Chemical Composition of Essential Oil and Hydrosol from *Picea mariana* Bark Residue

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For the first time, the essential oil of Black spruce (*Picea mariana*) bark residue was obtained using two types of hydrodistillations: steam distillation (SD) and water distillation (WD). Both gave similar yields and compositions as analyzed using gas chromatography and mass spectrometry. The essential oil composition is turpentine-like with the predominance of α-pinene (40.6% SD; 40.5% WD) and β-pinene (33.9% SD; 25.9% WD), followed by hydrocarbon monoterpenes β-phellandrene (4.8% SD; 3.6% WD), 3-carene (4.1% SD; 3.1% WD), and limonene (4.0% SD; 3.7% WD). Hydrosol's composition is rich in oxygenated compounds with α-terpineol (29.3% SD; 33.5% WD), *trans*-pinocarveol (5.2% SD; 3.7% WD), terpinen-4-ol (5.0% SD; 5.8% WD), verbenone (4.9% SD; 5.4% WD), borneol (4.9% SD; 3.9% WD), and pinocarvone (4.6% SD; 4.3% WD). These black spruce bark essential oils differ in composition from those from needles, which are commercially available and rich in bornyl acetate.

Keywords: Black spruce; Picea mariana; Bark; Valorization; Essential oil; Hydrosol; Chemical composition

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INTRODUCTION

Coniferous trees are known for their pleasant resinous and terpenic smell that is characteristic of the forest atmosphere. Several essential oils from softwoods that are obtained by hydrodistillation of the needles are available on the market, *i.e.*, essential oils of pine, fir, cedar, or spruce. Another well-known conifer essential oil is turpentine oil distilled from the oleoresin of *Pinus* species.

The essential oils and oleoresins of those conifers that contain resin canals can be found in all plant parts. However, the composition of the essential oils obtained from different parts of the same plant can vary from little differences (yields) to important dissimilarities (composition). For example, two different essential oils are produced from the cinnamon tree, one from leaves containing 87% eugenol as the major component and one from bark containing 97% of cinnamaldehyde (Singh *et al.* 2007). As previously reported, the composition of essential oils from conifers can also vary depending on the part analyzed (Kubeczka and Schultze 1987).

Black spruce (*Picea mariana* (Miller) B.S.P.) is one of the most important industrial species of the Canadian boreal forest. Its processing during logging and wood transformation generates huge amounts of biomass residues, consisting of 13% foliage, 6% branches, and 8% bark per tree on an oven dry basis (Desrochers 2011). The foliage is currently used to produce the essential oil of black spruce, which is widely used in aromatherapy. Shaw described its composition for the first time with bornyl acetate as its main compound (37%), followed by α-pinene (16%), camphene (10%), β-pinene (6.5%), and limonene (6.5%) (Shaw 1950; Guenther 1952). The hydrosol from black spruce needles obtained during hydrodistillation (also named distillation water), has been studied by Garneau *et al*. (2012). Its composition is rich in oxygenated monoterpenes, mainly composed of α-terpineol (14.8%), borneol (13.5%), bornyl acetate (7.8%), and terpinen-4-ol (6.5%). As for the bark, investigations have been made to produce a hot water extract enriched in polyphenols (Diouf *et al.* 2009; Garcia-Perez *et al.* 2012), but no study has yet dealt with its hydrodistillation to produce an essential oil. Moreover, very few reports exist to date on the chemical composition of an essential oil made from conifers' stem bark, and none was found concerning the *Picea* genus.

The present study aims to characterize the chemical composition, by gas chromatography and mass spectrometry, of essential oils and hydrosols of the residual stem bark of *P. mariana,* issued from two different procedures: steam distillation and water distillation.

EXPERIMENTAL

Materials

The analytical standard molecules for gas chromatography analysis, α-pinene, β-pinene, limonene, camphor, 4-ethylphenol, borneol, camphene, sabinene, α-phellandrene, 3-carene, p-cymene, α-terpineol, verbenone, cis-myrtanol, bornyl acetate, β-caryophyllene, and carvone were purchased from Sigma Aldrich (St-Louis, USA). The n-hexane and anhydrous sodium sulfate were purchased from Fisher Scientific (Tustin, Canada). Fresh bark of black spruce (*P. mariana*) was supplied by Boisaco Inc's sawmill, located in Sacré-Coeur, Québec, Canada. The bark was collected in June 2015 from the sawmill debarking of logs originating from Labrieville sector, 140 km from Forestville, Québec, Canada. The bark was milled and sieved to select particles from 2-mm to 1-mm and then stored at -20 °C in the dark.

