ORIGINAL ARTICLE

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Extraction and decomposition of hiba wood into valuable chemicals using stepwise temperature supercritical carbon dioxide treatment

Abstract Hiba (*Thujopsis dolabrata*) wood was treated with supercritical carbon dioxide ($scCO_2$) at stepwise temperature increments from 50° to 400°C continuously so that extractives (dichloromethane-soluble and -insoluble phases) and solid residues were obtained. The yield of extractives from hiba wood increased with increasing extraction temperature. The volatile compounds in the dichloromethane-soluble phase from $scCO_2$ extraction at 50°C contained only terpenoids. However, the volatile compounds in the dichloromethane-soluble phase from $scCO_2$ extraction at 300°C not only contained terpenoids but also phenols, furans, hydrocarbons, and organic acids. The yield of β-thujaplicin, which is a useful compound in hiba wood, increased with increasing extraction temperature from 50°C to 300°C; the optimal conditions for extracting β-thujaplicin were 300°C and 19.61 MPa. Further study of degradated compounds from the cellulosic and lignic materials of hiba wood after stepwise high-temperature $scCO_2$ treatment above 300°C may provide clues to its efficient use.

Key words Supercritical carbon dioxide · Stepwise temperature · β-Thujaplicin

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Introduction

Wood from hiba (*Thujopsis dolabrata*), an evergreen coniferous tree that grows in northern Japan,[1] contains β-thujaplicin (a naturally occurring aromatic seven-membered tropolone compound), which has important biological uses. Demand for the compound has been increasing and has surpassed the capacity to isolate it from hiba wood; consequently, chemically synthesized β-thujaplicin has come to be used instead. On the other hand, interest in natural foods is growing, and an efficient extraction method for β-thujaplicin from natural products has been developed.[2] However, the residue from such extractions has not provided clues to its efficient use.

Recently, supercritical fluid extraction has received great attention in the extraction of natural products. Supercritical carbon dioxide ($scCO_2$) has been attracting increasing attention as a solvent with great potential. Its properties, such as density, dielectric constant, diffusivity, viscosity, and solubility can be tuned by adjusting the pressure and temperature, which clearly distinguishes the fluid from conventional solvents; this property enables different solvent effects to be examined without changing the solvent itself. Separating CO_2 from the reaction mixture is energy efficient and a product can be obtained by simple treatments. In addition, CO_2 is inexpensive, nonflammable, nontoxic, environmentally friendly (compared to many other solvents), and can act as a reaction medium, which make it favored for green chemistry research.[3]

$scCO_2$ has been widely used for the supercritical fluid extraction of organic compounds, especially nonpolar compounds, such as anthraquinone extraction from paper and wood pulp;[4] for separating resin and fatty acids from sediment at pulp mill sites;[5] and for the selective extraction of valuable chemicals such as tropolones,[6] *cis*-abienol,[7] camphor,[8] ferruginol,[9] maltol,[10] paclitaxel,[11] and hinokitiol (β-thujaplicin),[12] among others. At present, $scCO_2$ is used as a medium in the following chemical reactions: enzyme-catalyzed reactions,[13] polymerizations,[14] radical reactions,[15] cycloaddition reactions,[16] transition metal-catalyzed reactions,[17] and Maillard reactions,[18] among others.

In general, scCO$_2$ extracts have no solvent residues, no "off-note" odors, and higher concentrations of the most valuable components when compared with conventional organic liquid solvent extracts. Most solvent extractions using carbon dioxide are run at temperatures between the critical point and 60°C, which are not likely to degrade or volatize heat-sensitive aroma compounds.[19] However, Hoyer has suggested that higher extraction temperatures would result in lower solvent density and in increased vapor pressure, which could lead to elevated solubility.[20] Therefore, high-temperature scCO$_2$ has been considered an effective medium for extraction.[20]

Generally, wood consists of cellulose, hemicelluloses, and lignin. Around 40%–45% of the dry substance in most wood species consists of cellulose, and about 20%–30% is hemicelluloses. Both materials can be readily hydrolyzed into monomeric sugars.[21] The rest of the wood consists mainly of lignin. Lignin is a complex polymer synthesized from phenylpropanoid monomers. It is one of the most abundant organic polymers on earth, exceeded only by cellulose. Pyrolysis (thermal degradation) of lignin during wood combustion yields a range of products, of which the most characteristic are methoxy phenols. The potential of woody biomass as a source of useful chemicals and fuels has been a subject of renewed interest in the current climate of reducing dependence on fossil resources.

Systematic uses of wood materials, such as cellulose, hemicelluloses, and lignin, have been suggested to be promising by Goldstein.[22] Various approaches to biomass conversion have been applied, such as pyrolysis, acid hydrolysis, and enzymatic hydrolysis. In addition to these approaches, supercritical fluid technology has recently received increasing attention.

