Water-Soluble Fractions of the Essential Oils

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In the usual processes of water-steam or hydrodistillation, or even in the process of preparing the cold-pressed essential oils, the oil comes into a close and prolonged contact with water. It can be said that all distillation processes yield an essential oil in two fractions; the first is the fraction that is insoluble in water and is decanted off from the separator in a traditional manner, and the second is the water soluble fraction which remains in the distillation water and is usually discarded with the water. We will refer to these as the "decanted fraction" and the "water soluble fraction" in this paper. This contact results in a portion of the essential oil being dispersed and carried away by the aqueous effluent. How seriously this phenomenon effects the yield of the essential oils can be seen from Table I.

Unfortunately, the problem of water contact does not just cause a diminished yield of the oil. The solubility of low flavor and odor value terpene and sesquiterpene hydrocarbons is negligible (being at the ppm level at best); however, the solubility of desirable oxygen-containing components, such as, esters, ketones, aldehydes, alcohols, phenols, etc., often reaches levels of 0.05-1.0%.

In essential oil production, the amount of steam required for oil recovery is normally comparable to the weight of the plant material. Since commercial essential oil-bearing botanicals usually yield between 0.1% and 1.0% of the oil, the amount of aqueous effluent exceeds that of recovered oil by a hundredfold or more. Due to the different solubilities, various essential oil components are disproportionately partitioned into the aqueous phase and, hence, the valuable polar components are either reduced or lost. Because of this phenomenon, relatively soluble minor components of the oil can escape completely resulting in an unbalanced odor and flavor profile when compared with that of the original plant. Therefore, the water soluble fraction is of importance to both the quantitative and qualitative outcome of the essential oil production.

The water soluble portion of an essential oil and its inherent problem was addressed long ago,[6] and over the years numerous technological solutions have been proposed for the recovery from aqueous dispersions of the lost components. However, only the oldest method of redistillation (cohobation) is commercially available and sometimes practiced by the industry.

The process of cohobation is, in fact, distillation of a multicomponent liquid system with a limited mutual solubility. In such a system, the vapor phase (and condensate)

Table I. Ratios of Water Soluble and Decanted Fractions of Essential Oils

Essential Oil	Botanical Source	Water Soluble/ Decanted Fraction Ratio	Reference Number
Basil (Eugenol type)	*Ocimum gratissimum* L.	1:1	1
Basil (Linalool methyl/chavicol type)	*Ocimum basilicum* L.	1:3	2
Basil (Linalool eugenol type)	*Ocimum basilicum* L.	1:1	2
Geranium	*Pelargonium graveolens* Thunb.	1:3	3
Caraway	*Carum carvi* L.	1:3	4
Dittany	*Dictamnus gymnostylis* Stev.	1:2	5
Hyssop	*Hyssopus cretaceous* Dub.	1:2	5

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always contain a higher proportion of least soluble components. Depending on the nature of the oil, 15-50% of the aqueous effluent must be distilled to allow recovery.[1] It must be emphasized that vaporization of more water soluble essential oil components requires the distillation of a larger quantity of the aqueous phase. This, in turn, causes a high degree of dissolution in the newly formed condensate.

Literature sources agree that cohobation leads to only partial and disproportional recovery of oil constituents.[1,7] In addition, prolonged heating of essential oil in the presence of water, undoubtedly results in various chemical changes and degradations. The resulting "cohobated oil" often exhibits an altered and inferior organoleptic profile.

Very little information can be found in the literature covering the study of the water soluble essential oil fractions. Everybody agrees that the cohobated oil contains a higher proportion of oxygenated components and that it should not be blended with decanted oil. Apparently, the low reputation of cohobated oils and the lack of a reliable and cost-effective method for oil recovery from the aqueous phase has obscured this aspect of essential oil production.

It is a clear desire of the manufacturer and user of natural aroma materials to produce and utilize a product which is as true to nature as possible. Our quality standard, in this case, is the smell of a flower, the aroma of a crushed leaf, or a freshly squeezed fruit. To achieve this, it is necessary to recover the full complement of aroma determining chemicals. In our opinion, the losses of essential oil components into the aqueous phase during distillation remains one of the major obstacles in reaching this goal.

