Equilibrium Distributions of Key Components of Spearmint Oil in Sub/Supercritical Carbon Dioxide

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Effects of temperature (at 35, 45 or 55°C) and pressure (10–110 atm) on the relative distribution coefficients of the twelve key components of spearmint oil (essential oil of *Mentha cardiaca*; Scotch spearmint) at equilibrium in dense CO_2 were investigated under conditions ranging from subcritical to supercritical regions. Effects of vapor pressure, molecular weight and polarity of the key components on their equilibrium distributions in sub/supercritical CO_2 are discussed. At 35°C, all key components of spearmint oil are equally soluble in dense CO_2 within the 12–102 atm pressure region. At 45 and 55°C, the key components are equally soluble for pressures greater than about 60 atm. However, around either 45°C/27 atm or 55°C/35 atm conditions, the relative distribution coefficients of all monoterpene hydrocarbons and of isomenthone (an oxygenated monoterpene) exhibit maxima, which are due to significantly higher vapor pressures of these components and significantly lower solvating power of the dense-gas solvent at these particular temperatures and pressures. Vapor-pressure effects, coupled with the decrease in solvating power, dominate the effects of polarity and molecular mass of the key components. Deterpenation of spearmint oil with dense CO_2 is possible around either 45°C/27 atm or 55°C/35 atm, where the monoterpene hydrocarbons tend to concentrate in the CO_2-rich phase.

KEY WORDS: Solubility, spearmint oil, sub/supercritical CO_2.

Essential oils are the volatile oils derived from plants. They are mixtures of organic compounds that carry the essential odor and the flavor of the parent plant. Essential oils are important raw materials in food, pharmaceutical, cosmetics and related industries. Therefore, extraction of essential oils from plants, and isolation and concentration of their valuable compounds/fractions, are of industrial importance.

Essential oils are separated from the cellular structure of various plants *via* a number of conventional methods. Among these methods are hydro-/steam-distillation, expression, enfleurage, adsorption and liquid–solvent extraction (1). These conventional separation techniques, as well as ensuing operations performed on raw essential oils for the purpose of isolation and concentration of desired compounds/fractions, have some important disadvantages (e.g., high operating temperatures and/or the use of possibly toxic liquid solvents) that impair product quality.

As an attractive alternative to such conventional techniques, supercritical fluid-aided extraction of essential oils from plants and their fractionation into desired products have received great interest (2,3). Advantageous properties of supercritical fluids (particularly those of supercritical CO_2), which make them favorable solvents especially for essential-oil applications, are well-known (2,4,5). Supercritical CO_2 with its low critical temperature (31°C) and moderate critical pressure (73 atm) is an exceptional nontoxic solvent, which permits extraction and fractionation operations on gentle essential oils to be carried out at mild conditions.

Experimental results prove the technical feasibility of supercritical fluid-aided extraction of essential oils from plants and fractionation of essential-oil extracts into desired products (e.g., deterpenation). For successful design, operation and optimization of such supercritical fluid-aided operations, it is necessary to know the phase behavior of the essential-oil/supercritical-solvent system over a wide range of operating conditions. Solubilities of several characteristic essential-oil compounds (e.g., limonene, citral, caryophyllene, eugenol) in supercritical CO_2 can be found in the literature (2,6). Most of the available solubility data, however, for the binaries of the characteristic essential-oil compounds (e.g., limonene–citral–CO_2 phase-equilibrium). Being complex multicomponent mixtures, phase behavior of essential oils is affected by both solute–solute and solute–solvent interactions. Typical essential oil extracts obtained from plants contain over 100 components; 10–20 of which constitute the bulk and thus characterize the essential oil. Undoubtedly, solubility of an isolated single essential-oil component in a supercritical fluid would be different from its solubility in the presence of other components of the essential oil due to solute–solute interactions. For the success of future industrial applications of supercritical-fluid technology to essential-oil extraction and processing, knowledge on the relative distributions of at least the key components of essential oils in supercritical solvents is more valuable than knowledge on the solubility of an isolated single essential-oil compound (selectivity information is as important as solubility information).

In this study, the effects of temperature and pressure on relative distribution of the twelve key components of spearmint oil (essential oil of *Mentha cardiaca*; Scotch spearmint) at equilibrium in both subcritical and supercritical CO_2 are investigated. The effects of various physicochemical properties (molecular weight, vapor pressure, polarity) of the key components on their equilibrium distributions in sub/supercritical CO_2 are also discussed.

