Ten Years of Hydrodiffusion of Oils

By Mans H. Boelens, Francisco Valverde, Leandro Sequeiros, Rafael Jimenez, Destilaciones Bordas Chinchurreta SA, Seville, Spain

Essential oils are isolated from plant material by steam and hydrodistillation and by hydrodiffusion.[1-7] Steam distillation is performed with indirect (dry) steam. Hydrodistillations are featured by the fact that the plant material is heated with water and the steam is generated within the still. Hydrodiffusion is carried out with low pressure steam (0.1 bar), replacing the volatiles from the intact plant material by osmotic action.

Comparison with Hydrodistillation

It will be clear, that the ease of isolation of a particular oil is dependent on the ease in which the plant cells release the oils. Essential oils can be present in isolated cells—organelles or idioblasts—(e.g. in Lauraceae, Rutaceae) or more at the surface of the plant material, e.g. in glandular hairs (as in Labiatae leaves), or in cavities, ducts or canals (like in Umbelliferous fruits).[8,9]

The thermodynamical aspects of steam distillation of essential oils from herb are well known.[7] The hydrodistillation and hydrodiffusion of essential oils from plant material, however, is more complicated. The oil has to diffuse from the inside of the material to the surface. Moreover the plant material also contains non-volatiles, e.g. fats (fatty oils), which retain the volatiles. Thus during the isolation of volatiles from plant material by means of steam, the following physical parameters play a role: partition coefficients, diffusion rates, water solubilities, partial vapour pressures, times and velocities of heat transfer.

Koedam et al.[1,2] compared the isolation procedures for essential oils and they found that during the hydrodistillation of oils from certain plant material the isolation sequence of the volatile components is determined more by their water solubilities than by their boiling points.

This phenomenon was explained by the fact that the isolation of the components was more depending of hydrodiffusion (related to water solubilities) than of hydrodistillation (related to partial vapour pressures, e.g. boiling points).

The approximated chemical composition, and the olfactive and organoleptic qualities of the following groups of essential oils, obtained by hydrodiffusion and hydrodistillation, were studied:

Leaf oils of: *Laurus nobilis* L., *Citrus aurantium* L. ssp. amara Engl., *Cistus ladanifer* L.

Fruit oils of: *Pimpinella anisum* L, *Carum carvi* L., *Coriandrum sativum* L., *Cuminum cyminum* L.

Flower/leaf oils of: *Rosmarinus officinalis* L., *Lavandula latifolia* L., *Salvia lavandulae Vahl*, *Thymus vulgare* L.

Experimental

Isolation—The essential oils were obtained by:

- Hydrodistillation of plant material in a 50 l stainless steel apparatus with grill and basket. Heating was performed with indirect steam (1-3 bar). The distillate water was recycled.
- Hydrodiffusion with low pressure steam of 0.05-0.1 bar at 90-95°C in a Schmid hydrodiffusor LS 500.

  The distillate water was not recycled.

Analysis—The oils were analysed on a Perkin-Elmer 8400 gas chromatograph equipped with a 60 m fused-silica capillary column, 60 m x 0.25 mm i.d.; stationary phase SE-54; N_2 flow 1.2 ml/min; oven temperature programmed 110-220°C, at 3°C/min; injection temperature 250°C. Peak area percentages were calculated using the normalization method in which the response factor for each component is supposed to be equal to one.

The identities of the quantified constituents were checked by comparison of their retention times with those of authentic compounds. The approximated chemical composition of the oils is shown in Table I.

Discussion

Hydrodiffusion—The principle of hydrodiffusion is the osmotic action of steam cq. water on vegetable cells. Koedam et al.[1] demonstrated that the sequence of evaporation of the volatile components during (hydro)distillation from uncomminuted plant mate-

 0272-2666/90/0005-1101$04.00/00

rial is governed by the rate of diffusion of the different constituents through the cell membranes, which in turn is determined by the degree of solubility of the compounds in the distillation water. Von Rechenberg[10] first recognized this type of diffusion and called it hydrodiffusion.

