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Bitter orange peel essential oil: a review of the different factors and chemical reactions influencing its composition

Short title: Composition of bitter orange peel essential oil: a review

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Abstract

This review summarizes the findings and discusses the results on the different factors that can influence the bitter orange peel oil composition. Small changes in composition can result in noticeable modifications of the odour profile of the essential oil. The analysis method appears to have a crucial effect on the number of compounds identified in the essential oil. Growing location, cultivar, ripening stage, storage conditions, and extraction methods are reported to impact the bitter orange essential oil. Bitter orange peel oil should be stored at -21°C to prevent changes in the composition and formation of artefacts when storing for a period of several months. The influence of cultivars should not be neglected, since a few cultivars differ a lot from the main cluster of *Citrus aurantium* L.. The geranyl pyrophosphate forms most of the terpenes present in the bitter orange, especially limonene which is the majority compound, by the action of the terpene synthases during growing of the fruit. The extraction method can also be responsible for some differences in the composition due to the absence of water-soluble compounds in cold-pressed oils and to acid-catalysed reactions in hydrodistilled oils such as the decomposition of the linalyl acetate forming many different terpene derivatives.

Keywords:

bitter orange peel; *Citrus aurantium* L.; essential oil, extraction method, ripening stage

1. INTRODUCTION

Bitter oranges, also called sour oranges or bigarades, belong to the genus *Citrus* in the family Rutaceae. The bitter orange tree was used as the main rootstock for citrus until the tristeza disease appeared.¹ The fruits from bitter orange tree are cultivated for the preparation of marmalade,^{1,2} and peels, leaves and flowers are used for the extraction of essential oil.

The major part of the production of bitter orange peel oil is used in perfumery, combined with other natural or synthetic aromas. The rest is used in pharmacology and aromatherapy, in the cosmetic and detergent industry as a fragrance component, but also in food industry as a flavouring agent. For instance, it can be used as an aroma for soft and alcoholic beverages.³ It was also reported that bitter orange peel oil can be used for its antioxidant properties^{4,5} and its antimicrobial activity.⁶

Essential oils (EO) are mostly obtained by hydrodistillation.⁷ Citrus essential oils are an exception, because on an industrial scale they are obtained by cold pressing. Nevertheless, many authors studied bitter orange peel oils extracted by hydrodistillation on a laboratory scale.

In 1991, Boelens⁸ published a review on the chemical composition of citrus oils, which listed only six articles dealing with bitter orange peel oils. Boelens can be acknowledged for highlighting that some erroneous data were published by Shaw,⁹ Lawrence,¹⁰ and Swaine and Swaine¹¹ due to the misunderstanding of publications originally from Ortiz *et al.*¹² and Maekawa *et al.*¹³ Since then, numerous articles have been published on the composition of bitter orange peel oil, and thanks to the advances in analytical chemistry many more volatile compounds have been identified. Many of these articles try to assess the influence of different factors on the bitter orange oil composition, such as the growing location, the cultivars, the ripening stages, the storage conditions and the extraction methods. The aim of the present review is to confront all the conclusions that were drawn on the subject and to explain the chemical or botanical mechanisms behind those changes in the composition of the bitter orange peel oil.

2. BITTER ORANGE TAXONOMY

The most common taxonomic systems (i.e. botanical classification) used for the genus *Citrus* are the Tanaka system¹⁴ which lists 162 species and the Swingle system¹⁵ which lists only 16 species.¹⁶ These two systems do not always classify citrus in the same way because of the ability of the *Citrus* species to hybridize easily and create interspecific hybrids that can be considered as new species.¹⁷

According to Tanaka system, bitter oranges are classified into four botanical species: *Citrus aurantium* L. which has a wide number of cultivars (i.e. cultivated varieties), and *Citrus myrtifolia* Raf., *Citrus natsudaoidai* Hay., and *Citrus neo-aurantium* Tan., which have a very small number of cultivars (Table 1). In total, there are more than 80 cultivars of bitter orange. All the cultivars of *Citrus myrtifolia* Raf., *Citrus natsudaoidai* Hay., and *Citrus neo-aurantium* Tan belonging to bitter oranges are listed in Table 1, while only a few examples of cultivars of *Citrus aurantium* L. are given.

3. GENERAL COMPOSITION OF BITTER ORANGE ESSENTIAL OIL

Bitter orange peel oils, like other citrus peel oils, are composed of two fractions: a non-volatile fraction and a volatile fraction.

The non-volatile fraction (1% to 15% of the essential oil) is constituted of waxes, oxygen heterocyclic compounds (coumarins, psoralens, polymethoxylated flavones), fatty acids, hydrocarbons, sterols (also known as steroid alcohols), and carotenoids.^{18,19} Obviously, the non-volatile residue is almost absent in oils obtained by hydrodistillation.^{19,20}

The volatile fraction of bitter orange essential oil, which represents 85% to 99% of the EO, is constituted of hydrocarbon monoterpenes and sesquiterpenes as well as oxygenated compounds derived from the following hydrocarbons: alcohols, aldehydes, ketones, esters, ethers and oxides.⁷ All the scientific papers agree on the fact that the majority component of bitter orange EO is limonene.

According to the ISO / FDIS 9844 standard requirements²¹ the volatile composition of the cold-pressed essential oil of *Citrus aurantium* L. should follow what is stated in Table 2 column 3. According to the ISO standard 9844, the bitter orange essential oil contains at least the 10 following volatile compounds: α -pinene, β -pinene, myrcene, limonene, linalool, linalyl acetate, geranyl acetate, β -caryophyllene, germacrene D, (*E*)- β -nerolidol.²¹ For those 10 volatile compounds the quantity is expressed as a relative percentage of the total peak area. Octanal and decanal are also mentioned as compounds potentially present in bitter orange oil, which means that all in all only 12 volatile compounds are mentioned as components of bitter orange oil in ISO standard 9844.²¹ The non-volatile compounds are not mentioned. Some analysis conditions of the essential oil are given in the ISO standard 9844 for quick and easy quality control, but they are not normative.

But actually, the composition of the bitter orange oil reported in all the studies tends to show that many more compounds can be found. Most of the authors identified more than 20 volatile compounds (Table 2, Table 3, Table 4, Table 5 and Table 7), with a maximum identification of 64 volatile compounds by Dugo *et al.*¹⁹

4. FACTORS INFLUENCING THE COMPOSITION OF THE VOLATILE FRACTION OF THE BITTER ORANGE PEEL OIL

The different factors that can influence the bitter orange oil composition are the growing locations (i.e. geographic origin), the cultivars, the ripening stages, the storage conditions, the extraction methods.²² The influence of the rootstock and the plant age are not detailed in this article, but they might as well impact the essential oil composition as indicated by Boussaada and Chemli²³ and Kale and Adsule.² Nevertheless, no literature was found on the subject as far as bitter orange peel oil is concerned.

4.1 Growing location

The world major producing countries of bitter orange oil are Brazil, Ivory Coast, Spain, Dominican Republic, Italy, Argentina, Haiti, France, Egypt, Tunisia, Morocco, Uganda,

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3 Paraguay, and China.^{24,25} The different growing locations of bitter orange EO that were
4 studied in the literature are: Brazil,^{26,27} China,²⁸ Cuba,²⁹ Egypt,³⁰ France,^{26,31} Greece,^{5,26,32}
5 Iran,^{7,33,34} Italy,^{6,35-40} Ivory Coast,⁴¹ Japan,⁴²⁻⁴⁶ Pakistan,¹⁸ Spain,^{35,47-49} Tunisia,^{4,23,50,51}
6 Turkey,^{52,53} United States,¹² Venezuela,⁵⁴ West Indies,⁵⁵ and several from unspecified
7 geographical origins.^{23,56-58} Even if Argentina, Haiti, Morocco, Uganda, and Paraguay are in
8 the top fifteen of the world major producing countries of bitter orange oil,^{24,25} to our
9 knowledge the composition of the bitter orange peel cultivated in those countries has never
10 been studied in the literature. Actually, the composition of a bitter orange essential oil from
11 Argentina was reported by De La Torre and Sardi⁵⁹, but as stated by Dugo *et al.*⁶⁰ the
12 composition is too different from a bitter orange oil to be genuine. Abderrezak *et al.*⁶¹
13 reported the analysis of a bitter orange peel essential oil from Algeria, but 0.25% limonene is
14 not compatible with the chemotype of a bitter orange peel oil. Thus, these two studies were
15 not taken into account in the present review.

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21 Some authors tried to compare bitter orange peel oils from different origins using previous
22 studies of different authors.^{41,52} It can be very tricky and conclusions should be taken with
23 cautiousness because many factors that could influence the bitter orange oil composition are
24 unknown. As a consequence, when combining results from different authors, the growing
25 location may not be the only parameter under review.

26
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28 For instance, Dugo⁴¹ compared the composition of bitter orange peel oils from Italy, Spain,
29 Ivory Coast and Brazil, but the cultivars were not specified for the Italian, the Ivorian, and the
30 Brazilian EO, whereas Lota *et al.*³¹ highlighted that the cultivar can influence a lot the
31 composition of bitter orange peel oil. Moreover, the differences in the percentages of linalool
32 and linalyl acetate were attributed to the different growing locations whereas these two
33 percentages are more likely to be representative of the ripening stage of the bitter oranges
34 (which are not specified) than of their growing location. Indeed, linalyl acetate and linalool
35 drastically decrease when citrus are ripening.⁶² Finally, designating more precise locations
36 would be more relevant, as it would be hard to conclude on the influence of a growing
37 location as big as Brazil.

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41 Boussaada *et al.*²⁶ compared the composition of bitter orange peel oils from Chania (Greece),
42 Roxani (Greece), Corsica (France), and Brazil. They mentioned being cautious in comparing
43 the essential oil from trees of approximately the same age, disease-free and submitted to the
44 same horticultural conditions. Nevertheless, none of the cultivars was specified. And once
45 more, the name of the location where the trees were grown in Brazil, was not stated.

