Extraction of Rosemary by Superheated Water

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Superheated water under pressure between 125 and 175 °C has been shown to rapidly extract the oxygenated fragrance and flavor compounds from *Rosmarinus officinalis*, while the monoterpenes are extracted slowly, and only very small amounts of the sesquiterpenes, waxes, and lipids are removed. The eventual yields of oxygenated compounds are higher than are obtained by steam distillation. Although larger amounts of water are needed for extraction by superheated water, the energy costs are competitive because it is not necessary to vaporize the water and most of the heat required can be recycled. The experiments conducted on a laboratory scale indicate that extraction by superheated water could be a viable process for the production of high quality plant extracts.

INTRODUCTION

For centuries, man has tried to isolate, concentrate, and purify the scents and flavors produced by nature. The common methods used currently for the isolation of essences from natural products are steam distillation and solvent extraction. Losses of some volatile compounds, low extraction efficiency, degradation of unsaturated compounds through thermal or hydrolytic effects, and toxic solvent residue in the extract may be encountered with these extraction methods. This has led to the consideration of supercritical fluids in extraction processes. The vast majority of supercritical fluid extraction has focused on the use of carbon dioxide, primarily because it meets the requirement of health and safety standards. For example, the supercritical fluid extraction of *Rosmarinus officinalis* has been compared with steam distillation (Reverchon and Senatore, 1992). In a search for alternative solvents, a number of workers have used liquid water under pressure above 100 °C but below its critical temperature of 374 °C. Under these conditions, it is referred to as superheated water or subcritical water.

Organic compounds are much more soluble in water under these conditions than at room temperature (i) because, in general, entropy causes solubilities to rise with temperature and (ii) because water becomes less polar at higher temperatures as its structure breaks up. At ambient temperature and pressure, water has a relative electric permittivity (dielectric constant) of ~80 (Haar et al., 1984). However, this value dramatically decreases with temperature to less than 10 at the critical point. The dielectric constant of water is also substantially lowered at much milder conditions by increasing the temperature at moderate pressures. At 250 °C, its dielectric constant is equal to that of methanol at ambient temperature. A number of studies of solubilities in superheated water have been carried out, although there are no solubility data on compounds from natural products. A number of studies of hydro-carbon–water phase diagrams have been made. For example, one of these (von Bröllos et al., 1970) showed that biphenyl forms a 10% mass solution in water at 300 °C. It was later shown (Sanders, 1984) that the heavier solutes benzo[*e*]pyrene and nonadecylbenzene reach the same concentration at 350 °C. More recent work has been carried out on polyaromatic compounds and pesticides between 25 and 200 °C (Miller and Hawthorne, 1998). Further data have also been obtained, and a wide range of data has been used to develop an estimation for solubilities in superheated water (Gizir et al., 1998). This gives an approximate expression for the solubility, x_2, at temperature T in terms that at a temperature, T_0, close to ambient, where the solubility is known:

$$\ln [x_2(T)] \approx (T_0/T) \ln[x_2(T_0)] + 15[(T/293) - 1]^3 \quad (1)$$

Comparisons of predictions from this equation for the pesticide choranthonil, the worst fitting compound, show agreement within a factor of about 5, even though the solubilities rise by several orders of magnitude over the temperature range. Although this is only an estimation method, it has the advantage of only requiring a room temperature solubility.

Both subcritical water (Zimmerman, 1954) and supercritical water (Model, 1982) have been used for the oxidative destruction of organic compounds with molecular oxygen. More recently, superheated water has been used to extract pollutants with a wide range of polarities from environmental samples (Hawthorne et al., 1994; Yang et al., 1995, 1997a; Hartonen et al., 1997). The elution of organic compounds from sorbents of varying polarity has also been studied (Yang et al., 1998), as has the partitioning of organic compounds from gasoline and diesel fuel (Yang et al., 1997b). Another recent application of superheated water is to achieve reversed-phase chromatographic separations by using pure water or water mixed with organic solvents at elevated temperatures (Miller and Hawthorne, 1997a; Smith and Burgess, 1997). Extraction of used automotive tires with both supercritical and subcritical water has been studied, and these experiments also involved

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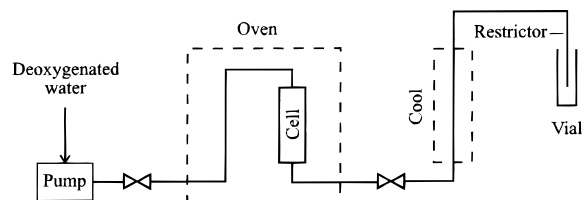
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Figure 1. Schematic diagram of the superheated water extraction apparatus.

the breakdown of natural rubber. Other processes studied involving natural products have been the hydrolysis of vegetable oils (Holliday et al., 1997) and starch (Brunner, 1998).

