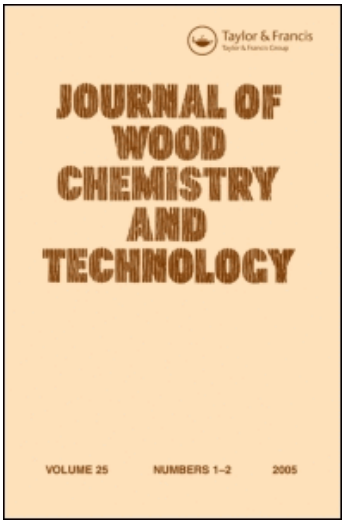

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Extraction and Analysis of the Essential Oil of the Needles and Twigs of White Spruce Picea Glauca (Moench) Voss

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EXTRACTION AND ANALYSIS OF THE ESSENTIAL OIL OF THE NEEDLES AND TWIGS OF WHITE SPRUCE PICEA GLAUCA (MOENCH) VOSS

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ABSTRACT

The constituents of the essential oil extracted from the needles and twigs of white spruce - Picea glauca (Moench) Voss - by steam distillation are analyzed by GC-MS and GC with authentic samples. The analysis allows for the identification of 39 constituents.

INTRODUCTION

White spruce - Picea glauca (Moench) Voss - is an abundant species in Canada; the extraction and analysis of its essential oil have been the subject of many publications[1-4].

This study describes improvements in a method of extraction by steam distillation and reports the identification of 39 constituents of white spruce essential oil, fifteen of which have not been previously reported. Some references are given on the chemicoecological role of the new products.

RESULTS AND DISCUSSION

Table 1 shows the distribution of the compounds identified in the essential oil of Picea glauca (Moench) Voss as obtained on a SE-30 column. Our results confirm previous studies[1-4] on this

essential oil. However, we have found some constituents not yet reported for this species of spruce. Most of the components reported here, including the new ones, have already been submitted to a wide variety of bioassays in order to determine their role on insects either as insecticidal, attractant, antifeedant or repellent. Recent references featuring these new compounds found in the essential oil of white spruce are given here following the name of the products. These constituents are α-terpinene[5], sylvestrene[6], fenchol[7], citronellal[8], ocimene[9], citronellol[10], nerol[11], trans-caryophyllene[12], longifolene[13], elemene[14], α-humulene[15], β-selinene[16], β-cadinene[17], β-eudesmol[18] and farnesol[19]. The identification of these and other compounds was based on capillary GC-MS analysis as well as their retention time and peak enhancement with authentic samples. However, the identity of sylvestrene and elemene is based only on GC-MS. It is to be noted that three components reported here exhibit mean concentrations significantly different from previous work[1-4]: these are myrcene, limonene and camphor. However, all concentrations previously reported fall within the ranges observed here.

In Table 1, the concentrations are based on the percentage composition obtained by summation of all the peak areas (excluding the solvent diethylether) with a reporting integrator; ninety nine peaks were integrated. The mean concentration is the arithmetic mean of the concentrations observed. The standard deviation for the range of concentrations observed is reported. Some difficulties associated with the identification of naturally occurring terpenes have been reported[20]; these difficulties arise from the limits of MS data due to the great similarity of the mass spectra. Also, it is known[20] that a variation in the temperature might reverse the order of elution of some compounds. Recently, a computer pattern recognition method has been proposed[21]; this approach should substantially reduce the time necessary for GC-MS analyses.

In order to identify further minor constituents, the next step in our work on essential oils will deal with the prefractionation of essential oils using both gas and liquid phase preparative chromatography. Recent advances in the preparative gas phase[22] and preparative liquid phase mainly as HPLC[23] will most likely permit substantial progress towards the economic feasibility of fractionation of complex natural mixtures and purification of valuable products.

TABLE 1

Components of the Volatile Oil of the Leaves and Twigs of White Spruce

EN	Peak No	Compound Formula RN	RRT	Concentration: Range (%) Mean (%) S.D. (%)	Ref.
01	3	santene C_9H_{14} 529-16-8	0.198	t-0.6 0.2	1,3,4
02	4	tricyclene $C_{10}H_{16}$ 508-32-7	0.238	0.5-0.7 0.6 0.08	1-4
03	5	α-pinene $C_{10}H_{16}$ 80-56-8	0.248	4.8-8.6 6.5 1.21	1-4
04	6	camphene $C_{10}H_{16}$ 79-92-5	0.264	8-11.8 9.7 1.45	1-4
05	7	sabinene $C_{10}H_{16}$ 3387-41-5	0.288	t-0.4 t	2,3
06	8	β-pinene $C_{10}H_{16}$ 127-91-3	0.296	3.4-6.1 4.5 0.84	1-4
07	9	myrcene $C_{10}H_{16}$ 123-35-3	0.309	4.8-16.5 8.2 4.37	1-4

(continued)

(Table 1 continued)

EN	Peak No	Compound Formula RN	RRT	Concentration: Range (%) Mean (%) S.D. (%)	Ref.
08	10	α-phellandrene $C_{10}H_{16}$ 99-83-2	0.333	t-0.2 t	3
09	11	3-carene $C_{10}H_{16}$ 13466-78-9	0.346	1.1-4.9 2.4 1.55	1-4
10	12	p-cymene $C_{10}H_{14}$ 99-87-6	0.353	0-t t	1,3
11	13	α-terpinene $C_{10}H_{16}$ 99-86-5	0.358	t t	n.r.
12	14	sylvestrene $C_{10}H_{16}$ 1461-27-4	0.372	0-t t	n.r.
13	15	limonene $C_{10}H_{16}$ 138-86-3	0.379	9.8-25.1 15.6 6.33	1-4
14	16	1,8-cineol $C_{10}H_{18}O$ 470-82-6	0.380	0.5-0.8 0.7 0.11	1-4
15	17	γ-terpinene $C_{10}H_{16}$ 99-85-4	0.433	t-0.4 t	1,3
16	18	fenchone $C_{10}H_{16}O$ 1195-79-5	0.448	0-t t	1,3
17	19	linalool $C_{10}H_{18}O$ 78-70-6	0.519	t t	3
18	20	fenchol $C_{10}H_{18}O$ 1632-73-1	0.572	t t	n.r.