The purpose of the present work was to evaluate the volatile compounds of hiba wood obtained from continuous treatment with stepwise temperature scCO$_2$; these are useful products (e.g., liquid fuels and /or chemicals) which should provide clues as to their efficient use.

Experimental

Sample preparation

The hiba wood samples were taken from trees about 200 years old in the Kanaki area, Aomori Prefecture, Japan. The wood was air dried and ground in a Willey mill to pass through a 40- to 60-mesh screen. Water content of the wood was in the range 15%–18%, which was determined by drying wood samples in an oven at 105°C for 6 h.

Supercritical carbon dioxide extraction

The supercritical fluid extraction apparatus used was a JASCO Super 201 (Tokyo, Japan); a schematic of the apparatus is shown in Fig. 1. The pressure was measured at the outlet of the extraction cell by using a pressure transducer with ±0.1% accuracy. The carbon dioxide carrier fluid
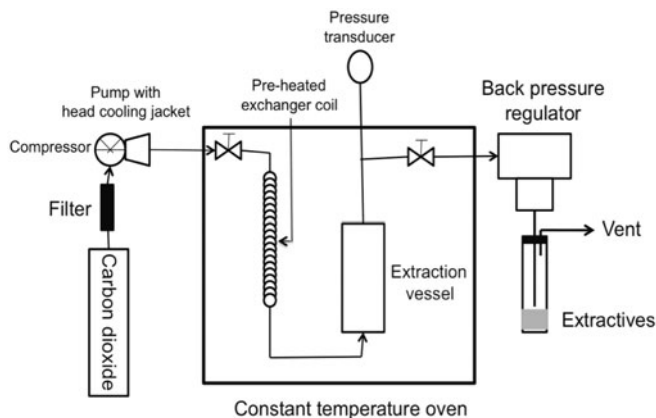

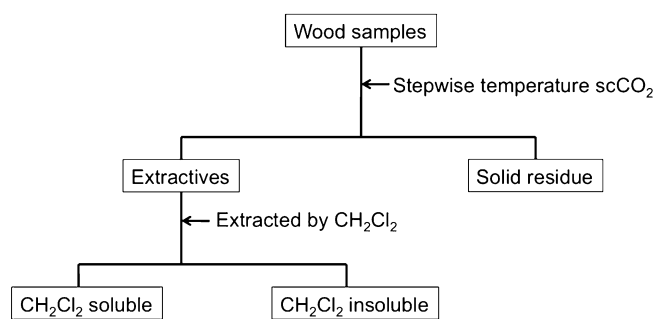Fig. 1. Schematic of the stepwise-temperature supercritical fluid extraction unit

Fig. 2. Scheme of extraction from hiba wood

(99.99%) was pressurized and delivered with a plunger pump. Each batch of extraction proceeded with scCO$_2$ at 19.61 MPa at 50°C, 200°, 300°, 380°, and 400°C for 20 min continuously. The flow rate of scCO$_2$ used was 1 ml/min. After expansion to atmospheric pressure, the extract was collected in a glass vial at 5°C. Extraction treatment was carried out in triplicate for each sample.

Extractives and extraction residue by stepwise temperature scCO$_2$

After treatment, the extractives were collected in a glass vial and the extraction residue was obtained from the extraction vessel. The extractives after scCO$_2$ treatment were left to stand for 24 h at room temperature so that the extractives could classify into two phases. The black solid residue could be obtained from the extraction vessel after stepwise temperature scCO$_2$ treatment (Fig. 2). Sodium chloride was added to the aqueous phase to increase extraction efficiency, then, the extractives were extracted twice with dichloromethane. The solvent-soluble phase was dried by passing through anhydrous sodium sulfate. Finally, the dichloromethane-soluble phase of extractives, i.e., a brown, highly viscous, oily phase, was obtained by removing dichloromethane using a rotary evaporator at 35°C. The dichloromethane-insoluble phase of extractives, i.e., a

yellowish clear phase, was obtained. The analysis of volatile compounds in the extractives after continuous treatment of hiba wood with stepwise temperature $scCO_2$ was performed in this study in consideration of its potential use as raw material for various processes.

The yield of extractives (Yield-e) was calculated using the following equation: Yield-e(%) = W_e / W_0 × 100, where W_0 is the oven-dried weight of hiba wood samples and W_e is the weight of extractives. The yield of the solid residue (Yield-r) was calculated from the following equation: Yield-r(%) = W_r / W_0 × 100. where W_r is the weight of solid residue.

