

Citrus Essential Oils: Extraction and Deterpenation

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ABSTRACT

The essential oils of citrus fruits are valuable raw materials in the scent and flavouring industries. As extracted, they are complex mixtures with large proportions of terpene hydrocarbons that make them easily oxidizable and insoluble in aqueous and alcoholic solutions. This mini-review surveys the main processes by which these essential oils are currently extracted and deterpenated, and also the current state of research into their deterpenation by means of ionic liquids.

Keywords: FMC in-line, ionic liquids, *pellatrice*, sesquiterpeneless and terpeneless oils, *sfumatrice*

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INTRODUCTION

An essential oil is in principle the volatile fraction obtained from a plant or from one or more of its parts by a physical separation process, usually distillation or cold-pressing (sometimes called “expression”). Although the product obtained by this latter process also includes certain non-volatile residues that can contribute positively to its properties (Dugo *et al.* 1997). It is essential oils that give plants their characteristic aromas and flavours. They are employed as combined aromatizers and flavourings in many foods and drinks (e.g. confectionery and spirits), and to mask bitterness in certain medicines. As pure aromatizers, they are used in perfumes, cosmetics, and soaps and other cleaning and personal hygiene products, and to mask unpleasant odours in the textile, plastics and paint industries. They are also employed in pharmaceutical or parapharmaceutical products, as well as in aromatherapy (Lawless 2002).

In the case of plants of the genus *Citrus*, most essential oil is contained in small glands in the peel of the fruit, and is made up of over a hundred components (terpenes, alcohols, aldehydes and esters, among others) that jointly determine the characteristics of the oil. Distillation of essential oil from the leaves of citrus plants is less common.

The chemical composition and quality of an essential oil depend on the soil and management practices in and by which the plant of origin was grown (e.g. available nutrients,

fertilizers and biotic components); geographical and climatic factors (insolation, temperature, rainfall, winds, altitude, latitude, etc.); and the ripeness of the fruit at harvest; post-harvest manipulation (washing, drying, packing, storage, transport). The chemical composition and quality of an essential oil as supplied to its users also depend on the method by which it was extracted from the plant, and on any processes to which it may have been subjected in order to improve its organoleptic characteristics (Guenther 1948).

This mini-review seeks to describe the main techniques by which the essential oils are extracted and their properties improved through deterpenation processes. This is established as a previous step to the discussion of the role that ionic liquids could bring to the performance of such processes.

CHEMICAL COMPOSITION

Essential oils are mixtures of dozens of components, sometimes more than a hundred, including monoterpenes, sesquiterpenes, their oxygenated derivatives, and low-molecular-weight aliphatic alkanes, alcohols, aldehydes, ketones, esters and acids. Associated non-volatile compounds (e.g. paraffins, waxes) are also sometimes found as components of essential oils. Terpene hydrocarbons contribute little to aroma and flavour, and their presence can give rise to problems deriving firstly from their insolubility in aqueous and alcoholic solution, and secondly from their oxidation when exposed

Table 1 Mass percent composition of major citrus essential oils (Shaw 1979). Adapted with permission of The American Chemical Society.

	Sweet Orange	Grape-fruit	Mandarin	Lemon	C. P. Lime	Dist. Lime	Bitter Orange	Bergamot
Acids								
Citronellic			0.006					
Decanoic			0.03					
Dodecanoic			0.006					
Heptanoic			0.004					
Nonanoic			0.01					
Octanoic			0.04			0.02		
Undecanoic			0.003					
Alcohols								
Benzyl alcohol			0.009					
Borneol						0.6		
<i>Cis</i> -carveol			0.01-0.04					
<i>Trans</i> -carveol			0.003-0.04					
Citronellol			0.01-0.03	0.5			0.2-1.1	
Decanol			0.04			0.06		
Elemol		0.04						
Fenchol						1.2		
Geraniol			0.01-0.04					
Heptanol			0.02					
Isopulegol			0.01-0.05				0.3-0.4	
Linalool	0.3-5.3	0.3-0.4	0.03-6.1	0.08-0.3	0.09-0.2	0.1	0.5-1	16-41
Nerol			0.05				0.1-0.3	
1-nonanol	0.1		0.1		0.1	0.01		
Octanol		0.8	0.09			0.01		
Sabinene hydrate			0.2					
Terpinen-1-ol						0.7		
Terpinen-4-ol	0.06-0.2	0.08	0.06-0.3	0.01-0.4		1.6	0.3-0.4	
α -terpineol	0.1-0.5	0.2	0.03-1.1	0.2-0.5	0.3-1.05	5.9	0.2-0.3	0.2-4
β -terpineol			0.4			0.7		
Tetrahydrogeraniol				0.1				
thymol			0.04-0.2					
α,α,p -trimethylbenzyl alcohol			0.03			0.6		
Aldehydes								
Citral	0.05-0.2	0.05-0.06		2-13.2	3.1-5.3	0.3		
Citronellal	0.1	0.14	0.1-0.2	0.03-0.2	1.4		0.3-0.4	
Decanal	0.1-0.7	0.3-0.6	0.04-0.9	0.06-0.2	0.1	0.09		
Dodecanal	0.05-0.2	0.1-0.2	0.006-0.15	0.1		0.006		
Furfural						0.005		
Geranial	0.06-0.2	0.1-0.2	0.06-0.3	0.6-2.3	5.1-6.8	0.1		
Heptanal	0.03-0.05	0.05-0.06		0.04				
Hexanal	0.006-0.02							
Neral	0.01-0.2	0.03	0.06	0.4-1.3	0.4-4.6			
Nonanal	0.06-0.2	0.04-0.1	0.03	0.09-0.3	0.2		0.1-0.4	
Octanal	0.2-2.8	0.3-0.7	0.04-0.3	0.1-0.15	0.8	0.03	1.4-2.2	
Perillaldehyde	0.02	0.2	0.003-0.1					
α -sinensal	0.03		0.2					
β -sinensal	0.06-0.09							
Tetradecanal	0.05-0.09	0.1	0.05					
Undecanal	0.01-0.2							
Esters								
Citronellyl acetate			0.04-0.1	0.04-0.2			0.2-0.6	
Citronellyl formate							0.1-1.1	
Decyl acetate		0.15	0.002-0.003	0.05	0.1			
Geranyl acetate			0.003-0.1	0.1-1	0.55-3.1	0.3		0.6
Geranyl formate							0.3-0.6	
Linalyl acetate							0.3-1	11.4-44
1,8pmenthadiene-9ylacetate			0.003					
1-p-menthen-9-yl acetate			0.001					
Neryl acetate	0.1	0.2	0.06-0.1	0.1-0.4	2.5-3.1	0.01		
Neryl formate	0.1				0.2			
Octyl acetate	0.1	0.1	0.02-0.04	0.04				
Perillyl acetate			0.008-0.1					
Terpinyl acetate			0.002-0.05					
Hydrocarbons								
α -bergamotene	0.06			0.4	2.5	0.5		
β -bisabolene				0.14-1.4	2.5-4	0.9		
γ -cadinene			0.02					
Δ -cadinene	0.1	0.1	0.2					
Camphene		0.2	0.01-0.4	0.2-0.5	0.5	0.8	0.4-0.9	
Δ -carene			0.004-0.06					0.02-0.1
Caryophyllene		0.3	0.02-0.09	0.3	2.5	0.3		
α -copaene		0.06	0.008-0.2					

