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How to make a green product greener: use of ionic liquids as additives during essential oil hydrodistillation

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The effect of addition of ionic liquids (ILs) during hydrodistillation of the essential oil of *Rosmarinus officinalis* L. on its yields has been evaluated. Four different chloride based ILs have been used, namely a hydroxyl functionalized imidazolium salt, (1-hydroxyethyl-3-methyl imidazolium chloride (IL-1), a morpholinium salt, (*N*,*N*-butylmethylmorpholinium chloride (IL-2), a Brønsted acidic ionic liquid, (N-methylimidazolium chloride (IL-3) and an ammonium salt, choline chloride (IL-4). ILs 1-3 permitted to obtain higher yields of essential oil with respect to the classic hydrodistillation. In particular, IL-1 permitted to improve the essential oil yield by about 25%. Noteworthy, no appreciable changes were observed in the composition of the essential oils when the ILs were added.

Introduction

Essential oils, also commonly known as essences or volatile oils or ethereal oils, according to the AFNOR NF T 75-006 rule (October 1987), somewhat restrictive, are 'products derived from plant material, both by steam distillation and by mechanical processes from the skin of Citrus, or by dry distillation. The essential oil is then separated by the aqueous phase by physical processes'. However, a very small number of essential oils can also not derive from plant material, such as ambergris, castoreum and musk.Essential oils are very complex mixtures, whose constituents can be mainly catalogued in two main classes: terpene derivatives and phenylpropanoids although some essential oil may be composed by high percentages of other chemicals (*i.e.* alkanes, alkenes, aldehydes, ketones, etc.).

Essential oils are extensively used in many industrial applications: medicinal products, cosmetics, flavor and fragrances, perfumery, foods. There are no reliable data on the scale of consumption of essential oils but, it can be estimated that the world market of these products, only as flavors and fragrances, has a value of 10-12 billion euro (about 12.5-15.5 billion U.S. dollars).[1] The most consumed essential oils are orange and cornmint (50,000 and 25,000 tons per year), largely employed in soft drinks, fragrances, oral care and confectionery. The essential oil of rosemary is instead used in quantities between 100 and 500 tons.[1] It is mainly demanded by the fast food and processed food industries for its spicy flavor. However, most of these amounts are probably underestimated because of the lack of domestic consumption in major producing countries, such as China, India and Indonesia.

The most used technique for the obtaining of these products is probably steam distillation, at both the hobbyist and industrial levels. The system is constituted by two immiscible fluids, water and essential oil, so the process is subjected to the Dalton's law. The relatively simple process of distillation has as main drawback the very low yield of product. These low yields and the high market demand make these substances high added-value products and it could be extremely interesting to improve the process yield to save considerable amounts of money. A further added value to these already expensive products, derives from their production from organic cultivation. The final price of these essential oils may be up to ten times that of standard quality one; *i.e.* the wholesale price for orange oil passed from 5.50 €/kg to 35 €/kg in 2007.[1] Very small improvements in the yields may result in a considerable gain.

This paper deals about the possibility to use some ionic liquids (ILs) as additives to improve the essential oils yields of the hydrodistillation process. Moreover, the effect of the IL structure on the essential oils extraction was evaluated. ILs are salts, usually constituted by a large organic cation and an organic or inorganic anion, liquid at/or near room temperature. Due to their ionic character, ILs exhibit important properties such as a negligible vapour pressure, low flammability, high thermal and chemical stabilities, broad liquid temperature range and high solvation ability for organic, inorganic and polymeric compounds,[2] including biopolymers such as cellulose, chitine and keratin.[3] For these unique properties, which can be tailored through an appropriate cation and anion selection, ILs have been proposed as efficient and "greener" solvents in the most diverse applications,[4] including as (co)solvents for the extraction of value-added compounds from natural sources. Starting from the pioneering work of Du et al.,[5] showing the successful application of IL aqueous solutions in microwave-assisted extraction of *trans*-resveratrol from a Chinese traditional medicine herb, the use of ILs in this field is slowly increased and an exhaustive review has been recently published.[6] The first report on the use of ILs for essential oil extraction was from Zhai *et al*. in 2009.[7] They used ILs as microwave absorption media during the hydrodistillation of the essential oils from *Illicium verum* and *Cuminum cyminum*. The comparison of the compositions of the resulting oils with those obtained with the classical hydrodistillation method evidenced no difference in the main constituents. However, the time necessary for a complete extraction was significantly shortened. In 2011, Ma *et al.* uses ILs to obtain the essential oil from *Schisandra chinensis* showing an increase in the extraction yield and reducing the time of hydrodistillation.[8] On the other hand, Jiao *et al.* (2013a,b) observed similar results, together with a significant increase in oil yield, during the extraction of the essential oils of *Dryopteris fragrans* and *Fructus forsythiae*.[9] Also *Rosmarinus*