Methods

Separation of volatile constituents

Essential oils were obtained *via* two different methods: steam distillation (SD) and water distillation (WD). The device used for the hydrodistillation was composed of an aluminum 20-L still (All American, Hillsville, USA) modified in the author's workshop to meet the experimental needs with a heating system, a connection to steam entrance (2 L/h steam flow) and a condenser (Schmidt 2015). To extract the essential oil by steam distillation, the steam was introduced through the plant material to carry the volatile molecules to the condenser to produce the floating essential oil and the hydrosol. The water distillation was performed using the same conditions except for the still, which was filled with 15 L of hot water to have plant material completely immersed during the process. Boiling water created a stream of steam carrying volatile compounds to the condenser (Boutekedjiret *et al.* 2003). For each, 200 g of fresh bark (corresponding to 73 g of dry matter) was processed for 6 h to obtain 34.3 mg of oil with SD and 38.7 mg with WD. Then, 350 mL of each hydrosol produced during WD and SD were submitted to extraction with 3 mL × 200 mL of n-hexane. The extractions were performed in triplicates. The obtained oils and hydrosol extracts were dried over anhydrous sodium sulfate and stored at 4 °C before analysis.

Gas chromatography analysis

Gas chromatography (GC) was performed on a Varian CP-3800 Gas Chromatography (Varian Inc., Walnut Creek, USA) equipped with a Flame Ionization Detector (FID). Separation was achieved on an Agilent J&W VF-5ms (Agilent Technologies, Santa Clara, USA) (30 m × 0.25 mm × 0.25 µm) with a 5% phenyl-methyl column according to the following temperature program: 50 °C to 200 °C at 3 °C/min. The injector and detector temperature were 250 °C and 285 °C, respectively, and the carrier gas He was applied at 1 mL/min. There was 1 µL of sample injected with a split ratio 1:10. Relative percentage amounts of the separated compounds were calculated from FID chromatograms.

Gas chromatography-mass spectrometry analysis

The gas chromatography-mass spectrometry (GC-MS) analyses were performed on a Varian Saturn 2200 GC/MS/MS (Varian Inc., Walnut Creek, USA). The mass spectrometry (MS) was operated in an electronic ionization mode by electronic impact at 70 eV and the MS signal acquisition was set between 30 m/z and 600 m/z. The column and conditions of temperature were identical to those used in the GC-FID analysis. Peak identification was performed by comparison of the mass spectra with those available in the NIST 02, Adams, and Essentia databases, and by comparison of their retention index values with literature reporting results using a VF-5ms column as often as possible (Hennebelle *et al.* 2006; De Pinho *et al.* 2009; Leffingwell and Alford 2011; Robinson *et al.* 2011; Rossi *et al.* 2011; Feijó *et al.* 2014; Guerrini *et al.* 2014; Nurzyńska-Wierdak 2014; Chaftar *et al.* 2016). The retention index values were calculated according to the Kovats equation using a mixture of saturated alkanes (C7-C30) (Supelco, Bellefonte, USA) as a reference. Identification was confirmed with analytical standards available in the author's laboratory when possible.

RESULTS AND DISCUSSION

Essential Oils Composition

The yields of the essential oils of black spruce bark produced either *via* steam distillation or water distillation were determined to the same value of 0.05%. For comparison, this yield was ten times lower than that reported for the hydrodistillation of *P. mariana*'s needles (0.4% to 0.6%) (Guenther 1952). Rudloff (1975) later reported a higher extraction yield of 1.3% from black spruce needles compared to 0.3% from the twigs.

