source and interface temperatures were 250°C. The acquisition was performed in scanning mode (mass range m/z 35–400 u).

Compounds were preliminarily identified by use of NIST 05, Wiley 6, NBS 75 k, Adams 2001 and in-house Flavorlib libraries. Their identities were confirmed by comparison of their linear retention indices with those of reference standards or with published data.

Odor detection threshold determination

A previously described multiple paired comparison test was used. [14] Samples were prepared in capped, wide-mouthed, 50-mL glass bottles. A group of 30–40 unscreened and untrained assessors were employed in determining the odor thresholds. In each case, panels were replicated a sufficient number of times, so that a minimum of 100 responses were obtained for each concentration used in determining a particular threshold. The test involved presenting the assessors with several samples, along with an aqueous solution for reference. Each sample was compared in odor individually with reference to determine a possible difference. Six samples were presented to each judge during each session. The first bottle contained the reference sample and the next five coded bottles contained four different dilutions and an aqueous solution identical to the reference. The four dilutions were placed in order of increasing concentrations to prevent fatigue. The position of the aqueous solution coded sample was arbitrarily changed from day to day. The statistical analyses for determining odor detection threshold values involved calculating the concentration corresponding to 50% of positive responses from the
total judgments. The calculation was made from the linear regression of percentage detection against log concentration. The 95% confidence limit calculated for the threshold values was used as a measure of error. Relative standard deviations were lower than 6%.

### Results and discussion

The total volatile compounds from ciruela, isolated by SDE, were evaluated by sniffing a drop of the extract on a cardboard smelling strip, as done by perfumers. Following evaporation of the solvent, all panelists agreed that the extract evoked the characteristic fruity and plum-like aroma of the fruit, thereby indicating that the method utilized for aroma isolation was appropriate.

A total of 119 volatile compounds were detected by GC-MS by means of two different isolation methods (SDE and HS-SPME) in the three varieties; 105 of them were positively identified (Table 2). Positive identifications were arrived at by comparison of linear retention indices and mass spectra with those of standard reference compounds. As a result of the use of SDE, 63 volatile compounds were additionally isolated, in comparison with the SPME. These results are explained based on the characteristics of each extraction method used. The SDE is an exhaustive method, in which the fruit pulp was completely dispersed in hot water and volatiles were steam distilled and extracted with dichloromethane; consequently, higher recoveries were obtained. Furthermore, the conditions of the SDE method may lead to artifact compounds. On the other hand, the HS-SPME method is a non-exhaustive procedure with mild conditions but is specific depending of the type of fiber used. Taking into account the nature of the identified compounds, their presence cannot be explained simply due to odorant degradation and/or artifact formation, with the exception of 2-furfural.

Certain compounds have been reported previously in ciruela\[3,4,8\] and consisted largely of 44 esters, 17 aldehydes, 16 alcohols, 12 terpenes, 8 ketones, 6 acids, 5 aromatics, 4 paraffins, 6 miscellaneous compounds, and 1 lactone. *Chi abal* showed the richest composition, with 81 volatile compounds. *Campech abal* and *Ek abal* had a moderate composition, with 57 compounds each.

The semiquantitative data in Table 2 show that in total 1.32, 2.97, and 5.10 mg of volatile compounds were obtained per kg of fresh fruit (excluding skin and stone) for *Campech abal*, *Ek abal*, and *Chi abal*, respectively. Alcohols, esters, and aldehydes predominated in the three ciruela fruits (91.5%, 97.9%, and 83.1% of total volatiles in *Campech abal*, *Ek abal*, and *Chi abal*, respectively), then followed terpenes, acids, and ketones. Of these, ethyl acetate, acetic acid, ethyl butanoate, (*E*)-2-hexenal, (*Z*)-3-hexen-1-ol, (*E*)-2-hexenol, and 1-hexanol were the main volatile compounds, according to their high concentrations in at least one of the three cultivars analyzed.