EXPERIMENTAL PROCEDURES

The equilibrium cell used in this study (7) (Fig. 1) was a bolted closure-type (six cap screws) high-pressure vessel manufactured from 316 stainless steel. The cell had an effective volume of 255.5 cm^3 (12 cm height, 6 cm i.d., 8 cm o.d.). Sealing of the cell was provided by an O-ring gasket made of Teflon. The sampling system consisted of a high-pressure on–off valve (V-1) with 1/4" i.d. and two high-pressure flow-regulating valves (V-2 and V-3) with 1/8" i.d. The valves were connected to each other (4.5 cm between V-1 and V-3) and to the body of the equilibrium cell (5 cm between V-1 and the cell body) with stainless-steel tubing of 0.4 cm i.d. The pressure of the cell was monitored within ±1 atm accuracy by a pressure gauge connected to the tubing between the cell body and the valve V-1.

At the beginning of each experiment, 15 cm^3 of Scotch spearmint oil (essential oil of *M. cardiaca*) was put into the equilibrium cell. Depending on desired pressure, the cell was then packed with a predetermined amount

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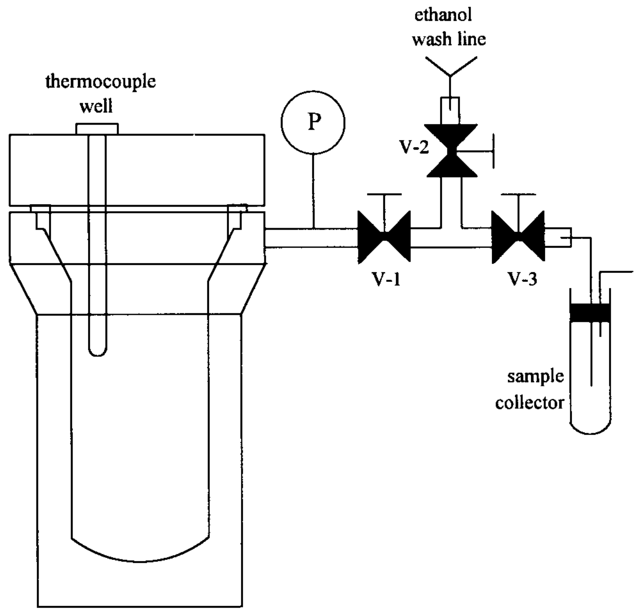

FIG. 1. Equilibrium cell and sampling system with valves V-1, V-2, V-3.

(90–250 g) of crushed dry ice (manufactured from 99.9% CO_2). The lid of the cell was closed quickly, and the cell was placed on a cradle in a water bath, which was being maintained at the preset temperature within ±1°C. Thorough mixing of the cell contents was provided through motor-driven horizontal movements of the cradle in the water. The temperature of the cell contents was continuously measured by a thermocouple within ±0.1°C. As the cell temperature approached the preset temperature of the water bath, the cell pressure also increased to desired level (it took about 15 min to reach thermal equilibrium). Mixing of the cell contents through horizontal movements of the cradle was continued for 90 min to ensure that thermodynamic equilibrium between the essential oil and CO_2 phases was attained (preliminary test runs showed that at least 60 min of equilibration time was necessary for the system to reach thermodynamic equilibrium). At the end of the equilibration time, the movement of the cradle was ceased, and they system was allowed to stay still at equilibrium conditions for an additional 90 min to eliminate the possibility of essential oil entrainment within the gas phase.

During sampling, the valve V-1 was quickly opened and closed to trap a sample of the gas phase within the space between vales V-1, V-2 and V-3 without significantly disturbing the equilibrium. After taking the cell out of the water bath, a glass test tube as a sample collector was attached to the outlet of valve V-3. Valve V-3 was then opened slowly, and CO_2 was released out of the space between valves V-1, V-2 and V-3 and was vented to atmosphere through the exit of the sample collector. Ethyl alcohol (1 cc) was then injected through valve V-2 to wash out the essential oil, which had precipitated within the sampling system during depressurization. In each experiment, about 1.5 cm^3 of sample (ethyl alcohol plus essential oil) was collected in the sample collector. Variations in the results of the experiments performed with two different sample collector temperatures (15 and 0°C) were not significant and were within the overall experimental error.

Sets of experiments were also performed by mixing 1 and 3 cm^3 ethyl alcohol as entrainer with 15 cm^3 of the original spearmint oil. However, within the overall experimental error, no significant effect of the addition of ethyl alcohol as a polar entrainer was observed.