Measurement of volatile compounds

A Hewlett–Packard 6890 gas chromatograph (Hewlett–Packard, Palo Alto, CA, USA) equipped with a fused silica capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness, HP-INNOWax: J&W Scientific, Folsom, CA, USA) and a flame ionization detector (FID) was used to analyze the $scCO_2$ extracts. The operating conditions were as follows: injection temperature, 230°C; detector temperature, 230°C; helium carrier flow rate, 1.0 ml/min; temperature program, 60°–240°C at 4°C/min and held at 240°C for 10 min. A split ratio of 40:1 and an injection volume of 1 μl were used.

Gas chromatography/mass spectrometry (GC-MS) analysis was accomplished by using a Hewlett–Packard 6890 gas chromatograph coupled directly to a Hewlett–Packard 5973 MSD mass spectrometer. An identical column and temperature program was carried out as that used in the GC analysis. The temperature of the transfer line was 220°C. The helium carrier flow rate was 1.0 ml/min. A split ratio of 40:1 was used and mass spectra were obtained with an electron multiplier voltage and an electron ionization energy of 1206 V and 70 eV, respectively. All mass numbers between 30 and 550 m/z were recorded (SCAN technique). Individual compounds were identified by comparing their mass spectra with data from the NIST Library, the literature,[23] and NMR spectra. The total emission of volatile organic compounds was first calculated by combining the peak areas of all identified compounds, after which the relative proportions of individual compounds from the total emission were calculated.

Results and discussion

Effects of temperature and water contents on extractives

Extraction time is an important parameter in the design of extraction apparatus. It determines the volume of the apparatus (20 ml) for a given reactive capacity. Using the developed equipment, extraction experiments were conducted with $scCO_2$ at 19.61 MPa/50°C and at 19.61 MPa/400°C, increasing the extraction time from 10 to 60 min in 10-min steps to determine the requisite time for extracting the maximum amount of extractives from the wood samples. As shown in Figs. 3 and 4, most extractives were extracted from wood samples after 20 min of extraction time for both
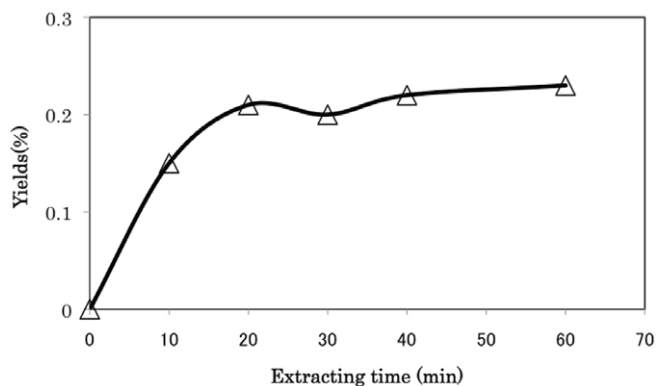
Fig. 3. Extractives yields from hiba woods obtained with supercritical carbon dioxide ($scCO_2$) at 19.61 MPa and 50°C. Extractives yields are the weight percentages of extractives by stepwise temperature $scCO_2$ based on the oven-dried weight of hiba wood
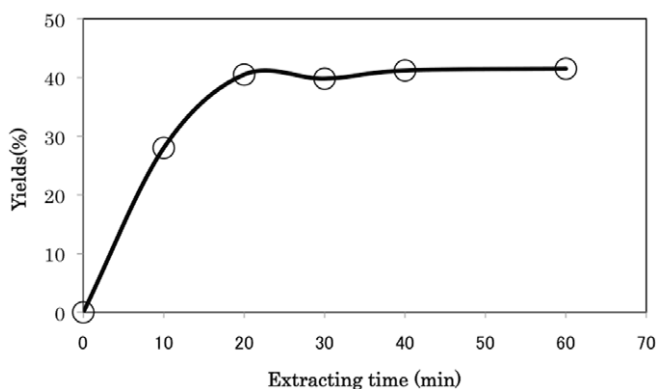
Fig. 4. Extractives yields from hiba woods obtained with $scCO_2$ at 19.61 MPa and 400°C
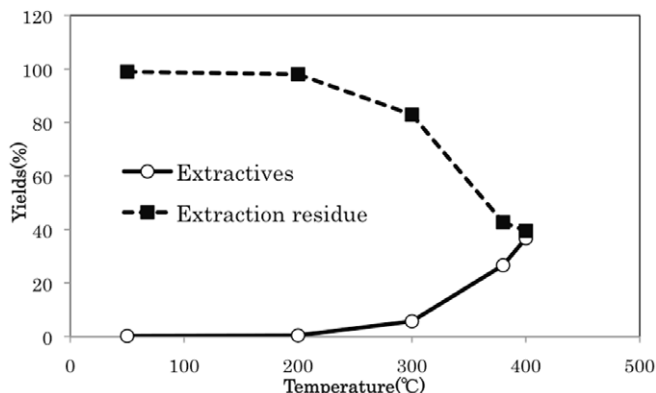
Fig. 5. The yields of extractives from hiba wood by stepwise temperature $scCO_2$. Extraction residue yields are the weight of residue after extraction by stepwise temperature $scCO_2$ based on the oven-dried weight of hiba wood. Each batch of extraction proceeded with $scCO_2$ at 19.61 MPa at 50°, 200°, 300°, 380°, and 400°C for 20 min

temperature conditions. Therefore, the extraction time for every experiment in this study was fixed at 20 min.