Table 1 (Cont.)

	Sweet Orange	Grape-fruit	Mandarin	Lemon	C. P. Lime	Dist. Lime	Bitter Orange	Bergamot
Hydrocarbons (cont.)								
<i>β</i> -copaene		0.01						
<i>β</i> -cubebene	0.1							
<i>p</i> -cymene	0.2	0.4	0.2-8.2	0.6-1.1	0.5-1.9	11.6		
<i>α</i> - <i>p</i> -dimethylstyrene						0.5		
<i>β</i> -elemene	0.05	0.06	0.07-0.8					
<i>γ</i> -elemene			0.2					
<i>Δ</i> -elemene			0.06-0.1					
Farnesene	0.02-0.07							
<i>α</i> + <i>β</i> -humulene			0.05	0.2				
Limonene	83-97	86-95	65-94	54-80	47-64	60	74-86	25-32
Longifolene			0.01					
Myrcene	0.9-2.1	1.4-2.1	1.2-7.6	0.9-12.7	0.7-10.3	0.8		
Nonane						0.06		
Ocimene		0.4	0.08					
<i>α</i> -phellandrene		0.8	0.03-0.3	0.2	0.2			
<i>β</i> -phellandrene		0.7	0.4-0.5	0.8	0.9			
<i>α</i> -pinene	0.1-0.6	0.2-1.6	0.3-2.5	0.4-5	1.2-2.4	0.8		0.8-2
<i>β</i> -pinene			0.9-2.1	2.2-13.9	10.1-11.9	0.9	0.9-5.5	4.1
Sabinene	0.1-0.6	0.7	0.4-2.1	0.5-1.5	1.6			4.1-4.2
<i>α</i> -selinene			0.02					
<i>γ</i> -selinene			0.008					
Sesquicictronellene						0.2		
<i>β</i> -sesquiphellandrene			0.2					
<i>α</i> -terpinene		0.1	0.1-0.4	0.7	0.8			
<i>γ</i> -terpinene	0.1	0.5-0.8	2.1-17.3	2.9-14	7.3-21.7	0.6		4.7-5.5
Terpinolene	0.1		0.2-1.1	0.6-0.9	0.6-1.2	0.8		
<i>α</i> -thujene			0.5		0.4			
Toluene						0.002		
Tridecane						0.02		
Undecane						0.03		
Valencene	0.1-0.2							
Ketones								
Carvone	0.02-0.1		0.005-0.03	0.04				
Methylheptenone				0.06		0.006		
Nootkatone	0.01	0.3-0.8	0.01	0.01	0.01		0.01	
Miscellaneous								
1,4-cineole						1.8		
1,8-cineole			0.002			0.7	0.8-8.1	
Dimethyl anthranilate			0.9					
2,2-dimethyl-5-(1-methyl-1-propenyl)-tetrahydrofuran						0.3		
<i>Cis</i> -linalool oxide		0.03						
<i>Trans</i> -linalool oxide		0.03						
Pinol						0.02		
Thymol methyl ether			0.1					
<i>α,α</i> - <i>p</i> -trimethylbenzyl alcohol methyl ether						0.2		
2,6,6-trimethyl-2-vinyl-tetrahydropyran						0.16		
Nonvolatiles	1-4.1	1.37-9.5	3.5-4.7	0.47-2.2	6.7-7.5		0.23	

to oxygen and their evolution to resins, both of which result in the deterioration of aroma and flavour. The essential oils of citrus fruit peel are about 95% monoterpene hydrocarbons. The organoleptic characteristics of these oils are mainly due to their small proportions of oxygenated terpene derivatives and certain other oxygenated compounds (aldehydes, ketones and esters).

