

Extraction of Peat Lipids with Supercritical Carbon Dioxide

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Waxy materials were removed from peat samples by supercritical carbon dioxide extraction and the extracts analyzed by gas chromatography. The extracts were lighter in colour and richer in lipids than those obtained by conventional neutral organic solvent extraction. In the carbon dioxide extract, however, the proportions of hydroxyalkanoic acids were much smaller. The yield of the carbon dioxide extract from 3 different peats using 20 MPa pressure at 60°C ranged from 12 to 17 mg/g dry peat. The proportion of identified lipids in the extracts was on average 80% and these lipids occurred predominantly in a free (unesterified) state. The dissolution of peat in carbon dioxide could, however, be affected by varying the pressure and temperature of extraction. The yields of supercritical extraction were only 4–32% of those obtained by conventional extraction with acetone.

Peat bitumens, which contain waxy and resinous substances, have for decades been of particular interest with regard to substitution of other natural waxes. They are traditionally isolated from peat by extraction with a neutral organic solvent.^{1–4} For example, benzene, acetone, hexane, petroleum ether, and petrol have been used. Peat extracts can be divided further into wax, resin and asphaltene fractions on the basis of their solubility characteristics. The yields of peat extracts and their fractions have been observed to be affected by many factors, such as the peat material, the extraction solvent and the extraction conditions. Methods for the determination of physical and chemical characteristics, such as melting point, density and acid and saponification numbers, of peat extracts, were established many years ago. Recently, the amount and detailed composition of the lipids in peat extracts have been determined by capillary gas chromatography and mass spectrometry.^{5–8} The main lipid classes in peat extracts are the long-chain alkanolic, hydroxyalkanoic and alkanedioic acids, alkanols and alkanes, in addition to sterols and triterpenoids.

The use of supercritical fluid extraction as a separation method has been increasing during recent years.^{9–11} Commercial applications have

been developed mainly in the food and petroleum industries. Carbon dioxide is a widely used solvent; it is well suited to the extraction of natural products and it could be an alternative to conventional peat extraction. Lipids and lipid-bearing materials have been extracted with supercritical carbon dioxide,^{12–16} but the supercritical extraction of peat has been studied to a limited extent. Peat has been extracted with pentane at

Table 1. SC-CO₂ extraction conditions in the different experiments.

Experiment No.	Mire	Moisture content of peat/ % w/w	Pressure of CO ₂ / MPa	Temperature/°C
1	Karanginneva	< 2	20	60
2	Piipsanneva	< 2	20	60
3	Kakkeriesuo	< 2	20	60
4	Karanginneva	20	20	60
5	– " –	45	20	60
6	– " –	20	20	40
7	– " –	20	20	80
8	– " –	20	50	60
9	– " –	20	50	40
10	– " –	20	50	80

Table 2. Yields of SC-CO₂ (20 MPa, 60 °C) and acetone extracts and their fractions in peat samples from different mires.

Mire	Experiment No.	Extraction solvent	Extract yield/ mg/g dry peat	Wax yield/ mg/g dry peat	Resin yield/ mg/g dry peat	Asphaltene yield/ mg/g dry peat
Karanginneva	1	SC-CO ₂	16.9	12.6	4.3	—
— " —	4	SC-CO ₂	14.8	11.3	3.5	—
— " —	5	SC-CO ₂	15.1	11.4	3.7	—
— " —	11	Acetone	131.9	83.7	48.2	—
Piipsanneva	2	SC-CO ₂	15.1	13.0	1.5	0.6
— " —	12	Acetone	71.7	50.8	20.9	—
Kakkeriasuo	3	SC-CO ₂	11.8	5.7	6.0	0.1
— " —	13	Acetone	36.6	14.3	22.3	—