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49 Kirbaslar and Kirbaslar⁵² compared the volatile composition of their Turkish EO with the
50 Spanish and Italian EO of Boelens and Jimenez.³⁵ They concluded that percentages of
51 nonanal, tetradecanal, myrtenol, neral, nootkatone and octanol were higher than 0.01% in
52 Italian and Spanish oils, whereas these compounds were not detected in Turkish oil. Actually,
53 the fact that fewer compounds were detected could possibly be due to an analysis method with
54 a more important dilution of the EO. Indeed, Kirbaslar and Kirbaslar⁵² did a split injection of
55 1 μ L of Turkish EO diluted 1/20 in hexane (no mention of the split ratio used, neither if the
56 dilution was by weight or by volume), and they identified between 23 and 27 compounds in
57 their samples, which is rather low compared to other studies (Tables 4, 5 and 7).

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3 Abderrezak et al.⁶¹ claimed that they did a comparative study of the compositions of essential
4 oils of citrus growing in different countries, but they did not take into account the extraction
5 method used by the different authors and compared cold-pressed oils with hydrodistilled oils.
6 Not to mention that the cultivars and the analysis methods were also different between the
7 EO.
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10 Boelens and Jimenez³⁵ are the only authors who accurately assessed the impact of growing
11 location on the bitter orange EO composition, using bitter oranges of the same cultivar, the
12 same year of harvest, with a similar extraction method (cold-pressing) and the same
13 chromatographic method. Though, there were a few errors in this article in the table listing the
14 chemical composition of Mediterranean orange oils: (1) octanol and decanol as well as octyl
15 acetate and decyl acetate were classified in aliphatic aldehydes, hopefully not counted in this
16 class, but a separate class for aliphatic alcohols and esters should have been created, (2) the
17 total of aliphatic aldehydes of bitter orange oil from Italy is 0.631, not 0.531, (3) the total of
18 monoterpenes of bitter orange oil from Spain is 97.406, not 96.85, (4) the total of
19 monoterpenes of bitter orange oil from Italy is 96.873, not 96.83. The conclusions drawn by
20 these authors were that α -pinene, β -pinene, sabinene, aldehydes, and monoterpenoid alcohols
21 and esters were more concentrated in Sicilian bitter orange oil than in Andalucian oil, whereas
22 limonene, sesquiterpenes, nerolidol and nootkatone were less concentrated. These conclusions
23 are based on the analysis of only one sample of each growing location. More studies on the
24 impact of growing location on the bitter orange EO composition would be needed to be able
25 to affirm that these conclusions could be generalized to the influence of coastal climate
26 (Sicilian) and desert-like climate (Andalucian).
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33 Thus, not much can be concluded for sure on the influence of the country in which bitter
34 orange trees are grown on the composition of the essential oil.
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37 4.2 Cultivars

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39 The study by Ortiz *et al.*¹² was meant to compare essential oils obtained by the same
40 laboratory extraction method, from numerous cultivars of bitter orange harvested in the same
41 period (June-July), all cultivated in the Citrus Research Centre at Riverside in California.
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44 Ortiz *et al.*¹² are not the only authors who rigorously examined the influence of the cultivar on
45 the volatile composition of the bitter orange peel oil. More recently, Lota *et al.*³¹ compared
46 the composition of 30 different cultivars of bitter orange EO while making sure that the
47 growing location (Corse, France), the cultural conditions, as well as the laboratory extraction
48 method were the same, so that the only parameter under review during the study was the
49 cultivar. They drew the conclusion that the 26 cultivars of *Citrus aurantium* L. that they
50 studied exhibited a weak chemical variability, except for the Espagne and the Gou Tou
51 cultivar, and were characterized by limonene as majority component. Actually, limonene was
52 also the majority component for the Espagne and the Gou Tou cultivar, but to a far less extent
53 (72.9% peak area for the Espagne cultivar and 84.2% peak area for the Gou Tou cultivar
54 versus between 87.6% to 95.1% peak area for the 24 other *Citrus aurantium* L. cultivars). The
55 fact that the peel EO of the Gou Tou cultivar differed from most of the *Citrus aurantium* L. is
56 probably linked to its supposed natural hybrid origin (possible hybrid between *Citrus*
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3 *aurantium* L. and *Citrus grandis*).^{63,64} The peel EO of the Tosu cultivar belonging to the
4 species *Citrus neo-aurantium* Tan. was similar to the Gou Tou cultivar: a lower percentage of
5 limonene and a higher percentage of β -pinene than the group of 24 cultivars of *Citrus*
6 *aurantium* L.. As far as *Citrus myrtifolia* Raf. is concerned, the peel EO of the Large Chinotto
7 cultivar had a profile similar to the 24 cultivars of *Citrus aurantium* L.. The peel EO of the
8 monovarietal *Citrus natsudaidai* Hay. also had a profile close to the 24 cultivars of *Citrus*
9 *aurantium* L., despite the fact that it does not contain α -pinene.
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13 4.3 Ripening stages

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15 Several studies concerning the influence of the ripening stages of bitter oranges on peel oil
16 composition have been reported in the literature.^{7,30,33,39,51,56,65} Citrus are non climacteric,
17 which means that once fruits are harvested, the maturation process stops and they do not ripen
18 further.¹ The colour of the peel is an indicator of the maturity of the fruit. When the bitter
19 orange is immature the peel is dark green. As it ripens, it passes through light green, then
20 yellow, and finally orange at the mature stage. The evolution of the gas chromatography
21 percentages of the compounds during the growing and the ripening of bitter oranges are listed
22 in Table 2. Only the compounds listed in the ISO standard 9844 are taken into account.
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27 First of all, one should be careful with the wording chosen by the authors of the studies
28 dealing with ripening stages, when in need to compare those results. When Ashour and El-
29 Kebeer³⁰ referred to immature fruits, they meant fruits which have reached the size of a bitter
30 orange but were still green in colour, whereas when Rowshan and Najafian⁷ referred to
31 immature fruits, they meant green fruits of the size of a lemon, that is to say smaller than a
32 bitter orange. Thus, the immature stage of Ashour and El-Kebeer³⁰ seems to be equivalent to
33 the semi-mature stage of Rowshan and Najafian⁷. Moreover, the size criteria chosen by
34 Rowshan and Najafian⁷ and by Ashour and El-Kebeer³⁰ to determine maturity were rather
35 imprecise since no real measurement was provided. Ashour and El-Kebeer³⁰ called setting
36 fruits, green fruits that were really small in size. According to the analysis results of the
37 setting fruits, it can be assumed that setting fruits were even less mature than the immature
38 stage stated by Rowshan and Najafian⁷. Azhdarzadeh and Hojjati³³ compared unripe peels and
39 ripe peels with no further details on the maturity stage (colour, size of the fruits, etc...). From
40 the analysis results of the unripe peels, one can hypothesize that they were slightly more ripe
41 than the setting fruits of Ashour and El-Kebeer³⁰ and less ripe than the immature fruits of
42 Rowshan and Najafian⁷. Bourgou *et al.*⁵¹ defined the immature, semi-mature and mature fruits
43 by their colour, just as Dugo *et al.*³⁹ used the colour to define ripe and unripe fruits. Once
44 more, neither of them gave any details on the precise colour, which could have been measured
45 with a colorimeter for instance, nor on the size measurement of the fruit.
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53 Boussaada and Chemli⁶⁵ found that the percentage of limonene rises at its maximum in the
54 middle of the productive period when fruits are normally harvested, and then decreases in the
55 end of the productive period to arrive at a percentage that is approximately the same as in the
56 beginning (Table 2). Rowshan and Najafian⁷ observed that the highest percentage of limonene
57 was obtained for the semi-mature stage (green colour, size of a bitter orange) and slightly
58 decrease at the mature stage (orange colour). The lowest percentage of limonene is at the
59 immature stage (green colour, size of a lemon). Ashour and El-Kebeer³⁰ found that during the
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3 ripening of the fruits (from immature to ripening fruits, no changing in size but changing of
4 colour), the percentages of limonene slightly decreased from 95.25% to 92.68%. The different
5 authors, except Bourgou *et al.*⁵¹, agree on the fact that limonene is formed during the growing
6 of the bitter orange and slightly decreases during the ripening of the bitter orange. Actually,
7 the analysis results of the semi-mature bitter orange peel obtained by Bourgou *et al.*⁵¹ seem
8 suspect: limonene percentage of only 67.90% and products of hydration and oxidation
9 percentages (1,8-cineole, (*Z*)-sabinene hydrate, octanol, (*Z*)-linalool oxide, terpinen-4-ol)
10 higher than at the immature and the mature stage.
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14 The compositions of unripe and ripe bitter orange peel obtained by Dugo *et al.*³⁹ are very
15 close to one another, apart from linalyl acetate, (*E*)- β -ocimene, (*E*) and (*Z*)-linalool oxide
16 which are higher in unripe peel.
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19 In Boussaada and Chemli⁶⁵ study, the linalool percentage gradually decreases along the
20 productive period. Rowshan and Najafian⁷ noticed that linalool percentage was maximum at
21 the immature stage and deeply decreases as the fruit grows and ripens. It is suggested that
22 limonene is formed during growing by decomposition of the linalool and the linalyl
23 acetate.^{47,65}
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26 Ashour and El-Kebeer³⁰ noticed that during growing of bitter oranges (from setting fruits,
27 which are really small in size, to immature fruits, which reached the size of the bitter orange
28 but are still dark green in colour) β -pinene, ocimene, linalool, linalyl acetate, and α -terpineol
29 decreased, while limonene increased from 46.19% to 95.25%. Ocimene and linalool were not
30 present any more in the ripening fruit.³⁰
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33 As far as β -pinene is concerned, Rowshan and Najafian⁷ came to the same conclusion as
34 Ashour and El-Kebeer³⁰: β -pinene decreased during growing. But contrary to Ashour and El-
35 Kebeer³⁰, Rowshan and Najafian⁷ found that α -pinene and myrcene decreased during
36 growing.
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39 Boussaada and Chemli⁶⁵ concluded that β -pinene and α -terpinolene percentages showed a
40 slight increase throughout the productive season. But, is this slight increase (from 0.2% to
41 0.3% and from 0.4% to 0.6% respectively) sufficient to be significant? The percentages of the
42 other monoterpenes were considered as being constant from unripe to ripe citrus oil.
43 α -terpineol, geraniol, nerol and geranyl acetate percentages were said to be fairly constant in
44 all the oils from unripe and ripe fruits. Actually, geraniol varies from 0.1% to 0.2% and
45 geranyl acetate from 0.2% to 0.3%. Boelens and Jimenez⁵⁶ also came to the conclusion that
46 α -terpineol, geraniol, and nerol were fairly constant during the ripening of bitter oranges,
47 whereas geranyl acetate and neryl acetate increased from 0.06% to 0.13% and from 0.02% to
48 0.04% respectively.
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52 As far as octanal and decanal are concerned, Azhdarzadeh and Hojjati³³, Ashour and El-
53 Kebeer³⁰, Boelens and Jimenez⁵⁶, Rowshan and Najafian⁷, as well as Dugo *et al.*³⁹ to a lesser
54 extent, all agree that these two aldehydes increase during the ripening of bitter oranges.
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57 Boelens and Jimenez⁵⁶ pointed out that the oxygen-containing sesquiterpenes (nerolidol,
58 farnesol, nootkatone and α -selinenone) appear to be formed during the ripening.
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3 All those authors drew conclusions on the evolution of the peel oil composition during
4 ripening based on comparisons of relative percentages of peak area. None of them quantified
5 using external or internal standard, or standard additions.
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8 4.4 Storage conditions 9