At the end of each experiment, analyses of the oil–ethanol mixtures collected in the sample collector were carried out with 1-μL samples in a gas chromatograph [HP5890 Series II (Hewlett-Packard, Palo Alto, CA); FID detector at 250°C; Carbowax 20 M capillary column (Hewlett-Packard); 30 m × 0.25 cm × 0.25 μ; carrier gas: N_2 at 1 cm^3/min rate and 1:100 split; temperature programming: 8 min at 70°C, 8°C/min to 130°C, 1 min at 130°C, 3°C/min to 190°C, 1 min at 190°C, 8°C/min to 220°C, 10 min at 220°C]. Spearmint oil, originally charged to the equilibrium cell, was also analyzed in the same way at the beginning of each experiment. Chromatograms of the original spearmint oil showed about 150 peaks.

The key components of the spearmint oil originally charged to the equilibrium cell were identified by a gas chromatograph equipped with a mass-selective detector [HP5890 Series II (Hewlett-Packard); HP5971 MS detector at 250°C; Carbowax 20 M capillary column; 50 m × 0.32 cm × 0.30 μ; carrier gas: He at 1 cm^3/min rate and 1:50 split; temperature programming: 8 min at 70°C, 8°C/min to 130°C, 1 min at 130°C, 3°C/min to 190°C, 1 min at 190°C, 8°C/min to 250°C, 10 min at 250°C]. The characteristic twelve components (8) constituted the bulk of the spearmint oil (about 94% of the total area count of about 150 peaks belonged to the selected twelve key components).

The details of the set-up, experimental procedure, raw data, chromatographic analyses and component identification procedure were described elsewhere (7).

RESULTS AND DISCUSSION

Figure 2 shows the chromatogram of the original spearmint oil charged to the equilibrium cell at the beginning of each experiment. Table 1 gives the selected major components of the original spearmint oil and their normalized area counts. Components labeled as a,b,c,d,e,f are monoterpene hydrocarbons, components labeled as g,i,k are oxygenated monoterpenes, and components labeled as h,j,l are sesquiterpene hydrocarbons. Carvone and limonene constitute the bulk of this spearmint oil.

Practically, it is not possible to determine the actual solubility values of the key components in the CO_2-rich phase because this requires an elaborate calibration of the chromatographic analysis. However, distributions of the key components in the CO_2-rich phase, relative to those in the original spearmint oil charged to the equilibrium cell, can be determined. The relative distribution coefficient, R_i, of a key component is defined as:

$$R_i = C_i^{eq}/C_i^o \qquad [1]$$

where C_i^{eq} is the normalized concentration (normalized area count) of key component i in the sample taken from the CO_2-rich phase, and C_i^o is the normalized concentration (normalized area count) of key component i in the original spearmint oil charged to the equilibrium cell.

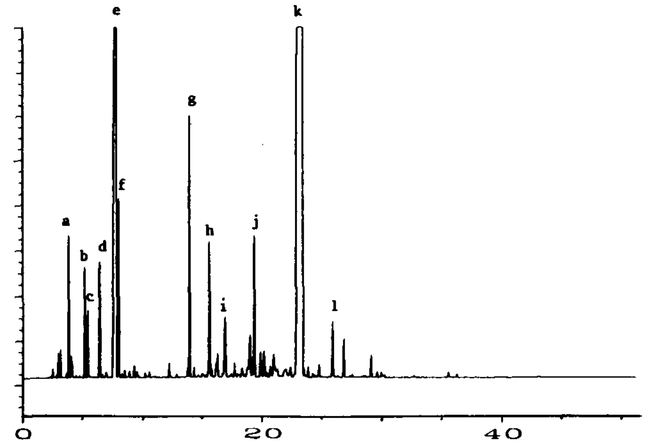

FIG. 2. Chromatogram of the original spearmint oil.

Hence, an R_i value greater than unity indicates that dense CO_2 preferentially dissolves key component *i*.