In the Schmid hydrodiffusor the low-pressure steam flow goes, according to the law of gravity, from the top through the vegetable load down to the condenser at the bottom. Due to the construction of the apparatus the hydrodiffusion, which is a slow-acting process, takes less time than hydrodistillation. With the hydrodiffusor 25-50% of the time and energy (steam) can be saved. A disadvantage is that the distillate water cannot be recycled, and eventually the water layers must be extracted with a suitable solvent.

According to experiments of the producer of the apparatus, the yields of essential oils obtained by hydrodiffusion should be equal or higher than those of oils processed by hydrodistillation (see Table II). In our experiments the yields of hydrodiffusion and hydrodistillation were more or less equal.

Separation of Oils[12,13]

The separation of oils from the condensate in the hydrodiffusion process in florentine flasks is not efficient.

During the hydrodiffusion of oils from intact (uncommunicated) plant material, the isolation sequence of the volatile components is determined to a great extent by their water solubilities. As a consequence, the condensate water is more or less saturated with the polar constituents of the oil.

There are three problems to overcome:

Table I. Approximated Chemical Composition of Oils Isolated by Hydrodiffusion and Hydrodistillation

	Hydrodiffusion %	Hydrodistillation %
Oils from Leaves with Internal Oil Cells		
Laurel Oil		
Monoterpene hydrocarbons	15.8	26.3
1,8-Cineole	28.0	43.0
Monoterpene alcohols/esters	42.3	25.9
α-Terpinyl acetate	13.5	7.5
α-Terpineol	2.3	4.5
Sesquiterpenoids	1.4	1.0
Benzenoids	12.0	3.5
Bitter Orange Oil		
Monoterpene hydrocarbons	6.2	12.8
Linalool	4.8	22.9
Linalyl acetate	83.8	49.1
Other monoterpene alcohols/esters	4.6	13.4
Sesquiterpenoids	0.6	1.8
Cistus Oil		
Monoterpene hydrocarbons	6.5	53.5
Monoterpene oxygen-derivatives	14.5	7.5
Sesquiterpene hydrocarbons	4.5	13.8
Sesquiterpene oxygen-derivatives and Benzenoids	74.5	25.2
Oils from Fruits with Oil Cavities		
Anise Oil		
Methyl chavicol	1.2	0.9
cis-Anethole	0.2	0.5
trans-Anethole	93.4	93.5
Anisyl-derivatives	5.2	5.1
Cumin Oil		
Monoterpene hydrocarbons	47.8	47.1
Other monoterpenoids	1.9	1.7
Cuminaldehyde and p-menthadienals	47.6	48.7
Sesquiterpenoids	2.7	2.5
Caraway Oil		
Limonene	38.7	44.2
Limonene oxides	0.2	1.0
Carvone	59.9	52.5
Carvone derivatives	1.2	2.3
Coriander Oil		
Monoterpene hydrocarbons	23.6	27.3
Linalool	70.4	66.2
Camphor	2.5	3.1
Other terpenoids	3.5	3.4
Oils from Flowers/Leaves with Glandular Hairs		
Spike Lavender Oil		
Monoterpene hydrocarbons	8.0	8.7
1,8-Cineole	17.3	28.2
Linalool	45.1	40.1
Camphor	19.6	13.6
Other Monoterpene alcohols/esters	5.1	5.1
Sesquiterpenoids	4.9	4.3
Spanish Sage Oil		
Monoterpene hydrocarbons	29.4	33.0
1,8-Cineole	19.8	22.1
Camphor	19.5	21.3
Monoterpene alcohols/esters	28.1	21.5
Sesquiterpenoids	3.2	2.1
Rosemary Oil		
Monoterpene hydrocarbons	56.0	46.1
1,8-Cineole	17.5	19.1
Camphor & Verbenone	13.3	18.3
Monoterpene alcohols/esters	10.2	13.0
Sesquiterpenoids and Benzenoids	3.0	3.5
Thyme Oil		
Monoterpene hydrocarbons	34.0	44.5
1,8-Cineole	13.8	7.6
Linalool	10.0	3.8
Monoterpene alcohols/esters	39.7	41.1
Thymol/Carvacrol	2.5	3.0

- part of the oil is dissolved in the condensate water: in practice about 1%, seldom higher than 2% and in exceptional cases (polar-like phenolic-constituents) up to 5%;
- another part of the oil is emulsified in the water: mostly less than 1%;
- finally, a part of the oil is strongly emulsified with water and other organic particles on the oil-water interface, the quantity could be up to 10%.

