

Essential Oils and Microwave Extracts of Cultivated Plants

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A recent patent gives an account of a new method for extracting natural products by using a microwave source of radiation.¹ Based on a relatively simple principle, this method involves immersing vegetable material in a transparent solvent with microwave radiation. The internal heating of water within the vegetable material distends it and makes the glands and oleiferous receptacles burst. This process thus frees organic liquids which disperse and dissolve in the solvent used.^{2,3}

It is certainly most propitious to investigate the potential of such a technique and to compare it with more classic methods, such as hydrodiffusion, due to the present technical and commercial situation, which calls for research into new extracts and new extraction techniques.

We have used these two methods to treat different cultivated plants: five Umbelliferae, one Compositae and seven Labiatae. There is a double purpose for this approach. First, we want to determine the advantages and disadvantages of this technique in terms of research. Secondly, we intend to make appropriate comparisons between microwave extracts and essential oils coming from the aerial part of these plants.

Methodology

Vegetable matter—Four species of the Umbelliferae family: dill (*Anethum graveolens* L.), caraway (*Carum carvi* L.), fennel (*Foeniculum vulgare* Mill.) and parsley (*Petroselinum crispum* (Mill.) Nym. ex A. W. Hill., syn. *P. sativum* Hoffm.); one of the Compositae family: tarragon (*Artemisia dracunculoides* L.); and six of the Labiatae family: hyssop (*Hyssopus officinalis* L.), marjoram (*Origanum majorana* L.), oregano (*Origanum vulgare* L.), Summer savory (*Satureja hortensis* L.), Sage (*Salvia officinalis* L.), and thyme (*Thymus vulgaris* L.) were sown in a Gothic greenhouse, 8 m x 12 m, located at Chicoutimi, Québec (48°26'N, 71°04'W) in the month of November 1989. The plants were grown in pots filled with sandy loam. They were

fertilized every two weeks with a nutritive solution containing 1.5 mg/L of 20-20-20 and 1.5 mg/L of 10-52-10. Between the fertilization periods, water was given when needed. The day/night temperatures in the greenhouses was maintained at 20/15°C during the autumn cultivation and 25/10°C during the spring cultivation. Care was thus taken to compare only the results of vegetable matter treated in the same way. The lavender (*Lavandula angustifolia* P. Miller) and the coriander (*Coriandrum sativum* L.) were grown by a private producer in the area of Baie-Saint-Paul, Québec (47°27'N, 70°30'W). They were therefore harvested during the summer. Each of the three crops of the vegetable matter is separated into two parts: one is intended for the extraction of essential oil by hydrodiffusion, and the other is reserved for the extraction technique using a microwave oven.

Hydrodiffusion—A quantity of 500 g of recently harvested (within 24 hours) or frozen vegetable matter is submitted to steam for a period of two hours. The Pyrex apparatus is at atmospheric pressure. The condensate is gathered into a flask containing water, on which approximately 100 mL of pentane is floating. The flask is surrounded by an ice bath.⁴ After separation of the organic phase, the distillation water is submitted to two other pentane extractions.

Microwave extracts—Approximately 15 g of generally fresh vegetable matter is immersed in a beaker containing 150 mL of an organic solvent (hexane, carbon tetrachloride, toluene). This beaker is put into a conventional microwave oven (750 W, 2450 MHz) for a period usually not exceeding 60 seconds. The organic extract is then filtered and concentrated by a factor of 15 with a rotary film evaporator in order to bring the oil concentrations to values suitable for a chromatographic analysis.

Analyses—The extracts of essential oils are analyzed by gas phase chromatography on 30 m polar (Sulpecowac 10)

Figure 1. Yields (weight/weight of dry material) obtained by hydrodiffusion (2 h) and of microwave extract (50 s in hexane)

