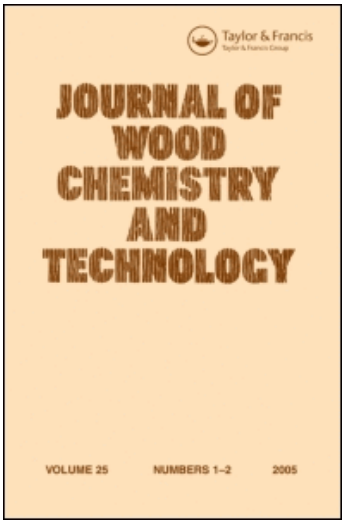

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INFLUENCE OF SAMPLE PREPARATION ON THE COMPOSITION OF THE ESSENTIAL OIL OF THE NEEDLES AND TWIGS OF *PICEA MARIANA* (MILL.) B.S.P.

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ABSTRACT

The needles and twigs of black spruce - *Picea mariana* (Mill.) B.S.P. - were analyzed for the composition of their essential oil after having been submitted to hydrodistillation. The composition of the essential oil is significantly influenced by the preparation of the samples: whether prepared as two-cm pieces or macerated in a blender. Depending upon the preparation of the samples, the major components are, respectively: α-pinene (7.4 and 13.5%), camphene (14 and 21.2%) and bornyl acetate (41.8 and 29.6%). Sixteen constituents are reported for the first time.

INTRODUCTION

The physical properties of the essential oil of *Picea mariana* (Mill.) B.S.P. were described long ago[1,2]; the composition of this oil in terms of major and minor constituents reported by Rudloff [3,4].

The economic importance[5-7] of this essential oil, due to its high content in bornyl acetate, prompted us to study further the influence of different physical factors on the quantity and quality of this oil. In this study, we examine the influence of the preparation of the samples on the composition and yield of the essential oil.

TABLE 1

Composition of the Volatile Oil of the Leaves and Twigs of Black Spruce

EN No	Peak No	Compound Formula	RN RRT	Concentration: Range (%): 2-cm pieces	(macerated samples)	Average (%): 2-cm pieces	(macerated samples)	Ref.
01	3	santene C_9H_{14}	529-16-8 0.198	1.3 - 3.8	(0.9 - 3.0)	2.5	(1.9)	4
02	4	tricyclene $C_{10}H_{16}$	508-32-7 0.238	0.9 - 1.7	(1.9 - 2.8)	1.2	(2.4)	4
03	5	α-pinene $C_{10}H_{16}$	80-56-8 0.248	6.2 - 8.8	(11.0 - 15.7)	7.4	(13.5)	4
04	6	camphene $C_{10}H_{16}$	79-92-5 0.264	11.5 - 17.9	(18.8 - 24.5)	14.0	(21.2)	4
05	7	sabinene $C_{10}H_{16}$	3387-41-5 0.288	t - 0.5	(t - 0.3)	t	(t)	4
06	8	β-pinene $C_{10}H_{16}$	127-91-3 0.296	1.3 - 3.0	(2.0 - 2.7)	2.4	(2.4)	4
07	9	myrcene $C_{10}H_{16}$	123-35-3 0.309	0.4 - 4.1	(2.8 - 4.1)	2.3	(3.6)	4
08	10	α-phellandrene $C_{10}H_{16}$	99-83-2 0.333	t	(t - 0.4)	t	(t)	4[a]
09	11	3-carene $C_{10}H_{16}$	13466-78-9 0.346	2.1 - 10.7	(1.7 - 4.6)	5.4	(2.9)	4

10	12	p-cymene $C_{10}H_{14}$	99-83-2 0.353	0 - t	(0 - t)	t	(t)	4
11	13	α-terpinene $C_{10}H_{16}$	99-86-5 0.358	0 - t	(0 - t)	t	(t)	4
12	14	limonene $C_{10}H_{16}$	138-86-3 0.379	2.5 - 5.9	(3.8 - 5.4)	4.5	(4.7)	4
13	15	1,8-cineol $C_{10}H_{18}O$	470-82-6 0.380	t	(0.3 - 0.7)	0.51	(0.5)	4
14	16	γ-terpinene $C_{10}H_{16}$	99-85-4 0.433	0 - t	(0 - t)	t	(t)	4
15	17	fenchone $C_{10}H_{16}O$	1195-79-5 0.448	0 - t	(0 - t)	t	(t)	4
16	19	linalool $C_{10}H_{18}O$	78-70-6 0.519	0 - t	(0 - t)	t	(t)	4
17	20	fenchol $C_{10}H_{18}O$	1632-73-4 0.572	t	(t - 0.4)	t	(t)	n.r.
18	21	camphor $C_{10}H_{16}O$	76-22-2 0.608	t - 1.2	(t - 0.6)	0.6	(t)	4
19	22	citronellal $C_{10}H_{18}O$	106-23-0 0.610	t	(t - 0.1)	t	(t)	n.r.
20	23	ocimene $C_{10}H_{16}$	29714-87-2 0.646	0 - t	(0 - t)	t	(t)	4

(Table 1 continued)

(Table 1 continued)