Chemical analysis of commercial essential oils cannot only determine their quality and purity, but also provide information on the technology used in their production and their geographical origin. For some essential oils, the appropriate physicochemical properties and analytical methods have been established by national and international (ISO) standards. For citrus oils, the variables of interest include specific weight, refractive index, optical rotation, nonvolatile residue content, solubility in ethanol and aldehyde content, although all these properties show considerable variability. Detailed analysis of oil composition is generally based on UV and IR spectroscopy and gas or liquid chromatography.

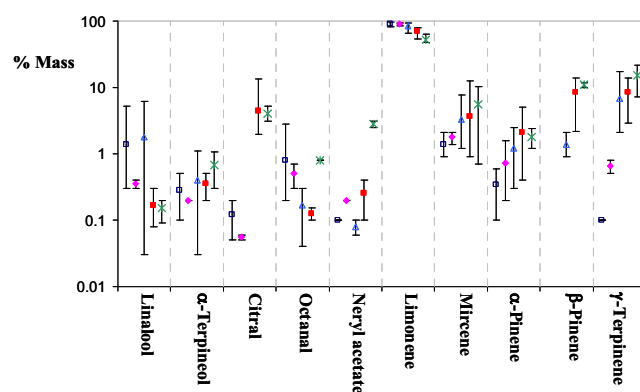


Fig. 1 Mass percent composition ranges of major components of citrus essential oils. Sweet orange \diamond Grapefruit \triangle Mandarin \square Lemon \bullet \ast Cold-pressed lime.

Many works about the composition of specific essential oils extracted under specific conditions can be found in the bibliography. Some reviews give a broader overview of the subject (Shaw 1979a; Shaw 1979b; Boelens 1991; Dugo and McHale 2002; Lawrence 2002; Mondello *et al.* 2002). A work that enables to compare the composition of different essential oils depending on the citrus type, origin, oil extraction method, analysis method used, etc. is the one from Shaw (1979b). **Table 1** has been built with data taken from that work. In this table it can be observed which are the constituent components of some citrus essential oils and the possible variation of their composition (showed in mass %) depending on all the factors previously cited. The major compound, by far in all cases, is limonene. **Fig. 1** shows the mean composition (symbols) for some characteristic components of citrus essential oils and the range in which these compositions may vary.

EXTRACTION PROCESSES

The essential oils of citrus fruits are contained in numerous glands or sacs that are irregularly distributed in the outer, coloured layer of their peel, the flavedo, which comprises the exocarp and several layers of subepidermal tissue (Spiegel-Roy and Goldschmidt 1996). As a result, most citrus fruits are somewhat exceptional in that the extraction of their essential oils without excessive loss of quality requires that their peel be treated separately from, or without affecting, the rest of the fruit. Pulping or pressing the whole fruit are generally not viable options. However, regardless of the particular extraction method used, three intermediate products are obtained: a mixture of juice and pulp (45-55%), essential oils (0.2-0.5%) and peel (45-55%). These intermediate products can then be subjected to further separation processes, depending on the intended final destination (**Fig. 2**).

Traditional and semi-industrial processes

The basic process for extraction of high-quality essential oils is cold pressing, of which there are several variants. The oldest is the completely manual sponge process: each fruit is cut in half, the flesh is extracted, and the peel is soaked in water for a few hours before being pressed between two sponges that absorb a mixture of essential oils, aqueous components, colloids, peel cells and other materials. Wringing the sponges then releases the liquid phase, from which the essential oil is separated by decantation. A less effective traditional method is the *ecuelle* process, in

which the fruit is rolled, under some pressure, in a shallow bowl that is covered with blunt teeth and has a central exit tube for collection of the expressed mixture of oil and aqueous components.

The basic principles of most mechanical processes for extracting essential oils from peel are the same as those of the sponge and *ecuelle* processes (Di Giacomo and Di Giacomo 2002; Guenther 1948; NIIR Board 2003). In the former case, there is the laceration of epidermis and oil sacs and the creation of pressure gradients down which the oil exits the peel. In the latter, the abrasion of the peel is included, resulting in the consequent formation of fine detritus. In machines developed for the sponge process (*sfumatrici*), the de-fleshed peel is rotated and compressed against fixed elements, and the expressed oil is carried away by fine jets of water. Though the yield is higher than in the manual sponge process, the pressure exerted must be kept low enough to avoid the contamination of the expressed oil with other components, particularly those contained in the mesocarp (pith, or albedo), the colloidal contents of which tend to emulsify and deteriorate the expressed oils.

In machines developed for the *ecuelle* process (*pellatrici*), whole fruits are grated, shedding a mixture of essential oils and peel detritus that is washed away and filtered before separation of the oils from the filtrate by centrifugation. The grating is performed by multiple toothed rollers that rotate at a speed that depends on the variety and ripeness of the citrus fruit in question, as does the time required by the grating process.

Both *sfumatrici*-type and *pellatrici*-type machines are capable of producing at an industrial scale when appropriate refinements are introduced (see below). In the case of the *sfumatrici*, the essential improvement is a pre-extraction stage in which the fruit is automatically cut and its flesh removed.

All the above processes should be performed as fast as possible in order to prevent deterioration of the oils extracted, to which multiple factors can contribute. Since the oxygenated compounds that are chiefly responsible for the aromas and flavours of essential oils are their most water-soluble components, lengthy contact with juice or with water used to wash the oils out of the extracting machinery can result in significant losses of important oxygenated terpenoids, aldehydes and esters. Contact with air leads to undesirable oxidation, hydrolysis and resinification reactions. Colloids extracted together with the oils promote emulsification, which hinders separation of the oil. Oils extracted by *ecuelle*-based processes also dissolve coloured and/or resinous materials present in the accompanying solid detritus.