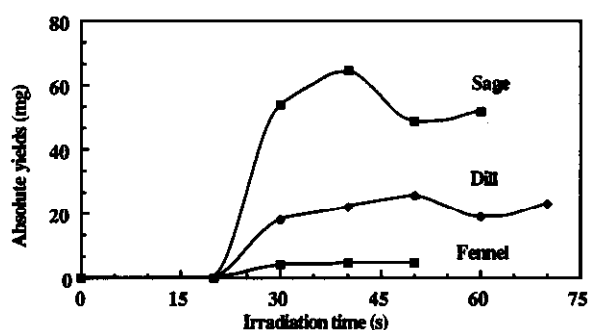


Figure 2. Yields (weight of extract in mg) obtained from 15 g of plant material through microwave (in hexane)

and apolar (DB5) capillary columns, with the following temperature program: 2 min at 40°C, then heating at the rate of 2°C/min to 210°C. This temperature is maintained for an extra 33 min. There is a flame ionization detector. The results are expressed in terms of the percentage of peak area. No correction was made to take account of the response factors of each analyzed product. In several cases, for those in which there existed a reasonable doubt about the identification of the product, analyses coupling chromatography and mass spectrometry were carried out. The yields in extracts (in relation to the humid or dry weight of vegetable matter) are calculated with chromatograms while adding to the solutions an internal standard, namely tetradecane in this instance.

Results

Extract yield—The extract yields, which are important elements for comparison, are relatively close to each other. Thus, the results obtained show a better yield in extracts by the hydrodiffusion technique for seven out of ten plants (Figure 1). In the case of savory, even if the yield is a little better with microwave extraction (0.5% as opposed to 0.4%) and practically identical in the case of marjoram (approximately 1%), the yields obtained by hydrodiffusion are generally better, in the order of one factor going from

Table I. Compositions and yields of essential oil and microwave extracts of Hyssop foliage

| Constituents | KI ^a | Autumn harvest | | Spring harvest | |
|--|-----------------|----------------------|-------------------|----------------------|-------------------|
| | | hydrod. ^b | m.w. ^c | hydrod. ^b | m.w. ^c |
| α-thujene | 927 | 0.22 | 0.17 | 0.21 | - |
| α-pinene | 933 | 0.47 | 0.17 | 0.42 | - |
| camphene | 947 | 0.11 | t | 0.10 | - |
| sabinene | 972 | 1.35 | 1.10 | 1.36 | 1.31 |
| β-pinene | 974 | 8.85 | 4.78 | 8.23 | 4.07 |
| 4,7-dimethyl-4-octanol | 981 | 0.20 | 0.33 | 0.09 | - |
| myrcene | 991 | 2.20 | 1.18 | 1.98 | 1.24 |
| limonene + β-phellandrene ^d | 1026 | 6.17 | 3.07 | 5.13 | 3.19 |
| trans-β-ocimene | 1050 | 0.77 | 1.31 | 1.07 | t |
| terpinolene | 1085 | 0.09 | t | 0.18 | - |
| linalool | 1097 | 0.61 | 0.70 | 0.64 | 0.42 |
| pinocamphone | 1155 | 5.56 | 22.82 | 8.14 | 31.23 |
| unidentified | 1157 | 3.12 | t | 5.88 | 6.30 |
| isopinocampone | 1168 | 43.29 | 55.17 | 40.64 | 39.21 |
| myrtenol | 1190 | 0.92 | 3.21 | 1.07 | 2.12 |
| unidentified | 1322 | 0.25 | 0.40 | 0.30 | - |
| β-caryophyllene | 1412 | 2.74 | 0.17 | 1.99 | - |
| α-humulene | 1447 | 0.45 | t | 0.35 | - |
| alloaromadendrene | 1455 | 1.20 | t | 1.66 | - |
| unidentified | 1457 | 0.55 | t | 0.32 | - |
| germacrene-D | 1475 | 9.02 | 0.61 | 9.00 | t |
| bicyclogermacrene | 1490 | 4.93 | 0.29 | 5.12 | t |
| unidentified | 1508 | 0.25 | - | 0.19 | - |
| myrtenyl-methyl ether | 1544 | 1.60 | 0.43 | 5.12 | - |
| unidentified | 1625 | 0.45 | t | 0.24 | - |
| unidentified | 1635 | 0.39 | t | 0.24 | - |
| unidentified | 1642 | 0.30 | t | - | - |
| unidentified | 1646 | 0.29 | t | - | - |
| unidentified | 1660 | 1.17 | 1.18 | 0.67 | - |
| unidentified | 1956 | t | 1.34 | - | 3.39 |
| unidentified | 2110 | 0.30 | - | - | - |

^a: KI: Kovats indices on DB-5 column; ^b: 2 h hydrodiffusion time; ^c: 50 s microwave extraction time; ^d: limonene/β-phellandrene ratio close to 1/8
t = trace (<0.01%)

one to three. Fennel presents the greatest difference in this respect.