The chemical compositions of the essential oils produced from black spruce bark by steam and water distillation were quite similar (Table 1). They were both mainly composed of hydrocarbon monoterpenes; some sesquiterpenes were also determined, due to water distillation being slightly more efficient to extract sesquiterpenes (2.9% compared to 0.8% of the total oil for steam distillation). The proportion of sesquiterpenes has been reported to rarely exceed 10% in conifer needle oils previously studied, and they seem to be very scarce in *Picea* oils in general (Kubeczka and Schultze 1987). Oxygenated monoterpenoids make up part of the composition of oils obtained from black spruce bark, being less important in the essential oil from SD than in the oil obtained from WD. Indeed, water distilled essential oil contained 18 oxygenated compounds that represented 6.3% of the oil against the 6 oxygenated monoterpenes for the steam distilled counterpart, which was 1.1%. This could have been explained partially by the chemical conversion that occurred in the presence of water during water distillation, which resulted from potential hydrolysis reactions of the hydrocarbon monoterpenes that led to monoterpene alcohol formation (Boutekedjiret *et al.* 2003).

The major black spruce bark essential oil constituent was the bicyclic monoterpene α-pinene that represented almost half of the total composition, 40.6% and 40.5% for the steam distilled and water distilled oils, respectively (Fig. 1). Its isomer β-pinene was the second major compound with a high rate of 33.9% for SD and 25.9% for WD. Thus, the pinenes represented more than two thirds of the black spruce bark essential oil, which showed the same characteristics as turpentine oils (Stevanovic and Perrin 2009), mostly from *Pinus* genus. For comparison, the chemical composition of *Picea abies* turpentine revealed the same pattern with a predominance of α-pinene (54.3%) and β-pinene (25.3%) (Borg-Karlson *et al.* 1993), which confirmed that the volatile part of oleoresins from the *Picea* genus have compositions comparable to those of volatile oils from *Pinus*. The wood of *P. mariana* extracted with hexane was reported to contain α-pinene and β-pinene as the main monoterpenes as well, at 19% (heartwood) and 15% (sapwood) of the total hexane extract along with heavier diterpenoids (Pichette *et al.* 1998). As was reported for the turpentine oil of *P. abies* (Borg-Karlson *et al.* 1993), three other main molecules 3-carene, limonene, and β-phellandrene were found in equivalent proportions in both the steam distilled and water distilled oils from black spruce bark studied in this research.

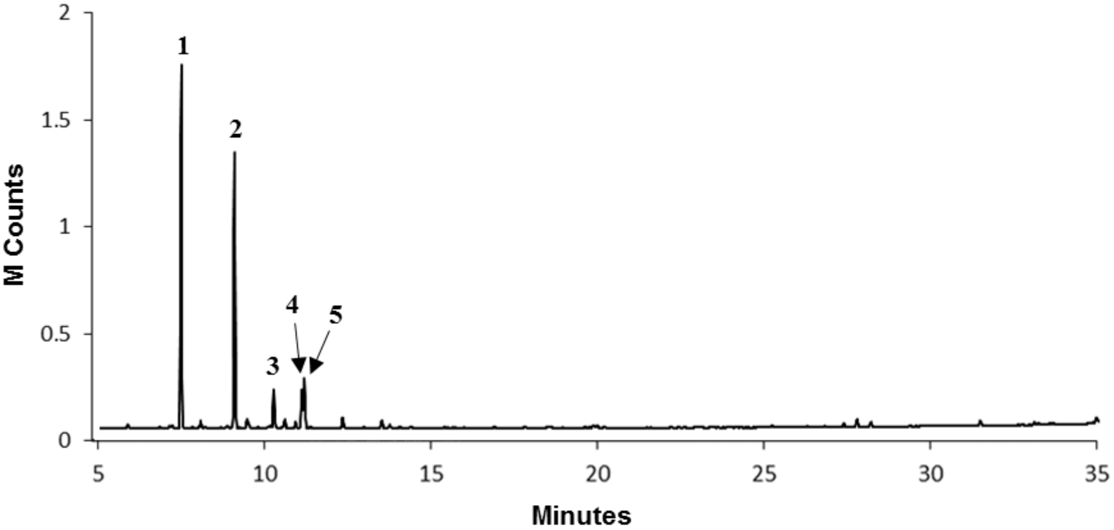

Fig. 1. Gas chromatogram of the essential oil of black spruce bark; Identification of the major peaks: 1: α-pinene; 2: β-pinene; 3: 3-carene; 4: limonene; and 5: β-phellandrene.