The distillation of citrus fruit peel, of whole fruit, or of the solid residue obtained from the crushing of whole fruit (which retains significant quantities of oils), usually affords essential oils of markedly inferior quality, with aromas and flavours that are very different from those of oils obtained by cold pressing. It is therefore employed basically to extract oils remaining in residues, such as peels, that have already been subjected to cold pressing. Generally, steam distillation under vacuum is performed.

Virtually the only citrus fruit from which essential oils are in some places still extracted following the crushing of the whole fruit is the lime. The waste peel is practically free of oil and juice and oil are separated by distillation. This process has been used for the production of high quality juice and a particularly popular distilled oil (NIIR Board 2003).

Industrial processes

On an industrial scale, essential oils are obtained from citrus fruits as a by-product of fruit juice production. Fruits entering the plant are transported to washing tanks on a conveyor belt on which they are examined and rejected if not well developed, firm, intact, sufficiently smooth-skinned, and free of bruises and signs of rotting or decomposition. After being washed clean of foreign bodies and microorganisms by means of jets of water containing detergent, so-

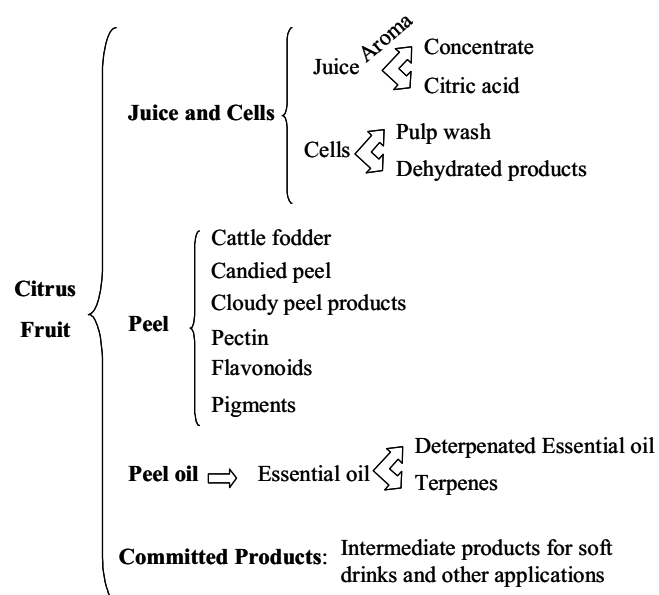


Fig. 2 Products that can be obtained from citrus fruits.

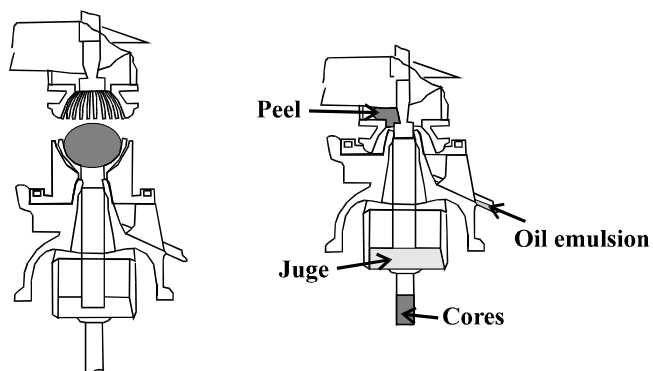


Fig. 3 The working of the FMC in-line citrus juice extractor.

dium hypochlorite or other appropriate agents, they are further rinsed and brushed while being conveyed to the extraction machinery. At some stage, they are also separated into different size classes.

Extraction of oils can either precede juice extraction in *pellatrici* style, as in Brown International Corp.'s oil extractors or the *pellatrici Indelicato* and *Speciale*; follow juice extraction (e.g. by Brown citrus juice extractors) in *sfumatrici* style; or take place simultaneously with juice extraction, as in the FMC whole citrus juice extractor of Food Machinery Corp. (now JBT FoodTech, a division of John Bean Technologies Corp.) (Di Giacomo and Di Giacomo 2002). The most widely used machines are the Brown oil extractor and the FMC in-line extractor.

The most recent Brown oil extractors feature over 3,000,000 teeth on rollers that are submerged in water to prevent loss of volatiles to the atmosphere, and implement post-laceration passage of the fruit through drying rollers that remove adherent water and oil. For elongated fruit, such as lemons, the lacerating rollers oscillate from side to side as they rotate, thus ensuring complete coverage of the peel.

The basic unit of the FMC in-line extractor consists of two opposing cups, one above the other, each split into fingers that fit between those of the other cup when the two are brought together (Fig. 3). At the centre of each cup is a circular cutter that penetrates the fruit when the upper cup clamps down on it. As the upper cup continues to descend, the juice, pulp, seeds and core of the fruit are forced through the lower cutter into an exit tube, where at the end of the cycle they are further compressed to separate juice and juice sacs by passage through a strainer; while essential oils from sacs ruptured by compression of the peel seep between the fingers of the cups and are washed away by water from a spray ring above the upper cup as the spent peel is forced through a gap surrounding the upper cutter. The two main products, juice and oils, are thus separated from the albedo throughout the extraction process.