21	24	isoborneol $C_{10}H_{18}O$	124-76-5 0.650	t	(t)	t	(t)	4
22	25	borneol $C_{10}H_{18}O$	507-70-0 0.676	t - 3.4	(t - 2.6)	2.0	(0.8)	4
23	26	4-terpineol $C_{10}H_{18}O$	562-74-3 0.709	t - 0.5	(t)	t	(t)	4
24	27	α-terpineol $C_{10}H_{18}O$	98-55-5 0.738	0.6 - 1.5	(t - 0.7)	1.1	(0.5)	4
25	28	estragole $C_{10}H_{12}O$	140-67-0 0.744	t	(t)	t	(t)	n.r.
26	30	citronellol $C_{10}H_{20}O$	106-22-9 0.852	0 - t	(0 - t)	t	(t)	n.r.
27	31	piperitone $C_{10}H_{16}O$	89-81-6 0.882	0 - t	(0 - 0.6)	t	(t)	4
28	32	nerol $C_{10}H_{18}O$	29714-87-2 0.916	t	(0.1 - 0.4)	t	(0.2)	n.r.
29	33	carvone $C_{10}H_{14}O$	99-49-0 0.915	t	(t - 0.2)	t	(t)	n.r.
30	34	geraniol $C_{10}H_{18}O$	106-24-4 0.918	t	(t)	t	(t)	4
31	36	bornyl acetate $C_{12}H_{20}O_2$	5655-61-8 1.000	36.4 - 48.8	(24.4 - 33.6)	41.8	(29.6)	4

32	42	geranyl acetate $C_{12}H_{20}O_2$	105-87-3 1.234	0 - t	(0 - t)	t	(t)	4
33	43	(-)-trans-caryophyllene $C_{15}H_{24}$	87-44-5 1.288	t	(t - 0.5)	t	(t)	n.r.
34	44	longifolene $C_{15}H_{24}$	11029-06-4 1.234	t	(t - 0.5)	t	(t)	n.r.
35	45	α-humulene $C_{15}H_{24}$	6753-98-6 1.356	t	(t - 0.1)	t	(t)	n.r.
36	50	β-selinene $C_{15}H_{24}$	17066-67-0 1.470	t	(t - 0.3)	t	(t)	n.r.
37	52	β-cadinene $C_{15}H_{24}$	523-47-7 1.488	t	(t)	t	(t)	n.r.
38	63	β-eudesmol $C_{15}H_{26}O$	473-15-4 1.817	0 - 1.2	(t - 5.5)	t	(1.5)	n.r.
39	64	farnesol $C_{15}H_{26}O$	4602-84-0 1.924	t	(t - 0.3)	t	(t)	n.r.

EN: Entry
RN: Registry Number in Chemical Abstracts
RRT: Relative Retention Time to Bornyl Acetate (29.6 min.)

t: trace amounts (conc. <0.1%)
n.r.: not previously reported
a: uncertain in ref. 4; confirmed in this study

RESULTS AND DISCUSSION

Our results shown in Table 1 illustrate the important influence of the sample preparation on the composition of the essential oil extracted from the leaves and twigs of black spruce. Our results are in agreement with previous work[4]; however, Table 1 shows the identification of sixteen new constituents. Fourteen of the new constituents found in *P. mariana* have also been detected in *P. glauca* and references to their chemicoecological role have been given[8].

From our results, the following observations can be made:

i) the concentration of bornyl acetate is markedly reduced from 41.8 to 29.6% after maceration ;

ii) the concentration of the other major compounds is significantly increased after maceration: α-pinene (7.4 and 13.5%); camphene (14 and 21.2%);

iii) the yield in essential oil, relative to fresh weight, is increased after maceration from 0.5% to 1.0%.

A thoroughly extracted essential oil obtained after maceration contains less bornyl acetate (29.6 vs 41.8%), more α-pinene (13.5 vs 7.4%) and more camphene (21.2 vs 14.0%) than the easily extractible oil obtained without maceration.

These results may be explained in different ways.

First, it has already been observed[9] that the concentration in bornyl acetate is far more important in the leaves (46.5%) than in the twigs (1.3%). For α-pinene, the corresponding results were reported: leaves (8.8%) and twigs (18.4%); however, for camphene, the concentrations are as follows: leaves (19.1%) and twigs (0.9%).

Secondly, assuming that the relative contribution of physical factors such as volatility and solubility in water as being negligible for bornyl acetate, camphene and α-pinene, chemical factors might also be involved to explain the decrease in the concentration of bornyl acetate and the increase in the concentration of camphene and α-pinene after maceration, such as the formation of the carbonium ion after elimination of the acetate group and the subsequent rearrangement of this ion into α-pinene and camphene. Similar routes have already been postulated in biogenetic relationships of terpenes[10].

The abundance of black spruce, its prime importance to the pulp and paper industry, the emergence of new techniques of extraction[11] and separation[12-14] operational at the industrial level combined with the techniques of biotechnology[15] applied to terpenes should enhance the economic development of wood by-products such as essential oils and their constituents.

EXPERIMENTAL

Collection and Preparation of Samples

The foliage of black spruce was collected from 20 to 25-year-old trees located in the Chicoutimi vicinity in winter 1984. The delay between the collection of the 3 samples from ten different trees was reduced to a minimum. Leaves and twigs were placed in plastic bags and kept in a cold room at -20°C two or three days before extraction. Maceration was performed on leaves and twigs using a blender in a cold (5°C) water suspension for 2 minutes.

Compounds were identified by retention time and GC-MS analysis as described previously[8].

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