10 Boelens and Jimenez⁵⁶ studied the impact of one to two weeks storage on picked ripe fruits.
11 They observed that linalool, linalyl acetate, nerolidol, nootkatone and α -selinenone kept on
12 increasing after picking up the fruits, and attributed the formation of these compounds to
13 enzymatic reactions. In plants, endogenous glycosidases are involved in enzymatic hydrolysis
14 of the glycosidic bond of glycosidic aroma precursors, releasing free aroma compounds.⁶⁶
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17 Njoroge *et al.*⁴³ studied the impact of storage conditions (temperature and time of storage) on
18 the volatile composition of Daidai (*Citrus aurantium* L. var. *cyathifera* Y. Tanaka)
19 cold-pressed peel oil (Table 3). Artefact compounds may be formed during storage of
20 essential oils upon oxidation, heat or chemical interactions between the compounds that are
21 initially present in the oil.⁴³ No changes were found over time when cold-pressed Daidai oil
22 was stored at -21°C. Changes occurred in the Daidai oil stored several months at 5°C and
23 20°C. The longer the oil was stored, the more important the changes in the composition were.
24 Limonene, myrcene, γ -terpinene and linalyl acetate percentages decreased when the
25 temperature and the time of storage increased. The decreases of myrcene and γ -terpinene were
26 observed when stored at 20°C or when stored 12 months at 5°C (Table 3). Under the same
27 conditions, terpinolene, *p*-cymene, α -terpineol, thujol and octyl acetate slightly increased,
28 while (*Z*)-carveol, limonene-10-yl acetate, (*E*)-*p*-mentha-2,8-dien-1-ol, linalool, nonyl acetate,
29 decyl acetate, β -caryophyllene, (*E*)- β -farnesene, α -humulene sharply increased. Germacrene
30 D decreased until disappearing. Some compounds that did not exist in the fresh oil were
31 formed upon storage: carvone, sabinene hydrate, (*Z,E*)-farnesol, and several oxygen
32 derivatives of the farnesene group. Their relative percentages increased with time and
33 temperature. Surprisingly neither linalool oxides nor limonene oxides were identified in the
34 oils after long storage periods.
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42 4.5 Extraction methods 43

44 In the literature, the extraction methods used to obtain peel oil from citrus are: cold pressing,
45 hydrodistillation, supercritical carbon dioxide⁵⁷ or solvent⁶⁷ extraction. The most common
46 methods are cold pressing and hydrodistillation, and the result of extraction is not called
47 essential oil when using supercritical carbon dioxide or solvent extraction.
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50 4.5.1 Cold pressing 51

52 On an industrial scale, bitter orange essential oils are obtained by cold pressing. All the
53 different mechanical systems for cold extraction of citrus oils are based on the following
54 steps.^{68,69} First, mechanical action on fruits or on peels breaks essential oil glands (utricles)
55 and releases the EO. Then, the citrus oil is dispersed in water which acts as a vehicle agent. In
56 most cases, the aqueous phase is continuously recycled to minimize the loss of oxygenated
57 compounds. Finally, the emulsion is centrifuged to obtain pure EO. The water-soluble
58 compounds are lost. The different methods are Sfumatrice, Torchi, Pelatrice, Brown Oil
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3 Extractor and FMC (Food Machinery Corporation, now called JBT).⁷⁰ Sfumatrice machines
4 work on peels without pulp; now these are not widely used and are replaced by Torchi, which
5 work on the entire fruits. Pelatrice machines work on the entire fruit, and the EO is obtained
6 by rolling the fruit over spikes. The Brown Oil Extractor is quite similar to the Pelatrice
7 method.⁷¹ FMC machines also process the entire fruit: the extraction of juice and EO are
8 performed simultaneously. The aqueous phase that carries the EO is easily recycled when oil
9 is produced using the Pelatrice and FMC processes. The ability to recycle the aqueous phase
10 is more difficult for Sfumatrice and Torchi machines because of the rapid increase of pectins
11 in the aqueous phase.^{41,72}
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15 On a laboratory scale, three different types of cold extraction were found in the bibliography.
16 (1) Lota⁷³ used a semi-automatic method (« Roze-Schwob ») consisting of two jaws that
17 rotate the bitter orange and a sharp point which breaks the oils glands.³ The dispersion that
18 was released (mix of EO and aqueous phase) was then centrifuged to obtain pure EO. (2)
19 Kirbaslar and Kirbaslar,⁵² Njoroge *et al.*,^{42,43} and Sawamura⁴⁵ applied manual pressure on the
20 flavedo to release the oil. Njoroge *et al.*^{42,43} added brine to the oil. Then, the oil was
21 centrifuged and dried over anhydrous sodium sulphate. (3) Boelens and Jimenez^{35,56} extracted
22 the peel oil by needle puncturing followed by centrifugation.
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26 Tables 4 and 5 compare the volatile composition of bitter orange essential oils obtained by
27 cold pressing on an industrial scale and a laboratory scale respectively. The compositions
28 reported in table 4 and 5 are not exhaustive since some authors found more than 50 volatiles,
29 but focused on the compounds that are found in bitter orange EO according to the ISO
30 standard.
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33 Among all the gas chromatographic analysis results of cold-pressed bitter orange oil that can
34 be found in the literature, the only ones which are in accordance with the ISO standard 9844
35 are Dugo *et al.*^{19,36} and Mondello *et al.*^{37,40} Veriotti and Sacks⁵⁸ are the ones who identified
36 the lowest number of compounds in cold-pressed bitter orange oil. The chromatographic
37 method used is to blame: the lowest volume injected and the highest split of all the studies on
38 bitter orange, when specified (Table 4).
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42 43 4.5.2 Hydrodistillation

44 Hydrodistillation is used to extract bitter orange essential oil on a laboratory scale for analysis
45 and quantification of oil contained in the peels. To our knowledge, all the bitter orange
46 hydrodistilled oils were obtained using a Clevenger type apparatus. The Table 6 gives
47 exhaustive details on the different methods used to obtain bitter orange essential oil with a
48 Clevenger apparatus.^{5-7,18,23,26,32,50,54,65}
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52 In general, authors give very few information on the methods employed for peel
53 hydrodistillation. Gorgorcena and Ortiz⁴⁹ also used hydrodistillation to extract essential oil
54 from bitter orange but they were not recorded in table 6 because no details are given on the
55 method. The study by Gonzalez de *et al.*⁵⁴ is quite terse. The methods used are not detailed
56 and only seven compounds were identified in this Venezuelan oil, but this can probably be
57 attributed to the analysis method not being adapted since very few compounds were also
58 found in the other *Citrus* species of this study. The essential oils can be obtained by
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3 hydrodistillation using dried or fresh peels. The mass of bitter orange peel used for one
4 extraction varies quite a lot: from 35 g of fresh peels to 100 g of dried peels. The time of
5 hydrodistillation varies from 1.5 hours⁴ to 6 hours.¹⁸ The only article which specifies the
6 distillate flow rate (3 to 3.5 mL/min) is Sarrou *et al.*⁵ It can be assumed that the extractions
7 by Protopapadakis and Papanikolaou³² and Rowshan and Najafian⁷ were done with a distillate
8 flow rate of 2 to 3 mL/min, since these authors claim that they followed the method described
9 in the European Pharmacopoeia⁷⁴. And, when specified, after extraction the essential oil is
10 dried over Na₂SO₄ anhydrous and stored in sealed vials between -20°C and 6°C.

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15 To compare the yields expressed in different units in the articles, they were all converted in
16 g/100g dry matter using values found in the literature. Dried bitter orange peels contain 90%
17 dry matter and fresh bitter orange peels contain 30% dry matter. According to the ISO
18 standard 9844, the bitter orange essential oil density ranges from 0.84 to 0.86 g/mL, so the
19 density of the different oils obtained was considered as being 0.85 g/mL. The yields obtained
20 vary from 0.21 to 1.12 g/100g dry matter (Table 6). These important differences in yield
21 obtained could be due to different factors: (1) part of the essential oil may be lost during
22 drying of peel, (2) the mass of peel from which the oil is extracted is too small to scale up
23 (concerning Sarrou *et al.*⁵), (3) the time of hydrodistillation is too short to extract the whole
24 quantity of essential oil contained in the peels, (4) the cultivars of bitter oranges are different,
25 (5) the ripening stage may be different, (6) the growing location is different.

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30 Concerning Azhdarzadeh and Hojjati³³, Boussaada and Chemli^{23,65}, Boussaada *et al.*²⁶ and
31 Bourgou *et al.*⁵¹, the yields given in the article were expressed for 100 g of fresh peel but it
32 was not specified if the figures given were in mL or in g. Thus, they could not be converted in
33 g/100g dry matter.

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37 The extraction method influences not only the yields but also the composition of the EO.
38 Indeed, the hydrodistillation requires heating during several hours and also the citrus peels,
39 when in water, form an aqueous acidic solution. According to Boelens,⁸ the pH of bitter
40 orange peels is between 2.5 and 4. Temperature, time and pH are the three main factors that
41 cause degradation of terpenes, elimination, rearrangement and cyclization of alcohols and
42 esters.