There have been no published reports on the extraction of plant material with superheated water, although an experiment on the extraction of rosemary by water at 125 °C (Miller and Hawthorne, 1997b) showed that the oxygenated compounds were preferentially extracted. The sensitivity of extracted compounds to degradation and hydrolysis at higher temperatures will obviously be a problem in some cases. Rosemary was therefore chosen as a "test" plant to investigate the principles involved in the superheated water extraction process for plant material, where this is possible, and an extensive study was carried out and reported here.

MATERIALS AND METHODS

Plant Material and Pure Standards. Rosemary leaves (*Rosmarinus officinalis*) were collected from plants growing in England between October and December. This is not the best period to carry out studies on rosemary leaves because the oil content is at the lowest level, and so the studies are comparative only.

All the pure standards used for the solubility measurements and chromatographic calibrations, the *n*-nonane used as an internal standard, NaCl used as a demulsifier, and Na_2SO_4 used as a drying agent, were provided by Aldrich (Gillingham, Dorset, U.K.), except for isobornyl acetate that was supplied by Lancaster (Morecambe, Lancashire, U.K.). HPLC grade hexane (Fisher Scientific U.K. Ltd., Loughborough, U.K.) was used to remove the compounds from the water extracts for analysis.

Extraction System. All extractions were performed using the apparatus shown schematically in Figure 1, which is similar to one described earlier (Yang et al., 1995). Distilled water was first purged for 2 h with nitrogen to remove dissolved oxygen. The water was then delivered at a constant flow rate by pump 1, which was a L6000A pump (Merck-Hitachi, U.K.), through a needle valve to a stainless steel preequilibrating coil (1 m × 0.76 mm i.d. × 1.6 mm o.d.) and, finally, to a 10.4 mL extraction cell (Keystone Scientific, Bellefonte, PA). Both the coil and the cell were placed in a gas chromatographic (GC) oven (Carlo Erba Fractovap) and kept at constant temperature. The extraction cell was mounted vertically inside the oven with the water flowing from top to bottom, so that any extracted materials were immediately swept from the cell. The outlet of the extraction cell was connected by stainless steel tubing to an outlet needle valve mounted just outside the oven wall, which was used as an on—off valve during an extraction and to control the flow during the filling of the cell. A 11 cm long, 100 μm i.d., stainless steel restrictor (Coopers Needle Works, Birmingham, U.K.) was required to maintain pressure in the system so that water remained liquid at all temperatures. The outlet was inserted in a collection vial. Since hot water may cause losses of volatiles, a cooling loop (cooled with room temperature water), made from a 40 cm length of stainless steel tubing, was connected between the outlet needle valve and the restrictor. A second pump, pump 2, which was also a L6000A pump (Merck-Hitachi, U.K.), was connected to the cooling coil

via a shut-off valve. This was used to flush through any organic compounds that were precipitated in the cooling coil as the temperature of the water cooled.

Superheated Water Extractions. For all the extractions, the cell was filled with weighed (~4.0 g) fresh rosemary leaves, and a glass wool plug was inserted at the outlet end to prevent the frit being plugged. After assembling the extraction cell in the oven, the cell was pressurized with ~20 bar of water by opening the inlet needle valve from the pump. The valve was then closed, and the oven was brought up to the desired temperature as quickly as possible and equilibrated for 20 min. The inlet and outlet valves were then opened, water was pumped through the cell at a given flow rate, and the extracts were collected in the vial. For kinetic experiments, the vial was replaced at given time intervals. Following the extraction, 3 mL of hexane was pumped through the cooling coil to sweep any precipitated compounds from the cooling coil. A further 15 mL of hexane was added to each of the extracts in a separating funnel, and about 1 g of NaCl was added to facilitate the breaking of the emulsion. The hexane layer was then separated and dried with ~3 g of anhydrous sodium sulfate, and an appropriate amount of *n*-nonane was added as internal standard before GC analysis.