Effect of the extraction time—The curves of production yields of microwave extracts are in the shape of an S and reveal that the first twenty seconds are not very productive (Figure 2). Most of the extract appears in the following 20 seconds. Beyond one minute, likelihood of boiling of the organic solvent becomes more and more probable.

Qualitative composition of extracts—Microwave oven extraction gives, by way of a first approximation, composition extracts that are similar to what is obtained by hydrodiffusion. Indeed, the products analyzed, whether they are in an essential oil or in microwave extracts, belong

Table II. Compositions and yields of essential oils and microwave extracts obtained from Savory foliage (autumn harvest)

| Constituents | KI ^a | Hydrodiffusion ^b | Microwave ^c |
|--|-----------------|-----------------------------|------------------------|
| α -thujene | 926 | 1.20 | 0.24 |
| α -pinene | 932 | 0.84 | t |
| camphene | 946 | 0.07 | - |
| sabinene | 972 | 0.17 | t |
| β -pinene | 973 | 0.49 | t |
| unidentified | 981 | 0.17 | 0.22 |
| myrcene | 991 | 1.93 | 0.39 |
| unidentified | 995 | 0.12 | 0.23 |
| α -phellandrene | 999 | 0.33 | t |
| α -terpinene | 1013 | 4.03 | 1.03 |
| p-cymene | 1021 | 2.59 | 1.25 |
| limonene + β -phellandrene ^d | 1026 | 0.47 | t |
| cis- β -ocimene | 1050 | 0.22 | - |
| γ -terpinene | 1058 | 44.17 | 12.38 |
| trans- β -ocimene | 1064 | 0.40 | 0.65 |
| unidentified | 1172 | 0.29 | t |
| unidentified | 1281 | t | 0.21 |
| carvacrol | 1297 | 39.81 | 83.40 |
| β -caryophyllene | 1411 | 1.39 | t |
| bicyclogermacrene | 1489 | 0.25 | t |
| unidentified | 1504 | 1.08 | t |
| Yields (% fresh matter) | - | 0.057 | 0.053 |

^{a,b,c}: same as in Table I; ^d: limonene/ β -phellandrene ratio close to 1/1
t = trace (<0.01%)

to the family of terpenes, and, more specifically, monoterpenes and sesquiterpenes. Thus, in the case of hyssop foliage, analyses of the essential oil and the microwave extract show the near identity of the constituents (Table I). Of the 31 compounds observed in the chromatography of the essential oil, 29 are found in the microwave extract. This "identicalness" is also observed in the essential oils and "microwave" extracts of other vegetable matters, although there are occasionally more pronounced discrepancies. The general tendency is that there are slightly fewer "visible" compounds (in terms of numbers) on the chromatograms of microwave extracts compared to what is observed with essential oils.

Quantitative composition of the extracts—The quantitative composition of the two kinds of extracts is subject to much more significant variation. Thus, the percentages of major products found in the hyssop foliage extracts (Table I) present some important differences. Although isopinocampheol is the major product in both cases (43% and 55%), pinocampheol is in greater concentration in the microwave extract (23% as opposed to 5.5%), and the concentration of β -pinene is almost twice as high in the essential oil (8.8% as opposed to 4.8%). The most important characteristic for differentiating the two types of extracts is the disproportion (by a factor of at least 10) between the much greater concentrations of sesquiterpenes (germacrene-

Table III. Compositions and yields of essential oils and microwave extracts obtained from Marjoram foliage