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officinalis has been the subject of a study that involves the use of ILs for essential oil extraction affording results in agreement with the above observations.[10] However, all these studies were carried out with microwave-assisted extraction (MAE) methods. MAE is surely an efficient approach for laboratory or small-scale applications, but when the process is scaled-up, metal (copper, stainless steel) distillers shielding the microwave energy prevent its application.

Moreover, although a large number of different cations is nowadays available, most of the papers related to the use of ILs in extraction processes are still focused on imidazolium salts.

Here, we report on the use of four chloride based ILs having imidazolium or onium cations: in particular, a hydroxyl functionalized imidazolium salt (1-hydroethyl-3-methyl imidazolium chloride, **1**), a morpholinium salt (*N,N*-butylmethylmorpholinium chloride, **2**), a Brønsted acidic ionic liquid (*N*-methylimidazolium chloride, **3**) and an ammonium salt, choline chloride (**4**), which is a natural compound , part of the vitamin B complex.

These ILs have been selected considering two important features that significantly can affect eventual large scale applications; IL price and IL environmental impact. Therefore, we selected four chloride based ILs, which can be prepared by single step processes, avoiding often expensive anion metathesis reactions. In particular, we included a protic IL (**3**) that is synthesized through simple neutralization of an organic amine (methylimidazole) with a mineral acid (HCl), to yield an IL that does not require purification.[11]

Moreover, the selected ILs present a significantly lower toxicity towards the aquatic compart with respect the widely used 1,3-dialkylsubstituted imidazolium salts, in particular, with respect those characterized by long alkyl chains.[12]

Since the main aim of our investigation was to verify the possibility to increase value-added compounds extraction using simple and cheap procedures, we avoided to apply microwave or sonication and/or to use of pure IL as extraction solvents; essential oil was extracted by hydrodistillation from mixtures of water-IL. This approach could indeed be easily scaled-up and applied to traditional existing essential oils manufactures.

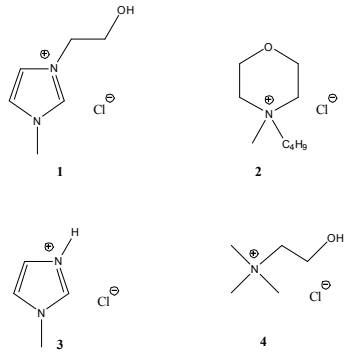

Figure 1. Chemical structures of ionic liquids 1-4

Experimental

Reagents. Chloline chloride (>99%, Sigma –Aldrich) was used without any purification. 1-(2-Hydroxyethyl)-3-methylimidazolium chloride and *N,N*-butylmethylmorpholinium chloride were prepared by addition of the selected alkyl chloride (2-chloroethanol and butyl chloride) to an equimolar solution (100 mmol) of methylimidazole or *N*-methylmorpholine in acetonitrile (100 mL) and the mixture were refluxed for 72h. The formed salts were separated by filtration, washed with hexane and dryed under vacuum. Methylimidazolium chloride was prepared by a dropwise addition of an equimolar amount of HCl (37%) to methylimidazole in water. The mixture was stirred for 4 to 5 h at 60 °C to ensure that all of the bases are reacted. Then, water was removed at reduced pressure to obtain a white solid. The IL structure and purity was confirmed by NMR analysis. The employed ILs were then dried under constant agitation in vacuo (7.5 x 10^{-4} Torr) at 40 °C (**3**) or 80 °C (**1**, **2** and **4**) for a minimum of 24 h to reduce the content of water and volatile compounds to negligible values (water < 100 ppm). Although in this case the ability of water to affect the ILs properties is not important, being ILs used as additives in hydrodistillation, the presence of residual water in ILs might be a source of weighing errors. Dried ILs have been therefore used.