Table II. Chemical Composition of the Water Soluble Fraction of Cedarleaf Oil

Constituent	%
3-pentanone	0.11
n-hexanol	0.07
3-methylethyl butyrate	0.04
fenchone	26.22
α-thujone	34.36
β-thujone	4.44
cis-linalool oxide (furanoid)	0.06
trans-linalool oxide (furanoid)	0.03
camphor	7.11
linalool	0.23
bornyl acetate	0.57
terpinen-4-ol	11.80
sabina ketone	0.41
α-terpineol	3.76
α-terpinyl acetate	0.31
borneol	1.01
verbenone	0.23
piperitone	0.25
carvone	0.22
geranyl acetate	0.11
myrtenol	0.11
trans-carveol	0.46
p-cymen-8-ol	0.11
cis-carveol	0.01
p-mentha-1,4-dien-7-ol	t
thymol	0.23

t = trace

Several years ago, the extraction method for oil recovery from distillate waters was developed in the University of Leningrad.[8,9] This method—the "poroplast extraction technique"—is based on partition chromatography with a number of modifications which make it suitable for low-cost, high efficiency commercial recovery of the essential oils from aqueous dispersions. A detailed description of the poroplast extraction technique was presented in the previous publications.[10,11]

The present work was motivated by our interest to revitalize and rehabilitate the subject of water soluble fractions of the essential oils, and to start a systematic study of this field.

The chemical composition of water soluble fractions of cedar leaf (*Thuja occidentalis*), peppermint (*Mentha piperita*), geranium (*Pelargonium graveolens*), and fir needle (*Abies balsamea*) essential oils are presented in Tables II, III, IV and V respectively.

For comparison purposes, Table V also contains the composition of a hydrocarbon-free fraction prepared from decanted fir needle essential oil.

Table III. Chemical Composition of the Water Soluble Fraction of Peppermint Oil

Constituent	%
dimethyl sulphide	0.08
isobutyraldehyde	0.24
valeraldehyde	2.48
2-ethyl furan	0.03
2,5-diethyltetrahydrofuran	0.07
isobutyl alcohol	0.05
n-hexanal	0.15
tiglic aldehyde	0.04
trans-2-pentenal	t
isoamyl alcohol	0.09
1,8-cineole	15.66
trans-2-hexenal	0.49
n-amyl alcohol	t
p-cymene	0.02
4-heptanol	t
isoamyl isovalerate	t
2-heptanol	t
2-penten-1-ol	0.34
3-methyl cyclohexanone	0.31
n-hexanol	0.30
cis-3-hexanol	0.69
3-octanol	0.40
trans-2-hexenol	0.41
1-octen-3-ol	0.23
menthone	16.63
isomenthone	4.66
benzaldehyde	0.19
linalool	0.44
isopinocamphone	0.09
terpinen-1-ol	0.33
menthyl acetate	0.17
isopulegol	0.35
isopulegone	0.08
terpinen-4-ol	0.14
neomenthol	6.21
trans-dihydrocarvone	0.09
neoisomenthol	2.22
menthol	36.67
pulegone	0.53
α-terpineol	0.72
borneol	0.08
piperitone	1.40
dihydrocarveol	0.02
methyl salicylate	t
myrtenol	t
trans-carveol	t
cis-carveol	0.04
benzyl alcohol	t
phenylethyl alcohol	t
piperitenone	0.07
cis-jasmone	0.07
anisaldehyde	0.16
thymol	t
eugenol	0.10
carvacrol	t
veratraldehyde	t

t = trace

Table IV. Chemical Composition of the Water Soluble Fraction of Geranium Oil

Constituent	%
acetone	0.85
ethanol	3.22
2-butanone	1.11
1-penten-3-ol	0.13
1,8-cineole	0.21
cis-3-hexenyl acetate	0.25
n-hexanol	0.16
cis-3-hexenol	1.12
cis-rose oxide	1.58
trans-2-hexenol	0.15
trans-rose oxide	1.58
cis-linalool oxide (furanoid)	0.36
trans-linalool oxide (furanoid)	0.14
menthone	0.25
isomenthone	11.35
linalool	9.44
citronellyl formate	0.63
menthol	0.54
terpinen-4-ol	0.31
α-terpineol	1.20
neral	0.78
citronellyl propionate	0.04
citronellol	42.44
geranyl acetate	t
geranial	1.36
piperitone	0.28
geraniol	19.38
geranyl propionate	0.07
phenylethyl propionate	0.03
phenylethyl tiglate	0.13

t = trace

In these cases, the yield of water soluble fractions of the essential oils was between 15-30% based upon a respective amount of a decanted fraction. Obviously, it is very important to increase the yield of the oil and the content of the main constituents. However, when similar materials are being compared, what determines the richness and fullness of the organoleptic profile are the contributions of the minor components. Therefore, the complete recovery of minor constituents is of ultimate importance. In this respect, the value of water soluble fractions is difficult to overestimate. It can be seen from the data that the water soluble fractions contain very little, if any, hydrocarbons, but are rich in oxygenated components, especially the minor low boiling ones. In many cases, these components can be seen only in the water soluble fraction of the essential oil. Among other components, attention must be paid to the C_6 aldehydes and alcohols, which are well known to provide fresh green character to aroma compositions. Under normal essential oil production conditions, these organoleptically powerful chemicals are almost completely lost into the aqueous phase.