The predominant class of compounds in all three ciruela were C₆ compounds according to their contents, i.e. (*E*)-2-hexenal (0.22–1.00 mg/kg), (*Z*)-3-hexen-1-ol (0.04–0.62 mg/kg), (*E*)-2-hexen-1-ol (0.13–0.52 mg/kg), and 1-hexanol (0.08–0.19 mg/kg). The highest content of (*E*)-2-hexenal and (*E*)-2-hexen-1-ol was present in *Ek abal*, whereas the lowest content was found in *Campech abal*. 1-Hexanol and (*Z*)-3-hexen-1-ol had the highest content in *Chi abal*, whereas the lowest content was found in *Campech abal*. The results parallel previous reports.\[3,4,8\] C₆ compounds are known to have a characteristic ‘green leaf’ odor, as released from green plant tissue following mechanical damage.\[15\] These volatile compounds are responsible for the ‘green’ odor perceived in fruits.\[16\] Other important C₆ compounds, but with fruity odors, were ethyl hexanoate (0.01–0.19 mg/kg) with the highest content in *Chi abal* and hexyl acetate (0.01–0.06 mg/kg) with the highest content in *Ek abal*, in comparison with the previous two cultivars. Among the esters identified, ethyl (*E*)-2-methyl-2-butenoate (ethyl tiglate) warrant attention because this type of ester is a less common plant volatile. The esters of branched chain acids can be derived from amino acid metabolism.\[15\] The presence of this ester has been reported previously in this fruit.\[4\] In general, ethyl esters were found to have higher amounts in *Chi abal*.

Table 3 lists the orthonasal odor detection threshold in water and the OAV for several volatile compounds found in ciruela. The significant contribution of each odorant to the characteristic flavor can be determined by the OAV, which is the ratio of concentration to the odor threshold of the compound. Although it is known that nonvolatile fruit compounds might influence odor thresholds, water is the
Table 2. Volatile compounds identified in ciruela varieties.