Steam Distillation. Steam distillation of rosemary leaves was performed in a simple laboratory quickfit apparatus comprising a 500 mL steam generator flask, a 500 mL distilling flask (insulated with a polystyrene box), a condenser, and a receiving vessel. The condenser was positioned vertically to facilitate the collection of the distillate. The receiving flask consisted of a separating funnel so that the solvent extraction could be straightforward accomplished in it, as reported in the previous section. The steam generator flask was filled with distilled water and heated with a heating mantle. As the water vaporized, the steam passed to the distilling flask containing 4 g of rosemary leaves. The vapor then passed through a cooled tube (the condenser) where it condensed back to its liquid state. The distillate was finally collected into the receiving flask, filled with 10 mL of hexane, and cooled with room temperature water. During the distillation, the volume of hexane in the receiving flask was kept constant by adding few more milliliters of solvent. At the end of the process, the condenser was washed out with 5 mL of hexane in order to recover any extracted compounds deposited in it.

Solubility Measurements at Ambient Conditions. The solubility measurements in water at ambient conditions were performed as follows. About 80 mg of pure standard and 40 mL of distilled water were placed in a beaker provided with a jacket in which water at 25 °C was circulated. A magnetic stirrer was also placed in the beaker to promote a more intimate mixing of the sample and water. After 1 h, 10 mL of water extract was pipetted and double-extracted with 15 mL of hexane in a separating funnel. A known amount of *n*-nonane was added to the solution in order to provide quantitative data. The hexane solution was then made ready for the GC analysis by drying it with ~3 g of anhydrous sodium sulfate.

GC Analysis. The analyses of the hexane extracts were all performed by using a Carlo Erba HRGC 5300-HT GC equipped with a flame ionization detector (FID). Aliquots (1 μL) of the extracts were injected on-column into a BPX5 fused silica capillary column (25 m × 0.32 mm i.d., 0.5 μm film thickness). The carrier gas (helium) was delivered at a constant pressure of 30 kPa, relative to atmospheric pressure. The detector temperature was 310 °C. The oven temperature was 50 °C for 5 min and then increased to 200 °C at a rate of 3 °C/min. For compound quantitation, calibrations of eight of the compounds extracted were established graphically by injecting solutions made of known amounts of internal standard and pure compound.

RESULTS AND DISCUSSION

Initial Experiments. These were carried out (always on 4 g samples of rosemary) for 30 min with a flow rate of 2 mL/min at 125, 150, and 175 °C. At 175 °C, the
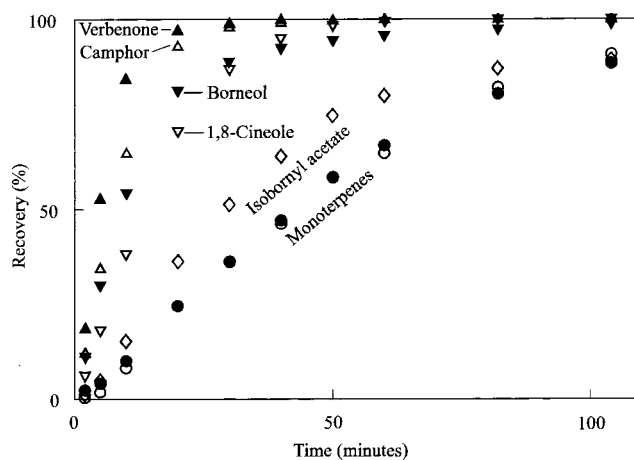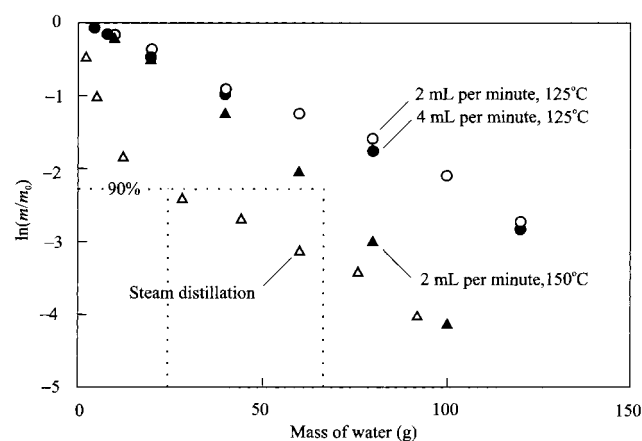
Superheated Water Extraction

