Distributions of Origanum-Oil Components in Oil and Sub/Supercritical Carbon Dioxide Phases

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The relative equilibrium distributions of origanum-oil *(Origanum Munituflorum)* components in the oil and sub/supercritical CO_2 phases are determined for 24 characteristic components at 35, 45, 55°C and within the 20–110 atm pressure range. The relative distributions of terpene hydrocarbons are the most sensitives to changes in temperature and pressure, and their relatively small molecules and high volatilities make them more soluble in the dense CO_2, especially in the supercritical region. At low temperatures, almost all components, except *limonene* and *carvacrol*, show similar relative distributions in the CO_2 and oil phases. At higher temperatures, deterpenation, i.e., the separation of the terpene portion, in the CO_2 phase is more favorable.

Introduction

Origanum oil and its fractions find use in industries such as pharmaceutical and food. As in other essential oils, many of the large numbers of origanum-oil components are heat-sensitive. Conventional methods like hydro or steam distillation may cause product degradation because of the high temperatures they employ. Thus, supercritical fractionation is considered to be the most advantageous method for the rectification and purification of higher-value oil fractions for industrial use. In the present study, the relative distributions of origanum-oil components in the oil and sub/supercritical CO_2 equilibrium phases with respect to the original oil feed are investigated to establish a basis for supercritical fractionation of origanum oil.

Experimental

The equilibrium cell and the constant-temperature agitation mechanism used in this study were basically those reported in [1,2]. Samples from both the liquid and sub/supercritical CO_2 phases were trapped in *T*-shaped enclosures equipped with three high-pressure on-off valves. In all experiments 15 ml of origanum oil was used. CO_2 was pumped into the cell, already at the desired temperature, until the desired pressure were attained. The agitation/equilibration and phase-separation periods were 90 min each. Entrained oils in the sampling-*T* were captured in refrigerated sampling bottles containing ethanol (1 ml for gas and 2 ml for liquid samples). After capturing the free oil in the sampling bottle during the initial CO_2 release from the sampling-*T*, some ethanol (2.5 ml for gas- and 4.5 ml for oil-phase samples) was used to recover the remaining oil in the sampling-*T*.

Analyses of the original origanum oil and the experimental samples were done [2] using a GC (HP 5890 Series II, FID, Innowax capillary column). Identification of the components was carried out [2] using a GC/MSD (HP 5971, Innowax capillary column). A full chromatogram of the original oil yielded about 60 components, 24 of which accounted for about 95% by weight of the oil. A total of 25 experiments, including six to check reproducibility, were performed at 35, 45, 55°C, within the 20–110 atm pressure range.

Results and Discussion

The normalized area per cents for each component in the original feed, C_i^o, and in samples, $C^*_{z,i}(T,P)$, were used to calculate the dense gas (*y*) and liquid (*x*) phase CO_2-free relative-distribution coefficients, defined as:

$$R_{z,i} = C^*_{z,i} \Big/ C^o_i \qquad i = 1,...,n\ (n \neq CO_2) \qquad (1)$$

for each phase separately ($z = y$ or x), with respect to the original oil. For example, the $R_{y,i} > 1$ means that the component concentration is more in the oil obtained from the CO_2 phase than in the feed. The $R_{y,i}$ and $R_{x,i}$ values for each of the 24 components determined in 25 experiments are given in [2]. In this short note, only the $R_{y,i}$ behaviors of different components at various experimental conditions will be discussed with possible supercritical fractionation in mind.

Table 1 summarizes the grouping of the origanum-oil components [3]. It is evident in Figures 1–3 that, depending upon the experimental T and P, the R_y values of some components are quite different from those of others, whereas some components have R_y values very close to each other. In other words, some of the oil components are identifiable on a component basis, whereas others seem to group together. In Figures 1-3 the numerals on points denote to pure components, whereas the ellipses with a *G* notation denote to group of components exhibiting very close R_y values. Tables 2–4 identify the components and the component groups in Figures 1-3. The components grouping together should not always be taken here as components with similar chemical structures, since no such correlation is clearly evident in all cases. Furthermore, a more useful interpretation of the R_y data given may be made if it is noticed that most of the components and groups lie in the range $0 < R_y < 2$ or 3, and only a few components are seen with R_y values between 2 and 8, 12, or 25, depending upon the experimental conditions. Grouping is needed when the

points are close to each other, and an easy separation seems to be impossible.