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45 Table 7 compares the volatile composition of bitter orange essential oils obtained by
46 hydrodistillation to the ISO standard obtained by cold pressing. The compositions of
47 hydrodistilled oils reported in table 7 are not exhaustive, but focused on the 12 compounds
48 that are mentioned in the ISO standard. The germacrene D percentage in hydrodistilled oils
49 appears to be always lower than the ISO standard. The linalyl acetate percentage is always
50 lower than the ISO standard (Table 7). This can be imputed to the decomposition of the linalyl
51 acetate present in peels during hydrodistillation due to low pH and heating. Except for Hosni
52 *et al.*,⁵⁰ the linalool percentage in hydrodistilled oils is always higher than the ISO standard.
53 This can be attributed to the formation of linalool during hydrodistillation. Thus, it can be
54 assumed that linalyl acetate is converted partially in linalool during hydrodistillation. Indeed,
55 linalyl acetate undergoes thermal degradation that generates linalyl carbocation. In aqueous
56 acid solution, the linalyl carbocation is hydrated to give linalool.⁷⁵

5. CHEMICAL REACTIONS HAPPENING DURING GROWING, RIPENING, STORAGE OF THE BITTER ORANGE AND DURING OIL EXTRACTION BY HYDRODISTILLATION

Adapted from the literature,^{3,47,75-90} the figure 1 is a review of the different reactions that can happen during growing, ripening and storage of the bitter orange and during hydrodistillation due to heating and acid pH.

Most of the terpene derivatives are produced during hydrodistillation by degradation of linalyl acetate, via rearrangements and cyclization of the linalyl carbocation.⁷⁵ During hydrodistillation, the major mechanism by which oxygen is added to the terpenes produced by degradation of linalyl acetate, is not oxidation but acid-catalysed reactions in aqueous acid conditions (due to the acidity of bitter oranges).⁸⁷ Baxter *et al.*⁸⁴ studied the products of the reactions of linalool, geraniol, nerol as well as their acetate esters in aqueous acid conditions (pH = 2.3) at 24°C during 10 to 20 days. Actually, 10 days is too long to be able to identify the different intermediate products of reaction. Cori *et al.*⁸⁹ studied the kinetics of those reactions and concluded that the hydration of the linalyl carbocation in linalool is faster than the allylic rearrangement of the linalyl carbocation in geranyl and neryl carbocation and than the cyclization in terpinyl carbocation. Solvolysis of linalyl acetate is 120 times faster than solvolysis of geranyl acetate and of neryl acetate.⁸⁸ The mechanisms of reaction appear to be different as well. The linalyl acetate forms the linalyl carbocation that is more stable than the geranyl and the neryl carbocation because it is a tertiary carbocation. Meanwhile the geranyl acetate and the neryl acetate proceed by deacylation to form directly geraniol and nerol respectively. Morin and Richard⁷⁵ studied the kinetics of linalyl acetate degradation simulating hydrodistillation by heating under reflux at different pH: 2, 4, 7 and 9 during periods of time varying between 0.3 to 6 hours. At pH 2 during 6 hours, the products the most abundant were terpenes: terpinolene (20.2%), (*E*)-ocimene (13.8%), α -terpinene (coeluted with 1,4-cineole 13.1%), limonene (9.3%), γ -terpinene (7.2%)... Many alcohols were also produced in smaller quantities, among which: α -terpineol (3.9%), (*Z*)- β -terpineol (0.4%) and terpinene-4-ol (1.1%), as well as linalool oxides (0.13%).

Another proof of the role of the acid pH was given by Boelens and Jimenez.⁵⁶ Those authors showed that, if the sampling was performed with a syringe rinsed with an ethanol solution of triethanolamine, it was possible to avoid the following reactions which are due to acid pH of bitter orange peels: linalyl acetate degradation into monoterpenes, formation of α -terpineol by cyclisation, as well as allylic rearrangement of linalool and linalyl acetate to form nerol and geraniol and their acetates.

In 1966, Attaway *et al.*⁹¹ stated that linalool could form limonene during growing, but it is not the only precursor⁶² and the most likely hypothesis at present is that limonene is derived from geranyl pyrophosphate (GPP) (also known as geranyl diphosphate) by the action of enzymes called terpene synthases or cyclases.⁹² Terpenes are synthesized by the condensation of isopentenyl pyrophosphate (IPP) (also known as isopentenyl diphosphate) and dimethylallyl pyrophosphate (DMAPP) (also known as dimethylallyl diphosphate) which forms GPP. IPP

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3 and DMAPP can be formed through two different pathways which are located in two different
4 cellular compartments: the cytosolic mevalonate pathway and the plastic methylerythritol
5 phosphate pathway. GPP is the precursor of monoterpenes such as ocimene and limonene.
6 Monoterpene synthase genes were characterized in citrus^{93–95}. A high expression of those
7 genes appears to have an important role in the formation of citrus essential oils.⁹² Indeed,
8 terpenes synthases are responsible for the synthesis of monoterpenes.
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12 When submitting β -pinene to hydrodistillation in harsh acid conditions during 3 hours using a
13 Clevenger apparatus, Haro-Guzmán and Huet obtained important quantities of α -terpineol,
14 terpinolene and 1,4-cineole, as well as lesser quantities of 1,8-cineole and *p*-cymene.⁹⁶
15 Muneyuki *et al.* reviewed the acid catalysed rearrangements of α -pinene and β -pinene.⁹⁷
16 Under acidic conditions, the degradation of pinenes mainly gave α -terpineol, and smaller
17 amounts of α -fenchol and borneol. When pH is even lower, some hydrocarbons such as
18 limonene, terpinolene, camphene and fenchene can be formed as well.
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23 The major hydration products of acid-catalysed reaction of sabinene and α -thujene are:
24 terpinen-4-ol, γ -terpinene, α -terpinene, terpinolene, sabinene hydrate and 1,4-terpin.⁸²
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28 In plants, not all aroma compounds are found in a free state. Some are glycosidically bound
29 aroma compounds: they are called aroma precursors since they are able to release free
30 odorous aroma compounds when the glycosidic bond is hydrolysed,⁹⁸ but they are not
31 odorous as such, when glycosidically bound. Glycosidic aroma precursors are preferential
32 storage and transport forms probably due to the toxicity of the free form in the cells above a
33 certain concentration.⁶⁶ Deglycosylation occurs by enzymatic or acid hydrolysis of the
34 glycosidic bond⁹⁹ during fruit maturation, spontaneously when the pH is acid enough or
35 because of heat treatment. Thus, it can be assumed that due to the acidity of bitter orange
36 peels in aqueous solution,⁸ hydrodistillation of peels induces deglycosylation and release of
37 aroma precursors, but no literature was found on this point.
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41 Oxidations of the terpenes and the sesquiterpenes can happen in the presence of dioxygen.
42 Boelens and Sindreu⁴⁷ stated that nerolidol can form various sesquiterpenes such as
43 germacrene D, α -humulene, caryophyllene, α -selinene that can oxidise in α -selinenone, and
44 valencene that can oxidise in nootkatone.
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47 Ikeda *et al.*⁷⁶ were the first authors to assume that when γ -terpinene is exposed to air at room
48 temperature it could possibly form *p*-cymene as γ -terpinene concentration decreases while *p*-
49 cymene concentration increases. Kimura *et al.*⁷⁷ studied the impact of storage on lemon oil
50 and on different compounds: citral, limonene, β -pinene, and γ -terpinene, in acidic conditions
51 at 38°C. They found out that citral and β -pinene concentrations significantly decreased after
52 60 days of storage at these temperature and pH conditions, while α -terpineol and *p*-cymene
53 which are more stable increased, due to low degradation of limonene and γ -terpinene
54 respectively. As the storage time increases, the concentration of *p*-cymene increases.¹⁰⁰ In
55 2014, Lorjaroenphon *et al.*⁸⁵ studied the degradation products of citral when stored three days
56 in citric acid solution. They proposed rearrangement pathways for citral in aqueous acidic
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3 solution very similar to the ones by Clark *et al.*⁸⁷ dating from 1977. These reaction schemes
4 are more detailed than the ones presented by Kimura *et al.*⁷⁷
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6. CONCLUSION