The extractives yields from hiba wood samples are shown in Fig. 5. The yield of extractives from hiba woods increased

with increasing extraction temperature. Although the yield of extractives increased with the extraction temperature from 50° to 400°C, the increments for temperatures above 340°C were large. In contrast, the yield of extraction residue from hiba woods decreased with increased extraction temperature. The yield of extractives at 300°C was 29 times the yield of extractives at 50°C under constant pressure (19.61 MPa).

At a temperature of 300°C, hydrolysis or pyrolysis of cellulose, hemicelluloses, and lignin may have taken place, and therefore the measured mass difference may have been a combination of extractives removal and loss of cellulosic materials and lignins.

The components of volatile compounds in the dichloromethane-soluble phase from hiba wood extractives are shown in Table 1 and Fig. 6. Five different categories (terpenoids, phenols, organic acids, furans, and hydrocarbons) were obtained in the dichloromethane-soluble phase of extractives. Only terpenoids were detected from the dichloromethane-soluble phase at 50°C as volatiles. The extractives at 50°C mainly consisted of two monoterpenoids amounting to 3.7% of total extractives (mainly β-thujaplicin and α-pinene), and 15 sesquiterpenoids amounting to more than 96.3% of total extractives (mainly thujopsene, cedrol, nootkatone, nerolidol, α-cedrol, and α-cedrene). The components of volatile compounds in the dichloromethane-soluble phase at 200°C were similar to those at 50°C. In contrast, not only terpenoids but also phenols, furans, hydrocarbons, and organic acids were detected from the dichloromethane-soluble phase at 300°C as volatiles. The extractives at 300°C consisted mainly of 13 terpenoids (mainly anethol, β-thujaplicin, cuparenal, γ-costol, cuparene, *epi*-cubenol, and thujopsene), amounting to 43.1% of extractives; 10 phenols (mainly 4-hydroxy-3-methoxy-cinnamaldehyde, 6-methyl-6-[3-methyl-3-methylethyl]-1-cyclo-propen-1-yl)-2-heptanone, and isoeugenol), amounting to 50.9% of extractives; 1 hydrocarbon (3a,7a-dihydro-5-methyl-1H-indene-1,7-(4H)-dione), amounting to 1.5% of extractives; 2 organic acids (hexadecanoic acid and octadecanoic acid), amounting to 2.6% of extractives; and 2 furans (furfural and 5-hydroxymethylfurfural), amounting to 1.9% of extractives.

From the dichloromethane-soluble phase at 380°C, phenols, terpenoids, furans, hydrocarbons, and organic acid were detected as volatiles. The extractives at 380°C consisted mainly of 16 phenols (mainly 2-methoxy-*p*-cresol, isoeugenol, 4-ethylguaiacol, and guaiacol), amounting to 62.1% of extractives; 14 terpenoids (mainly 5,6-dihydroalaskene, β-thujaplicin, and cuparene), amounting to 16.4% of extractives; 6 furans (mainly furfural, 5-methyl-furfural, and 5-hydroxymethylfurfural), amounting to 12.9% of extractives; 4 hydrocarbons [mainly 1-(acetyloxy)-2-butanone and 1-(acetyloxy)-2-propanone], amounting to 6.7% of extractives; and 3 organic acids (mainly acetic acid and butanoic acid), amounting to 1.9% of extractives.

Phenols, terpenoids, furans, hydrocarbons, and organic acids were detected from the dichloromethane-soluble phase at 400°C as volatiles and mainly consisted of 16 phenols (mainly 2-methoxy-*p*-cresol, guaiacol, and 4-ethylguaiacol), amounting to 68.9% of extractives; 14 terpenoids (mainly 5,6-dihydroalaskene, β-thujaplicin, and cuparene), amounting to 17.6% of extractives; 6 furans (mainly furfural, 5-methyl-furfural, and maltol), amounting to 8.6% of extractives; 5 hydrocarbons (mainly 1-(acetyloxy)-2-propanone and 1-(acetyloxy)-2-butanone), amounting to 4.1% of extractives; and 4 organic acids (mainly acetic acid and butanoic acid), amounting to 0.8% of extractives.