| Constituents | KI ^a | Autumn harvest | | Spring harvest | |
|--|-----------------|----------------------|-------------------|----------------------|-------------------|
| | | hydrod. ^b | m.w. ^c | hydrod. ^b | m.w. ^c |
| α -thujene | 933 | 0.34 | 0.15 | 0.29 | 0.21 |
| α -pinene | 938 | 0.69 | 0.16 | 0.62 | 0.15 |
| sabinene | 974 | 7.60 | 3.48 | 6.25 | 2.90 |
| β -pinene | 976 | 0.34 | t | 0.31 | t |
| myrcene | 992 | 2.10 | 0.83 | 1.79 | 0.64 |
| α -phellandrene | 999 | 0.11 | t | 0.11 | t |
| α -terpinene | 1015 | 5.91 | 0.05 | 6.39 | t |
| p-cymene | 1025 | 0.07 | t | 0.15 | t |
| limonene + β -phellandrene ^d | 1030 | 3.16 | 1.52 | 2.78 | 1.23 |
| γ -terpinene | 1066 | 9.96 | 0.14 | 10.88 | t |
| cis-para-menth- 2-en-1-ol | 1074 | 4.70 | 3.07 | 4.21 | 3.26 |
| terpinolene | 1097 | 2.23 | 0.01 | 2.46 | t |
| linalool | 1107 | 22.97 | 43.95 | 18.54 | 54.75 |
| cis-sabinene hydrate | 1111 | 2.37 | 2.35 | 2.94 | 2.70 |
| unidentified | 1128 | 1.35 | t | 1.47 | t |
| unidentified | 1145 | 0.47 | t | 0.60 | t |
| terpinene-4-ol | 1177 | 18.67 | 0.64 | 22.08 | 0.75 |
| α - and β -terpineol | 1187 | 2.54 | 2.31 | 2.65 | 2.29 |
| unidentified | 1191 | 0.41 | 0.13 | 0.44 | t |
| unidentified | 1197 | 0.15 | 0.14 | 0.12 | 0.11 |
| unidentified | 1201 | 0.24 | t | 0.33 | - |
| 4-thujanyl- 4-acetate ^e | 1257 | 1.63 | 27.60 | 0.91 | 16.21 |
| linalyl acetate | 1263 | 5.09 | 3.90 | 5.11 | 4.44 |
| β -caryophyllene | 1413 | 2.89 | 0.62 | 3.76 | 0.86 |
| α -humulene | 1451 | 0.12 | t | 0.16 | t |
| bicyclogermacrene | 1498 | 2.04 | 0.44 | 2.49 | 0.54 |
| unidentified | 2004 | 0.24 | 0.28 | 0.27 | 0.21 |
| unidentified | 2199 | 0.23 | 1.21 | 0.30 | 1.27 |
| unidentified (hydrocarbon ?) | 2288 | 0.32 | 6.16 | 0.25 | 6.04 |
| unidentified (hydrocarbon ?) | 2328 | - | 0.23 | 0.22 | t |

^{a,c}: same as in Table I; ^d: limonene/ β -phellandrene ratio close to 1/1;
^e: mass spectrum very similar to that of sabinene hydrate (20);
t = trace (<0.01%)

D and bicyclogermacrene) in the essential oil. In the case of fennel, the major products measured in the essential oil are trans-anethole (55.5%) and limonene (35.7%), whereas the microwave extract gives the following respective percentages: 78.6% and 14.8%.⁵

In the case of savory, there are more or less the same characteristics (Table II). Even if the γ -terpinene and carvacrol have more or less the same concentrations in the essential oil (respectively 44% and 40%), their concentration in the microwave extract is very different: respectively 12.4% and 83.4%. In the case of marjoram foliage, the variation of concentrations of major products is even greater (Table III). In the microwave extract, the concentrations of α - and β -phellandrene and terpinene-4-ol practically disap-

Table IV. Microwave extracts from Marjoram foliage: solvent effects^a

| Constituents | toluene+ | | | | |
|------------------------|--------------|------------------|--------------|--------------|-------------------------------|
| | toluene | CCl ₄ | hexane | toluene | CCl ₄ ^b |
| α-thujene | 0.15 | 0.29 | 0.15 | 0.22 | 0.33 |
| α-pinene | 0.29 | 0.54 | 0.16 | 0.40 | 0.58 |
| sabinene | 4.07 | 20.71 | 3.48 | 5.01 | 5.99 |
| β-pinene | t | 0.26 | t | t | t |
| myrcene | 1.27 | 1.53 | 0.83 | 1.36 | 1.58 |
| α-phellandrene | 0.15 | 0.07 | t | 0.07 | t |
| α-terpinene | 0.03 | 0.07 | 0.05 | 0.05 | t |
| limonene + | | | | | |
| β-phellandrene | 2.07 | 2.24 | 1.52 | 2.19 | 2.35 |
| γ-terpinene | 0.31 | 0.18 | 0.14 | 0.19 | 0.28 |
| cis-p-menth-2-en-1-ol | 2.65 | 3.09 | 3.07 | 3.20 | 3.94 |
| linalool | 39.58 | 32.82 | 43.95 | 36.11 | 30.91 |
| 1111 ^c | 1.75 | 1.68 | 2.35 | 1.54 | 1.39 |
| 4-terpineol | 0.75 | 0.61 | 0.64 | 0.67 | 0.63 |
| α- and β-terpineol | 2.04 | 1.93 | 2.31 | 2.18 | 1.96 |
| 1257 ^c | 28.12 | 37.34 | 27.60 | 32.84 | 38.14 |
| linalyl acetate | 4.73 | 2.19 | 3.90 | 3.59 | 4.35 |
| β-caryophyllene | 2.19 | 2.64 | 0.62 | 2.43 | 2.85 |
| bicyclogermacrene | 1.60 | 1.77 | 0.44 | 1.27 | 1.77 |
| 2199 ^c | t | 0.43 | 1.21 | t | t |
| 2288 ^c | t | 1.40 | 6.16 | 0.21 | t |
| Yield (% fresh matter) | 0.52 | 0.51 | 0.11 | 0.56 | 0.17 |
| Yield (% dry matter) | 1.24 | 1.17 | 1.02 | 0.92 | 0.28 |