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Table 1. Comparison of Yields of Eight Compounds from Rosemary Using Steam Distillation and Water Extraction in mg/1 g Sample[a]

	steam distillation	water extraction at 150 °C
α-pinene	0.080 (0.019)	0.163 (0.056)
camphene	0.019 (0.005)	0.039 (0.011)
limonene	0.007 (0.001)	0.025 (0.011)
1,8-cineole	0.082 (0.022)	0.161 (0.010)
camphor	0.033 (0.008)	0.060 (0.002)
borneol	0.010 (0.002)	0.017 (0.003)
verbenone	0.016 (0.003)	0.025 (0.002)
isobornyl acetate	N/D	0.004 (0.001)

[a] Standard deviations in parentheses N/D, not detected.

separation of the water and hexane layers was very slow and incomplete, so accurate quantitative analysis was not possible. However, from the chromatograms, it appeared qualitatively that the yield increased with temperature. Nevertheless, because of the difficulty with analysis, further experiments were only carried out at 125 and 150 °C. A comparison was then made of extraction at 150 °C and steam distillation both for a period of 60 min. A single sample was mixed thoroughly and used for both experiments. The flow rate for extraction was 2 mL/min, and the amount of water passed in the steam distillation was approximately the same. As will be seen later from the results of kinetic experiments, the conditions used means that both processes are close to exhaustive. Both the extractions and steam distillations were carried in triplicate, and the results are reported in Table 1. Product from both processes contain substantially the same main compounds, but the extract obtained by superheated water extraction gives higher yields. The total yield of the eight compounds extracted using superheated water at 150 °C is 0.05% of the plant mass. The total yield of essential oils compounds from rosemary in these experiments can be approximately estimated from the chromatograms to be 0.075%, assuming that the chromatographic response factors of the other compounds are equal to the average of those of the measured compounds. This is a low yield by commercial standards and reflects the fact that the rosemary was not grown in an ideal climate and not collected at an ideal time of year.

Kinetic Experiments. Experiments were carried out at water flow rates of 1, 2, and 4 mL/min and at cell temperatures of 125 and 150 °C by changing the collection vial periodically, and thus obtaining curves of recovery versus time. Figure 2 shows recovery curves for extraction from rosemary at 150 °C with a flow rate of 2 mL/min. They are plotted as the percentage of a final mass, m_0, recovered at a given time. The quantity m_0 is obtained using an extrapolation formula that relies on the fact the tail of the extraction curve is exponential in form, which is invariably found to be the case (Bartle et al., 1990). The monoterpenes extract slowly, with α-pinene shown as the open circles and camphene and limonene, whose extraction curves are indistinguishable on this figure, shown as filled circles. The apparent initial slow extraction of α-pinene may be due to the fact that it is oxidized by residual oxygen in the system to verbenone. The ester isobornyl acetate (open diamonds) is extracted somewhat more rapidly than the monoterpenes. A more rapidly extracted group is formed by the cyclic ether 1,8-cineole (open inverted triangles) and the alcohol borneol (closed inverted triangles). The ketones are removed most rapidly. Of the latter, verbenone (closed triangles), which has a double carbon–carbon bond conjugated with the ketone bond, extracts

Figure 2. Recovery curves for compounds extracted from rosemary by water at 150 °C.

Figure 3. Recovery of 1,8-cineole from 4 g of rosemary using superheated water extraction and steam distillation.

more rapidly than camphor (open triangles). Very small and unquantifiable amounts of heavier hydrocarbons were extracted.

Figure 3 shows kinetic curves for 1,8-cineole, the most important oxygenated compound, plotted as the natural logarithm of the mass remaining in the plant, m, divided by m_0, against the mass of water passed at a particular time. It can be seen that the two curves at 125 °C and the curve at 150 °C are all approximately straight lines. Furthermore, the two curves at 125 °C, obtained at two different flow rates, lie almost on the same straight line, indicating that the extraction rate depends only on the amount of water passed. Both these features show that the rate of extraction is determined by the partition of the compound between the plant material and the water and not by the rate of diffusion of the compound out of the plant material, as will be discussed more fully in the next section. Thus, the more soluble compounds will be extracted more quickly. Moreover, increasing the temperature increases the rate of extraction, as can be seen by comparison of the curves at 125 and 150 °C, with the rate at the higher temperature being almost double that at the lower temperature. In a process, it is likely that even higher temperatures would be better provided that the extracted compounds were not degraded and separation of the oil could be satisfactorily carried out.