Substrate preparation:

Flowering aerial parts of rosemary (*Rosmarinus officinalis L.*) were dried in the shadow till constant weight. The plant material (2000 g) was coarsely cut and used to prepare forty identical 50 g samples, which were put into a 2 L spherical flask treated as follows:

-500 mL of water were added and immediately hydrodistilled;

-500 mL of NaCl (5%) water solution were added and immediately hydrodistilled;

-500 mL of water were added and hydrodistilled after 24 hours maceration;

-450 mL of water and 50 ml of IL were added and hydrodistilled after 24 hours maceration.

Each experiment was performed at least in triplicate.

Hydrodistillation

Hydrodistillation was accomplished using a water-recycling Clevenger-type apparatus accordingly to the European Pharmacopoeia.[13] The plant material was put in a 2000 mL spherical flask accordingly to the above-described experimental protocol and heated with a heating mantle to the boiling point for two hours. The essential oil was recovered from the lateral arm of the apparatus and stored in amber glass vials at 5°C until analysis.

In all cases, the residual water containing the dissolved IL has been reused at least three times with fresh rosemary without significant modification in oil composition and yield.

GC and GC-MS analyses

The GC analyses were accomplished with a HP-5890 Series II instrument equipped with HP-WAX and HP-5 capillary columns (30 m x 0.25 mm, 0.25 μm film thickness), and with the following conditions: temperature program of 60°C for 10 min, followed by an increase of 5°C/min to 220°C; injector and detector temperatures at 250°C; carrier gas helium (2 mL/min); detector dual FID; split ratio 1:30; injection of 0.5 μL of a 10% hexane solution of the essential oil).

For both the columns, identification of the chemicals was performed by comparison of their retention times with those of pure authentic samples and by means of their Linear Retention Indices (LRI) relative to the series of n-hydrocarbons.

GC-EIMS analyses were performed with a Varian CP-3800 gas-chromatograph equipped with a HP-5 capillary column (30 m x 0.25 mm; coating thickness 0.25 μm) and a Varian Saturn 2000 ion trap mass detector. Analytical conditions: injector and transfer line temperatures at 220 and 240°C respectively; oven temperature was programmed from 60°C to 240°C at 3°C/min; carrier gas helium at 1 mL/min; injection of 0.2 μL (10% hexane solution); split ratio 1:30. Identification of the constituents was based on comparison of the retention times with those of authentic samples, comparing their Linear Retention Indices relative to the series of n-hydrocarbons, and by computer matching against commercial (NIST 98 and ADAMS 95) and home-made library mass spectra built up from pure substances and components of known essential oils and MS literature data, as previously described.[14]The compositions and the

yields of its essential oil obtained with the different methods are reported in Table 1.

Table 1. Composition of the essential oils of *Rosmarinus officinalis* obtained using the different ILs

Constituents	l.r.i.	water	water macer.	water NaCl	IL 1	IL 2	IL 3	IL 4
α-thujene	933	0.2	0.2	0.2	0.2	0.2		
α-pinene	941	25.5	27.2	28.3	33.1	27.6	27.5	28.6
camphene	955	4.0	4.4	4.0	5.2	4.3	4.4	4.7
thuja-2,4(10)-diene	959	0.8	0.9	1.0	1.1	0.9	1.0	1.0
sabinene	977	0.9	0.9	0.9	1.0	0.9	0.7	0.9
β-pinene	981	2.3	2.3	2.2	2.4	2.2	2.3	2.2
3-octanone	988	0.1	0.2	0.2		0.1	0.1	0.1
α-phellandrene	1006	0.3	0.3	0.3	0.3	0.3	0.4	0.3
α-terpinene	1020	0.7	0.6	0.7	0.7	0.7	0.7	0.7
p-cymene	1028	1.0	1.2	1.2	1.2	1.2	1.3	1.3
limonene	1032	3.7	4.1	3.9	4.3	3.8	4.3	3.4
(Z)-β-ocimene	1041	0.1						
1,8-cineole	1042	10.6	10.6	8.9	11.0	8.9	9.1	9.3
γ-terpinene	1063	1.1	1.0	1.0	1.1	1.0	0.9	0.9
cis-sabinene hydrate	1070	0.1						
terpinolene	1090	1.2	1.1	1.1	1.2	1.1	1.6	1.0
linalool	1101	3.2	3.1	3.0	2.8	3.0	3.0	3.4
exo-fenchol	1119	0.1	0.1	0.1		0.1	0.2	0.1
cis-p-menth-2-en-1-ol	1123	0.1						
chrysanthenone	1125	1.1	1.1	0.8	0.7	0.8	0.5	0.6
trans-pinocarveol	1141	0.2	0.2	0.2		0.2	0.1	0.2
trans-p-menth-2-en-1-ol	1142	0.1	0.1			0.1		
camphor	1145	5.6	5.8	5.0	4.7	5.0	5.1	5.3
camphene hydrate	1150			0.1		0.1		
trans-pinocamphone	1162	0.5	0.4	0.5	0.4	0.3	0.3	0.4
pinocarvone	1164	0.2	0.1	0.3	0.2	0.1	0.1	0.1
borneol	1167	6.3	6.8	6.6	5.7	6.7	6.6	7.1
cis-pinocamphone	1175	0.6	0.6	0.6	0.5	0.5	0.5	0.5
4-terpineol	1179	1.3	1.4	1.4	1.2	1.3	1.3	1.4
p-cymen-8-ol	1185	0.1	0.1	0.2		0.2	0.2	0.2
α-terpineol	1191	2.2	2.1	3.4	1.9	2.2	4.1	2.5
myrtenol	1195	0.5	0.5	0.5	0.4	0.5	0.5	0.5
verbenone	1206	12.7	11.7	12.5	10.0	12.2	11.8	10.9
trans-carveol	1219	0.1	0.1	0.2		0.1	0.1	0.2
citronellol	1228	0.2	0.2	0.2	0.1	0.2	0.3	0.3
carvone	1244	0.2	0.1	0.2		0.1	0.2	0.1
geraniol	1256	2.5	2.6	2.8	1.7	2.8	1.6	0.1
isobornyl acetate	1287	3.4	3.7	3.8	3.7	4.3	3.8	3.9