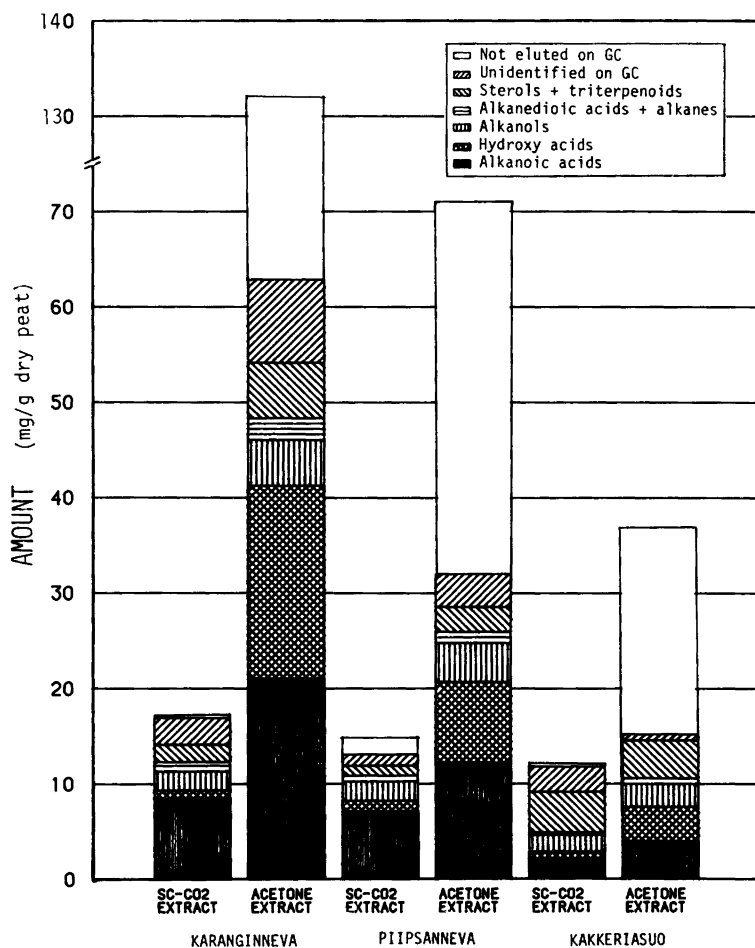


Fig. 1. The amounts of lipid component groups in the SC-CO₂ (20 MPa, 60 °C) and acetone extracts of peat samples from different mires.

Table 3. Amounts and compositions of SC-CO₂-soluble (20 MPa, 60°C) and acetone-soluble lipid compound groups in peat samples from different mires.

Compound group or component	Karanginneva Amount/ mg/g dry peat		Piipsanneva Amount/ mg/g dry peat		Kakkeriasuo Amount/ mg/g dry peat	
	SC-CO ₂ - soluble lipids	Acetone- soluble lipids	SC-CO ₂ - soluble lipids	Acetone- soluble lipids	SC-CO ₂ - soluble lipids	Acetone- soluble lipids
Total	14.2	54.2	11.9	28.7	9.2	14.6
Straight chain components	12.3	48.4	10.8	26.0	4.9	10.6
Alkanoic acids	8.4	21.0	7.1	12.2	2.0	3.9
C ₁₄	+	+	-	0.1	-	0.1
C ₁₆	0.2	0.5	0.1	0.2	0.4	0.5
C ₁₈ (+ unsat. acids)	0.6	1.1	0.1	0.5	0.2	0.3
C ₁₉	+	0.1	-	-	-	-
C ₂₀	0.3	1.0	0.2	0.4	0.1	0.2
C ₂₁	+	0.1	+	+	+	+
C ₂₂	0.6	1.4	0.8	1.3	0.2	0.3
C ₂₃	0.2	0.5	0.1	0.3	+	0.1
C ₂₄	1.6	3.9	1.5	2.6	0.4	0.8
C ₂₅	0.3	0.6	0.2	0.4	+	0.1
C ₂₆	2.3	6.0	2.0	3.3	0.5	0.8
C ₂₇	0.2	0.5	0.2	0.3	+	0.1
C ₂₈	1.5	3.2	1.2	1.9	0.2	0.4
C ₂₉	-	-	-	-	-	-
C ₃₀	0.6	1.8	0.7	0.9	0.1	0.2
C ₃₂	-	0.3	-	-	-	+
Hydroxyalkanoic acids	0.9	20.3	1.1	8.6	0.8	3.7
C ₁₂	+	0.2	-	-	-	-
C ₁₄	-	0.2	+	+	0.2	0.2
C ₁₆ (mono + di- hydroxy acids)	0.1	1.2	+	0.3	-	+
C ₁₈ (mono + tri- hydroxy acid)	0.2	0.8	+	0.4	+	0.2
C ₂₀	+	1.1	-	0.3	-	0.1
C ₂₁	-	0.1	-	-	-	-
C ₂₂	0.1	1.7	0.1	1.0	0.1	0.5
C ₂₃	-	0.8	0.1	0.1	-	-
C ₂₄	-	2.5	0.1	1.1	0.1	0.4
C ₂₅	-	0.3	0.1	0.1	+	0.1
C ₂₆	0.4	6.4	0.5	2.7	0.3	0.5
C ₂₇	-	-	-	-	-	-
C ₂₈	0.1	5.0	0.2	2.6	0.1	1.6
C ₃₀	-	-	-	-	-	-
Alkanedioic acids	0.2	1.3	0.1	0.2	-	0.3
C ₂₂	-	0.2	-	0.1	-	0.1
C ₂₄	0.1	0.2	0.1	0.1	-	-
C ₂₆	0.1	0.4	+	+	-	-
C ₂₈	+	0.5	+	+	-	0.2
Alkanols	2.0	4.8	2.0	4.1	1.8	2.4
C ₁₆	+	-	+	0.7	0.1	0.1