Thus, the essential oil of *P. mariana* bark was mainly composed of hydrocarbon monoterpenes, whereas the *P. mariana* needle essential oil was constituted of 37% to 46.5% (Guenther 1952; Rudloff 1975) of the oxygenated monoterpene bornyl acetate. Bornyl acetate was determined only in trace amounts in the black spruce bark essential oil. This result was in accordance with previous literature (Rudloff 1975), where bornyl acetate represented only 1.3% of the oil from twigs (rich in bark and juvenile wood) while it was the major constituent of the oil from *P. mariana* needles. Rudloff also reported great amounts of α- and β-pinene (18.4% and 9.8%, respectively) in the twigs but the highest compound present was 3-carene, which constituted for half of the total twig oil composition. These differences could perhaps have been explained by the degree of maturity of the plant tissue: juvenile bark and wood in twigs were compared with mature stem bark in this study. Thus, hydrocarbon monoterpenes are the most common constituents of conifers resins, especially pinenes, sabinene, 3-carene, and limonene (Kubeczka and Schultze 1987), whereas the oxygenated monoterpenoids were more abundant in the flowers or leaves' essential oils (Stevanovic and Perrin 2009). This can be easily seen in the chromatogram (Fig. 1): the essential oil chromatogram shows a noticeable abundance of compounds in the region of hydrocarbon monoterpenes, whereas the oxygenated monoterpenes region was nearly empty.

Hydrosols Composition

The hydrosols produced during both procedures were rather similar in composition and showed comparable concentrations of terpenoids (60 mg/L for SD and 56 mg/L for WD) (Table 2). They were exclusively composed of oxygenated monoterpenoids; α-terpineol was the major constituent, that represented one third of the total identified hydrosol constituents amongst *trans*-pinocarveol, terpinen-4-ol, borneol, verbenone, and pinocarvone (Fig. 2). The only noticeable difference between the two hydrosols was the absence of hydrocarbon monoterpenes and sesquiterpenes in the water distilled hydrosol. The SD hydrosol contained α- and β-pinenes (1.1% and 1.5 %, respectively), limonene, β-phellandrene, and some sesquiterpenes. However, the presence of hydrocarbon monoterpenes remained very low in hydrosols due to their poor solubility in water compared to oxygenated monoterpenoids (Rao *et al.* 2002); α-terpineol solubility in water reached 710 mg/L compared to 2.49 mg/L and 4.89 mg/L for α- and β-pinenes (Garneau *et al.* 2012).

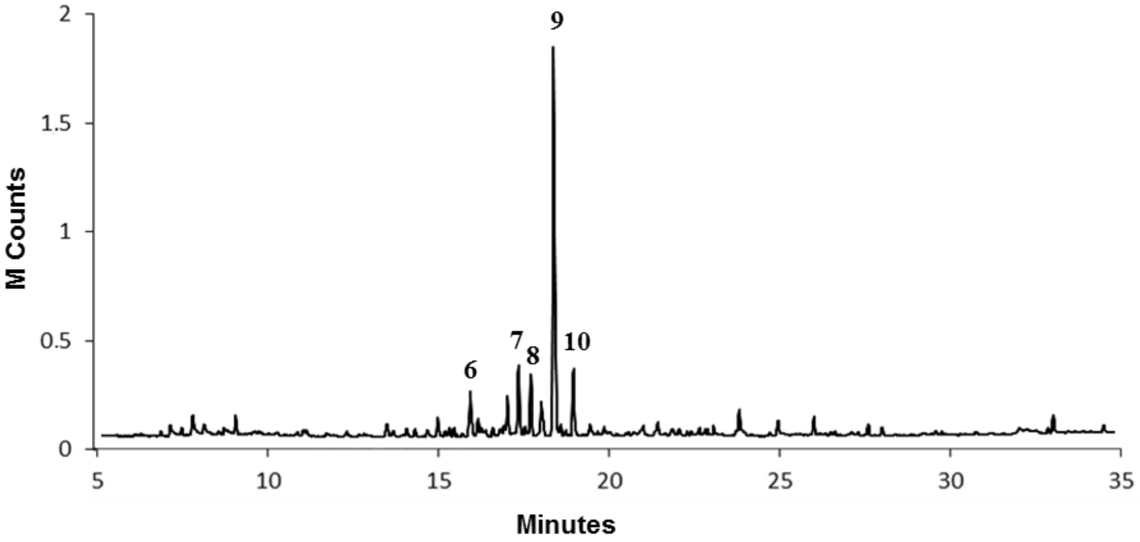

Fig. 2. Gas chromatogram of the hydrosol of black spruce bark; Identification of the major peaks: 6: *trans*-pinocarveol; 7: borneol; 8: terpinen-4-ol; 9: α-terpineol; and 10: verbenone

Interestingly, in black spruce needle hydrosol, α-terpineol was also identified as the main constituent along with borneol, bornyl acetate, and terpinen-4-ol (Garneau *et al.* 2012). The presence of α-terpineol was also reported in the hexane extract of black spruce wood (Pichette *et al.* 1998).