^a: 50 s irradiation in microwave oven (spring harvest); ^b: results obtained in CCl₄ following a pre-extraction made with toluene (preceding column);

^c: Kovats indices on DB-5 column

t = trace

Table V. Composition and yield of essential oil and microwave^c extracts obtained from Thyme: solvent effects

| Constituents | Hydro-diffusion ^b | toluene | | |
|-----------------------------|------------------------------|------------------|--------------|--------------|
| | | CCl ₄ | hexane | |
| α-thujene | 0.40 | 0.18 | 0.80 | t |
| α-pinene | 0.17 | t | 0.34 | t |
| β-pinene | 0.07 | 0.17 | 0.23 | t |
| 4,7-dimethyl-4-octanol | 0.69 | 0.44 | 0.82 | 0.89 |
| 6-methyl-5-hepten-2-one | 0.46 | 0.40 | 1.42 | 1.44 |
| myrcene | 1.03 | 0.27 | 1.05 | t |
| 3-octanol | 0.20 | t | 1.11 | 0.92 |
| α-phellandrene | 0.05 | 0.27 | 0.14 | t |
| α-terpinene | 0.56 | 0.20 | 0.37 | t |
| p-cymene | 2.23 | 1.14 | 2.91 | 0.95 |
| limonene + | | | | |
| β-phellandrene ^d | 0.23 | - | - | t |
| 1,8-cineole | - | t | 1.18 | t |
| cis-β-ocimene | 0.32 | 0.17 | 0.43 | t |
| trans-β-ocimene | 0.46 | 0.55 | t | t |
| γ-terpinene | 4.47 | 2.89 | 7.71 | 2.45 |
| trans-sabinene hydrate | - | 0.25 | 0.42 | - |
| terpinolene | - | 0.84 | t | - |
| linalool | 7.33 | 8.65 | 1.35 | 5.76 |
| 1126 ^a | 0.95 | 1.55 | t | 0.86 |
| terpinene-1-ol-4 | - | 1.29 | t | - |
| 1237 ^a | 1.37 | 0.59 | 5.69 | t |
| 1242 | 0.93 | - | 0.59 | 1.15 |
| carvone | 1.02 | 0.62 | 0.75 | t |
| 1251 | - | 0.94 | 1.45 | - |
| geraniol | 1.02 | - | 1.23 | 2.61 |
| linalyl acetate | 42.50 | 50.54 | 14.02 | 23.17 |
| 1276 | 1.22 | t | 1.62 | 4.01 |
| bornyl acetate | - | 0.66 | - | - |
| thymol | 9.35 | 6.28 | 31.29 | 43.10 |
| carvacrol | 5.07 | 4.25 | 10.92 | 6.96 |
| 1345 | t | 0.26 | 0.59 | 1.42 |
| 1357 | 0.18 | 0.15 | 0.38 | 0.87 |
| α-copaene | 0.09 | 0.26 | 0.54 | 2.10 |
| β-caryophyllene | 3.56 | 3.10 | 2.67 | t |
| α-humulene | 0.12 | 0.16 | t | - |
| germacrene-D | 2.31 | 1.67 | 1.25 | t |
| 1513 | 3.55 | 2.39 | 3.88 | t |
| 1958 | t | t | 0.85 | - |
| Yields (% fresh material) | 0.10 | 0.10 | 0.08 | 0.02 |

^{a-c}: same as in Table I; ^d: limonene/β-phellandrene = 1/1

pear, while the concentration of linalool doubles and an unidentified compound appears.