| Compound                        | RI  | ID | Campech abal | Ek abal | Chi abal |
|---------------------------------|-----|----|--------------|---------|----------|
|                                 |     |    | SDE          | SPME    | SDE      | SPME    |
| Ethanol                         | 527 | A  | tr           | *       | 0.01     | *       |
| Acetic acid                     | 610 | A  | tr           | *       | –        | –       |
| Ethyl acetate                   | 613 | A  | 0.16         | *       | 0.59     | *       |
| 2-Methyl-3-buten-2-ol           | 618 | B  | 0.23         | –       | –        | –       |
| 2-Methylpropan-1-ol             | 622 | A  | –            | –       | –        | –       |
| Methyl propanoate               | 642 | A  | tr           | *       | –        | –       |
| 1-Butanol                       | 650 | A  | –            | –       | –        | –       |
| 3-Methylbutanal                 | 654 | A  | tr           | *       | 0.01     | –       |
| 2-Methylbutanal                 | 662 | A  | 0.01         | –       | –        | –       |
| 1-Penten-3-one                  | 680 | A  | –            | –       | tr       | –       |
| 3-Pentanone                     | 700 | A  | tr           | –       | –        | 0.01    |
| Pentanal                        | 707 | A  | –            | –       | tr       | –       |
| Ethyl propanoate                | 709 | A  | tr           | *       | tr       | *       |
| Propyl acetate                  | 711 | A  | –            | –       | tr       | *       |
| 3-Hydroxy-2-butanol             | 714 | A  | –            | –       | 0.01     | –       |
| 3-Methyl-3-buten-1-ol           | 720 | A  | –            | –       | 0.02     | –       |
| Methyl butanoate                | 724 | A  | tr           | *       | –        | tr      |
| 3-Methyl-2-butenal              | 730 | B  | –            | –       | tr       | –       |
| 2-Methylbutan-1-ol              | 736 | A  | –            | –       | 0.01     | –       |
| Ethyl 2-methylpropanoate        | 751 | A  | tr           | *       | –        | –       |
| (E)-2-Pentenal                  | 754 | B  | –            | –       | 0.01     | –       |
| 1-Pentanol                      | 760 | A  | 0.05         | –       | 0.03     | –       |
| (Z)-2-Penten-1-ol               | 767 | B  | –            | –       | 0.03     | –       |
| 3-Methyl-2-buten-1-ol           | 774 | B  | –            | –       | 0.01     | –       |
| Methyl 3-methylbutanoate        | 790 | A  | 0.01         | *       | 0.01     | *       |
| 4-Methyl-3-penten-2-one         | 797 | B  | –            | –       | 0.01     | –       |
| Hexanal                         | 802 | A  | –            | –       | tr       | *       |
| Ethyl butanoate                 | 804 | A  | 0.06         | *       | 0.02     | –       |
| Butyl acetate                   | 812 | A  | –            | –       | 0.05     | –       |
| 2-Furfural                      | 831 | A  | 0.02         | –       | 0.02     | –       |
| Ethyl 2-methylbutanoate         | 845 | A  | 0.01         | *       | 0.02     | –       |
| (E)-2-Hexenal                   | 854 | A  | 0.22         | –       | 1.00     | *       |
| Ethyl 3-methylbutanoate         | 858 | A  | 0.01         | *       | 0.01     | –       |
| (Z)-3-Hexen-1-ol                | 860 | A  | 0.05         | *       | 0.05     | *       |
| p-Xylene                        | 863 | A  | 0.01         | –       | –        | –       |
| 2-Methylpropyl butanoate        | 865 | A  | –            | –       | –        | –       |
| (E)-2-Hexen-1-ol                | 867 | A  | 0.13         | –       | 0.52     | *       |
| 1-Hexanol                       | 871 | A  | 0.08         | *       | 0.11     | –       |
| 4-Penten-1-yl acetate           | 874 | B  | tr           | –       | –        | 0.04    |
| Ethyl (E)-2-methyl-2-butoate    | 877 | A  | 0.01         | *       | tr       | *       |
| 3-Heptanone                     | 884 | A  | –            | –       | 0.02     | –       |
| Propyl butanoate                | 896 | A  | –            | –       | –        | 0.01    |
| Heptanal                        | 905 | A  | –            | –       | tr       | *       |
| 3-Methyl-2-butenyl acetate      | 911 | B  | –            | –       | tr       | *       |
| 2-Cyclohexen-1-one              | 914 | A  | 0.01         | –       | tr       | –       |
| Methyl hexanoate                | 927 | A  | tr           | *       | 0.02     | –       |
| 5-Methyl-3-heptanone            | 943 | B  | –            | –       | tr       | –       |
| 5-Methyl-2-furfural             | 946 | A  | –            | –       | –        | –       |
| (E)-2-Heptanal                  | 954 | A  | –            | –       | 0.02     | –       |
| Benzaldehyde                    | 960 | A  | 0.01         | –       | tr       | –       |
| Methyl (E)-2-hexenoate          | 966 | A  | –            | –       | 0.01     | –       |
| 3-Octanone                      | 984 | A  | –            | –       | tr       | *       |
| Butyl butanoate                 | 994 | A  | –            | –       | tr       | –       |
| 1,3,5-Trimethylbenzene          | 996 | A  | tr           | –       | –        | –       |
| Ethyl hexanoate                 | 998 | A  | 0.01         | –       | 0.06     | *       |
| 2-Methylpropyl 3-methylbutanoate| 1002| A  | –            | –       | 0.06     | –       |
| Ethyl (E)-3-hexenoate           | 1004| A  | –            | –       | tr       | –       |
| (Z)-3-Hexenyl acetate           | 1006| A  | 0.01         | *       | 0.11     | *       |
| Hexyl acetate                   | 1009| A  | 0.01         | *       | 0.06     | –       |
| Hexanoic acid                   | 1017| A  | –            | –       | –        | 0.02    |
| p-Cimene                        | 1023| A  | tr           | –       | –        | 0.01    |
| Limonene                        | 1028| A  | 0.01         | *       | 0.01     | *       |