EN	Peak No	Compound Formula RN	RRT	Concentration: Range (%) Mean (%) S.D. (%)	Ref.
19	21	camphor $C_{10}H_{16}O$ 76-22-2	0.608	8.5-24.5 15.3 5.72	1-4
20	22	citronellal $C_{10}H_{18}O$ 106-23-0	0.610	t t	n.r.
21	23	ocimene $C_{10}H_{16}$ 29714-87-2	0.646	t t	n.r.
22	24	isoborneol $C_{10}H_{18}O$ 124-76-5	0.650	t t	1,3
23	25	borneol $C_{10}H_{18}O$ 507-70-0	0.676	0.2-5.6 2.4 2.14	1-4
24	26	4-terpineol $C_{10}H_{18}O$ 562-74-3	0.709	0.5-1.5 0.8 0.34	2-4
25	27	α-terpineol $C_{10}H_{18}O$ 98-55-5	0.738	0.4-2.5 1.4 0.72	2-4
26	28	citronellol $C_{10}H_{20}O$ 106-22-9	0.852	t-1.5 t	n.r.
27	29	piperitone $C_{10}H_{16}O$ 89-81-6	0.882	t-1.6 0.8	2-4
28	30	nerol $C_{10}H_{18}O$ 106-25-2	0.915	t t	n.r.
29	31	geraniol $C_{10}H_{18}O$ 106-24-1	0.918	t t	3

(continued)

(Table 1 continued)

EN	Peak No	Compound Formula RN	RRT	Concentration: Range (%) Mean (%) S.D. (%)	Ref.
30	32	bornyl acetate $C_{12}H_{20}O_2$ 5655-61-8	1.000	11.3-19.6 15.6 2.84	1-4
31	33	geranyl acetate $C_{12}H_{20}O_2$ 105-87-3	1.234	0-t t	3
32	34	trans-caryophyllene $C_{15}H_{24}$ 87-44-5	1.288	t t	n.r.
33	35	longifolene $C_{15}H_{24}$ 475-20-7	1.312	t t	n.r.
34	36	elemene $C_{15}H_{24}$ 11029-06-4	1.325	t t	n.r.
35	37	α-humulene $C_{15}H_{24}$ 6753-98-6	1.356	t t	n.r.
36	43	β-selinene $C_{15}H_{24}$ 17066-67-0	1.470	t t	n.r.
37	45	β-cadinene $C_{15}H_{24}$ 523-47-7	1.488	t t	n.r.
38	54	β-eudesmol $C_{15}H_{26}O$ 473-15-4	1.817	0.9-4.0 2.3 1.15	n.r.
39	55	farnesol $C_{15}H_{26}O$ 4602-84-0	1.921	t t	n.r.

RN: Registry Number to Chemical Abstracts.
RRT: Relative Retention Time to bornyl acetate (29.6 min.).
S.D.: Standard Deviation.
t: trace amounts (conc. < 0.1%).
n.r.: not previously reported.

EXPERIMENTAL

Collection and Preparation of Samples

The plant material was collected in the Chicoutimi urban area in January 1984. Fifteen samples were prepared from three different 20 to 25-year-old white spruce trees. The delay between the collection of samples and the steam distillation 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.

In a typical experiment, 250 g of freshly harvested leaves and twigs of white spruce were ground in cold water (5°C) and steam-distilled during 90 min. The observed pH was 5.5 at the beginning and 4.5 at the end of the extraction. In order to reduce the losses by evaporation or solubilization, the following procedure, which constitutes an original contribution in regard to the method described earlier[2], was applied. The distillate was collected through a specially designed long-neck condenser adapter under a layer (ca. 1 cm) of diethyl ether in a saturated NaCl aqueous solution kept at 5°C. The aqueous layer (ca. 1000 ml) was then extracted three times with 50 ml of Et_2O. Afterwards, the organic fraction was dried over anhydrous Na_2SO_4 and Et_2O was carefully removed by distillation under atmospheric pressure. In order to minimize possible losses, all the ether was not completely evaporated. A GC-Analysis performed before and after the distillation of the solvent Et_2O gave no significant differences in the essential oil composition. The yields of essential oil relative to the fresh samples varied from 0.3 to 0.7% in weight (average 0.6%, 15 samples).

GC-MS Analyses

The essential oil was analyzed on two glass capillary columns: SE-30, 30 m x 0.25 mm for GC and DB-1, 25 m x 0.25 mm for GC-MS. GC analyses were as follows: Temperature programming: 60°C up to 190°C at a rate of 2°C/min. Temperatures: injector (300°C),

detector (250°C). GC-MS facilities were provided by INRS-Santé, Montréal, and Environment-Québec (Montréal).

General conditions for GC-MS: electron impact (70 eV), temperatures: injector (250°C), ion source (250°C), oven (temperature programming: 50°C for 2 min. and 5°C/min. up to 280°C). Injection mode: split, ratio 60:1. Mass range: 30 to 500 amu. Sweep speed: 1 sec./decade. Trap current: 100 μA.

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