Figure 3 shows the pressure dependence of the relative distributions of the twelve key components of the spearmint oil in the CO_2-rich phase at 45°C (20–110 atm, 0.029–0.61 g/cm^3). At this temperature, CO_2 shows significant selectivity to monoterpene hydrocarbons for pressures less than about 30 atm. The relative distribution coefficients of all the monoterpene hydrocarbons attain maxima around 27 atm. This behavior may be explained as follows: Monoterpene hydrocarbons definitely possess the highest vapor pressures among the key components of the spearmint oil. This property, coupled with their lower molecular mass and lower polarity (CO_2 is a nonpolar solvent), makes them easily soluble in CO_2 (2). It is also known that vapor-pressure effects on solubility of typical essential-oil components in dense-gas solvents are revealed distinctly at pressures lower than the critical pressure of the solvent, and that the fractional contribution of the vapor pressure to solubility enhancement falls with increasing total pressure, i.e., with increasing solvating power of the solvent (2). Furthermore, solubility isotherms of various solid solutes (4) and pure essential-oil components (2) go through temperature-dependent minima within the 20–40 atm region. Hence, to the left of this minimum-solubility region, relative contribution of the vapor pressure effect falls with decreasing pressure. Therefore, being highly volatile substances, the relative distribution coefficients of the monoterpene hydrocarbons go through maxima due to the dominating effect of their high vapor pressures while the solvating power of the solvent goes through a minimum. As the effect of solvating power of the solvent increases in either direction of the minimum solubility region, the relative distribution coefficients of all the key components show an asymptotic approach to unity (equal solubility). This argument also explains the maximum in the relative distribution coefficient of isomenthone. Although isomenthone is not a monoterpene hydrocarbon (it is an oxygenated monoterpene), its vapor pressure is close to those of the monoterpene hydrocarbons. The other oxygenated monoterpenes (dihydrocarvone and carvone) and β-cadinene (sesquiterpene hydrocarbon) show minima in their relative distribution coefficients around 27 atm because their lower vapor pressures, higher polarities and higher molecular masses impair their solubility around this pressure region which corresponds to the minimum in solvating power of the solvent. Compared to other sesquiterpene hydrocarbons, the relative distribu-

TABLE 1

Key Components of Spearmint Oil

Peak identification	Component	Retention time (min)	Molecular weight	Temperature (°C) at which vapor pressure is 100 mmHg/760 mmHg	Normalized area count (%)
a	α-Pinene $C_{10}H_{16}$	3.8	136.24	90/155	0.63
b	β-Pinene $C_{10}H_{16}$	5.1	136.24	94/158	0.68
c	Sabinene $C_{10}H_{16}$	5.4	136.24	—/—	0.42
d	Myrcene $C_{10}H_{16}$	6.4	136.24	106/171	0.92
e	Limonene $C_{10}H_{16}$	7.8	136.24	108/175	18.09
f	γ-Terpinene $C_{10}H_{16}$	8.0	136.24	—/—	1.35
				Total monoterpene hydrocarbons	22.09
g	Isomenthone $C_{10}H_{18}$	13.9	154.25	138/209	1.62
i	Dihydrocarvone $C_{10}H_{16}$	16.8	152.25	—/—	0.86
k	Carvone $C_{12}H_{14}$	23.3	150.25	157/228	72.72
				Total oxygenated monoterpenes	75.20
h	β-Bourbonene $C_{15}H_{24}$	15.5	204.36	—/—	0.98
j	β-Caryophyllene $C_{15}H_{24}$	19.3	204.36	—/261	1.24
l	β-Cadinene $C_{15}H_{24}$	25.8	204.36	—/274	0.49
				Total sesquiterpene hydrocarbons	2.71

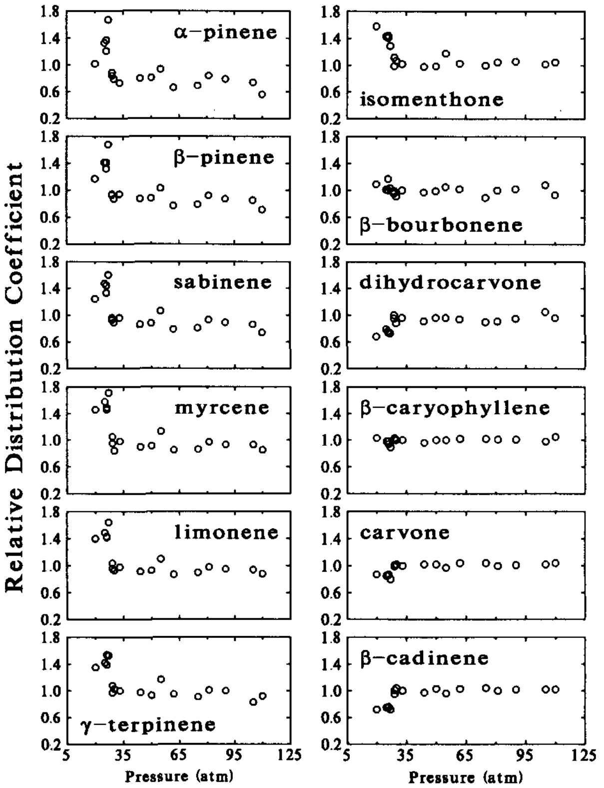

FIG. 3. Relative distributions of the key components at 45°C.