Hydrosols could be used in the perfume industry, cosmetics, or as food ingredients. They could also be further extracted with another lipophilic solvent to obtain the "secondary" oil in opposition to the primary one that naturally evaporates during distillation. According to Rao *et al*., blending the primary and the recovered oil from hydrosols gave more richness and fullness to the oil (Fleisher 1991; Rao *et al.* 2002).

Table 1. Compositions of Essential Oils from Steam Distillation and Water Distillation

		(%)		
Compounds	RI	SD EO[a]	WD EO[b]	Identification[c]
Santene	881	0.3	0.4	MS, RI
Tricyclene	924	0.2	0.4	MS, RI
α-Thujene	926	0.2	trace	MS, RI
α-Pinene	934	40.6	40.5	Std, MS, RI
Camphene	951	0.6	1.1	Std, MS, RI
2,4(10)-Thujadiene	954	0.1	trace	MS, RI
Sabinene	973	0.2	0.1	Std, MS, RI
β-Pinene	980	33.9	25.9	Std, MS, RI
Myrcene	988	1.7	1.1	MS, RI
α-Phellandrene	1008	0.3	trace	Std, MS, RI
3-Carene	1010	4.1	3.1	Std, MS, RI
α-Terpinene	1018	0.6	0.6	MS, RI
p-Cymene	1026	0.5	0.5	Std, MS, RI
Limonene	1030	4.0	3.7	Std, MS, RI
β-Phellandrene	1032	4.8	3.6	MS, RI
γ-Terpinene	1059	0.9	1.2	MS, RI
Terpinolene	1086	0.6	1.0	MS, RI
Dehydro-p-cymene	1092	0.3	0.3	MS, RI
Linalool	1100	-	0.2	MS, RI
1,3,8-p-Menthatriene	1114	trace	0.1	MS, RI
exo-Fenchyl alcool	1122	-	0.2	MS, RI
α-Campholenal	1129	-	0.2	MS, RI
trans-Pinocarveol	1144	-	0.4	MS, RI
Camphor	1151	-	0.1	Std, MS, RI
cis-β-Terpineol	1159	-	0.1	MS, RI
Pinocarvone	1165	0.2	0.1	MS, RI
Borneol	1175	-	0.3	Std, MS, RI
Pinocamphone	1180	-	0.2	MS, RI
Terpinen-4-ol	1183	-	0.7	MS, RI
α-Terpineol	1199	0.1	1.2	Std, MS, RI
Verbenone	1212	-	0.1	Std, MS, RI
Thymol methyl ether	1231	0.3	0.1	MS, RI
4-Ethylguaiacol	1275	-	0.1	MS, RI
Phellandral	1282	0.1	trace	MS, RI

Bornyl acetate	1286	-	0.1	Std, MS, RI
(E,E)-2,4-Decadienal	1297	0.2	1.0	MS, RI
2-Methoxy-4-vinylphenol	1313	-	0.9	MS, RI
(E,Z)-2,4-Decadienal	1321	0.2	0.3	MS, RI
Longicyclene	1399	0.3	1.5	MS, RI
Longifolene	1414	0.3	1.0	MS, RI
β-Caryophyllene	1423	0.2	0.3	Std, MS, RI
α-Humulene	1458	-	0.1	MS, RI
Monoterpenoids	-	95.0	89.9	-
Sesquiterpenoids	-	0.8	2.9	-
Oxygenated compounds	-	1.1	6.3	-
Total compounds	-	95.8	92.8	-

*Notes: a: steam distilled essential oil; b: water distilled essential oil; c: MS (Mass Spectra), RI (Retention Index), and Std (Standard molecule). Molecules in bold are major compounds.