carvacrol	1301					0.1		
myrtenyl acetate	1326				0.3	0.1		
piperitenone	1348	0.3	0.3	0.3	0.2	0.3	0.3	0.3
geranyl acetate	1385	0.2	0.2	0.2	0.2	0.3	0.2	0.2
(Z)-jasmone	1394	0.2	0.2	0.2		0.2	0.2	0.2
methyl eugenol	1402	0.2	0.1	0.1		0.1	0.1	0.1
β-caryophyllene	1419	0.6	0.4	0.7	0.6	0.9	0.6	0.4
α-humulene	1455	0.1		0.1		0.2	0.1	
caryophyllene oxide	1582	0.2	0.1			0.2		
caryophylla-4(14),8(15)-dien-5-ol	1636	0.1				0.1		
selin-11-en-6-α-ol	1645	0.3	0.3	0.3		0.4	0.3	0.3
Monoterpene hydrocarbons		41.8	44.2	44.8	51.8	44.2	45.1	45.0
Oxygenated monoterpenes		52.4	51.9	51.8	45.7	50.5	49.9	47.6
Sesquiterpene hydrocarbons		0.7	0.4	0.8	0.6	1.1	0.7	0.4
Oxygenated sesquiterpenes		0.6	0.4	0.3	0.0	0.7	0.3	0.3
Phenylpropanoids		0.2	0.1	0.1	0.0	0.1	0.1	0.1
Others		0.3	0.4	0.4	0.0	0.3	0.3	0.3
Total identified		96.0	97.4	98.2	98.1	96.9	96.4	93.7
Essential oil yield (%w/w)		1.58	1.46	1.64	1.93	1.84	1.77	1.67

Results and discussion

Rosmarinus officinalis was selected of because it is wide available, inexpensive, widely used in cosmetics, food and medicine and give a reasonable yield of essential oil for easy laboratory tests.

The compositions and the yields of its essential oil obtained with the different methods are reported in Table 1. Altogether, 49 constituents were identified in the samples, accounting for 93.7 to 98.2% of the whole essential oil compositions: α-pinene was the main chemical, followed by verbenone and 1,8-cineole. In terms of chemical compound classes, the essential oils were almost exclusively formed by monoterpenes, both hydrocarbons and oxygenated ones.

The GC-MS analysis allowed us to classify this essential oil as a α-pinene chemotype, the most common one in Italy.[14]

The classic hydrodistillation method gave a 1.58% essential oil yield (Table 1). Contrary to previously reported data for other essential oils, no significant differences were obtained by preventive 24 h maceration in water or addition of NaCl to increase the ionic strength.[15,16] The same oil composition and yield was found also adding **4**. On the contrary, the yield increased significantly (from 15 to 25%), when the other ILs were used, particularly in the case of **1**, that permitted to improve the essential oil yield of almost 25%. No differences were observed if the plant material was macerated for 24 h with the IL before hydrodistillation (data not shown). This increase in the yield is very important in the case of essential oils being high value added products.