(Continued)
| Compound                          | RI   | ID | Campech abal | Ek abal | Chi abal |
|----------------------------------|------|----|--------------|---------|----------|
| 1,8-Cineol                       | 1031 | A  | tr           | tr      | 0.01     |
| Phenylacetaldehyde               | 1040 | A  | tr           | tr      |           |
| Butyl 3-methylbutanoate          | 1046 | A  | tr           | tr      |           |
| 3-Methylbutyl butanoate          | 1054 | A  | tr           | tr      |           |
| γ-Terpinene                      | 1056 | A  | 0.01         | 0.01    | 0.01     |
| (E)-2-Octenal                    | 1057 | A  | –            | –       |          |
| γ-Hexalactone                    | 1059 | A  | tr           | tr      |          |
| 5-Nonanone                       | 1073 | B  | tr           | tr      | tr       |
| 4-Nonanol                        | 1078 | B  | –            | 0.01    | tr       |
| (Z)-Linalool oxide (furanoid)    | 1087 | A  | tr           | –       |          |
| Methyl benzoate                  | 1091 | A  | 0.03         | –       | 0.01     |
| 2-Methylbenzofuran               | 1094 | A  | tr           | –       |          |
| Ethyl heptanoate                 | 1098 | A  | tr           | tr      | tr       |
| Nonanal                          | 1102 | A  | –            | 0.02    | 0.02     |
| Methyl octanoate                 | 1126 | A  | –            | –       | 0.01     |
| Methyl 2-methyloctanoate         | 1158 | B  | 0.08         | 0.07    | 0.08     |
| Benzy1 acetate                   | 1162 | A  | tr           | –       | tr       |
| (E)-2-Nonenal                    | 1165 | A  | –            | tr      | tr       |
| Ethyl benzoate                   | 1170 | A  | tr           | tr      | tr       |
| Octanoic acid                    | 1197 | A  | tr           | –       |          |
| (E)-3-Hexenyl butanoate          | 1185 | A  | tr           | tr      | tr       |
| Heptyl butanoate                 | 1193 | A  | –            | –       | tr       |
| Ethyl octanoate                  | 1195 | A  | tr           | tr      | 0.02     |
| Safranal                         | 1198 | A  | –            | tr      |          |
| Decan                           | 1206 | A  | tr           | 0.01    | –        |
| Ethyl salicylate                 | 1270 | A  | –            | –       | 0.01     |
| Nonanoic acid                    | 1277 | A  | –            | –       | tr       |
| Ethyl nonanoate                  | 1293 | A  | –            | –       | tr       |
| α-Cubebene                       | 1351 | A  | tr           | –       | tr       |
| α-Copaene                        | 1375 | A  | 0.01         | tr      | 0.01     |
| Methyl (E)-cinnamate             | 1378 | A  | tr           | –       | tr       |
| (E)-β-Damascenone                | 1384 | A  | tr           | tr      | –        |
| Decanoic acid                    | 1387 | A  | –            | –       | tr       |
| Ethyl decanoate                  | 1391 | A  | –            | –       | 0.01     |
| Dodecanal                       | 1411 | A  | tr           | tr      |          |
| β-Caryophyllene                  | 1420 | A  | 0.02         | –       | tr       |
| (E)-α-Bergamotene                | 1436 | A  | tr           | –       |          |
| Dehydro-β-ionone                 | 1438 | B  | tr           | –       |          |
| Geranylacetone                   | 1444 | A  | tr           | –       |          |
| α-Humulene                       | 1450 | A  | tr           | –       |          |
| 1-Dodecane                       | 1472 | A  | tr           | 0.02    |          |
| γ-Curcumene                      | 1479 | A  | 0.01         | tr      |          |
| (E)-β-Ionone                     | 1486 | A  | –            | –       | 0.01     |
| α-Selinene                       | 1498 | A  | –            | 0.01    | –        |
| γ-Cadinene                       | 1514 | A  | tr           | –       | tr       |
| Dodecanoic acid                  | 1570 | A  | –            | –       | tr       |
| Ethyl dodecanoate                | 1597 | A  | –            | –       | 0.01     |
| Benzophenone                     | 1603 | A  | –            | –       | tr       |
| 1-Tetradecanol                   | 1673 | A  | –            | –       | tr       |
| 2-Ethylhexyl benzoate            | 1692 | B  | tr           | –       | –        |
| Ethyl tetradecanoate             | 1794 | A  | –            | –       | tr       |
| 1-Octadecane                     | 1800 | A  | 0.02         | –       | –        |
| 1-Nonadecane                     | 1900 | A  | 0.01         | –       | –        |
| Methyl hexadecanoate             | 1927 | A  | –            | –       | tr       |
| Isopropyl hexadecanoate          | 2013 | A  | tr           | –       | tr       |
| 1-Eicosane                       | 2000 | A  | tr           | –       | –        |
| 1-Docosane                       | 2100 | A  | tr           | –       | tr       |