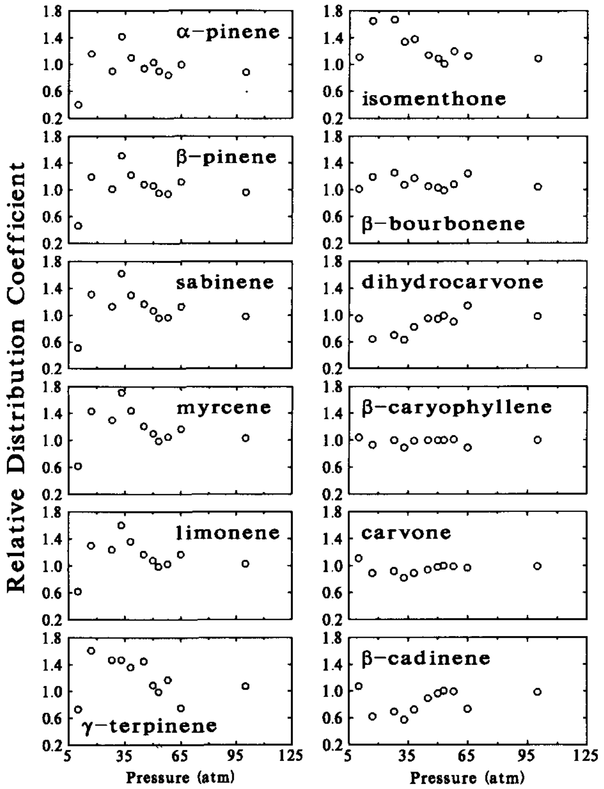

FIG. 4. Relative distributions of the key components at 35°C.

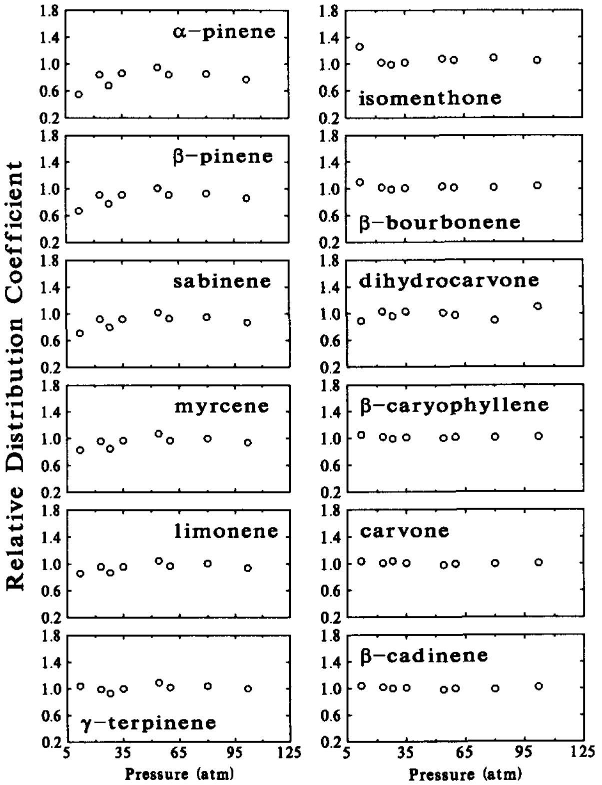

FIG. 5. Relative distributions of the key components at 55°C.

tion coefficient of β-caryophyllene does not show a significant minimum, even though it has a high molecular mass, because the vapor pressure of this substance is close to that of limonene.

Figure 4 shows the pressure dependence of the relative distributions of the twelve key components of the spearmint oil in the CO_2-rich phase at 35°C. At this temperature, all the key components are equally soluble in CO_2 (R_i vales are close to unity) within 12–102 atm pressure (0.016–0.72 g/cm^3 pure CO_2 density) region. Compared to Figure 3, no maxima in relative distribution coefficients of the monoterpene hydrocarbons are observed at low pressures because the vapor pressure of these substances drop significantly with decreasing temperature (2). Furthermore, at 35°C, the gas-phase density approaches the density of liquid CO_2 at high pressures, and it is known that liquid CO_2 dissolves essential oils and flavor substances readily (2,5,9).