Table 3. Continued

Compound group or component	Karanginneva Amount/ mg/g dry peat		Piipsanneva Amount/ mg/g dry peat		Kakkeriasuo Amount/ mg/g dry peat	
	SC-CO ₂ - soluble lipids	Acetone- soluble lipids	SC-CO ₂ - soluble lipids	Acetone- soluble lipids	SC-CO ₂ - soluble lipids	Acetone- soluble lipids
C ₁₈	0.1	0.2	+	0.1	+	0.1
Phytol	+	0.1	-	0.1	+	0.1
C ₂₀	0.1	0.7	0.1	0.1	0.1	0.1
C ₂₁	+	+	+	+	-	-
C ₂₂	0.3	0.8	0.3	0.6	0.2	0.2
C ₂₃	0.1	0.1	0.1	0.1	+	+
C ₂₄	0.4	1.0	0.3	0.5	0.3	0.4
C ₂₅	0.1	0.2	0.1	0.1	0.1	0.1
C ₂₆	0.4	1.1	0.4	0.6	0.4	0.5
C ₂₇	0.1	0.2	0.1	0.4	+	0.2
C ₂₈	0.4	0.8	0.6	0.8	0.4	0.5
C ₃₀	-	-	-	-	-	-
Alkanes	0.8	1.0	0.5	0.9	0.3	0.3
Sterols and triterpenoids	1.9	5.8	1.1	2.7	4.3	4.0

*Amounts below 0.05 mg/g are designated + and compounds not detected -.

5.8 MPa and 220–250 °C,¹⁷ with acetone at 10 and 28 MPa and 350 °C¹⁸ and with methanol at 12 MPa and 240–260 °C¹⁹ primarily in order to produce liquid fuels.

The aim of the present study was to obtain information on differences between the yields and lipid compositions of extracts obtained with supercritical carbon dioxide and those obtained with organic solvents. Moreover, the effects of pressure and temperature on the dissolution of peat constituents in supercritical carbon dioxide were studied.