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9 More than 50 studies have been published on the composition of the bitter orange essential
10 oils. Many factors can influence its composition. Up until now, the following factors have
11 been discussed in the literature: growing location, cultivars, ripening stage, storage conditions,
12 and extraction methods.
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15 First of all, it may be underlined that only one article did a true quantification of the
16 compounds of a sample of bitter orange essential oil using internal standards.⁵⁵ All the studies
17 that compared different samples of bitter orange essential oils draw conclusions based on raw
18 GC percentages. It ensues from the comparison of the number of compounds identified in
19 each study, that some authors should have injected a volume of essential oil more important
20 or have lowered the split, in order to identify more compounds. When trying to identify more
21 compounds, authors should be cautious when it comes to the saturation of limonene, or inject
22 the limonene separately for its quantification.
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26 It results from the examination of the compositions of the bitter orange peel oils published in
27 the literature, that 50 out of the 53 cold-pressed peel oils extracted from *Citrus aurantium* L.
28 reported in this review would not be identified as bitter orange peel oil according to the ISO
29 standard 9844, because they do not comply with the normative ranges of values for the 10
30 compounds of the standard. The only three results of analysis of cold-pressed oils which are
31 compliant with the ISO standard 9844 are Dugo *et al.*,^{19,36} the Maroc cultivar from Lota *et*
32 *al.*,³¹ and Mondello *et al.*^{37,40} Moreover, the means of the percentages of limonene, linalyl
33 acetate, and germacrene D of the 24 cultivars of *Citrus aurantium* L. which have a similar
34 chemotype according to Lota *et al.*³¹ are not compliant with the standard. Hence, the ISO
35 standard 9844, may consider broadening some of its normative ranges of values.
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40 Bitter orange peel essential oil coming from some of the major producing countries such as
41 Argentina, Haiti, Morocco, Uganda, and Paraguay have not been studied yet in the literature.
42 Boelens and Jimenez³⁵ tried to assess the influence of the growing location, but more
43 experiments are needed to draw firm conclusions.
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46 Only half of the authors mentioned the name of the cultivar they used for their study, whereas
47 it has been established that some cultivars such as the Espagne and the Gou Tou cultivar
48 differ a lot from the other cultivars of *Citrus aurantium* L..³¹
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51 All the authors agree on the fact that limonene is the majority compound of the bitter orange
52 peel oil by far. Seven studies were published on the influence of the growing and the ripening
53 stage of the bitter orange on the composition of its essential oil. The limonene percentage
54 increases during growing of the fruit by cyclisation of geranyl pyrophosphate. The linalool
55 percentage dramatically decreases during growing as the limonene increases, so it could be
56 possible that the limonene is also partly formed by the degradation of the linalool. The
57 question remains if two pathways can coexist as far as the formation of limonene is
58 concerned. If so, the predominance of one of them would probably be determined by the gene
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3 pool and the environment of the bitter orange. The cultivars being examples of genetic
4 variability among bitter oranges, and the growing location (climate, soil quality...) a factor of
5 the environment. β -pinene seems to decrease during growing. α -terpineol, geraniol, and nerol
6 appear to be fairly constant during the ripening of bitter oranges. Aldehydes (mainly octanal
7 and decanal) which are known to have an important odorant impact ⁵⁵ increase during the
8 ripening of bitter oranges.
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11 Boelens and Jimenez⁵⁶ are the only authors who studied the impact of storage of bitter
12 oranges on the composition of its oil. Unfortunately, only one analysis was done at the end of
13 a short storage time (one to two weeks). According to this analysis compared with the
14 analysis of the ripe fruit right after picking up, they concluded that linalool, linalyl acetate,
15 nerolidol, nootkatone and α -selinenone increased after picking up the fruits. Enzymatic
16 reactions were accounted for the formation of these compounds.
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20 Njoroge *et al.*⁴³ are the only authors who assessed the impact of storage of bitter orange
21 essential oil on its composition. It can be concluded from this study that bitter orange EO
22 should be stored at -21°C to prevent any degradation caused by long storage period. The main
23 changes in composition are observed when stored at 20°C or stored at 5°C during at least 12
24 months. Structural rearrangements of monoterpenes such as limonene and γ -terpinene due to
25 temperature and oxidation form *p*-cymene via terpinolene when the temperature and the time
26 of storage increase. The oxidation of limonene explains the sharp increases of (*Z*)-carveol,
27 carvone, limonene-10-yl acetate, and (*E*)-*p*-mentha-2,8-dien-1-ol, and the slight increase of α -
28 terpineol. The increase of linalool was probably due to the decrease of linalyl acetate and
29 maybe as well to the autoxidation of myrcene.⁸³ It can be hypothesized that both thujol and
30 sabinene hydrate came from sabinene, by structural rearrangement followed by hydration and
31 simply by hydration respectively.
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36 The main extraction methods used to obtain oil from bitter orange peel are cold pressing and
37 hydrodistillation. Cold pressing consists in applying mechanical pressure on the peels to
38 release the essential oil. Then, water is added to the EO. The mixture is centrifuged and
39 finally the aqueous phase is discarded which means that soluble compounds such as
40 glycosidic aroma compounds are thrown away. Actually, the presence of glycosidic aroma
41 compounds in bitter orange peels has never been proved yet in the literature, but their
42 presence has been reported in several citrus species (three cultivars of mandarin, one cultivar
43 of sweet orange, one cultivar of pink grapefruit and one cultivar of white grapefruit).⁹⁸
44 Hydrodistillation is exclusively used to extract bitter orange peel oil on laboratory scale. The
45 use of a Clevenger apparatus provides the advantage of measuring directly the volume of oil
46 extracted per mass of peels involved. Despite the use of a Clevenger, the different parameters
47 of the hydrodistillation method appear to vary a lot (mass of peel involved, time of
48 hydrodistillation, distillation rate), and so does the quantity of essential oil extracted per mass
49 of peel. During hydrodistillation, the aroma compounds of the bitter orange peels are
50 submitted to acid-catalysed reactions, due to the acidity of the bitter orange peels which lower
51 the pH of the aqueous solution. At acid pH, linalyl acetate is decomposed in many terpene
52 derivatives, which explains that the percentages of linalyl acetate are much lower in
53 hydrodistilled oils than in cold pressed oils. The main differences between cold pressed bitter
54 orange oils and hydrodistilled oils are due to the acid-catalysed reactions during
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3 hydrodistillation and possibly to the release of aroma compounds by deglycosylation of the
4 glycosidic bound.
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6 Understanding all these reactions is essential because the odour profile of the bitter orange
7 peel oil can be impacted a lot. Monoterpenes do not play a major role in the flavour of bitter
8 orange peel oil,¹⁰¹ but many of their reaction products formed by acid-catalysed
9 rearrangement followed by hydration are extremely important to the flavour of the essential
10 oil. For instance, the hydration of a relatively weak flavorant such as limonene leads to a
11 temporary increase in flavour until the terpineols are converted to terpins.⁸⁸
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TABLE 1

Family	Rutaceae			
Genus	Citrus			
	Bitter orange / Sour Orange / Bigarade			
Species	<i>Citrus aurantium</i> L.	<i>Citrus myrtifolia</i> Raf.	<i>Citrus natsudaidai</i> Hay.	<i>Citrus neo-aurantium</i> Tan.
Cultivars	Country of origin	Cultivars examples		
	Algeria	Algerian, Trabou		
	Brazil	Azeda, Brazilian, Jaboticaba		
	China	Gou Tou, Huahong, Kabusu		
	Cuba	Cajel, Cuban		
	France	Cardosi, De Grasse, Donnet, Filippi, Luisi, Menton, Santucci	Large chinotto	Tosu
	Italy	Bizzarrio, Gallesio, Palermo,	Small chinotto	Natsudaidai
	Jamaica	Jacmel		Konejime
	Japan	Daidai, Du Japon, Shuto	Crispifolia	
	Spain	Bouquetier de Nice à fleurs doubles, Espagne, Sevillano (Seville)		
	Tunisia	Alibert, Petit Pierre, Tunisian		
	United States	Bittersweet, Keen, Standard		
		

TABLE 2

	ISO standard 9844 ²¹	Ashour and El-Kebeer ³⁰	Azhdarzadeh and Hojjati ³³		Boelens and Jimenez ⁵⁶				
Extraction method	Cold-pressed	Steam distillation		Hydrodistillation		Laboratory cold-pressed			
Cultivar		Egypt			Iran (Khuzestan province)				
Growing location		Egypt			Iran (Khuzestan province)				
Growing / Ripening		Setting fruits (very small in size)	Immature fruits (size of a bitter orange)	Ripening fruits	Unripe fruits	Ripe fruits	Unripe fruits on tree	Ripe fruits on tree	
ISO standard 9844 compounds	α -pinene	0.30-0.65	0.38	0.43	0.55	2.56*	1.96*	0.60	0.65
	β -pinene	0.30-1.15	2.38*	0.14*	0.11*	0.51	0.56	0.13*	0.14*
	myrcene	1.60-1.95	1.69	1.82	2.25*	3.93*	5.74*	2.12*	1.95
	octanal	X	-	-	-	0.39	0.83	0.23	0.30
	limonene	92.95-95.00	46.19*	95.45*	92.68*	59.9*	81.6*	94.50	93.20
	linalool	0.10-0.35	25.23*	0.38*	0*	1.33*	2.19*	0.20	0.24
	decanal	X	0	0	1.63	-	-	0.14	0.20
	linalyl acetate	0.6-1.02	4.50*	0.03*	0.12*	0.52*	0*	0.23*	0.28*
	geranyl acetate	0.10-0.25	1.33*	0.13	0*	2.09*	0.33*	0.06*	0.13
	β -caryophyllene	0.05-0.15	-*	-*	-*	0*	0.22*	0.07	0.06
	germacrene-D	0.08-0.18	-*	-*	-*	0*	0.22*	0.09	0.08
	(E)- β -nerolidol	0.06-0.18	-*	-*	-*	0*	0.09	0.03*	0.10
Total volatile compounds identified		14	12	8	21	39	44		

*percentages of peak area out of the ISO range tr: traces

TABLE 2 Continued

	ISO standard 9844 ²¹	Bourgou <i>et al.</i> ⁵¹			Boussaada and Chemli ⁶⁵				Dugo <i>et al.</i> ³⁹		Rowshan and Najafian ⁷		
Extraction method	Cold-pressed	Hydrodistillation			Hydrodistillation				Cold-pressed		Hydrodistillation		
Cultivar	Larange												
Growing location	Tunisia (Menzel Bouzelfa)					Egypt				Iran			
Growing / Ripening		Immature green colour	Semi-mature yellow colour	Mature orange colour	November	December	January	February	Unripe green colour	Ripe orange colour	Immature (green - size of a lemon)	Semi-mature (green - size of a bitter orange)	Ripe (orange)
α-pinene	0.30-0.65	0.13*	0.03*	0.36	0.4	0.4	0.4	0.3	0.33	0.34	1.17*	0.44	0.43
β-pinene	0.30-1.15	0.11*	0.07*	0.38	0.2*	0.3	0.3	0.3	0.15*	0.10*	0.58	0.07*	0.1*
myrcene	1.60-1.95	0.09*	0.48*	0.07*	1.7	1.6	1.6	1.4*	1.44*	1.56*	3.43*	1.87	1.78
octanal	X	-	-	-	-	-	-	-	0.05	0.07	1.38	0.40	0.68
limonene	92.95-95.00	80.54*	67.90*	90.95*	87.7*	88*	92.2	87*	94.54	96.52*	78.14*	94.72*	93.47*
linalool	0.10-0.35	0.03*	tr*	0.1*	1.3*	1*	0.8*	0.6*	0.06*	0.06*	8.19*	0.91*	1.25*
decanal	X	-	-	-	-	-	-	-	0.08	0.09	0.34	0.15	0.20
linalyl acetate	0.6-1.02	0.07*	0.09*	0.01*	0.1*	0.2*	0.2*	0.2*	0.12*	0.08*	0.54*	0.16*	0.22*
geranyl acetate	0.10-0.25	tr*	0.11	0.02*	0.2	0.2	0.2	0.3*	0.08*	0.08*	0.16	0.07*	0.13
β-caryophyllene	0.05-0.15	-*	-*	-*	tr*	tr*	tr*	tr*	0.04*	0.04*	0.02*	0.03*	0*
germacrene-D	0.08-0.18	0.10	0.25*	0.04*	-*	-*	-*	-*	0.02*	0.03*	0.07*	0*	0*
(E)-β-nerolidol	0.06-0.18	-*	-*	-*	tr*	tr*	tr*	0.1	0.04*	0.03*	-*	-*	-*
Total volatile compounds identified		31			26				56	58	31	22	24