The classification of fruits by size before arrival at a battery of FMC extractors with variously sized cups is particularly important, as size mismatch between cup and fruit can result in undesirable forms of peel damage that result in the mixing of juice and oil. Other critical factors include the direction and uniformity of the jets of water from the spray ring, the nozzles of which must therefore be kept scrupulously clean; the amount of water used (underspraying resulting in suboptimal oil recovery, and overspraying increasing unnecessarily the capacity demands on downstream units); and the pressure used for spraying, since excessive pressure can lead to loss of oil-loaded droplets, and insufficient pressure to oil being left on the extractor instead of being washed away. A related factor is the need for efficient delivery of fruits to the extractor so that each cup is always occupied when it should be, since spraying empty cups dilutes the mixture of oil and water leaving the extractor.

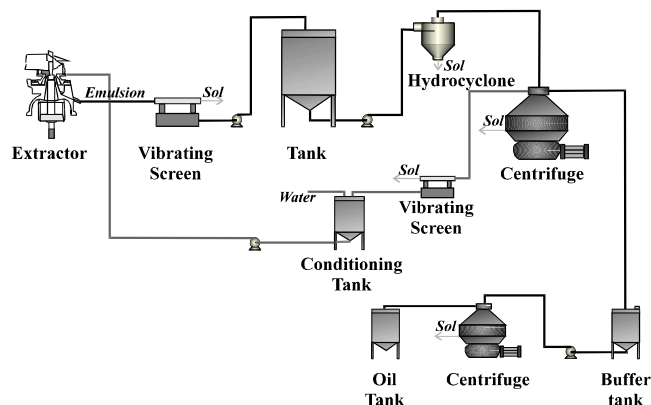


Fig. 4 Post-extraction purification of citrus essential oils.

Purification of oil

All the cold pressing processes described above afford mixtures of essential oils with water and other components from which they must be separated. This is usually achieved by a centrifugation-based process (Fig. 4), although the first stage is the removal of gross solids by passage through a screen and, if necessary, the use of a hydrocyclone. The outflow from this stage, which has an essential oil content of about 0.5-2% by volume (depending on the type of citrus fruit), is pumped to a desludging centrifuge that separates it into an aqueous phase, a sludge containing almost all the remaining solids, and an emulsion with an essential oil content of 70-80%. "Polishing" by a second centrifuge removes the remaining water and also any remaining solids.

Excessive water consumption and the excessive generation of undesirable wastewaters can be avoided, and oil yield slightly increased, by re-using the aqueous centrifuge outflows as extractor spray following appropriate treatment. Such treatment may include, in particular, the use of enzymes to remove pectins, considerable quantities of which can be present in the oil-bearing outflow from extractors. Indeed, since pectins increase flow viscosity and can make the final product turbid, enzyme treatment of the high-oil outflow from the primary centrifuge may also be beneficial (Braddock and Kesterson 1979; Coll *et al.* 1996).

An alternative oil purification method is steam distillation. This method less commonly used than the centrifugation-based method because, as noted above, heat degrades essential oils. When employed, the outflow from the extractors is collected in a vat and heated by the injection of steam, the resulting vapour is condensed, the condensate is allowed to stand until water and oil separate, and the oil is decanted off.

Following purification by the above methods, essential oils are in some cases subjected to "winterization", i.e. removal of waxes by storage for a week or more at a temperature between -25 and -5°C.

For purified essential oils to maintain their quality requires storage in vessels made of appropriate materials (stainless steel, aluminium, tinfoil and permitted plastics may be used) under an inert atmosphere at temperatures no higher than 15-20°C. If water has been completely removed during purification, there will be no hydrolysis reactions, and the oxidation of limonene and other terpenes is prevented by the inert atmosphere.

DETERPENATION

As noted previously, terpene hydrocarbons contribute little to, and can jeopardize, the aroma and flavour of essential oils. Although the natural, non-deterpenated oil may be preferable for some purposes, the removal of terpenes concentrates the more desirable components; increases stability by slowing oxidation and resinification; and increases the solubility of the oils in water, ethanol, and other solvents used in food technology. Essential oils can be deterpenated by ad-

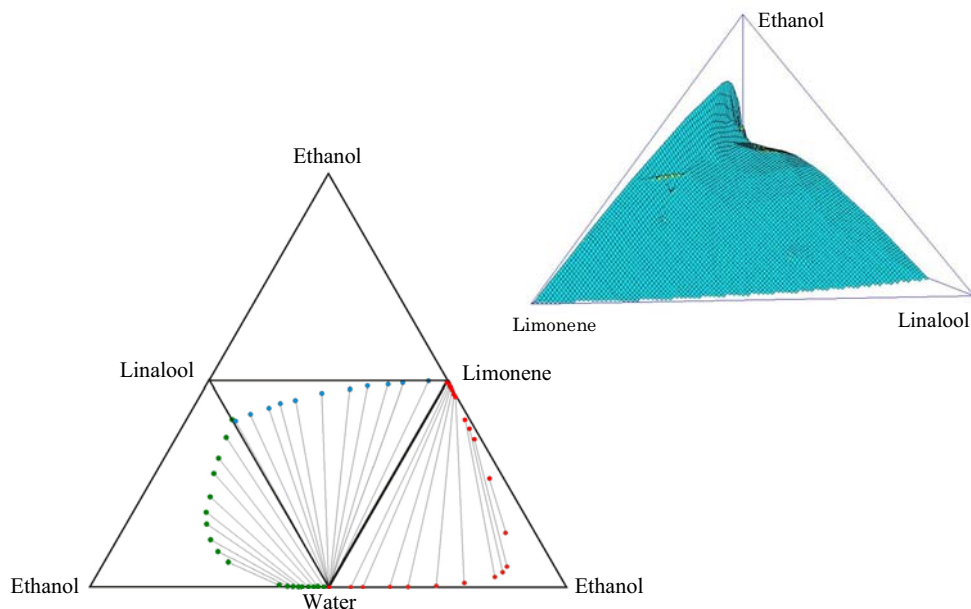


Fig. 5 Equilibrium data for the quaternary system limonene + linalool + ethanol + water at 298.15 K.