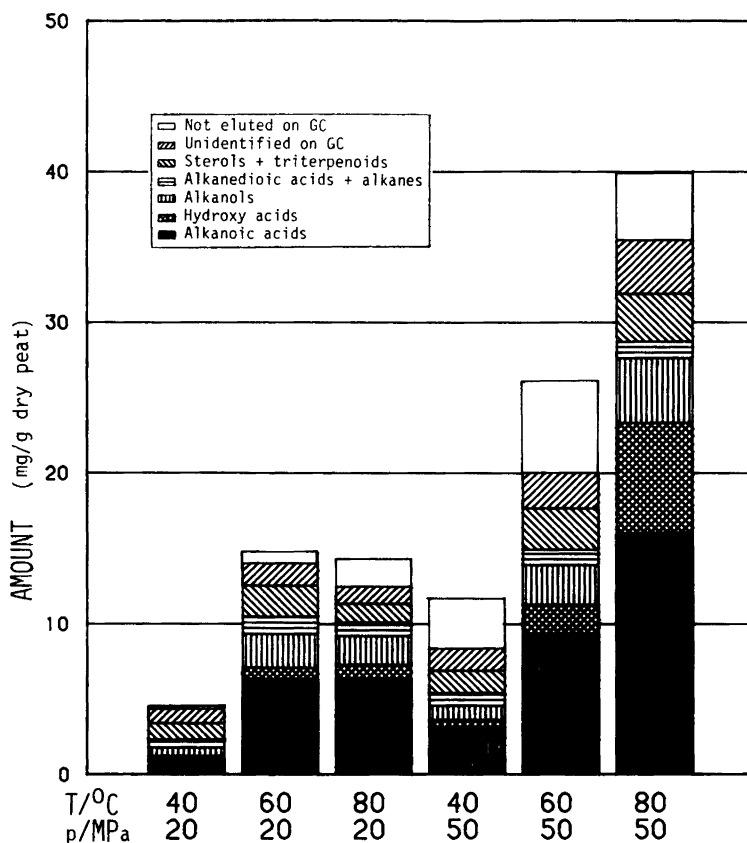
Experimental

Material. The peat samples were collected from the mires of Karanginneva and Piipsanneva, which are aapa mires in Central Finland, and Kakkeriasuo, a raised bog in southwest Finland. The samples were taken from the top 1 metre layer of the mires. The sample from Karanginneva consisted mainly of *carex* and *sphagnum* materials; the sample from Piipsanneva was *carex*- and *ligni*-dominant, that from Kakkeriasuo *sphagnum* peat. The ash content of the sam-

ple from Karanginneva was 12.3 % w/w dry peat, that of the sample from Piipsanneva 3.6 %, and Kakkeriasuo 1.9 % according to DIN 51719. The degrees of decomposition were H₇, H₇, and H₂, respectively, according to von Post.²⁰

Sample pretreatment and extractions. The moist peat samples from each mire were freeze-dried to a final moisture content of less than 2 % and ground with a hammer mill to less than 0.5 mm in particle size. In addition, portions of the peat from Karanginneva were air-dried (moisture contents 20 % and 45 %). The freeze-dried samples (200 g each) from each mire were extracted with supercritical carbon dioxide (SC-CO₂) at 20 MPa and 60 °C with a Nova Werke AG (Effretikon, Switzerland) extraction unit for 5.5 h using an average gas flow rate of 3 kg h⁻¹. Further, aliquots of the same samples (10 g each) were extracted with 250 ml acetone and an aliphatic hydrocarbon (LIAV 110, delivered by Neste Oy, Kulloo, Finland, b.p. 80–110 °C) in Soxhlet extractors for 8 h. The air-dried peat samples from Karanginneva were also extracted with SC-CO₂ at 20 MPa and 60 °C. In addition, in order to

Fig. 2. Effects of pressure and temperature on the amounts of lipid component groups in the SC-CO₂ extract from peat.



study the effects of pressure and temperature in supercritical extraction, the samples from Karanginneva (moisture content 20%) were extracted with SC-CO₂ at 20 MPa at temperatures of 40 and 80 °C, and at 50 MPa at temperatures of 40, 60 and 80 °C. The SC-CO₂ extraction conditions used in the different experiments are presented in Table 1.

After evaporation *in vacuo*, the extracts were fractionated by ethanol using an adaptation of a commonly used procedure.⁴ The dry extract was dissolved in hot ethanol (1:50 v/v) and the insoluble asphaltene fraction isolated. The solution was cooled to -20 °C, the precipitated wax fraction removed by filtration, washed with cold ethanol and vacuum-dried. The soluble resin fraction was obtained by vacuum evaporation to dryness of the filtrate. The dry extracts and their fractions were weighed. For the determination of the chemical composition, heptadecanoic acid

was added to the extracts and their fractions to serve as a quantitative internal standard in gas chromatographic analysis.

Gas chromatographic (GC) analysis. The lipid components of the extracts were analyzed according to a method⁵ reported recently. GC analyses were carried out with a Hewlett Packard 5790-A gas chromatograph equipped with an SE-30 fused silica capillary column (30 m×0.32 mm, film thickness 0.25 μm) and a flame ionization detector. Helium was used as the carrier gas, the flow rate being 1.8 mL min⁻¹. The temperature of the oven was programmed at 4 °C/min heating rate from 150 to 290 °C. The split injection mode was used and peak areas determined with a Hewlett Packard integrator 3390-A. The retention times of the lipid components were based on those of the acetone extract analyzed earlier by GC combined with mass spectrometry.