Studying the figures and tables in somewhat more detail, one can see that points *1–6*, and *11* and *14* denote *limonene*. This indicates that this component has high solubility in dense gas, especially under subcritical conditions. The points *7–10* on Fig.1 refer to *carvacrol*, indicating that *carvacrol* can also be recovered together with *limonene* as a fraction at this temperature and at pressures up to 60 atm; in the subcritical region. Remaining components are not separable throughout the pressure range, even if the scale is magnified. At 60 atm, a fraction rich in *p-cymene* and *carvacrol* can be obtained, since they have a slightly higher R_y value as compared to the other constituents. Further increase in pressure can not be used for any increased separation, because at about 100 atm R_y values of the components are so close to each other that they are grouped in one ellipse, *G9* (Fig.1).

Referring to Fig.2 and Table 4, the points and the groups demonstrate that at 45°C a more effective fractionation can be carried out. Especially in the 60–90 atm pressure region, some terpene fractions composed of *p-cymene* and *limonene* can be recovered. However, further processing may not result in any more separation.

At 55°C, Fig.3, separations may be easily observed among the groups. The obvious result at 55°C is that the aromatic component *butyl-benzene* could be separated as a near-pure component at this temperature at all pressures in the CO_2 phase; this result may not be of practical importance since the composition of this component in the original feed is very low. In the subcritical region, especially between 30–40 atm, deterpenation of the origanum oil is possible. In this region, all the terpene fraction of the oil can be separated. The remaining portion, i.e., *G31* and *G33*, is composed of alcohols, *thymol* and some higher-molecular-weight components. At 60 atm, the terpene fraction of *G32* and *G30* at 30 atm and 40 atm, split into two groups, *G34* and *G35*. *G34* is composed entirely of terpenes. *G35* still carries some *carvacrol* in addition to terpenes. At this pressure (60 atm), points *29*, *30*, and *31* on Fig.3 denote the high tendency of monoterpenes to dissolve in the dense gas. In the supercritical region, the groups of components are more observable. Terpenes, *α-pinene*, *camphene*, *β-myrcene* and *p-cymene* may be obtained as an upper fraction in *G37* and *G41*. In the 80–90 atm region, the terpenes appear as two groups and the lower group includes *carvacrol* with *limonene* and *α-terpinolene*. At pressures more than 100 atm, most of the terpenes are contained in *G42* and *carvacrol* is more isolated at a lower R_y value. However, the recovery of *carvacrol* from the gas phase is not practical, because at this pressure R_y is less than one; indicating that *carvacrol* will preferentially remain in the liquid phase with the remaining alcohol and sesquiterpene portions; *G44*. The possible fractionation of origanum oil at this temperature and above the critical pressure would provide effective deterpenation of the oil. The remaining part which would be rich in oxygenated components like alcohols and phenolics *(carvacrol* and *thymol)* will have the essential odor and properties of the origanum oil. It should be noted that the results shown here are for the mixtures as shown and that the R_y values may possibly change considerably when stepwise separation of some components in appreciable quantities take place; as they would in a fractionation column.

Conclusions

The results obtained are informative towards the design of a supercritical fractionation equipment operating at the conditions of the experiments. Especially, at supercritical pressures and around 55°C, effective separation of the terpene fraction may be achieved and the remaining product may be rich in heavier-molecular-weight sesquiterpenes, alcohols and phenolics. The phenolic content of the origanum oil which is the most valuable part of the oil from the pharmaceutical point of view, is mostly recoverable in the liquid-phase samples. The relative distributions in the gas phase are usually low as compared to the terpene fraction of the oil. An exception is that at 35°C and at subcritical pressures, *carvacrol* may be obtained in the gas phase together with *limonene*. As the temperature is raised to 55°C, a decline in the relative distribution of this component in the gas phase is observed. The R_y value for *carvacrol* is near to, but less than one, showing that *carvacrol* preferentially remains in the liquid phase. Thus, a deterpenated, *carvacrol*-rich fraction may be obtained from the origanum oil. The remaining components may be further extracted for the recovery of the phenolic content.

Acknowledgment

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Table 1. Grouping of the origanum-oil components. (MT: Monoterpene, ST: Sesquiterpene, AL: Alcohol, OX: Oxygenated, PH: Phenolic)

Components	%	MT	ST	AL	OX	PH
α-pinene	4.20	▮				
camphene	1.28	▮				
β-pinene	0.48	▮				
butyl-benzene	0.04				▮	
δ-3-carene	0.15	▮				
β-myrcene	2.31	▮				
α-terpinene	2.79	▮				
limonene	0.69	▮				
1-8-cineole	1.07				▮	
γ-terpinene	11.8	▮				
p-cymene	12.5	▮				
α-terpinolene	0.40	▮				
3-octanol	0.15			▮		
1-octen-3-ol	0.91			▮		
terpinen-4-ol	1.32	▮				
linalool	2.45			▮		
t-caryophyllene	7.97		▮			
aromadendrene	0.58		▮			
α-humulene	0.32		▮			
α-terpineol	0.79			▮		
endo-borneol	4.84			▮		
spathulenol	0.44			▮		
thymol	1.32					▮
carvacrol	41.2					▮

Table 2. Pure-component numbers of the origanum-oil components in Figures 1–3.