The components of volatile compounds in the dichloromethane-insoluble phase of extractives are shown in Table 2 and Fig. 7. No compounds were found in those extractives at 50°C. A small amount of volatile compounds were detected from the dichloromethane-insoluble phase at 200°C. These mainly consisted of one organic acid (acetic acid), amounting to 65%; one hydrocarbon (1-hydroxy-2-propanone), amounting to 20%; and one furan (5-hydroxymethyl-furfural), amounting to 15%. From the dichloromethane-insoluble phase of extractives at 300°C, furans, hydrocarbons, and organic acids were detected as volatiles. These mainly consisted of one organic acid (acetic acid), amounting to 72%; one hydrocarbon (1-hydroxy-2-propanone), amounting to 15.3%; and one furan (5-hydroxymethyl-furfural), amounting to 12.7%. Furans, hydrocarbons, organic acids, and phenols were detected from the dichloromethane-insoluble phase of extractives at 380°C as volatiles. These consisted mainly of five organic acids (mainly acetic acid and 3-ethylbutanoic acid), amounting to 56.2%; three hydrocarbons (mainly 1-hydroxy-2-propanone and cyclobutanol), amounting to 22%; three furans (mainly 5-hydroxymethylfurfural and tetrahydro-2-methyl-2-furanol), amounting to 15.6%; and three phenols (mainly cyclotene and 4-hydroxy-3-methoxy-phenylacetic acid), amounting to 6.2%.

From the dichloromethane-insoluble phase of extractives at 400°C, furans, hydrocarbons, organic acids, and phenols were detected as volatiles. These consisted mainly of five organic acids (mainly acetic acid and 3-ethylbutanoic acid), amounting to 58.3%; two hydrocarbons (1-hydroxy-2-propanone and cyclobutanol), amounting to 15.6%; three furans (5-hydroxymethylfurfural and tetrahydro-2-methyl-2-furanol), amounting to 16.4%; and two phenols (cyclotene and 4-hydroxy-3-methoxy-phenylacetic acid), amounting to 9.7%.

Only volatile compounds in the extractives were analyzed by GC or GC/MS, since useful products (e.g., liquid fuels and/or chemicals) can be obtained from the volatiles. However, nonvolatile compounds such as degradation/condensation products from polysaccharides and polyphenols may be included in the extractives.[24] The analysis of nonvolatile compounds in the extractives will be performed in a later study.

In general, the properties of the scCO$_2$ extraction medium at 50°C, e.g., density, viscosity, and diffusion coefficient, are controlled by various operational parameters. When applying scCO$_2$ extraction to natural samples such as plants or soil, the effect of these parameters on the scCO$_2$ extraction yield of the target analyte is not predictable, since the sample matrix has a profound effect on the extraction

Table 1. Components of volatile compounds in the dichloromethane-soluble phase of extractives from hiba wood by stepwise temperature scCO$_2$ treatment