sorption chromatography, but large-scale deterpenation is generally carried out by vacuum distillation and/or extraction into dilute alcohol or other solvents. As we shall see below, newer technologies are also being used, one of the most interesting approaches currently under development being the use of ionic liquids. Whatever the method employed, three gross grades of product can be distinguished: “concentrated oils”, from which only part of the hydrocarbons have been removed; “terpeneless oils”, from which the all or most monoterpenes have been removed; and “sesquiterpeneless and terpeneless oils” (sometimes just called “sesquiterpeneless oils”), which are free of monoterpenes, sesquiterpenes and waxes (Guenther 1948).

Distillation

Some 95% of citrus essential oils are monoterpenes, which at atmospheric pressure have boiling points approximately in the range 150-180°C. Sesquiterpenes, with boiling points of 240-280°C, are also present. Most of the oxygenated compounds responsible for aroma and flavour have boiling points between these two ranges. Accordingly, most monoterpenes can be removed by fractional distillation *in vacuo*. However, this process can never remove all monoterpenes without also removing some of the desired oxygenated compounds, and further fractionation to recover these losses not only courts degradation due to prolonged heating, but also tends to nullify the main advantage of the distillation approach, its speed.

Once monoterpenes have been wholly or partially removed, fractional distillation or steam distillation can also be used to separate oxygenated compounds from sesquiterpenes and waxes. However, even when performed *in vacuo* these distillation processes result in loss of quality due to polymerization and resinification reactions (Fleisher *et al.* 1987). Once monoterpenes have been removed, oxygenated compounds are therefore generally extracted from the residue with dilute alcohol or some other appropriate extractant.

Extraction with conventional solvents

For efficient extraction of a solute from a solution, an extractant should both dissolve the solute well (Distribution Coefficient $\beta > 1$) and dissolve it selectively (Selectivity $S > 1$). Other factors to be considered in choosing an extractant include its physical properties, recoverability, toxicity, and cost. Several extractants that have been employed for the deterpenation of essential oils include ethanol, methanol, aqueous solutions of ethanol or methanol, ethyl acetate, and acetone.

In investigating the extractive deterpenation of citrus essential oils, Arce and coworkers (2005) have modelled them as mixtures of the monoterpene limonene and the desired monoterpene alcohol linalool. **Fig. 5** shows the immiscibility region of the quaternary system formed by this mixture with the aqueous solution of ethanol used as extracting agent (Arce *et al.* 2005). In this figure, the equilibrium data (Arce *et al.* 2004a) corresponding to the constituent ternary systems are also shown. Ternary equilibrium established between ethanol and water with limonene or linalool show tie lines with opposite slope, a sign of their plausible separation using this solvent. In the quaternary system, linalool is predominantly located in the aqueous phase ($\beta_{\text{linalool}} > 1$) if the proportion of ethanol in the extractant is high, and predominantly in the organic phase ($\beta_{\text{linalool}} < 1$) if it is lower and since the selectivity $\beta_{\text{linalool}}/\beta_{\text{limonene}}$ is greater than unity throughout the region in which aqueous and organic phases separate, slightly diluted ethanol is a satisfactory deterpenation agent for the model essential oil considered (Arce *et al.* 2004a, 2005). Ethylene glycol, diethylene glycol, propane-1,2-diol, butenediol and aminoethanol are all inferior to dilute ethanol (Arce *et al.* 2002a, 2002b, 2003, 2004b, 2006). In any case the desired essential oil components can be separated from solvent by vacuum distillation.

Essential oils have also been deterpenated by counter-current liquid-liquid extraction, terpenes being taken up by pentane and the desired oxygenated components by dilute methanol or, if destined for human consumption, dilute ethanol. Both solvents are recovered by distillation, the pentane at atmospheric pressure and the methanol or ethanol under reduced pressure so as to avoid thermal degradation of the oxygenated target compounds.

Newer technologies in industrial use

The main drawback of the deterpenation methods described above is that they all involve distillation processes that inevitably cause some degree of degradation of the product. Two types of newer technology have, in some production plants, been introduced to avoid such degradation: membrane-based separation techniques, and extraction with supercritical fluids.

Membrane separation

Membrane separations can afford a higher-quality product than distillation due to their low working temperatures and the absence of a vapour-liquid interface. In general, they have the additional advantages of low energy requirements and operational costs, small space requirements, and great

versatility. Their handicap is the tendency for membranes to become clogged, and their maintenance costs. The terpene fraction – limonene especially – can be successfully removed by either ultrafiltration or reverse osmosis (Braddock 1982; Braddock and Adams 1984; Sakamoto *et al.* 2003).