Table 2. Compositions of Hydrosols from Steam Distillation and Water Distillation

		(%)		
Compounds	RI	SD hyd[a]	WD hyd[b]	Identification[c]
α-Pinene	934	1.1	-	Std, MS, RI
β-Pinene	980	1.5	-	Std, MS, RI
Limonene	1030	0.6	-	Std, MS, RI
β-Phellandrene	1032	1.0	-	MS, RI
p-Guaiacol	1087	1.1	1.1	MS, RI
Linalool	1100	0.8	0.5	MS, RI
Phenyl ethyl alcohol	1115	0.5	0.6	MS, RI
exo-Fenchyl alcool	1122	1.5	1.0	MS, RI
α-Campholenal	1129	1.4	0.3	MS, RI
p-Menth-3-en-1-ol	1137	-	0.4	MS, RI
***trans*-Pinocarveol**	1144	5.2	3.7	MS, RI
(E)-Verbenol	1149	1.2	-	MS, RI
Camphor	1151	0.8	0.3	Std, MS, RI
p-Mentha-1,5-dien-8-ol	1153	0.6	0.9	MS, RI
cis-β-Terpineol	1159	0.9	0.6	MS, RI
Pinocarvone	1165	4.6	4.3	MS, RI
4-Ethyl-phenol	1172	0.8	4.2	Std, MS, RI
Borneol	1175	4.9	3.9	Std, MS, RI
Pinocamphone	1180	1.0	-	MS, RI
Terpinen-4-ol	1183	5.0	5.8	MS, RI
p-Cymen-8-ol	1189	3.0	4.4	MS, RI
α-Terpineol	1199	29.3	33.5	Std, MS, RI
Verbenone	1212	4.9	5.4	Std, MS, RI

trans-Carveol	1217	0.9	1.4	MS, RI
cis-Carveol	1234	-	0.4	MS, RI
Carvone	1246	-	0.4	Std, MS, RI
Piperitone	1258	1.6	0.9	MS, RI
cis-Myrtanol	1268	1.4	1.3	Std, MS, RI
4-Ethylguaiacol	1275	0.7	2.6	MS, RI
p-Cymen-7-ol	1292	0.7	0.7	MS, RI
(E,E)-2,4-Decadienal	1297	4.6	0.5	MS, RI
2-Methoxy-4-vinylphenol	1313	-	5.8	MS, RI
(E,Z)-2,4-Decadienal	1321	3.1	0.9	MS, RI
p-1,4-Menthadien-7-ol	1331	-	0.3	MS, RI
1,2,4-Trimethoxybenzene	1370	1.5	0.3	MS, RI
Vanillin	1398	-	0.4	MS, RI
Longifolene	1414	0.8	-	MS, RI
β-Caryophyllene	1423	1.2	-	Std, MS, RI
α-Bisabolene	1475	2,9	-	MS, RI
Monoterpenoids	-	86.2	86.8	-
Sesquiterpenoids	-	4.9	0.0	-
Oxygenated compounds	-	82.0	86.8	-
Total compounds	-	91.1	86.8	-

*Notes: a: steam distilled hydrosol; b: water distilled hydrosol; c: MS (Mass Spectra), RI (Retention Index), and Std (Standard molecule). Molecules in bold are major compounds.

The results obtained in this study indicated the potential of valorization of two products, essential oil and hydrosol, issued from black spruce bark steam or water distillation. The essential oil was mainly composed of terpene hydrocarbons that resembled the composition of turpentine oils that corresponded to the volatile part of spruce oleoresins. Each of these products could find appropriate specific applications.

CONCLUSIONS

1. This was the first study that reported the characterization of volatile oil and hydrosol obtained by steam or water distillation of black spruce bark.
2. The essential oil from black spruce bark was constituted of monoterpene hydrocarbons, with a predominance of α- and β-pinene.
3. Oxygenated volatile components, with the major constituent α-terpineol, were determined to be concentrated in the hydrosol, water-soluble fraction of the oil.
4. The results obtained for steam distillation and water distillation of black spruce bark were comparable both in terms of volatile oils and hydrosols yields and their compositions. The essential oil production from black spruce bark, even though it led to a very low yield, could be optimized to reach a more acceptable rate using more material in a scale-up process.

5. This study represents a new approach to the valorization of bark as a wood transformation waste *via* production of a new essential oil of black spruce bark that could be extrapolated to bark residues of other conifer species.

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