Quantitative determinations were based on peak areas relative to heptadecanoic acid. Calibration of the GC system with quantitative reference mixtures relative to the internal standard indicated that peak area multiplication factors of 1.00–1.27 were needed to obtain correct results.

Results and discussion

Yields and lipid compositions of SC-CO₂ extracts from peat. A yellowish waxy product was obtained from peat by supercritical carbon dioxide extraction. The yield of extract recovered from dry peat at 20 MPa and 60°C ranged from 12 to 17 mg/g dry peat for the 3 different samples (experiments 1, 2 and 3 in Table 2). The proportion of the wax fraction in the extract ranged from 48 to 86%, that of the resin fraction from 10 to 51% and that of the small asphaltene fraction from 0 to 4%. On average, 80% w/w of the SC-CO₂ extracts were lipid compounds tentatively identified by GC (Fig. 1). The rest of the extracts consisted of unidentified compounds (on average, 15% w/w) and of substances not eluted in GC (on average 5% w/w). The amount of lipid components in the 3 extracts ranged from 9 to 14 mg/g dry peat. The lipid component groups were C₁₂–C₃₂ alkanolic and alkenolic acids, hydroxyalkanoic and hydroxyalkenoic acids, alkanedioic acids, alkanols, and alkanes, as well as sterols and triterpenoids (Table 3). Among the straight chain compounds, the largest group consisted of alkanolic acids followed by alkanols and hydroxyalkanoic acids. The sterols were β -sitosterol, β -sitostanol, stigmasterol and campesterol; the triterpenoids were cycloartenol, methylene cycloartanol, lupeol, betulinol, betulinic acid, oleanolic acid and ursolic acid.

The lipids occurred predominantly in unesterified state. Accordingly, supercritical carbon dioxide dissolves free lipid components more easily than esterified ones, although it is generally assumed that esters are easily dissolved by carbon dioxide, because it is a nonpolar solvent. Obviously, this is due to the lower molecular weights of the unesterified compounds. Supercritical extraction is especially effective for the isolation of substances of medium molecular weight.⁹

The yield and composition of the SC-CO₂ extract were highly dependent on the peat material. This was also found previously for acetone ex-

tracts of Finnish peat.⁸ The SC-CO₂ extract of *carex*-dominant humified peat from an aapa mire consisted mainly of straight chain lipid components, while only about half of the extract of weakly humified *sphagnum* peat from a raised bog consisted of straight chain lipids, the other half being sterols and triterpenoids. The moisture content of the peat did not affect significantly the yields or the proportions of wax, resin and lipids in the extract over the moisture range of 2–45% (experiments 1, 4 and 5 in Table 2). The proportions of different lipid component groups in the extracts were also independent of the moisture content.

Comparison of SC-CO₂ extracts with liquid organic solvent extracts. Compared to extracts obtained with organic solvents, the SC-CO₂ extracts were lighter in colour and richer in lipid components. The yields of the SC-CO₂ extracts obtained at 20 MPa and 60°C from the Karanginneva, Piipsanneva and Kakkeriasuo peat samples were, however, only 13–32% w/w of the yields of the acetone extracts (Table 2) and 20–38% of those of the hydrocarbon extracts. The proportions of identified lipids in the SC-CO₂ extracts were on average 80%, while those in the acetone and hydrocarbon extracts were on average only 40 and 50%, respectively. The SC-CO₂ extracts contained the same lipid classes as the acetone and hydrocarbon extracts of the same peat samples, though in different ratios (Fig. 1). As previously reported, acetone and high-boiling hydrocarbons remove lipid components from peat in equal amounts, except hydroxyalkanoic acids which are less soluble in hydrocarbons than in acetone.⁸