| Note | |
|------|---|
| a    | Lineal retention indices in AT-5ms capillary column. |
| b    | The reliability of the identification proposal is indicated by the following: A, compound definitely identified (comparison of RI and mass spectra with reference compound); B, by mass spectra and RI data from literature. |
| c    | Values expressed in mg/kg. |
| d    | tr: Lower than 0.01 mg/kg. |
| e    | Detected. |
| f    | Not detected. |
main constituent of the fruit. If a compound has an OAV \(\geq 1\), then it will contribute significantly to the overall fruit odor. If we look at the threshold concentration of a compound as a separate quantity, the OAV for that compound gives the number of threshold concentrations of that compound present in the fruit. The probability of a compound’s odor being detected should be greater than the number of OAVs. This value should then provide some indication of the importance of that compound in the overall odor. However, at least two simplifications of this concept should be scrutinized: the assumption that the perceived intensity is proportional to OAV and the frequent use of thresholds determined in model media other than the original food. Despite these limitations, the OAV concept is still considered a very useful tool in aroma research.\(^{[17]}\)

Due to the unavailability of the pure standard or the odor threshold data in the literature, the OAV of some compounds was omitted. From the odor threshold concentrations determined in this work or obtained from the literature, 22 compounds were present in amounts higher than their threshold concentrations (OAVs >1) (Table 3).

According to the odor notes of the 22 odor-active compounds, there is a balance between fruity and grassy notes in the aroma profile of this fruit. Only six compounds (methyl 3-methylbutanoate, ethyl butanoate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, ethyl hexanoate, and hexyl acetate) with fruity odor notes, plus five [(E)-2-hexenal, (Z)-3-hexen-1-ol, (E)-2-hexen-1-ol, 1-hexanol, and (Z)-3-hexenyl acetate] with grassy odor notes, and limonene (citrus-like) were common to the three cultivars. Clear differences in the OAVs of some odorants, between each of the cultivars, suggested that they contributed to the unique sensory profiles of the individual cultivars. Some compounds were detected as potential odorants only in one cultivar, for example, ethyl propanoate, ethyl 2-methylpropanoate, 1,8-cineol, and (E)-β-ionone in Chi abal, methyl butanalan and decanal in Ek abal, and 2-methyl-3-buten-1-ol in Campech abal. 3-Methyl-3-buten-1-ol and nonanal were identified as potential odorants only in Ek abal and Chi abal, whereas methyl benzoate was detected in Campech abal and Chi abal.

Since odor detection thresholds of some volatiles have not been determined, their contribution to ciruela aroma is still undefined. Sensory studies with aroma models and omission experiments warrant being conducted to determine the actual contribution of those volatiles to ciruela aroma.