Effect of the growing season—Despite the differences in temperature (see Methodology) and especially the noticeable differences in sunshine, Tables I and III show that the quantitative compositions of essential oils and those of microwave extracts are relatively similar.

Effect of the solvent—An interesting parameter is that the microwave extraction technique allows a choice of solvent.² In several cases, the differences observed after substituting one solvent with another are generally not great. Thus, in the case of marjoram foliage, the choice of solvent has little influence on the composition of the extract (except, perhaps, for the concentration of sabinene in the presence of CCl₄ or on the yields obtained (Table IV).

The extraction in two successive stages while changing the solvent has been proposed as a possible variant.² The extraction in carbon tetrachloride of a plant sample which was first subjected to extraction in toluene produces an extract whose composition is almost identical to that obtained in the first stage. The yield of the second stage is clearly weaker (0.28% as opposed to 0.9%).

The case of thyme foliage⁶ is, on the contrary, an extreme one among those recorded in the present study (Table V). The concentrations of oxygenated products and major products (linalyl acetate, thymol and carvacrol) are quite different. Linalyl acetate is the major product obtained in toluene (50.5%), whereas thymol is the major substance found in extracts in the presence of CCl₄ (31.3%) and hexane (43.1%). The variation of extract yields is more significant. Whereas toluene and CCl₄ produce yields of the same order of

Table VI. Microwave assisted extraction from isolated Sage plants (spring harvest)

| Constituents ^a | Hydrodif. ^b | 1 ^c | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | M(σ) ^d |
|--|------------------------|----------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|----------------------------|
| α -pinene | 2.53 | 1.65 | 0.67 | 0.77 | 1.09 | 0.83 | 1.94 | 1.24 | 3.66 | 2.38 | 0.57 | 1.5(1.0) |
| camphene | 2.42 | 1.62 | 2.16 | 0.84 | 1.07 | 0.60 | 3.21 | 1.57 | 0.75 | 1.89 | 2.46 | 1.6(0.9) |
| β -pinene | 2.42 | 0.89 | 1.11 | 1.22 | 1.09 | 0.68 | 2.16 | 1.44 | 1.62 | 1.36 | 1.16 | 1.3(0.4) |
| myrcene | 1.05 | 0.71 | 0.65 | 0.73 | 0.66 | 0.73 | 0.78 | 0.96 | 1.05 | 0.98 | 0.93 | 0.9(0.2) |
| limonene + 1,8-cineole ^e | 6.82 | 2.87 | 7.21 | 11.12 | 13.58 | 9.43 | 7.22 | 14.53 | 16.13 | 10.96 | 7.86 | 10.9(3.3) |
| α -thujone | 39.42 | 0.64 | 40.99 | 53.84 | 49.56 | 58.08 | 47.23 | 48.89 | 49.05 | 47.94 | 40.28 | 48.4(5.6) |
| β -thujone | 8.87 | 59.25 | 4.87 | 3.88 | 3.46 | 5.83 | 3.95 | 4.44 | 3.77 | 3.60 | 3.80 | 4.2(0.8) |
| camphor | 12.12 | 18.49 | 26.13 | 11.45 | 14.34 | 12.30 | 13.35 | 10.02 | 8.17 | 10.08 | 21.86 | 14.2(6.0) |
| borneol | 0.61 | 0.89 | 2.77 | 0.28 | 1.21 | 0.19 | 4.69 | 1.09 | t | 0.51 | 2.23 | 1.4(1.5) |
| 1168 ^f | 0.56 | t | 0.99 | 0.49 | 0.79 | 0.47 | t | 0.94 | 0.41 | 0.51 | 1.05 | 0.6(0.3) |
| bornyl acetate | 0.73 | 0.48 | 1.22 | 0.17 | 0.50 | 0.22 | 1.59 | 0.70 | 0.05 | 0.15 | 1.21 | 0.7(0.6) |
| β -caryo- phyllene | 2.38 | 0.43 | 0.31 | 0.63 | 0.51 | 0.28 | 0.48 | 0.42 | 0.77 | 0.86 | 0.67 | 0.5(0.2) |
| α -humulene | 6.02 | 0.62 | 0.88 | 0.84 | 1.38 | 1.05 | 1.39 | 0.92 | 1.31 | 1.80 | 0.84 | 1.2(0.3) |
| viridiflorol | 4.99 | 1.63 | 2.34 | 3.18 | 1.61 | 1.55 | 2.90 | 3.10 | 4.85 | 4.04 | 3.29 | 3.0(1.1) |
| 2050 ^f | 2.63 | 1.18 | 1.63 | 2.42 | 1.05 | 1.51 | 1.71 | 2.02 | 1.84 | 2.56 | 2.81 | 2.0(0.6) |