Components	Figure 1	Figure 2	Figure 3
limonene	1–6	11,14	
carvacrol	7–10		26
β-pinene		12	
3-octanol		13	
butyl-benzene		15,17	18–25
camphene		16	
p-cymene			27,31
γ-terpinene			28
δ-3-carene			29
β-myrcene			30

Table 3. Component groups in Figure 1 (35°C).

Components	*G 1*	*G 2*	*G 3*	*G 4*	*G 5*	*G 6*	*G 7*	*G 8*	*G 9*
α-pinene	▮	▮	▮	▮		▮	▮		▮
camphene	▮	▮	▮	▮		▮	▮		▮
β-pinene	▮	▮	▮	▮		▮	▮		▮
butyl-benzene	▮	▮	▮	▮		▮	▮		▮
δ-3-carene	▮	▮	▮	▮		▮	▮		▮
β-myrcene	▮	▮	▮	▮		▮	▮		▮
α-terpinene	▮	▮	▮	▮		▮	▮		▮
limonene								▮	▮
1-8-cineole	▮	▮	▮	▮		▮	▮		▮
γ-terpinene	▮	▮	▮	▮		▮	▮		▮
p-cymene	▮	▮	▮	▮	▮	▮	▮		▮
α-terpinolene	▮	▮	▮	▮		▮	▮		▮
3-octanol	▮	▮	▮	▮		▮	▮		▮
1-octen-3-ol	▮	▮	▮	▮		▮	▮		▮
terpinen-4-ol	▮	▮	▮	▮		▮	▮		▮
linalool	▮	▮	▮	▮		▮	▮		▮
t-caryophyllene	▮	▮	▮	▮		▮	▮		▮
aromadendrene	▮	▮	▮	▮		▮	▮		▮
α-humulene	▮	▮	▮	▮		▮	▮		▮
α-terpineol	▮	▮	▮	▮		▮	▮		▮
endo-borneol	▮	▮	▮	▮		▮	▮		▮
spathulenol	▮	▮	▮	▮		▮	▮		▮
thymol	▮	▮	▮	▮		▮	▮		▮
carvacrol					▮	▮	▮		▮

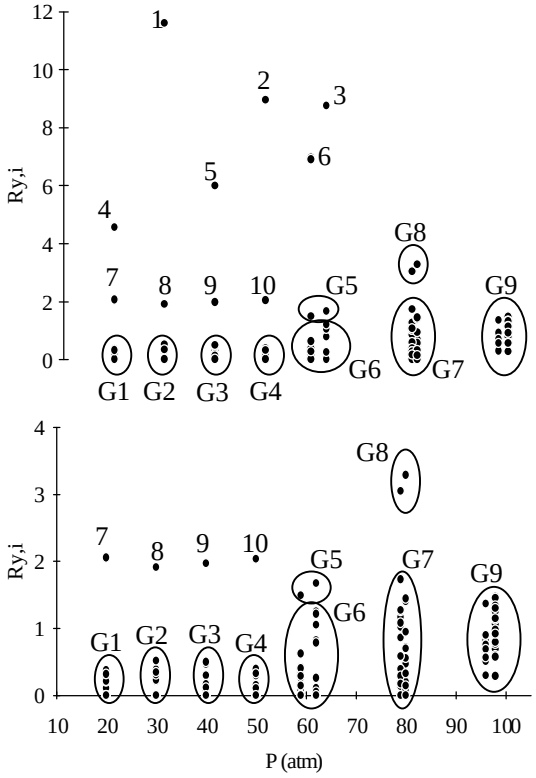


Figure 1. Relative distributions at 35°C.

References

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Table 4. Component groups in Figure 2 (45°C) and Figure 3 (55°C).