To overcome some of these problems, two possibilities are at hand, namely:

- to centrifuge the condensate and separate the oil by decantation, which can be efficient for most of all emulsified oil, but is not suitable for dissolved oil;
- to extract the condensate with a suitable solvent. For this purpose often a hydrocarbon, like hexane or toluene, is used.

In our opinion, for analytical purposes, a pentane/diethyl ether (1:1 v/v) is more suitable.

Because the oil is virtually not in contact with (acidic) water, but only steam, the decomposition of labile compounds, like linalyl acetate, is reduced to a minimum in the hydrodiffusor. The purpose of this investigation was to study whether there is higher concentrations of oxygen-containing terpenes c.q. sesquiterpenes in hydrodiffusion oils than in hydrodistilled oils; and to see if decomposition of important constituents could be circumvented.

Table II. Test Results of Schmid Hydrodiffusor LS 500 compared with Hydrodistillation (according to Schmid Hydrodiffusion SA, Switzerland, May 1981).

Product (Origin)	Hydrodiffusion Time h	Hydrodiffusion Average yield %	Hydrodistillation Time h	Hydrodistillation Average yield %
Cistus leaves (France)	8	0.13	16	0.04
Cistus leaves (Spain)	8	0.15	16	0.05
Lavender (France)	0.5	0.73	1	0.75
Lavandin (France)	0.5	1.7	1	1.4
Cumin fruits (Poland)	4	5.0	12	3.7
Caraway fruits (Poland)	4	3.6	10	4.5

Oils from leaves with internal oil cells—Leaves of plants from the families Lauraceae, Rutaceae, Myrtaceae and Cistaceae have isolated cells, so-called organelles or idioblasts.[7,8] The oils are rather slowly released from these cells and hydrodiffusion plays an important role.

Laurel leaf oil, obtained by hydrodiffusion, contained higher concentration of oxygen-containing monoterpenes and benzenoids than an oil processed by hydrodistillation.[11] The organoleptic quality of hydrodiffused laurel leaf oil is preferred to that of the hydrodistilled oil, due to the higher concentration of benzenoids.

Bitter orange leaf oil, obtained by hydrodiffusion, is quite different from the hydrodistilled oil, mainly due to the high concentration of linalyl acetate in the former oil. It seems that a high proportion of the linalyl acetate hydrolyzes and decomposes during hydrodistillation. The olfactive quality of hydrodiffused bitter orange leaf oil was preferred to that of hydrodistilled oil.

The differences between the chemical compositions of the hydrodiffused and hydrodistilled oils from cistus leaves are quite big, due to higher concentrations of oxygen-containing sesquiterpenes and benzenoids in the former oil. The olfactive quality of the hydrodiffused cistus oil is strongly woody balsamic, whereas the hydrostilled oil has a harsh terpene-like odour.

Oils from Umbelliferous Fruits with Oil Cavities—Umbelliferous fruits contain volatiles in cavities, ducts or canals.[9] Although the oils are not quickly released and hydrodiffusion plays a role, the fruits swell in time and the cells break open. Thus the hydrodiffusion process with these fruits is time dependent.[1]

As can be seen from Table I, the oils isolated from Umbelliferous fruits by hydrodiffusion and hydrodistillation do not show big differences in the concentration of their main constituents.

The olfactive and organoleptic qualities of anis and cumin oil obtained by both methods were the same for each oil.

The hydrodiffused oils from caraway and coriander were organoleptic slightly preferred to the hydrodistilled oils.