It is noteworthy that no appreciable changes were observed in the composition of the essential oils when the ILs were added, probably because the IL exerts its activity mainly on the plant matrix, allowing a better extraction of the oil. This is a very important result because it permits to obtain without any artifact the classic essential oil, which can be employed as usual by the end-user.

With respect to the mechanism determining the effect of ILs on hydrodistillation process, it is noteworthy that the inability of NaCl to increase significantly essential oils yield allows to conclude that the ionic strength is a not relevant factor in the extraction process. Furthermore, since all the investigated salts are chloride-based, these results are also an indication of the significant role exerted by the IL organic cation. The ability of the added ILs to favor cell walls modification, probably by hydrogen-bonding interactions between both IL ions (chloride and IL cation) and cell wall constituents (mainly cellulose) can be though the principal factor determining plant tissue disruption and oil release.

Furthermore, it is necessary to stress that when dealing with volatile compounds, such as essential oils, the negligible vapour pressure of most ILs and their thermal stability are fundamental properties which can improve the oils–IL isolation/separation. Also the IL non-flammability is another useful property in particular in the case of small and medium-sized craft enterprises that use open-flame to heat the still apparatus.

Surely, ILs **1**, **2** and **4** guarantee the higher stability also at high temperatures under vacuum (IL **3**, arising from an equilibrium process, can give methylimidazole and HCl at sufficiently low pressure). Nevertheless, all the employed ILs were stable under hydrodistillation conditions and we have also tested the hydrodistillation process as a final step for purification of ILs. Determination of physical constants and spectroscopic measurements evidenced no appreciable degradation of the tested ILs in these conditions (the same used in the present study).

The potentiality of a series of 1-alkyl-3-methylimidazolium ionic liquids differing in composition of anion and cation as alternative solvents for extraction of chemical constituents from *R. officinalis* has been recently investigated also in association with microwave.[17] This method required however large amounts of ILs (solid–IL ratio was indeed 1:12, g/mL, *i.e.* IL is used as a solvent) and, although it was able to improve greatly the extraction yields of carnosic and

rosmarinic acids, the total essential oil extraction remained practically unchanged. Furthermore, the extracted essential oil was characterized by a different composition: higher amounts of oxygenated compounds have been detected in the essential oil arising from IL-microwave hydrodistillation extraction.
Hydrodistillation with addition of a small amount of a proper IL appears therefore the more efficient way to increase oil essential extraction yield without affecting oil composition. Recently, the use of plant-derived products (*i.e.* pesticides, insecticides, drugs, etc.) has been proposed as a more environmental-friendly alternative to synthetic products. The emergence of drug-resistance to herbicides or to insecticides or antimicrobials is a serious challenge that, together with the environmental damage and the toxicity of many synthetic chemicals, increases the importance of plant-derived compounds. These latter are indeed generally more easily degradable and could show a smaller negative environmental impact. Furthermore, their use is generally admitted in organic cultivation and animal farming.[18,19] In addition, it has been calculated that natural products (and essential oils in particular) have a lower carbon footprint than synthetic ones and so they are even more environmentally friendly.[20]
In this contest, even a 25 % increase in extraction yield by addition of a relatively small amount of an IL (in this case, solid–IL ratio 1:1, g/ml) can further contribute to the sustainability of the process and to its greener nature.

Conclusions

In this work, some chloride based ionic liquids were successfully used as additives for an efficient extraction of the *Rosmarinus officinalis* L. essential oil by hydrodistillation. In particular, with the addition of a relatively small amount of 1-(2-hydroxyethyl)-3-methylimidazolium chloride the yield of essential oil improves significantly (around 25%) but positive effects have been observed also using the less expensive methylimidazolium chloride. Since no appreciable changes in the composition of the oils were determined when ILs were added (49 constituents have been identified and quantified, accounting for 93.7 to 98.2% of the whole essential oil compositions), the proposed method allows to obtain without any artifact the classic essential extracts.

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Graphical Abstract

How to make a green product greener: use of ionic liquids as additives during essential oil hydrodistillation

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This paper reports on the possibility to use simple ILs as additives during hydrodistillation to increase significantly essential oil yield without modification in composition