| Compound                  | Odor threshold (µg/kg) | Odor quality | Campech abal | Ek abal | Chi abal |
|---------------------------|------------------------|--------------|--------------|---------|----------|
| 2-Methyl-3-buten-1-ol     | 10^b                   | Fruity, faint scent | 23           | –       | –        |
| 3-Methylbutanal           | 0.5^c                  | Malty        | –            | 20      | –        |
| Ethyl propanoate          | 10^a                   | Fruity       | –            | –       | 10       |
| 3-Methyl-3-buten-1-ol     | 10^b                   | Pungent      | –            | 2       | 5        |
| Ethyl 2-methylpropanoate  | 0.1^b                  | Sweet-fruity | –            | –       | 100      |
| Methyl 3-methylbutanoate  | 0.4^b                  | Fruity       | 25           | 25      | 100      |
| Ethyl butanoate           | 1^c                    | Fruity       | 60           | 20      | 930      |
| Ethyl 2-methylbutanoate   | 2^b                    | Fruity       | 5            | 10      | 4        |
| (E)-2-Hexenal             | 17^a                   | Green-intense fruity | 13           | 59      | 20       |
| Ethyl 3-methylbutanoate   | 0.023^c                | Fruity, blueberry-like | 435          | 435     | 2174     |
| (Z)-3-Hexen-1-ol          | 50^d                   | Grassy       | 1            | 1       | 12       |
| (E)-2-Hexen-1-ol          | 100^b                  | Grassy       | 1            | 5       | 3        |
| 1-Hexanol                 | 0.01^b                 | Grassy, floral | 8000         | 11,000  | 19,000   |
| Ethyl hexanoate           | 1^b                    | Fruity, pineapple-like | 10           | 60      | 190      |
| (Z)-3-Hexenyl acetate     | 13^c                   | Green, banana-like | 1            | 8       | 2        |
| Hexyl acetate             | 2^a                    | Sweet-fruity | 5            | 30      | 5        |
| Limonene                  | 10^d                   | Citrus-like  | 1            | 1       | 1        |
| 1,8-Cineol                | 1.1^e                  | Green, herb  | –            | –       | 10       |
| Methyl benzoate           | 0.5^b                  | Fruity, sweet | 60           | –       | 20       |
| Nonanal                   | 1^f                    | Fatty, flowery | –            | 20      | 20       |
| Decanal                   | 0.1^b                  | Orange peel  | –            | 100     | –        |
| (E)-β-Ionone              | 3.5^c                  | Woody        | –            | –       | 3        |

\(^a\)According to the Leffingwell web page.\(^{[18]}\)
\(^b\)Determined in the present work.
\(^c\)Czerny.\(^{[19]}\)
**Conclusion**

In the present study, SDE and SPME were used for extraction of volatiles in *Campech abal*, *Ek abal*, and *Chi abal* ciruela fruits. A total of 119 compounds were identified in three cultivars. Of these, ethyl acetate, acetic acid, ethyl butanoate, \((E)-2\)-hexenal, \((Z)-3\)-hexen-1-ol, \((E)-2\)-hexenol, and 1-hexanol were the main volatile compounds, based on their high concentrations in at least one of the three cultivars. The determination of odor activity values provided a satisfactory assessment of the most volatile compounds that play a major role in odor perception. Methyl 3-methylbutanoate, ethyl butanoate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, ethyl hexanoate, hexyl acetate with fruity odor notes, \((E)-2\)-hexenal, \((Z)-3\)-hexen-1-ol, \((E)-2\)-hexen-1-ol, 1-hexanol, and \((Z)-3\)-hexenyl acetate with grassy odor notes, and limonene (citrus-like), responsible for the fruity and grassy character of the ciruela, were the potentially important common odorants in all cultivars. In addition, 2-methyl-3-buten-1-ol, 3-methylbutanal, ethyl propanoate, 3-methyl-3-buten-1-ol, ethyl 2-methylpropanoate, 1,8-cineol, methyl benzoate, nonanal, decanal, and \((E)-\beta\)-ionone were potentially important common odorants in all the ciruela cultivars. From the present results, it was concluded that the aroma profiles were similar in the tree cultivars, but significant variations were found in the contributions of these compounds to each cultivar. In future investigations, sensory studies with aroma models and omission experiments warrant being conducted to determine the actual contribution of those volatiles to ciruela aroma.

**Acknowledgment**

The authors would like to extend their appreciation to Dallant (Barcelona, Spain) for providing material without cost.

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