Oils from Labiatous Flowers/Leaves with Glandular Hairs—Leaves from Labiatae species contain superficial oil glands, which easily release the oil. Hydrodiffusion does not play an important role during the isolation of the oils. As can be seen in Table I, for Labiatous oils some differences exist between hydrodiffused and hydrodistilled oils. For instance, the concentration of the monoterpene hydro- carbons and of 1,8-cineole fluctuates to some extent in both types of oils.

This fluctuation may be due to the solubility of oxygen-containing monoterpenes in the distillate water, which was not recycled during hydrodiffusion. There were no significant differences in the olfactive and organoleptic qualities of both types of oils from a particular plant.

Conclusions

The differences between the chemical composition, and the olfactive and organoleptic qualities of essential oils obtained by hydrodiffusion or hydrodistillation, can be explained by the way in which the oil is present in the plant material.

Plant material with isolated oil cells affords different oils, from which the hydrodiffused oils contain higher concentrations of oxygen-containing monoterpenes and benzenoids and possess preferred olfactive and organoleptic qualities.

Plant material with oil cavities yields oils with slight differences, whereas plant material with glandular hairs gives oils with non-conclusive differences.

Acknowledgment: *The authors are greatly indebted to Prof. Dr. J. J. C. Scheffer, Center for Bio-Pharmaceutical Sciences, Gorlaeus Laboratories, Leiden, The Netherlands, for his most valuable suggestions and his critical review of the manuscript.*

References

1. A Koedam, JJC Scheffer and A Baerheim Svendsen, Comparison of Isolation Procedures for Essential Oils. II. Ajowan, Caraway, Coriander and Cumin, *Z Lebensm Unters Forsch* **168**, 106 (1979)
2. A Koedam, JJC Scheffer and A Baerheim Svendsen, Comparison of Isolation Procedures for Essential Oils. IV. Leyland Cypress, *Perf & Flavorist* **5**(7), 56 ((1981)
3. B Meyer-Warnod, Natural Essential Oils, Extraction Processes and Application to Major Oils, *Perf & Flavorist* **9**(2), 93 (1984)
4. E Legast and L Peyron, in: Proceedings of the 9th Intl Congress of Ess Oils, Fragrances & Flavors, Singapore, March (1983)
5. J Pellecuer et al, in: Proceedings of the 9th Intl Congress of Ess Oils, Fragrances & Flavors, Singapore, March (1983)
6. G Gaudin and A Guenet, Contribution a la Connaissance de l'Huile Essenielle de Ciste, in: Proc of the Intl Congress of Ess Oils, Digne (France), September (1988) 155-167
7. EFK Denny, Steam Distillation of the Subcutaneous Essential Oils, in: *Flavors and Fragrances: a World Perspective,* Ed by BM Lawrence, BD Mookherjee and BJ Willis, Elsevier, Amsterdam-Oxford-New York-Tokyo, 85-98, (1988)
8. ThM Malingré, Chemotoxonomy of Spice Plants, Perf & Flavorist **6**(6), 15 (1982)
9. K-H Kubeczka and I Bohn, New Constituents from the Essential Oils of Pimpinella Species, in: *Progress in Essential Oil Research,* Ed by E-J Brunke, Walter de Gruyter & Co., Berlin-New York, 279-298 (1986)
10. C von Rechenberg, Theorie der Gewinnung und Trennung der Aetheriscen Oele durch Destillation, Miltitz bei Leipzig, Selbstverlag von Schimmel & Co, p 423ff (1910)
11. MH Boelens and R Jimenez Sindreu, The Chemical Composition of Laurel Leaf Oil, obtained by Steam Distillation and Hydrodiffusion, in: *Progress in Essential Oil Research,* Ed by E-J Brunke, Walter de Gruyter & Co, Berlin-New York, 99-110 (1986)
12. E Legast and L Peyron, Proc of the IXth Intl Congress of Ess Oils, Singapore, Book 1, 69 (1983)
13. J Pellecuer, V de Lauzun, M Attiso, M Simeon de Beochberg, M Jacob and M Iderne, Proc of the IXth Intl Congress of Ess Oils, Singapore, Book 5, 115 (1983)