*percentages of peak area out of the ISO range tr: traces

TABLE 3

		ISO standard 9844 ²¹	Boelens and Jimenez ⁵⁶		Njoroge <i>et al.</i> ⁴³				
Extraction method		Cold-pressed	Laboratory cold-pressed		Laboratory cold-pressed				
Cultivar		Daidai							
Growing location		Japan							
Storage			ripe fruits on tree	ripe fruits stored 1-2 weeks	fresh oil	5°C		20°C	
						during 3 months	during 12 months	during 3 months	during 12 months
ISO standard 9844 compounds	α-pinene	0.30-0.65	0.65	0.55	0.5	0.6	0.5	0.6	0.5
	β-pinene	0.30-1.15	0.14*	0.20*	0.7	1.0	0.6	0.7	0.5
	myrcene	1.60-1.95	1.95	2.00*	1.6	1.6	0.5*	0.8*	0.1*
	octanal	X	0.30	0.12	0.1	0.1	<0.05	0.1	0.1
	limonene	92.95-95.00	93.20	92.20*	94.7	92.1*	85.8*	88.5*	65.1*
	linalool	0.10-0.35	0.24	0.34	0.2	0.2	0.4*	1.3*	1.0*
	decanal	X	0.20	0.14	0.1	0.1	0.1	0.2	0.1
	linalyl acetate	0.6-1.02	0.28*	0.75	1.1*	1.6*	0.7	0.9	0.5*
	geranyl acetate	0.10-0.25	0.13	0.15	-*	-*	-*	-*	-*
	β-caryophyllene	0.05-0.15	0.06	0.13	<0.05*	0.1	0.5*	0.4*	1.1*
	germacrene-D	0.08-0.18	0.08	0.10	0.1	<0.05*	0.1	<0.05*	0*
(E)-β-nerolidol	0.06-0.18	0.10	0.23*	0*	0*	<0.05*	<0.05*	0.1	
Total volatile compounds identified			44	18	41	58	55	58	

*percentages of peak area out of the ISO range

TABLE 4

References	Extraction method	Industrial cold-pressed extraction										
	Cold-pressed	ISO standard 9844 ²¹	Boelens and Jimenez ³⁵	Boelens and Oporto ⁴⁸	Dugo <i>et al.</i> ^{19,36} Dugo ⁴¹	Dugo <i>et al.</i> ³⁹	Koketsu <i>et al.</i> ²⁷	Mondello <i>et al.</i> ^{37,40}	Pino and Rosado ²⁹	Veriotti and Sacks ⁵⁸		
Cultivar		Seville		Seville								
Growing location		Spain (Andalucia) 1987	Italy (Sicily) 1987	Spain	Italy	Italy	Egypt ripe fruits extraction by Pelatrice	Brazil extraction by FMC	Italy	Cuba		
Ripening stage												
ISO standard 9844 compounds	α -pinene	0.30-0.65	0.447	0.592	0.383	0.563	0.38	0.34	0.89*	0.62	0.9*	0.94*
	β -pinene	0.30-1.15	0.295*	0.900	0.440	0.940	0.59	0.10*	1.17*	1.01	0.6	0.91
	myrcene	1.60-1.95	1.806	2.073*	1.733	1.789	1.38*	1.56*	3.10*	1.90	4.9*	2.05*
	octanal	X	0.130	0.239	0.065	0.135	0.07	0.07	-*	0.20 (α -phellandrene)	-*	0.03
	limonene	92.95-95.00	94.338	92.430*	93.770	95.363 (<i>p</i> -cymene, β -phellandrene)	93.43	96.52*	92.29*	93.26 (<i>p</i> -cymene)	86.2*	93.42
	linalool	0.10-0.35	0.152	0.371*	0.220	0.270	0.30	0.06*	0.21	0.32	0.3	0.10
	decanal	X	0.137	0.193	0.130	0.123	0.07	0.09	0.12	0.13	<0.1	-
	linalyl acetate	0.6-1.02	0.284*	0.775	0.426*	0.894	0.81	0.08*	0.37*	1.04*	-*	0.16*
	geranyl acetate	0.10-0.25	0.133	0.094*	0.142	0.098	0.07*	0.08*	tr	0.12	0.5*	0.11
	β -caryophyllene	0.05-0.15	-*	-*	0.103	0.052	0.04*	0.04*	0.10	0.06	-*	0.05
	germacrene-D	0.08-0.18	-*	-*	0.135	0.108	0.06*	0.03*	-*	0.12	0.2*	-*
	(<i>E</i>)- β -nerolidol	0.06-0.18	-*	-*	0.112	0.062	0.06	0.03*	-*	0.09	-*	-*
Total volatile compounds identified			44	58	64	60	58	37	54	30	12	
Dilution EO			-	-	1:10 (v/v) in hexane	1:10 (v/v) in hexane	-	1:10 (v/v) in hexane	-	-	-	
Volume injected			0.2 μ L	-	1 μ L	1 μ L	-	1 μ L	-	0.2 μ L	-	
Split			-	-	1:25	1:50	-	1:26	-	150:1	-	

*percentages of peak area out of the ISO range tr: traces

TABLE 5

Extraction method	Cold-pressed			Laboratory cold-pressed extraction						
	References	ISO standard 9844 ²¹	Boelens and Jimenez ⁵⁶	Gionfriddo <i>et al.</i> ³⁸	Huang and Wu ²⁸		Kirbaslar and Kirbaslar ⁵²			
Cultivar				Morocco	Bangan	Daidai				
Growing location	ripe fruits			Italy (Calabria) 2001	China (Chongqing)		Turkey (Antalya) 1999	Turkey (Antalya) 2000	Turkey (Marmaris) 2000	
Ripening stage										
ISO standard 9844 compounds	α -pinene	0.30-0.65	0.65	0.367	0.52	0.32	0.51	0.42	0.45	0.39
	β -pinene	0.30-1.15	0.14*	0.749	0.78	0.24*	0.51	0.40	0.42	0.57
	myrcene	1.60-1.95	1.95	1.498*	1.93	1.90	1.89	1.81	1.86	1.73
	octanal	X	0.30	0.146	-	-	-	0.08	0.10	0.16
	limonene	92.95-95.00	93.20	91.522*	92.96	92.53*	94.29	94.25	94.32	93.68
	linalool	0.10-0.35	0.24	0.378*	0.35	0.37*	0.16	0.38*	0.33	0.46*
	decanal	X	0.20	0.137	0	0	0	0.22	0.16	0.21
	linalyl acetate	0.6-1.02	0.28*	0.960	0.73	0.32*	0.32*	1.32*	1.27*	1.17*
	geranyl acetate	0.10-0.25	0.13	0.091*	0.20	0.34*	0.16	0.13	0.08*	0.04*
	β -caryophyllene	0.05-0.15	0.06	0.065	0.07	0.12	0.08	0.09	0.06	0.16*
	germacrene-D	0.08-0.18	0.08	0.094	_*	_*	_*	_*	_*	_*
	(<i>E</i>)- β -nerolidol	0.06-0.18	0.10	0.050*	0.11	0.32*	0.10	0.07	0.05*	0.03*
	Total volatile compounds identified		44	46	41	42	43	23	26	27
Dilution EO		-	pure		-		1/20 in hexane			
Volume injected		-	0.3 μ L		-		1 μ L diluted			
Split		-	1:60		-		split			

* percentages of peak area out of the ISO range

TABLE 5 Continued

Extraction method	Cold-pressed			Laboratory cold-pressed extraction				
	References	ISO standard 9844 ²¹	Lota <i>et al.</i> ³¹					
Species	<i>C. aurantium</i> L.			<i>C. neo-aurantium</i> Tan.	<i>C. myrtifolia</i> Raf.	<i>C. natsudaidai</i> Hay.		
Cultivar	Espagne	Gou Tou	24 other cultivars of <i>C. aurantium</i> L.**		Tosu	Large Chinotto	Natsudaidai	
Growing location	France (Corsica)							
Ripening stage								
ISO standard 9844 compounds	α -pinene	0.30-0.65	0.4	0.9*	0.4 ± 0.1	0.8*	0.5	0*
	β -pinene	0.30-1.15	1.2*	4.0*	1.0 ± 0.5	5.2*	1.0	0.7
	myrcene	1.60-1.95	1.0*	1.6	1.6 ± 0.1	1.5*	1.8	1.4*
	octanal	X	0	0.1	0.1 ± 0.1	0.1	tr	0.1
	limonene	92.95-95.00	72.9*	84.2*	92.7* ± 1.9	82.2*	94.9	93.5
	linalool	0.10-0.35	5.2*	0.8*	0.3 ± 0.3	1.1*	0.1	0.1
	decanal	X	0	0	0.1 ± 0.1	0.1	0.1	0
	linalyl acetate	0.6-1.02	5.0*	0*	1.2* ± 0.9	0*	0.2*	0.6
	geranyl acetate	0.10-0.25	0.6*	0.1	0.2 ± 0.1	0.1	0.1	0.2
	β -caryophyllene	0.05-0.15	0.9*	0.2*	0.1 ± 0.1	0.1	tr*	0.2*
	germacrene-D	0.08-0.18	2.1*	0.8*	0.2* ± 0.1	1.0*	tr*	0*
	(<i>E</i>)- β -nerolidol	0.06-0.18	3.2*	0.1	0.2 ± 0.1	0.1	0.1	0.4*
	Total volatile compounds identified		19	19		27	22	19
Dilution EO	-							
Volume injected	-							
Split	-							