In Figure 3, the recovery curve for steam distillation is also given, which is no longer linear. A horizontal dotted line corresponding to 90% recovery on the graph

Table 2. Dimensional Rates of Extraction, k_i, Compared with Mole Fraction Solubilities at 25 °C, x_2(298), and 150 °C x_2(423), Vapor Pressures at 100 °C, p_v(373), and Boiling Points, T_b

	k_i	x_2 (298)	x_2 (423)	p_v(373) (bar)	T_b (°C)
α-pinene	0.0391			0.184	156
camphene	0.0398	4.8×10^{-7}	0.006	0.138	159
limonene	0.0382	4.2×10^{-7}	0.005	0.094	176
isobornyl acetate	0.0522	3.8×10^{-6}	0.025		
1,8-cineole	0.139	1.3×10^{-4}	0.301	0.093	174
camphor	0.251	4.0×10^{-5}	0.132	0.026	209
borneol	0.139	1.1×10^{-5}	0.052		210
verbenone	0.355	4.7×10^{-5}	0.149		228

is shown from which it can be read that in order to recover 90% of 1,8-cineole from 4 g of rosemary by steam distillation 25 g of water is needed, against the 70 g required by superheated water extraction. In practice, much less water is used in steam distillation, and only a small fraction of the oxygenated compounds are recovered with the product being composed principally of monoterpenes.

Mechanism of Extraction. The form of the curve of amount extracted versus time can give information about the relative importance of the steps in the extraction process. This subject has been examined in a number of contexts other than extraction by superheated water, for example, in the field of supercritical fluid extraction (Clifford, 1998). Possible rate-determining steps involved include (a) surmounting an energy barrier, for example, during passage through a cell wall or desorption from a surface; (b) transport through the containing matrix by diffusion through the bulk material or down its pores; and (c) removal by partitioning into the flowing solvent. An extraction curve that is exponential in form indicates that the last of the three steps is relatively slow and determines the rate of extraction. When this is the case, the rate of extraction is also proportional to flow rate, and if the amount extracted is plotted against the amount of solvent passed, the results for different flow rates fall on the same curve. When removal by solvation and solvent flow is rate-determining, the equations for extraction, which can be complex in other circumstances, simplify to

$$m = m_0 \exp(-k_i M_w/M_p) \qquad (2)$$

where M_p is the mass of plant material, M_w is the mass of water passed, and k_i is a dimensionless rate for a particular compound.

Linear plots such as that given for 1,8-cineole in Figure 3 were found for all eight compounds shown in Figure 2. Thus, the quantity m/m_0 is exponentially related to the amount of water passed, and the curves indicate that the extraction mechanism is a partition between the plant material and the water, followed by removal in the water flow. The rates, k_i, were obtained for all the compounds from logarithmic plots, such as are shown in Figure 3, and are given in the first column of Table 2.

Comparison of Extraction Rates with Solubilities. Solubilities for the compounds were measured in water at 25 °C and are shown in the second column. No result for α-pinene was obtained, possibly because of its property of being readily oxidized to verbenone by molecular oxygen. The solubilities at 150 °C were then estimated using eq 1 and shown in the third column. These estimates are only approximate but
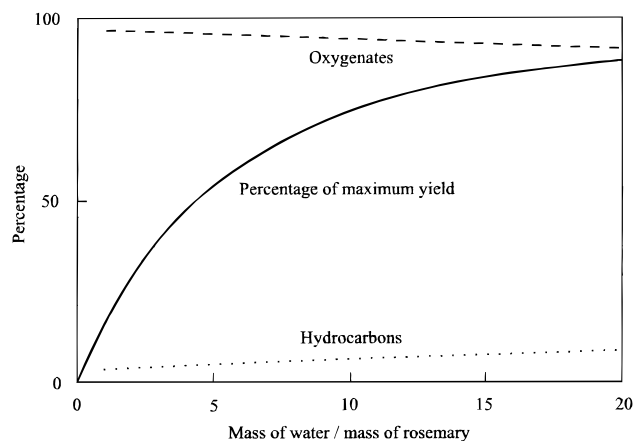

Figure 4. Percentages of the total obtainable yield recovered (continuous curve) of oxygenated compounds in the product (dashed curve) and hydrocarbons in the product (dotted curve) plotted against the mass of water used per unit mass of rosemary.

indicate that some of the oxygenated compounds are expected to be nearly completely miscible with water at 150 °C, whereas the hydrocarbon are still fairly insoluble. There is some correlation between the solubilities at 150 °C and the extraction rates, although the variation of affinity of the compounds to the plant material will have some effect.