	Rt	50°C	200°C	300°C	380°C	400°C	Category
α-Pinene	1.0	0.6	–	–	–	–	t
1-Hydroxy-2-propanone	1.9	–	–	–	1.1	0.2	h
Acetic acid	3.2	–	–	–	1.3	0.4	o
Furfural	3.4	–	1	1.0	4.5	2.8	f
1-(Acetyloxy)-2-propanone	3.4	–	–	–	2.1	1.2	h
1-(2-Furanyl)-ethanone	3.7	–	–	–	1.3	1.0	h
1-(Acetyloxy)-2-butanone	4.0	–	–	–	2.1	1.3	h
5-Methyl-furfural	4.3	–	–	–	2.8	2.3	f
Thujopsene	4.4	44.2	35.6	2.8	1.1	0.9	t
α-Muulrolene	4.6	1.4	1.6	–	–	–	t
α-Cedrene	4.7	4.0	2.0	–	–	–	t
Butanoic acid	4.7	–	–	–	0.4	0.3	o
Longipinene	4.8	3.5	3.0	–	–	–	t
2-Furanmethanol	5.0	–	–	–	1.6	0.6	f
β-Calacorene	5.1	0.8	0.4	–	–	–	t
epi-Cubenol	5.3	0.6	0.6	–	–	–	t
Nootkatone	5.8	7.7	6.0	–	–	–	t
1(10)-Cadinene-4β-ol	5.8	2.2	0.5	–	–	–	t
α-Cadinol	6.1	5.1	4.0	–	–	–	t
Cuparene	6.1	3	3.1	3.7	2.2	2.3	t
Longicycrene	6.2	1.3	0.3	–	–	–	t
2-Hydroxy-3-methyl-2-cyclopenten-1-one	6.4	–	–	–	3.1	2.0	p
Caryophylla-3,8-(13)-dien	6.4	2.5	2.0	–	–	–	t
Nerolidol	6.6	5.3	4.0	–	–	–	t
Guaiacol	6.6	–	–	–	5.8	7.5	p
2-Methoxy-p-cresol	7.3	–	–	–	9.3	14.2	p
Maltol	7.4	–	–	–	1.3	1.4	f
4-Ethylguaiacol	7.9	–	–	–	6.4	9.1	p
p-Cresol	8.3	–	–	–	0.3	0.6	p
Cedrol	8.4	11.1	8	3.1	0.8	0.9	t
Eugenol acetate	8.4	–	–	–	4.2	6.3	p
Widdrol	8.6	3.6	2	1.0	–	0.6	t
Eugenol	8.9	–	1.2	0.7	3.0	2.8	p
p-Vinyl-guaiacol	9.1	–	2	2.2	2.6	2.3	p
5-Acetoxymethyl-2-furaldehyde	9.1	–	–	–	0.8	0.7	f
Carvacrol	9.2	–	2.7	2.2	0.8	1.0	t
β-Thujaplicin	9.3	3.1	3.3	8.4	2.8	2.8	t
3a,7a-Dihydro-5-methyl-1H-indene-1,7(4H)-dione	9.9	–	0.5	1.5	–	0.4	h
Isoeugenol	10.1	–	3.2	5.6	12.1	9.3	p
4-Ethenyl-1,2-dimethylbenzene	10.2	–	–	1.0	0.2	0.2	p
6-Methyl-6-[3-methyl-3-(1-methylethenyl)-1-cyclopropen-1-yl]-2-heptanone	10.2	–	–	3.8	0.5	0.7	p
Cuparenol	10.3	–	0.5	4.4	0.8	1.3	t
Aromadendrene epoxide	10.4	–	0.5	1.0	0.2	0.4	t
1,2-Dimethyl-3,5-bis(1-methylethenyl)cyclohexane	11.0	–	–	0.8	0.2	0.3	p
γ-Costol	11.0	–	1	4.3	1.2	1.3	t
5-Hydroxymethylfurfural	11.2	–	–	0.8	1.8	0.7	f
5,6-Dehydroalaskene	11.5	–	0.5	8.6	3.9	3.6	t
Aceto-vanillone	12.1	–	–	0.6	1.7	2.0	p
Anethol	12.5	–	1	16.5	3.6	3.8	p
β-Thujaplicliol	12.6	–	–	–	1.1	1.1	t
Cuparophenol	13.0	–	0.5	0.6	0.4	0.4	t
Hexadecanoic acid	13.7	–	1	1.1	–	0.1	o
3-Methoxy-4-hydroxybenzeneacetic acid	14.1	–	3	3.4	4.4	4.2	p
Sandaracopimarinol	14.8	–	2	2.2	0.6	0.4	t
Octadecanoic acid	14.8	–	0.5	1.5	0.2	–	o
4-Hydroxy-3-methoxy-cinnamaldehyde	15.0	–	1	16.3	4.7	3.8	p
Cuparenic acid	16.2	–	1.5	1.0	0.5	0.5	t
Furans		0.0	1.0	1.9	12.9	8.6	f
Hydrocarbons		0.0	0.5	1.5	6.7	4.1	h
Organic acids		0.0	1.5	2.6	1.9	0.8	o
Phenols		0.0	3.2	50.9	62.1	68.9	p
Terpenoids		100.0	93.8	43.1	16.4	17.6	t

Figures show the percentages of components in the extractives based on the peak area by gas chromatography

Rt, retention times are relative to that of α-pinene; t, terpenoids; p, phenols; h, hydrocarbons; f, furans; o, organic acids; –, not present in detectable amounts

efficiency. Yarita has reported the effect of water content in soil samples on scCO$_2$ extraction recovery yields using triazine and thiolcarbamate herbicides as target analytes. The presence of small amounts of water in the matrix was considered to increase the recovery yields of analytes by acting as an internal modifier. In addition, adsorption sites on the matrix might be removed by the presence of water. In contrast, the recovery yields of target analytes from soil containing 30% water were poorer than those from soil containing 10%–20% water.[25] In this study, the water contents of hiba wood samples were in the range 15%–18%; these values are for air-dried conditions at which the cell cavities contained no liquid water, but the cell walls were fully saturated with water.[26] The water content of the extractives was very small in the extraction process at 50°C. The above results suggest that the water was not extracted at 50°C and remained in the sample until extraction at a higher temperature.

The water content in the wood samples might play a key role in assisting the scCO$_2$ extraction at higher temperatures (200°–400°C) of organic substances. When an organic sample is fresh, the water content should help it to absorb enough heat energy from scCO$_2$ extraction at higher temperature and transfer more heat energy to organic molecules contained in the sample.

Heat enhances the transfer of organic substance from the inner part to the surface of samples. In addition, for organic substances with large molecules, solubility in the intrinsic water increases when the samples are heated during scCO$_2$ extraction at higher temperatures, and then the dissolved components diffuse through the cell membranes, assisted by a driving force derived from evaporation of intrinsic water and evaporation of compounds themselves.