* percentages of peak area out of the ISO range

** mean ± standard deviation

tr: traces

TABLE 5 Continued

Extraction method	Cold-pressed		Laboratory cold-pressed extraction									
	References	ISO standard 9844 ²¹	Njoroge <i>et al.</i> ⁴²	Njoroge <i>et al.</i> ⁴³	Sawamura <i>et al.</i> ⁴⁴			Sawamura ⁴⁵		Song <i>et al.</i> ⁴⁶		
Cultivar		Daidai**	Daidai**	Daidai**	Kabusu	Bittersweet	Daidai**	Kabusu	Figaradia Hooker	Tokosu	Daidai**	
Growing location		Japan (Kochi)	Japan (Kochi)	Japan	Japan	Italy	Japan	Japan	Japan	Japan	Japan (Kochi)	
Ripening stage		ripe fruits	ripe fruits								ripe fruits	
ISO standard 9844 compounds	α -pinene	0.30-0.65	0.470	0.5	0.6	0.28*	0.51	0.54	0.57	0.47	0.6	
	β -pinene	0.30-1.15	0.684	0.7	0.7	0.03*	0.18*	0.91	1.05	0.69	0.4	
	myrcene	1.60-1.95	1.565*	1.6	1.6	1.7	1.73	1.73	1.65	1.68	1.64	2.2*
	octanal	X	0.103	0.1	0.1	0.2	0.10	0.09	0.14	0.16	tr	0.6
	limonene	92.95-95.00	94.682	94.7	94.7	92.0*	96.28*	95.85*	92.03*	92.99	94.36	92.5*
	linalool	0.10-0.35	0.149	0.2	0.2	1.1*	0.34	0.18	1.04*	0.62*	0.15	0.2
	decanal	X	0.090	0.1	0.1	0.1	0.10	0.07	0.07	0.09	0.01	0.2
	linalyl acetate	0.6-1.02	1.111*	1.1*	0*	0*	0*	0*	0*	0*	0*	1.4*
	geranyl acetate	0.10-0.25	0.085*	-*	0.1	0.1	tr*	0.06*	0.09*	0.13	0.01*	0.2
	β -caryophyllene	0.05-0.15	0.042*	<0.05*	-*	-*	tr*	0.02*	0.01*	0.02*	0.18*	tr*
	germacrene-D	0.08-0.18	0.090	0.1	-*	-*	0.01*	0.04*	0.04*	0.09	0.47*	0.1
	(E)- β -nerolidol	0.06-0.18	0.049*	-*	-*	-*	0*	0.03*	0.04*	0.08	0*	0.1
	Total volatile compounds identified		62	18	16	12	48	45	44	47	55	54
Dilution EO		pure	pure	pure			pure				-	
Volume injected		1 μ L	0.2 μ L	0.1 μ L			1 μ L				-	
Split		50:1	32:1	32:1			1:34				1:34	

*percentages of peak area out of the ISO range

** *Citrus aurantium* L. var. *cyathifera* Y. Tanaka tr: traces

TABLE 6

	Species and cultivar if indicated	Growing location	Peels state	Mass (g)	Time of HD (hours)	Distillation rate (mL/min)	Details after extraction and before analysis	Yield (as stated in the article)	Yield (g/100g dry matter)
Ali <i>et al.</i> ¹⁸	<i>C. aurantium</i>	Pakistan	fresh	-	6	-	stored in a sealed vial at 4°C	1.0 (mL/100g fresh peel)	0.26
Azhdarzadeh and Hojjati ³³	<i>C. aurantium</i>	Iran (Khouzestan province)	fresh	100	3	-	dried over Na ₂ SO ₄ anhydrous passed through membrane filter (Whatman filter No.1) stored at 4°C	unripe: 0.66% ripe: 0.86%	
Bourgou <i>et al.</i> ⁵¹	<i>C. aurantium</i>	Tunisia (Menzel Bouzelfa)	fresh	100	2	-	dried over Na ₂ SO ₄ anhydrous stored at 20°C in darkness	Immature: 0.23% Semi-mature: 0.12% Mature: 0.46%	
Boussaada and Chemli ²³	<i>C. aurantium</i> L. ssp. <i>amara</i>	Tunisia (Nabeul)						February: 0.7%	
		Greece (Chania)						0.8%	
Boussaada <i>et al.</i> ²⁶	<i>C. aurantium</i> L. ssp. <i>amara</i>	Brazil						0.8%	
		France (Corsica)	fresh	(peel of ten fresh ripe fruits)	3	-	dried over Na ₂ SO ₄ anhydrous stored in sealed glass vials in a refrigerator at 4-5°C	0.8%	
		Greece (Roxani)						1.1%	
Boussaada and Chemli ⁶⁵	<i>C. aurantium</i> L. ssp. <i>amara</i>	-						November: 1.0% December: 1.2% January: 1.3% February: 0.8%	
Caccioni <i>et al.</i> ⁶	<i>C. aurantium</i>	Italy (Lentiny)	fresh at ripening stage	500 to 900	until there was no significant increase in the volume of oil collected	-	dried over Na ₂ SO ₄ anhydrous stored under N ₂ in sealed vials	-	

TABLE 6 Continued

	Species and cultivar if indicated	Growing location	Peels state	Mass (g)	Time of HD (hours)	Distillation rate (mL/min)	Details after extraction and before analysis	Yield (as stated in the article)	Yield (g/100g dry matter)
Gonzalez de et al. ⁵⁴	<i>C. aurantium</i> L. ssp. <i>amara</i>	Venezuela (Tachira)	fresh	-	-	-	-	-	-
Hosni et al. ⁵⁰	<i>C. aurantium</i> L.	Tunisia (Zaghouan)	air dried ground	100	3	-	dried over Na ₂ SO ₄ anhydrous stored in amber and air-tight sealed vials at 0°C	1.24 (g/100g dry peel)	1.12
Jabri Karoui and Marzouk ⁴	<i>C. aurantium</i> L.	Tunisia (Cape Bon)	fresh	100	1.5	-	collected in diethyl ether using liquid-liquid isolation	-	-
Protopapadakis and Papanikolaou ³²	<i>C. aurantium</i> L. Chania	Greece (La Canée)	dried cut into small pieces	-	-	2 to 3	method of the European Pharmacopoeia	0.78 (mL/100g dry peel)	0.60
	<i>C. aurantium</i> L. Brazilian		immersed in water for 2 hours					0.48 (mL/100g dry peel)	0.37
	<i>C. aurantium</i> L. Keen		before					0.78 (mL/100g dry peel)	0.60
	<i>C. aurantium</i> L. Bittersweet		before					1.09 (mL/100g dry peel)	0.83
Rowshan and Najafian ⁷	<i>C. aurantium</i> L.	Iran	air-dried at ambient temperature in the shade until semi-dried	100	3	2 to 3	method of the European Pharmacopoeia. dried over Na ₂ SO ₄ anhydrous and stored in sealed vials at 4°C	-	-
Sanei-Dehkordi et al. ³⁴	<i>C. aurantium</i>	Iran (Babol)	fresh	50	3	-	dried over Na ₂ SO ₄ anhydrous and stored into an air-tight amber coloured vial at 4°C	0.7 ± 0.12 (g/100g fresh peel)	0.21
Sarrou et al. ⁵	<i>C. aurantium</i> L.	Greece	fresh	35	3	3 to 3.5	dried over Na ₂ SO ₄ anhydrous and stored at 4-6°C	1.67 (mL/100g fresh peels)	0.43

TABLE 7

Extraction method	cold-pressed		hydrodistilled oils											
	ISO standard 9844 ²¹	Ali <i>et al.</i> ¹⁸	Azhdarzadeh and Hojjati ³³	Bourgou <i>et al.</i> ⁵¹	Boussaada and Chemli ²³	Boussaada <i>et al.</i> ²⁶			Boussaada and Chemli ⁶⁵					
Cultivar	Larange													
Growing location	Pakistan	Iran (Khouzestan province)	Tunisia (Menzel Bouzelfa)	Tunisia (Nabeul)	Greece (Chania Crete)	Brazil	France (Corsica)	Greece (Roxani Crete)	November	December	January	February		
Ripening stage		ripe peel	ripe peel											
Harvest date														
ISO standard 9844 compounds	α -pinene	0.30-0.65	0.6	1.96*	0.36	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.3	
	β -pinene	0.30-1.15	0.21*	0.56*	0.38	0.3	0.5	0.2*	0.5	0.3	0.2*	0.3	0.3	
	myrcene	1.60-1.95	2.57*	5.74*	0.07*	1.6	1.5*	1.6	1.6	1.6	1.7	1.6	1.6	1.4*
	octanal	X	0.14	0.83	-	-	-	-	-	-	-	-	-	
	limonene	92.95-95.00	91.98*	81.6*	90.95*	90.6*	89.6*	93	91.8	92*	87.7*	88*	92.2	87*
	linalool	0.10-0.35	1.78*	2.19*	0.1*	1.5*	2*	0.8*	1.4*	1*	1.3*	1*	0.8*	0.6*
	decanal	X	0.08	-	-	-	-	-	-	-	-	-	-	-
	linalyl acetate	0.6-1.02	-*	0*	0.01*	0.2*	0.5*	0.2*	0.3*	0.2*	0.1*	0.2*	0.2*	0.2*
	geranyl acetate	0.10-0.25	0.08*	0.33*	0.02*	0.2	0.3*	0.2	0.3*	0.2	0.2	0.2	0.2	0.3*
	β -caryophyllene	0.05-0.15	0.05	0.22*	-*	tr*	tr*	tr*	tr*	tr*	tr*	tr*	tr*	tr*
	germacrene-D	0.08-0.18	0.06*	0.22*	0.04*	-*	-*	-*	-*	-*	-*	-*	-*	-*
	(<i>E</i>)- β -nerolidol	0.06-0.18	0.05*	0.09	-*	0.1	0.1	0.1	0.1	0.1	tr*	tr*	tr*	0.1
	Total volatile compounds identified		25	39	31	26		26			26			
Dilution EO		pure	pure	-	1% solution (diluted in pentane)		-			1% solution (diluted in pentane)				
Volume injected		1 μ L	0.5 μ L	-	0.1 μ L		-			0.1 μ L				
Split		1:50	-	60:1	1:50		-			1:50				