^a: Products with concentration >0.5%; ^b: 2 h hydrodiffusion with several sage plants; ^c: 40 s exposition to microwave irradiation;

^d: M(σ): mean(standard deviation) on #2 - #10 plants; ^e: limonene/1,8-cineole ratio close to 1/3; ^f: Kovats indices on DB-5 column;

t = trace (<0.01%)

magnitude (0.49% and 0.30%), hexane turns out to be of poor quality. It yields only 0.07%.

The use of more polar solvents (esters, ketones, alcohols, etc.) is also possible. In these cases, it is extremely easy to extract pigments, especially chlorophyll. The microwave extracts obtained in the presence of a solvent that is not very polar are generally microwave transparent, whereas those obtained in the presence of a polar solvent are opaque and of a dark green color whose origin is obvious.

Extraction on isolated individuals—Because of the quantity of vegetable matter required to perform an extraction in a microwave oven, it is possible to carry out a study plant by plant. Table VI shows the variability of the extract composition of ten sage plants treated in hexane for 40 s in a microwave oven. Relative stability in the composition of the nine extracts can be noted. The concentration of the major product, α -thujone, is 48.4% (σ = 5.6%), while that of β -thujone is 4.2% (σ = 0.8%). Mention must of course be made of sample No. 1, which presents an inverse composition: 59.2% of β -thujone and only 0.64% of α -thujone.

This approach can also be used to test the productivity of certain parts of the plant. We have been able to show, in the case of lavender, that almost all of the essential oil is located in the flowers. The stems holding these flowers contain at least ten times less oil (w/w), and this oil contains approximately 70-75% of coumarin, whereas the essential oil of lavender contains less than 1%.

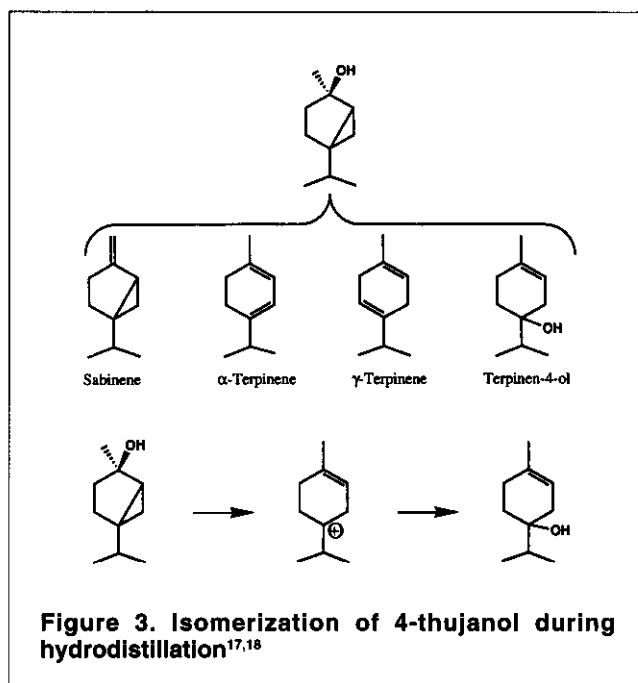
Discussion

The cultivation techniques used, the climate (or the microclimate of greenhouses) and the pedological conditions introduce variants which are bound to influence the

essential oil quantity. It can be noted, however, that the compositions of oils produced by microwave extraction are similar to those shown in the literature. This is true for the foliage of parsley,⁷ hyssop,⁸ savory,⁹ sage,¹⁰ marjoram,¹¹ fennel,¹² etc. Nevertheless, there are important differences in the case of the essential oil of oregano. Although there are two well-known chemotypes, with thymol and carvacrol, as well as several variants,^{13,14} we have not found any references relative to an oregano essential oil that was rich in sabinene (2-6%), cis- β -ocimene (8-12%), γ -terpinene (9-12%), germacrene-D (10-18%) and practically without any borneol. In a general way, although the relative compositions can be easily reproduced, this does not seem to be the case for thyme foliage. Does this mean that it is difficult to obtain a small sample (15 g) that is representative of the whole population? Is there great variability in the composition of oils within the vegetable matter? Is it possible that the presence of different known chemotypes of this plant can explain this relative non-productivity of the results?¹⁶