The extraction selectivity of β-thujaplicin using stepwise temperature scCO$_2$ extraction

As shown in a previous report,[12] the yields of β-thujaplicin from hiba wood using methanol extraction were greater than those for other solvents. However, the problem with solvents is that it is virtually impossible to remove all the solvent, and any residual solvent can be undesirable in a flavor or fragrance ingredient. Compared with classic solvent extraction procedures, scCO$_2$ extraction is quicker, less labor intensive,
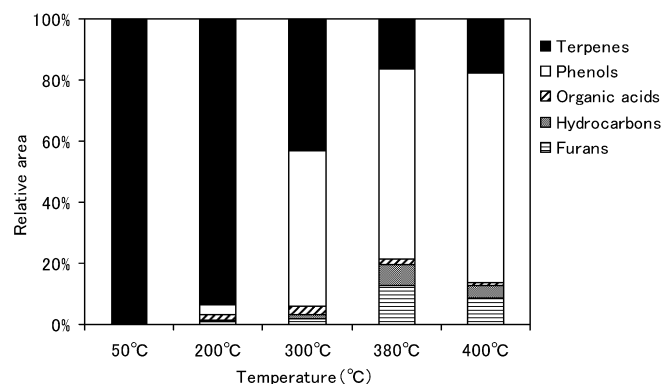
Fig. 6. The contents of volatile compounds in the dichloromethane-soluble phase of extractives from hiba wood by stepwise temperature scCO$_2$
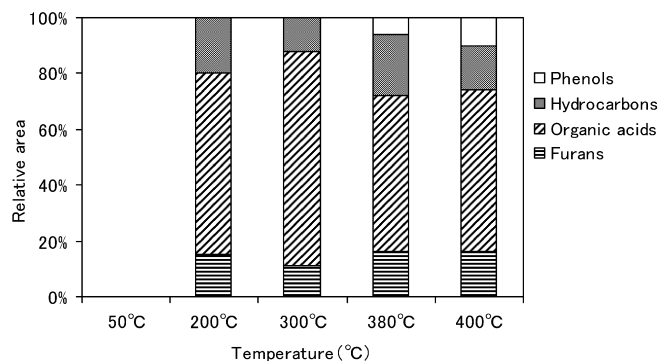
Fig. 7. The contents of volatile compounds in the dichloromethane-insoluble phase of extractives from hiba wood by stepwise temperature scCO$_2$

Table 2. Components of volatile compounds in the dichloromethane-insoluble phase of extractives from hiba wood by stepwise temperature scCO$_2$ treatment

	Rt	50°C	200°C	300°C	380°C	400°C	Category
1-Hydroxy-2-propanone	1.9	–	15	12.0	14.8	11.9	h
1-Hydroxy-2-butanone	2.6	–	–	–	1.3	–	h
Acetic acid hydroxy methyl ester	2.7	–	–	–	1.6	1.7	o
Acetic acid	3.2	–	56	72.0	36.4	37.6	o
Propanoic acid	4.1	–	7	5.3	2.1	3.4	o
2-Furanmethanol	5.0	–	–	–	3.2	3.3	f
2-Hydroxycyclopent-3-en-1-one	6.1	–	–	–	0.8	–	p
Cyclotene	6.6	–	–	–	2.9	4.8	p
Cyclobutanol	8.5	–	–	–	6.0	3.6	h
Tetrahydro-2-methyl-2-furanol	9.1	–	3.5	1.3	5.2	6.2	f
Levulic acid	10.2	–	–	–	1.0	1.5	o
5-Hydroxymethylfurfural	11.2	–	18.5	9.4	7.2	7.0	f
4-Hydroxy-3-methoxyphenylacetic acid	14.5	–	–	–	2.5	4.9	p
3-Ethylbutanoic acid	16.8	–	–	–	15.0	14.2	o

Figures show the percentages of components in the extractives based on the peak area by gas chromatography
Rt, retention times are relative to that of α-pinene; p, phenols; h, hydrocarbons; f, furans; o, organic acids; –, not present in detectable amounts

and has no hazardous solvents or waste. For these reasons, supercritical fluid technology can be applied effectively to the extraction of β-thujaplicin from hiba woods. The extraction selectivity of β-thujaplicin (the content of β-thujaplicin in the extractives) with scCO$_2$ without an entrainer was greater than for methanol extraction.