Supercritical fluid extraction

A pure fluid is in a supercritical state when its temperature and pressure are both greater than those of its critical point. To be of industrial interest, the density of a supercritical fluid should also be near or in excess of that of the critical point. The advantage of these fluids for extraction processes is that they have liquid-like densities (which can furthermore be fine-tuned by small pressure or temperature changes, thereby adjusting their solvent capacity) but negligible surface tension and gas-like transport properties, their viscosities being much lower than those of conventional solvents and their coefficients of diffusion considerably greater. Their use for the deterpenation of essential oils avoids both the thermal degradation associated with the higher working temperatures of direct distillation processes, and the need for post-extraction distillation to recover the solvent (the extractant can be recovered from the extracted terpenes or the purified essential oil by slight adjustment of temperature or pressure). The compound most commonly employed as a supercritical fluid for the deterpenation of essential oils is carbon dioxide. Carbon dioxide is non-toxic, non-flammable and environmentally friendly, is available as a high-purity product at low cost, and has a critical temperature of only 31°C. However, ethane has recently been put forward as a more advantageous alternative (Raeissi *et al.* 2008). Details of the use of supercritical fluids for deterpenation of essential oils may be found in papers by Danielski *et al.* (2008; Chapter of this book), Brignole and coworkers (Espinosa *et al.* 2000; Díaz *et al.* 2005), and the Goto group (Sato *et al.* 1995, 1996, 1997, 1998; Goto *et al.* 1997, 1999; Kondo *et al.* 2002; Fang *et al.* 2004; Roy *et al.* 2005, 2007), among others.

Extraction with ionic liquids

In recent decades, the possibilities of ionic liquids as environmentally friendly solvents, that can in principle be designed to optimize specific processes, have been increasingly explored (Holbrey and Rogers 2002; Plechkova and Seddon 2008). Among the many applications for which they

are now being considered is the deterpenation of essential oils.

Ionic liquids are being defined as salts with melting temperatures below 100°C. They are composed of large, generally asymmetric, organic cations and smaller anions (Seddon 1997; Brennecke and Magin 2001; MacFarlane and Seddon 2007; Wilkes 2002). Partly because of this size mismatch and asymmetry, many are liquids at room temperature. They are excellent and often highly selective solvents of both organic and inorganic compounds, including polymers, whether polar or nonpolar. Most of them are thermally and chemically stable in a wide range of temperatures, non-flammable and non-corrosive. Though not necessarily non-toxic, they are all environmentally friendly in that their vapour pressures are virtually zero, which not only eliminates health risks associated with the volatility of conventional organic solvents, but also means that they can easily be recovered quantitatively when used for the synthesis or extraction of relatively volatile organic compounds (Zhao *et al.* 2005). Their efficiency in liquid-liquid extraction is furthermore helped by selecting low viscosity and surface tension ionic liquids, which facilitate the achievement of good between-phase contact by mere shaking. In addition, they can behave as superacids, be good catalysts, be highly selective as reagents, resist both oxidation and reduction, have high ionic conductances, and conduct heat better than water (Chiappe and Pieraccini 2005; Seddon 1997; Welton 1999). They are relatively easy to prepare (although some are very hygroscopic and accordingly require careful handling), and many are currently available commercially. The design of an ionic liquid for a particular purpose starts with the choice of a cation and an anion with appropriate chemical, physical and/or biological properties, and often continues with the optimization of the length and/or ramification of alkyl side chains on the cation (Freemantle 1998; Hough *et al.* 2007; Plechkova and Seddon 2007). The most widely used cations have been di- or tri-substituted imidazolium, substituted pyridinium, tetraalkylammonium and tetraalkylphosphonium; while anions have included halides, sulphate, sulphonate, triflate, amides, imides, borates and phosphates. In Fig. 6, the more common cations and anions in the formulation of ionic liquids are shown, although many more exist making a growing number of combinations. Although ionic liquids are still expensive, in comparison with most conventional solvents on a mass basis, this disadvantage can sometimes be offset by their efficiency. This means that much smaller quantities are required; this, together with