* percentages of peak area out of the ISO range

TABLE 7 Continued

Extraction method	cold-pressed					hydrodistilled oils							
	ISO standard 9844 ²¹	Caccioni <i>et al.</i> ⁶	Gonzalez de <i>et al.</i> ⁵⁴	Hosni <i>et al.</i> ⁵⁰	Jabri Karoui and Marzouk ⁴	Protopapadakis and Papanikolaou ³²			Rowshan and Najafian ⁷	Sanei-Dehkordi <i>et al.</i> ³⁴	Sarrou <i>et al.</i> ⁵		
Cultivar						Chania	Brazilian	Keen	Bittersweet				
Growing location						Italy (Lentiny)	Venezuela (Tachira)	Tunisia (Zaghouan)	Tunisia (Cape Bon)	Greece (La Canée)	Iran mature: orange	Iran (Babol)	Greece
Ripening stage													
Harvest date													
ISO standard 9844 compounds	α -pinene	0.30-0.65	0.40	0.64	0.27*	0.55	0.38	0.38	0.39	0.37	0.43	0.30	0.53
	β -pinene	0.30-1.15	0.33	3.25*	1.37*	0.44	0.51	0.23*	0.48	0.33	0.1*	0.65	0.62
	myrcene	1.60-1.95	1.88	1.74	0*	0.04*	1.55*	1.62	1.61	1.60	1.78	1.00*	2.00*
	octanal	X	0.08	0	-	-	-	-	-	-	0.68	-	0.24
	limonene	92.95-95.00	94.27	90.04*	96.9*	90.25*	89.95*	93.00	91.80*	92.20*	93.47*	94.81	94.67
	linalool	0.10-0.35	0.8*	2.87*	0.17	1.56*	1.97*	0.82*	1.44*	1.05*	1.25*	-*	0.76*
	decanal	X	0.11	-	-	-	-	-	-	-	0.20	-	0.16
	linalyl acetate	0.6-1.02	-*	-*	0*	0.29*	0.47*	0.19*	0.28*	0.21*	0.22*	0.32*	0.18*
	geranyl acetate	0.10-0.25	0*	-*	0*	0.11	0.26*	0.23	0.25	0.22	0.13	0.13	0*
	β -caryophyllene	0.05-0.15	0.07	-*	-*	0.05	-*	-*	-*	-*	0*	0.03*	0*
	germacrene-D	0.08-0.18	-*	-*	tr*	-*	-*	-*	-*	-*	0*	0.08	0*
	(E)- β -nerolidol	0.06-0.18	0.07	-*	0*	0.35*	-*	-*	-*	-*	-*	0.06	0*
	Total volatile compounds identified		36	7	13	27			21		24	21	12
	Dilution EO		-	-	-	-			1:9 in pentane		-	-	-
Volume injected		-	-	-	-			1 μ L		-	-	-	
Split		-	-	-	60:1			-		1:50	-	1:30	

* percentages of peak area out of the ISO range

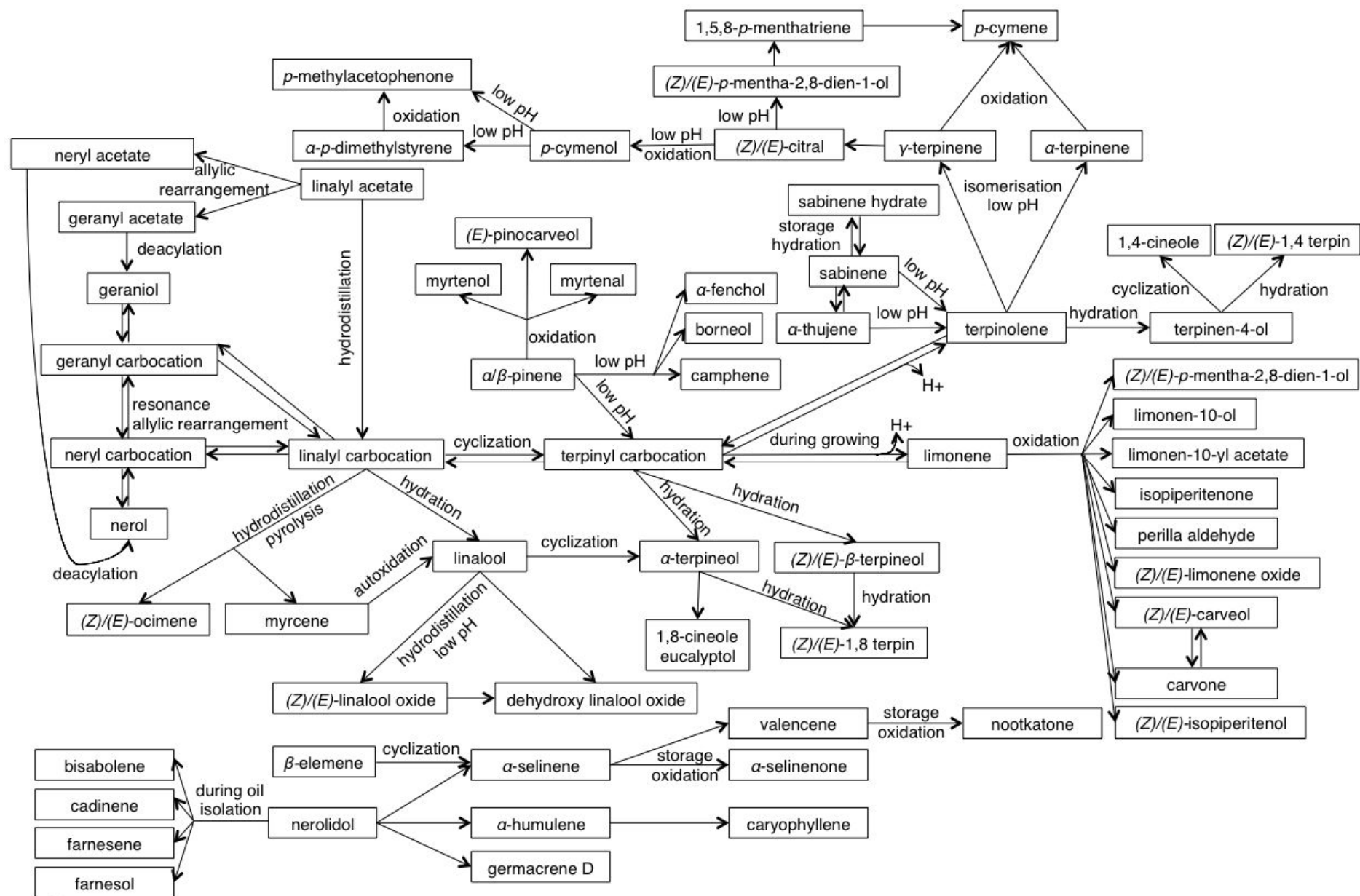
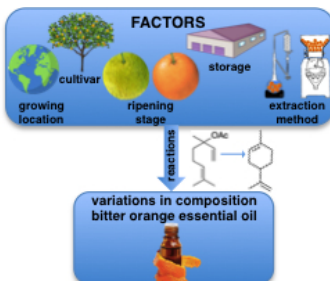


FIGURE 1

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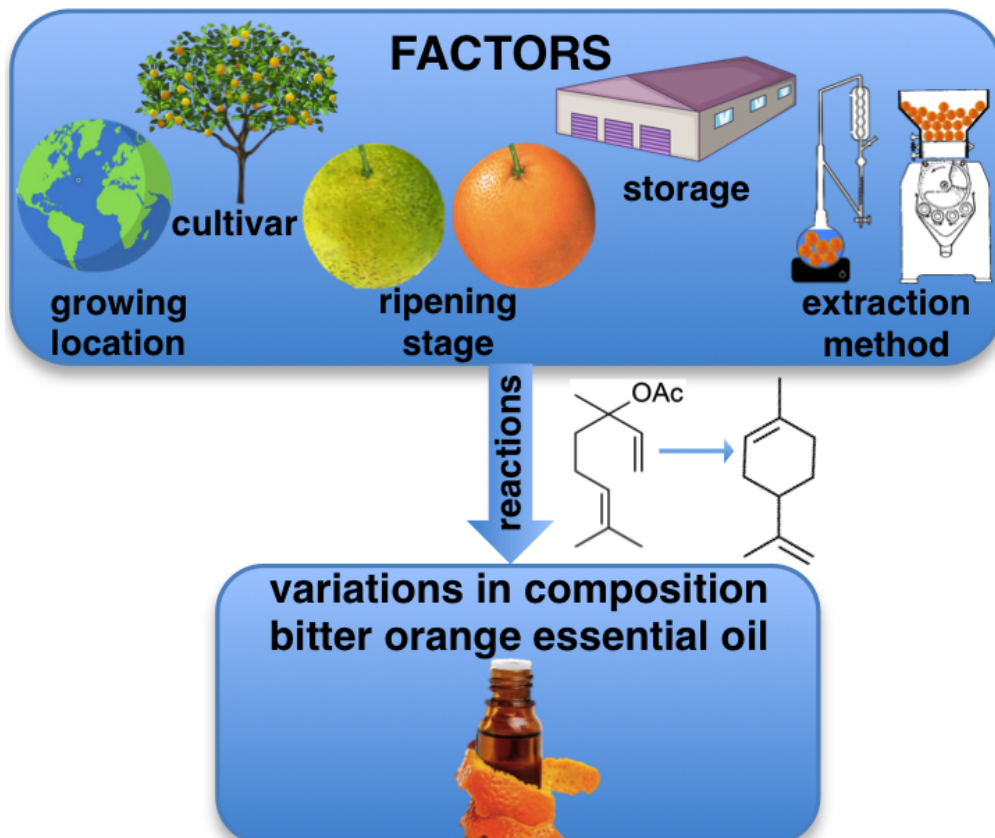
The influence of the growing location, the cultivar, the ripening stage, the storage and the extraction method on the composition of bitter orange peel essential oil is critically reviewed. The chemical reactions underlying the changes in composition due to these factors are presented.



Bitter orange peel essential oil: a review of the different factors and chemical reactions influencing its composition

Marion Gaff, Martine Esteban-Decloux and Pierre Giampaoli

254x70mm (72 x 72 DPI)



253x211mm (72 x 72 DPI)