Figure 5 shows the pressure dependence of the relative distributions of the twelve key components of the spearmint oil in the CO_2-rich phase at 55°C (10–100 atm, 0.012–0.34 g/cm^3). In general, the behavior is similar to that at 45°C. However, the peaks of the relative distribution coefficients of the monoterpene hydrocarbons and of isomenthone are more dilated and shifted toward higher pressure (to about 35 atm). These changes, which occurred with increase in temperature, also corroborate the validity of the argument based on the relative effects of vapor pressure of the key components and the decrease in solvating power of the solvent because, as temperature increases, minima in solubility isotherms of various solid solutes (4) and pure essential-oil components (2) occur at slightly higher pressures with a higher degree of dilation.

TABLE 2

Comparison of Spearmint Oil Compositions

		Normalized area count (%)		
Peak identification	Component	Original spearmint oil	Oil recovered in the vapor phase at 45°C/27 atm	Oil recovered in the vapor phase at 55°C/35 atm
a	α-Pinene	0.63	1.05	0.90
b	β-Pinene	0.68	1.14	1.04
c	Sabinene	0.42	0.68	0.69
d	Myrcene	0.92	1.61	1.61
e	Limonene	18.09	29.86	29.26
f	γ-Terpinene	1.35	2.15	2.04
	Monoterpene hydrocarbons	22.09	36.49	35.54
g	Isomenthone	1.62	2.10	2.19
i	Dihydrocarvone	0.86	0.70	0.60
k	Carvone	72.72	58.20	59.20
	Oxygenated monoterpenes	75.20	61.00	61.99
h	β-Bourbonene	0.98	1.04	1.07
j	β-Caryophyllene	1.24	1.11	1.11
l	β-Cadinene	0.49	0.36	0.29
	Sesquiterpene hydrocarbons	2.71	2.51	2.47

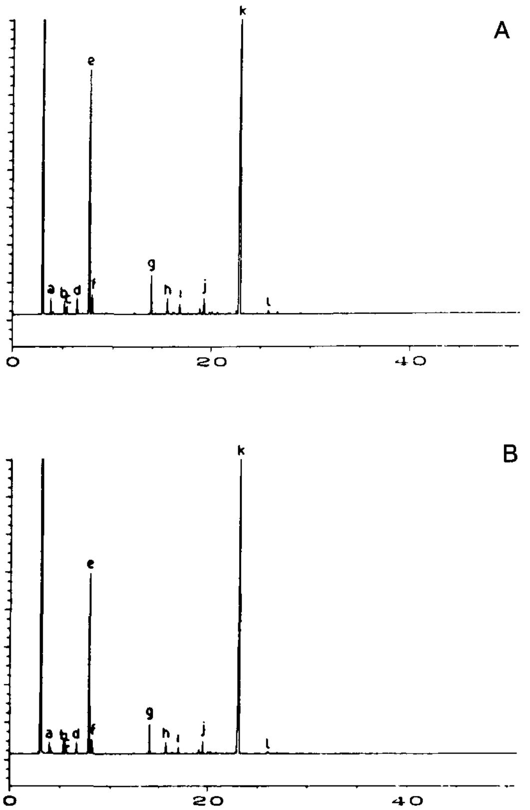

FIG. 6. (A) Chromatogram of the oil recovered in the vapor phase at 45°C/27 atm; (B) Chromatogram of the oil recovered in the vapor phase at 55°C/35 atm.

The quality of essential-oil products decreases with an increasing fraction of the monoterpene hydrocarbons. These hydrocarbons, which constitute the major part of essential oils, are unstable substances, and their decomposition products impair the quality of the essential-oil products. On the other hand, the real aroma of essential oils is due to oxygenated hydrocarbons. The results of this work show that deterpenation of spearmint oil with dense CO_2 is possible around either 45°C/27 atm or 55°C/35 atm conditions (both correspond to a pure CO_2 density of about 0.05 g/cm^3) through the preferential recovery of the monoterpene hydrocarbons in the dense-CO_2 phase. Table 2 compares the compositions of the original spearmint oil with the oils recovered in the vapor phase at 45°C/27 atm and 55°C/35 atm equilibrium conditions (Figs. 6a and 6b, respectively, show the chromatograms of the oils recovered in the vapor phase).

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