In this study, the extraction selectivity of β-thujaplicin increased with increasing extraction temperature from 50° to 300°C. The largest extraction selectivity of β-thujaplicin was 8.4% when extracted with scCO$_2$ at 300°C and 19.61 MPa, which roughly corresponds to a carbon dioxide density[27] of 0.1882 g/cm^3. These extraction conditions for β-thujaplicin can be considered optimal. The characteristics of scCO$_2$ could change depending on the pressure and temperature used for extraction. Ritter and Campbell have studied the volatility of resinous extract such as abietic acid, which probably increased at higher temperatures (180°C and 27.6 MPa, which roughly correspond to a carbon dioxide density[27] of 0.3923 g/cm^3), resulting in a higher extract yield.[28] The solubility of a solute in general is proportional to the solvent density. Hoyer indicated that a higher extraction temperature at constant pressure might result in higher vapor pressure and higher solubility. This suggests that the solubility of extractives may be controlled to a greater degree by vapor pressure than solvent density.[20] As the temperature increases, the vapor pressure of the solute increases, which tends to increase solubility. Concomitantly, carbon dioxide density decreases, which tends to decrease solubility. The solubility of solutes in scCO$_2$ is related to the characteristics of fluids such as density, diffusion, and vapor pressure. These characteristics could change according to the pressure and temperature used for extraction. However, Miller et al. have suggested that the solubility of polycyclic aromatic hydrocarbons in scCO$_2$ increases much more rapidly with higher temperatures (at constant pressure) than with higher pressures (at constant temperature) over pressures from 100 bar to 450 bar and temperatures from 313 to 523 K.[29] Jaffe et al. have also suggested that the extraction of aliphatic and aromatic hydrocarbons from new Albany shale by scCO$_2$ at an elevated temperature (300°C) resulted in significant increments in the relative recoveries of all compounds, but particularly for aromatic hydrocarbons. They have also suggested that the shale samples extracted by stepwise scCO$_2$ extraction at temperatures between 50° and 350°C resulted in the highest relative extraction yields for aliphatic and aromatic hydrocarbons at 350°C. Those recovered at high temperature (300° and 350°C) are the product of release of hydrocarbons "trapped" within macromolecular organic material.[30] Although supercritical fluid technology is more costly than chemical synthetic technology from an economical viewpoint, scCO$_2$ extraction is an excellent method for obtaining β-thujaplicin.

The decomposition of hiba wood into valuable chemicals after stepwise temperature scCO$_2$ treatment

In this study, the decomposition of cellulosic materials and lignin of hiba wood using scCO$_2$ at 200°C and above and 19.61 MPa resulted in the formation of organic acids, furans, hydrocarbons, and phenols. The yields in the dichloromethane-soluble phase of extractives at temperatures above 300°C were in the following order: phenols > terpenoids > furans > hydrocarbons > organic acids. The yields in the dichloromethane-insoluble phase of extractives at temperatures above 300°C were in the following order: organic acids > hydrocarbons > furans > phenols.

The reaction pathways that yielded organic acids, phenols, furans, and hydrocarbons from hiba woods using stepwise temperature scCO$_2$ at temperatures above 300°C remain unclear. The decomposition of cellulose under subcritical water conditions results initially in the formation of soluble oligomers and individual glucose monomers. Furthermore, glucose could isomerize into fructose or dehydrate into furans (hydroxymethylfurfural and furfural) and/or could decompose into several other small organic compounds.[31] 5-Hydroxymethylfurfural (HMF), a kind of furan, was produced by the dehydration of 6-carbon sugars obtained from the hydrolysis of cellulose, while furfural was a result of the dehydration of 5-carbon sugars resulting from the hydrolysis of the hemicellulosic part of wood.[32] Lignin degradation produced various phenols under subcritical water conditions. These compounds were found to consist of condensed-type linkages of lignin due to the preferential degradation of ether linkages that occurred in supercritical water.[33]

The detectable compounds in those extractives were very similar to those of wood vinegar and wood tar, which are by-products of wood carbonization (thermal degradation).[34-36] Carbonization of wood, like other lignocellulosic biomass, is a very complex process. scCO$_2$ treatment at above 300°C may have a similar reaction process and result in carbonization or hydrothermal processing[37] of woody materials.

This method is a new effective method for the continuous extraction and decomposition of constituents from woody materials using flow-type systems of scCO$_2$. This method should be applicable to extractives and to the thermal degradation of any waste biomass, such as rice straw, paper, cotton, and other cellulosic materials.

Conclusions

Extractives from hiba wood samples after stepwise temperature scCO$_2$ continuous treatment were evaluated to provide clues as to their effective use. These extractives were found to consist of terpenoids, phenols, hydrocarbons, furans, and organic acids. β-Thujaplicin is a useful compound in hiba wood, and its yield increased with increasing extraction temperature from 50° to 300°C; the optimal extraction conditions for β-thujaplicin were 300°C and 19.61 MPa. Further study of degraded compounds from the cellulosic and lignin materials of hiba wood after stepwise high-temperature scCO$_2$ treatment (above 300°C, 19.61 MPa) may provide a clue to its efficient use. This method is a new effective method for the continuous extraction and decomposition of constituents from woody materials using flow-type systems of scCO$_2$.

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