Of the four essential oils studied in this work, the fir needle oil is the least known one; therefore, we paid special

Table V. Chemical Composition of Decanted, Water Soluble and Hydrocarbon Free Fractions of Fir Needle Oil

Constituent	Decanted Oil	Water Soluble Fraction	Hydrocarbon Free Fraction
santene	1.62%	-	-
tricyclene	1.23	-	-
α-pinene	13.06	0.04%	-
camphene	5.56	0.01	-
n-hexanal*	-	0.06	0.02%
1,4-cineole*	-	0.09	t
β-pinene	31.62	-	0.02
sabinene	1.64	-	-
δ-3-carene	14.08	-	-
myrcene	1.76	-	-
α-phellandrene	0.18	-	-
α-terpinene	0.21	-	-
limonene	6.43	0.11	0.02
1,8-cineole	0.11	0.10	0.11
hexyl butyrate*	-	-	0.03
cis-3-hexenol*	-	0.87	0.03
β-phellandrene	6.08	-	-
γ-terpinene	0.36	-	-
para-cymene	0.07	-	-
terpinolene	1.09	-	-
cis-3-hexenyl acetate*	0.05	t	t
fenchone*	0.08	0.94	1.03
α-thujone*	0.05	1.08	0.44
cis-linalool oxide (furanoid)*	-	0.37	t
β-thujone*	t	0.38	0.10
trans-sabinene hydrate*	t	0.24	0.07
trans-linalool oxide (furanoid)*	-	0.32	-
citronellal*	-	0.04	t
α-copaene*	0.02	-	-
campholenic aldehyde*	t	0.05	0.26
camphor	0.32	3.62	3.83
benzaldehyde*	t	0.18	t
linalool	0.19	0.42	1.08
bornyl acetate	7.03	6.46	67.10
terpinen-4-ol	0.28	10.15	2.55
β-caryophyllene	0.15	-	t
myrtenal*	0.10	2.34	0.65
isoborneol*	-	0.14	0.05
α-terpineol*	0.72	51.80	6.65
borneol	0.65	3.91	6.06
verbenone*	-	0.30	0.08
piperitone	0.25	3.14	2.89
carvone*	-	0.27	1.91
citronellol*	-	0.40	0.25
myrtenol*	0.03	0.43	0.04
a carveol	-	0.05	0.02
maltol	t	0.44	t
methyl eugenol*	0.02	0.11	0.09
nerolidol*	-	t	0.18
thymol	0.07	0.68	0.76

* Newly identified constituents
t = trace

attention to the detailed investigation of this oil.

From the data in Table V, it can be seen that out of the 33 oxygenated components identified in fir needle oil, 19 were either completely absent from the decanted oil or present only in trace amounts. On the contrary, their concentration in the water soluble fraction is easily noticeable. Within this fraction, cis-3-hexenol, benzaldehyde, verbenone, maltol and nerolidol, compounds whose impact on an organoleptic profile is highly pronounced, can be found. It should be added that with the exception of bornyl acetate, the rest of

the oxygenated components are concentrated in the water soluble fraction.

It is well known that monoterpene and sesquiterpene hydrocarbons contribute very little to the organoleptic character of an essential oil. In many cases, their presence creates a serious application difficulty in fragrance and flavor products. From Table V, it can be seen that both hydrocarbon-free and water soluble fractions contain essentially the same components. Although the relative proportion of various constituents in water soluble and hydrocarbon-free fractions is extremely different, it must be emphasized that only from a combination of the two fractions can a close replica of the natural fir aroma be achieved.

The yield of a hydrocarbon-free fraction of the fir needle oil is approximately 10%, while the yield of water soluble fractions is 15%. This means that under normal production conditions, for each pound of organoleptically valuable fraction produced, 1.5 pounds is dumped down the drain.

It seems to us that the recovery of the water soluble fractions for any essential oil is advantageous; however, it is of utmost importance for oils containing mainly hydrocarbons or oils possessing components of high water solubility.

The water soluble fractions of several other essential oils are currently under study and the results will be reported at a later date.

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