It is therefore more useful here to compare the results to each other than to compare them to those shown in the literature. Tables I-V show the chemical differences found between the essential oil and the microwave extracts. Generally speaking, it can be seen that the extracts have simpler compositions. Several minor products of essential oils are found at most as traces in the extracts. This is the case for the foliage of hyssop, savory and marjoram (Tables I-III). Inversely, the principal compounds of essential oil have a higher concentration in the extract. This is true of carvacrol in the extract of savory foliage (Table II) and of myristicin in the case of parsley.⁵

Another observation, which follows to some extent from the previous one, is that the concentration of sesquiterpe-



nes generally is much greater in the essential oil than in the microwave extracts. The relative compositions appearing in Table VII, multiplied by absolute yields, emphasize this point. The reason for such behavior is not obvious. It is easy to imagine that during the time that the essential oil is being produced, the organic matter is subject to the temperature of steam for a relatively long period, ranging from one to several hours.

In a microwave extraction, the much shorter exposure time does not favor the physical and chemical processes, which are subject to a potentially considerable barrier. On the other hand, certain molecules can be bound chemically to an organic matter or rather encapsulated in a vegetable matrix somewhere other than in the oil-bearing glands. The rupture of this (physical) matrix or the (chemical) hydrolysis reactions, which are possible in hydrodiffusion, but which are not possible in a microwave oven for lack of time, means that these products cannot be extracted in less than one minute. Such reactions of hydrolysis, decomposition or dehydration have already been proposed. However, the already proposed transformation of trans-sabinene hydrate into terpinen-4-ol by heating in the presence of water, in the case of marjoram,¹⁵ is not observable in the results (Table III). The results reported here, which agree with the observations of Fisher et al.,¹⁶ show that the compound present in the plant is rather thujanyl-4 acetate (or sabinene hydrate acetate), a tertiary alcohol acetate (Figure 3). This compound must be very unstable in the presence of steam, and it decomposes rapidly into sabinene, α- and γ-terpinene and terpinen-4-ol. It should be recalled here that a special case of extreme divergence between the composition of essential oil and the microwave extract is that of garlic (*Allium sativum* L.).² This divergence can be explained by the important content of sulphur compounds whose S-S bonds are relatively sensitive to temperature.

Table VII. Sesquiterpene concentrations in some essential oils and microwave extracts

| | germacrene-D | bicyclogermacrene | β -caryophyllene | α -caryophyllene |
|-------------------|--------------|-------------------|------------------------|-------------------------|
| oregano | | | | |
| Essential oil | 18.45 | - | 9.06 | 0.99 |
| microwave extract | t | - | - | - |
| sage | | | | |
| Essential oil | - | - | 2.38 | 6.02 |
| microwave extract | - | - | 0.3-0.7 | 0.6-1.8 |
| fennel | | | | |
| Essential oil | 0.37 | - | 0.33 | - |
| microwave extract | - | - | - | - |
| marjoram | | | | |
| Essential oil | - | 2.49 | 3.76 | 0.16 |
| microwave extract | - | 0.66 | 0.86 | - |
| hyssop | | | | |
| Essential oil | 9.02 | 4.93 | 2.74 | 0.45 |
| microwave extract | 0.61 | 0.29 | t | t |
| caraway | | | | |
| Essential oil | 69.06 | 3.90 | 2.91 | - |
| microwave extract | 42.36 | t | 2.14 | - |

t = trace

Conclusion

The technique of preparing natural product extracts using a microwave oven in the presence of an appropriate solvent is far from having been exploited in all its dimensions. In terms of the laboratory, it is a method that certainly complements those that already exist, as it has the benefit of being a rapid method, using samples with less vegetable matter, and having composition extracts that are closer to reality. In comparison to the traditional preparation of essential oils, a method that can affect the nature of the oil components,¹⁹ the microwave technique presents a definite advantage.

This same quality should also find very timely industrial applications. Without going any deeper into this field, the example of marjoram shown above should encourage researchers to further investigate this technique, especially if the industrial technology of microwave ovens is open to technological improvements.

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