SC-CO₂ dissolves nonpolar substances better than polar ones. In addition, an increase in the number of hydroxyl and carboxyl groups in the lipid compound has been found to decrease its solubility in SC-CO₂.¹⁵ These facts might be the reason for the poor dissolution of hydroxyalkanoic, especially di and polyhydroxyalkanoic acids, and alkanedioic acids in SC-CO₂ compared to their dissolution in other solvents. Their proportions in the SC-CO₂ extracts from the 3 different peat samples were on average only 15% of those dissolved with acetone. The proportions of alkanolic acids and alkanols in the SC-CO₂ extracts were on average 53% and of alkanes, 76% of the amounts dissolved in acetone. Of the

straight chain compounds, the longer chain ones were predominant in all extracts. The yield of sterols with SC-CO₂ was on average 46%, and that of triterpenoids 26%, of the yields obtained with acetone from the humified peat samples, while the respective compounds from the weakly humified peat were as soluble in SC-CO₂ as in acetone.

In the fractionation of the SC-CO₂ extracts using cold ethanol, the distribution of the lipid components between the wax and resin fractions was selective and resembled that previously obtained with acetone and alkaline extracts.⁷ About 90% of the straight chain lipids in the SC-CO₂ extracts were recovered in the wax fractions and 10% in the resin fractions. The wax fractions consisted nearly exclusively of lipids, about 90%, while the resin fractions contained on average 54% lipids.

Effect of pressure and temperature on the yield and lipid composition of SC-CO₂ extracts. The pressure and temperature of extraction affected the dissolution of peat in supercritical carbon dioxide. The yield of the SC-CO₂ extract from Karanginneva peat ranged from 4.4 to 40 mg/g dry peat at different pressures and temperatures (experiments 4, 6–10 in Table 1). The proportion of the wax fraction in the extracts ranged from 50 to 76%, that of the resin fraction from 20 to 48% and of the asphaltene fraction from 0 to 8% in this peat. When the pressure was raised from 20 MPa to 50 MPa at constant temperature, the yields of the SC-CO₂ extract, its lipids, wax and resin fractions increased (Fig. 2). In addition, the extracts obtained at 50 MPa contained a small asphaltene fraction. However, the increase in pressure contributed more to the increase of the non-lipid part of the extract, as the proportions of lipids were smaller in the extracts obtained at 50 MPa than at 20 MPa.

The effect of temperature was dependent on the pressure, during extraction (Fig. 2). At 20 MPa pressure, the rise of temperature from 40 to 60°C increased the yields of the SC-CO₂ extract, its lipids and the wax fraction. On the other hand, there were no great differences in the yields obtained at 60°C and 80°C. Further, the proportion of lipids in the extract remained relatively constant at all temperatures. In contrast, at 50 MPa pressure, a rise of temperature from 40 to 80°C increased significantly the yields of the

SC-CO₂ extract, its lipids and the wax fraction. The proportion of lipids in the extract also increased with temperature increase.

These results conform with the general principles of supercritical fluid extraction^{9–10} and other studies on the extraction of lipid-bearing materials.¹⁶ In general, the solubility of a substance in supercritical fluid increases with pressure and the effect of temperature on the solubility changes with pressure. At lower pressures, the solubility of the substance may be reduced by an increase in temperature due to a reduction in the density of the gas. At high pressures, the decrease in density caused by the temperature rise is so insignificant that the increase in vapour pressure of the solid gives higher concentrations in the carbon dioxide phase.

For the extraction of peat samples from different mires, a pressure of 20 MPa and a temperature of 60°C were chosen to obtain a high yield of the lipid-rich product.

Conclusions

Supercritical carbon dioxide extraction proved to be a selective method to produce waxy substances from peat. The yield and lipid composition of the extract is dependent on the extraction pressure and temperature, and on the peat material, i.e. on its typical plant species composition and degree of decomposition. Compared to the conventional solvent extraction of peat, the advantages of supercritical carbon dioxide extraction are the lighter colour of the extract and the significantly higher proportion of lipids in the extract. The best lipid yield, relative to that achieved by acetone extraction, is obtained with the *sphagnum*-dominant weakly humified raised bog peat. In addition, technical advantages of the supercritical carbon dioxide extraction method are that removal of solvent from the extract by distillation is eliminated and the separation of wax and resin from the extract may not be needed because of the high lipid content of the extract. However, drawbacks of the supercritical carbon dioxide extraction method are the significantly smaller extract yields compared to normal solvent extraction and the high capital costs of the high pressure equipment required.

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