Thus, by controlling the amount of water used relative to the mass of plant material, the composition and quality of the oil can be adjusted. If small amounts of water are used the yield is low, but the proportions of oxygenates and thus quality are higher. If larger amounts of water are used, the yield is higher, but the quality is lower. Vapor pressures at 100 °C and, because these are not always available, boiling points are shown in the final two columns. These are known to affect rates of recovery by steam distillation but are found, as expected, not to explain the extraction rates.

Figure 2 indicates that if the amount of water used in extraction is relatively small, the proportion of the oxygenated aroma compounds will be higher. The rates shown in Table 2 can be used to quantify this effect. Of course, if smaller amounts of water are used, not all the total extractable compounds will be removed, and the extent of this can also be calculated. Figure 4 shows the results of such calculations, which assume that all the extracted compounds behave in the same way as the eight compounds studied, which make up two-thirds of the extract. The figure shows that if the ratio of the mass of water to that of rosemary used is 10:1, 74% of the available extract is obtained and contains 94% oxygenated compounds.

Energy and Water Costs. Only 505 kJ kg^{-1} is necessary to heat water from 30 to 150 °C under 15 bar pressure against 2550 kJ kg^{-1} needed to convert water at 30 °C to steam at 100 °C (Haar et al., 1984). Moreover, much of the heat in a superheated water extraction process can be recycled, but little can be recovered in a steam distillation. The amount that can be recovered depends on the size of the heat exchangers chosen. For example if a 30 °C difference in the temperature of the streams in the heat exchangers is designed, 75% of the heat can be recovered. In steam distillation, the cooling water from the condenser can be used in the boiler, but the maximum temperature of this is likely to be 70 °C. This means that only 6.5% of

the heat can be recovered. The heat advantage of superheated water extraction per kilogram of water is therefore about 20. More water would be used in the extraction process, say 10 kg of water to 1 kg of rosemary, as compared with a weight ratio of 1:1 in steam distillation. However, although 10 times as much water would be used in extraction, there is still a possible energy advantage. The water in the extraction process would be recycled, whereas recycled water is rarely put into a boiler in steam distillation. Some water will be necessary for cooling in the extraction recycle, and this is estimated to be 3 times the amount of water in the recycle. However, 15 kg of water is need to condense 1 kg of steam if the temperature of water leaving the condenser is 70 °C.

Comparison with Carbon Dioxide Extraction. The failure of steam distillation to obtain the oxygenated aroma and flavor compounds from plant materials has led to the use of extraction by carbon dioxide both as a liquid and a supercritical fluid. The required compounds are not very soluble in liquid carbon dioxide, and a high mass ratio of carbon dioxide to plant material is required. The compounds are more easily dissolved in supercritical carbon dioxide, but the extracts obtained contain plant waxes and are typically oleoresins. Moreover, plant materials often need to be dried to make extraction by carbon dioxide effective, as water is not very soluble in it and tends to mask the desired compounds. Drying is an additional cost and risks losing volatile aroma compounds. The process plant for superheated water extraction is likely to be less expensive, as the pressures involved are much lower. At 150 °C, the vapor pressure of water is 5 bar (Haar et al., 1984).

CONCLUSIONS

This study suggests that extraction by superheated water may be an effective way of obtaining aroma compounds from plant materials, while leaving behind the monoterpenes, higher hydrocarbons, and lipids. It is argued that the process has advantages over steam distillation and extraction with carbon dioxide and will have environmental advantages over solvent extraction. It also appears that the total amount of oxygenated compounds extractable by this method is greater than in steam distillation, perhaps because of the better penetration of the solvent under pressure. Energy and water costs are competitive with steam distillation, and capital costs will certainly be competitive with carbon dioxide extraction. However, experiments have so far been conducted on a small scale, no extract has yet been isolated, and there may be separation problems. A pilot plant is currently being constructed to continue the study.

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