Component	Groups in Figure 2 (45°C)										Groups in Figure 3 (55°C)																	
	G 10	G 11	G12			G13		G 14	G 15	G 16	G22		G23		G24		G25			G26				G27			
			G 17	G 18	G 19	G 20	G 21				G 28	G 29	G 30	G 31	G 32	G 33	G 34	G 35	G 36	G 37	G 38	G 39	G 40	G 41	G 42	G 43	G 44
α-pinene	▮	▮	▮			▮			▮	▮		▮	▮		▮				▮	▮				▮			
camphene	▮	▮	▮			▮			▮			▮	▮		▮		▮			▮				▮			
β-pinene		▮	▮			▮			▮			▮	▮		▮			▮			▮				▮		
butyl-benzene	▮				▮			▮		▮		▮															
δ-3-carene	▮	▮	▮			▮			▮	▮	▮		▮			▮					▮				▮		
β-myrcene	▮	▮	▮			▮			▮	▮		▮	▮		▮						▮			▮			
α-terpinene	▮	▮	▮			▮			▮	▮	▮		▮		▮		▮				▮				▮		
limonene					▮		▮		▮			▮	▮		▮		▮					▮			▮		
1-8-cineole	▮	▮	▮			▮			▮	▮		▮		▮		▮			▮				▮				▮
γ-terpinene	▮	▮		▮		▮			▮	▮	▮				▮		▮				▮				▮		
p-cymene	▮	▮		▮			▮		▮	▮	▮				▮					▮				▮			
α-terpinolene	▮	▮	▮			▮			▮	▮	▮		▮		▮			▮				▮			▮		
3-octanol		▮	▮			▮			▮			▮		▮		▮		▮					▮				▮
1-octen-3-ol	▮	▮	▮			▮			▮	▮		▮		▮		▮			▮				▮				▮
terpinen-4-ol	▮	▮	▮			▮			▮	▮		▮		▮		▮			▮				▮				▮
linalool	▮	▮	▮			▮			▮	▮		▮		▮		▮			▮				▮				▮
t-caryophyllene	▮	▮	▮			▮			▮	▮		▮	▮		▮				▮				▮				▮
aromadendrene	▮	▮	▮			▮			▮	▮		▮		▮		▮			▮				▮				▮
α-humulene	▮	▮	▮			▮			▮	▮		▮		▮		▮			▮				▮				▮
α-terpineol	▮	▮	▮			▮			▮	▮		▮		▮		▮			▮				▮				▮
endo-borneol	▮	▮	▮			▮			▮	▮		▮		▮		▮			▮				▮				▮
spathulenol	▮	▮	▮			▮			▮	▮		▮		▮		▮			▮				▮				▮
thymol	▮	▮	▮			▮			▮	▮		▮		▮		▮			▮				▮				▮
carvacrol	▮	▮	▮		▮	▮			▮	▮			▮		▮			▮				▮				▮		

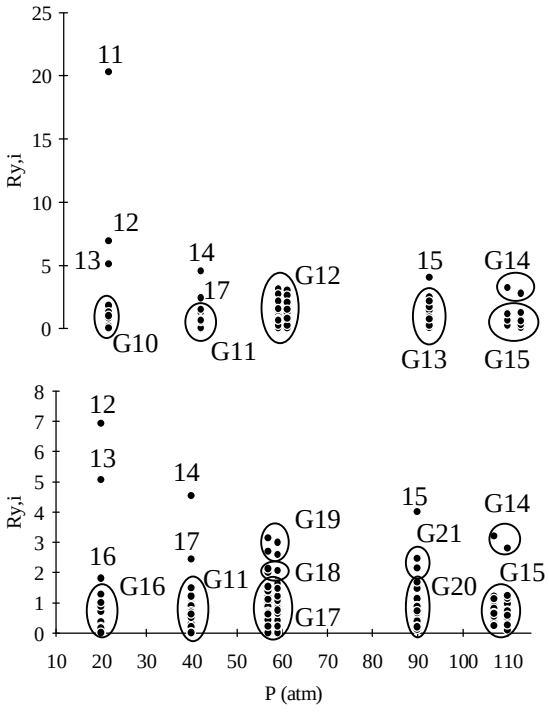


Figure 2. Relative distributions at 45°C.

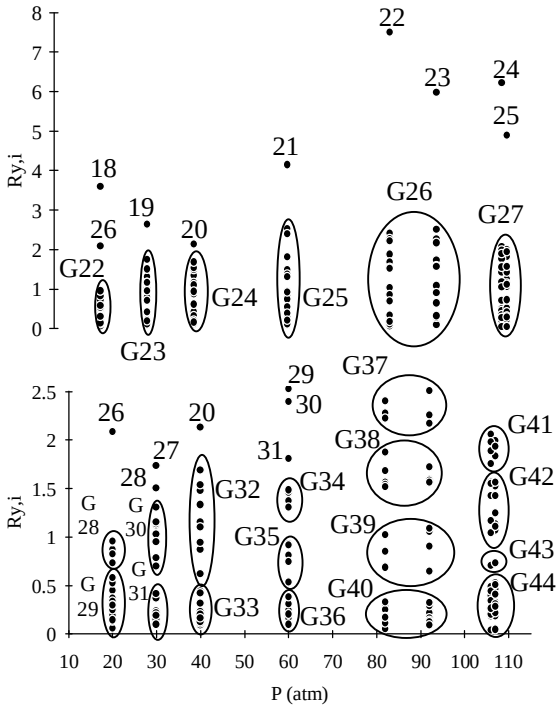


Figure 3. Relative distributions at 55°C.