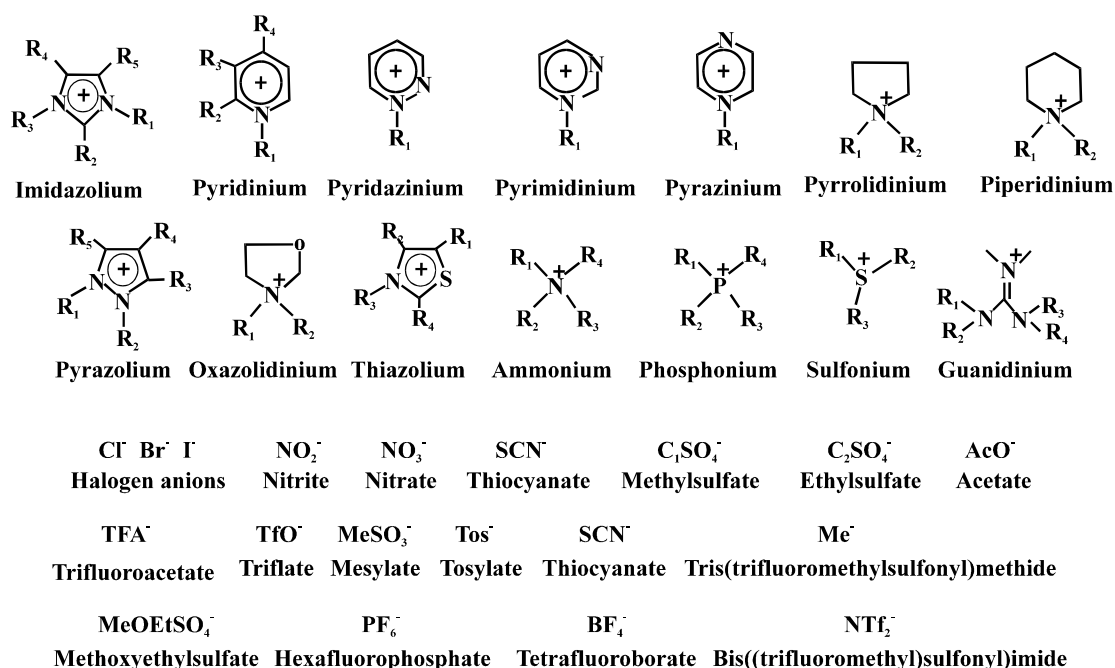
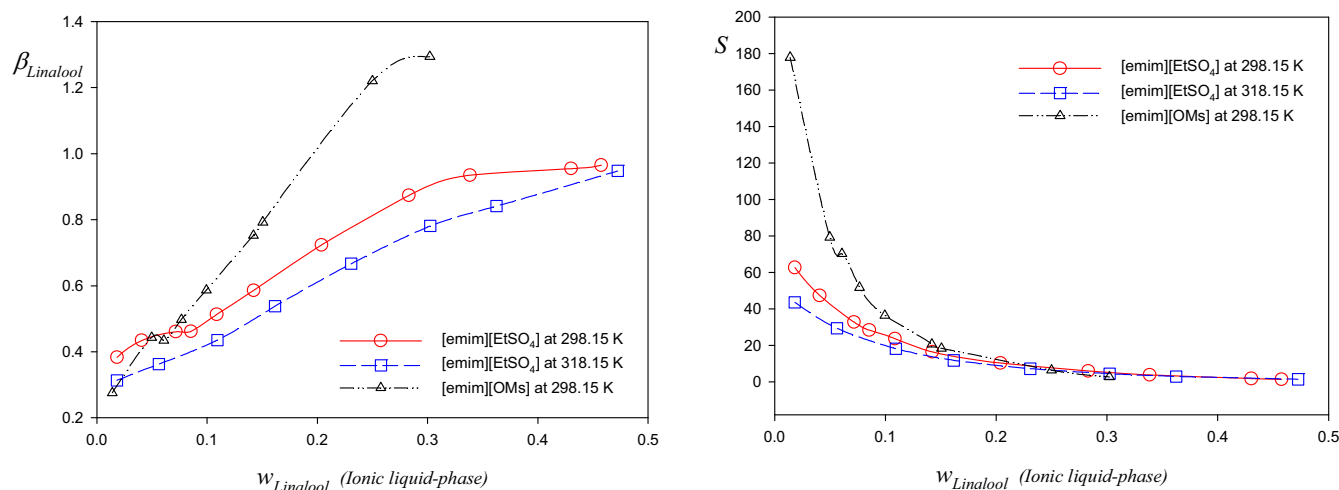


Fig. 6 Cations and anions commonly used in ionic liquids.

Table 2 Comparison of organic and ionic liquid solvents (Plechko and Seddon 2008). Reproduced with permission of The Royal Society of Chemistry.

Property	Organic solvents	Ionic liquids
Number of solvents	>1000	>1000000
Applicability	Single function	Multifunction
Catalytic ability	Rare	Common and tuneable
Chirality	Rare	Common and tuneable
Vapour pressure	Obeys the Clausius-Clapeyron equation	Negligible vapour pressure under normal conditions
Flammability	Usually flammable	Usually nonflammable
Solvation	Weakly solvating	Strongly solvating
Polarity	Conventional polarity concepts apply	Polarity concept questionable
Tuneability	Limited range of solvents available	Virtually unlimited range means "designer solvents"
Cost	Normally cheap	Typically between 2 and 100 times the cost of organic solvents
Recyclability	Green imperative	Economic imperative
Viscosity/cp	0.2-100	22-40000
Density/g·cm ⁻³	0.6-1.7	0.8-3.3
Refractive index	1.3-1.6	1.5-2.2

**Fig. 7** Linalool distribution ratio $\beta_{Linalool}$ and selectivity $S = \beta_{Linalool}/\beta_{Limonene}$ in the systems limonene + linalool + [emim][EtSO₄] (○, 298.15K; □, 318.15K) and limonene + linalool + [emim][OMs] (Δ, 298.15K), as functions of the mass fraction of linalool in the ionic-liquid-rich phase.

their other advantages (Table 2), has led to their increasing use in industrial processes (Pagni 2003; Plechkova and Seddon 2008).

The feasibility of using ionic liquids to deterpenate citrus essential oils is supported by the results of Arce *et al.* (2006, 2007), who modelled essential oils as mixtures of limonene and linalool. Fig. 7 shows the solubilities (β) and selectivities ($S = \beta_{Linalool}/\beta_{Limonene}$) obtained in the extraction of linalool using two ionic liquids 1-ethyl-3-methylimidazolium methanesulfonate ([emim][OMs]) and 1-ethyl-3-methylimidazolium ethylsulfate ([emim][EtSO₄]). Both ionic liquids showed high selectivity for linalool. The low solubilities of linalool in these particular ionic liquids mean that large quantities are required for efficient separation, so their use on an industrial scale could not be competitive even though their recovery is practically quantitative. Nevertheless, research is actively being pursued on the design of an ionic liquid with the required properties to carry out the desired separation (not only with good solubility and selectivity but low viscosity, non-toxicity and low cost).

CONCLUSIONS

Citrus essential oils are valuable raw materials in the scent, flavouring and parapharmaceutical industries. Their quality depends largely on the way in which they are extracted from the fruit, purified, and deterpenated. While conventional distillation-based deterpenation methods cannot avoid some loss of quality, higher-quality products are achieved by newer technologies, notably membrane-based separation and extraction with supercritical fluids. Research on the application of ionic liquids to the deterpenation of citrus essential oils is being actively pursued.

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