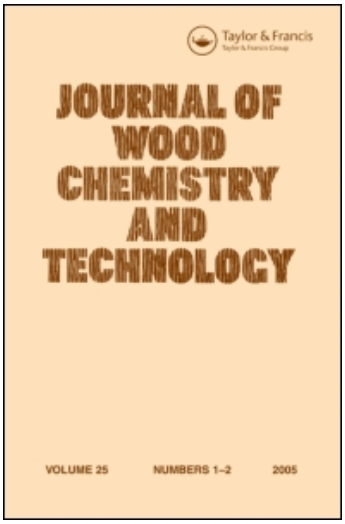

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THE VARIATIONS OF ESSENTIAL OIL COMPOSITION DURING THE EXTRACTION PROCESS. THE CASE OF *Thuja occidentalis* L. AND *Abies balsamea* (L.) MILL.

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ABSTRACT

From analyses of various samples of essential oils extracted by hydrodistillation from the branches of *Thuja occidentalis* L. and *Abies Balsamea* (L.) Mill., it was shown that there are extensive variations in the concentrations of the main components. The content in thujones and fenchone reaches a maximum value of 80 % after 40-50 minutes for cedarleaf oil. After 60 minutes, the concentrations in α-pinene and β-pinene in balsam fir oil are maximum at 15 % and 40 %, respectively.

INTRODUCTION

The northeastern part of United States and eastern part of Canada (particularly, the southeastern part of the Quebec Province) produce high quantities of essential oils obtained from *Thuja occidentalis* (L.) -white cedar- and *Abies balsamea* (L.) Mill. -balsam fir. In the Quebec Province alone, although it is not very easy to know the actual figures for production [1],

TABLE 1

Specifications of Essential oils*

Norms	Cedarleaf oil	Balsam fir oil
d_{25}	0.910 - 0.920	0.872 - 0.878
n_D^{20}	1.4560-1.4590	1.4730-1.4760
$[\alpha]_D$	-14 to -10°	-24 to -19°
chemical composition	ketone content calc. as thujone: min. 60 %	ester content calc. as bornyl acetate: 8 to 16 %.

*: See references 2-6.

several units are known to produce on a year around basis. Both oils are well-known and are described in the literature in terms of norms: see ref. 2, 3, and 4 for cedarleaf oil and 5 and 6 for balsam fir oil. For example, the essential oil from the leaves of *Thuja occidentalis* must contain at least 60% of ketones determined as thujone and that of *Abies balsamea* must include between 8 and 16% of esters determined as bornyl acetate. Other properties such as refractive index, specific gravity, optical rotation, solubility,... are also described (Table 1).

The purpose of this paper is to evaluate some parameters, and more specifically the time effect, in the production process of the above-mentioned essential oils.

EXPERIMENTAL

Two kind of data were collected. Hydrodistillations of essential oils were conducted at the laboratory level. In order to follow as closely as

possible the industrial procedure, no attention has been paid to the differentiation between leaves, buds, and twigs. In typical experiments, 200 g of fresh foliage were immersed in a two-liter three-vertical-neck flask containing ca. 1 liter of water. The steam distillation was carried out during 90 minutes, unless otherwise indicated, according to a procedure described previously [7]. Pressure of the whole system was maintained at atmospheric pressure. Finally, the organic fractions were injected on two different capillary gas-chromatographs: one equipped with a polar carbowax 20 M (30 m x 0.25 mm) and the other one with a nonpolar DB-5 Plus column of the same size. The oven temperature was programmed as followed: constant at 60 °C for 12 min., then heated at a rate of 2 °C/min. up to 210 °C and constant at 210 °C for 33 min. Analyses of oils were based on electronic integration of the signals on the chromatograms.

Several samples were also collected from various extraction factories. They were analyzed through the same chromatographic procedure, after having been diluted in diethyl ether (ca. 1:500). In these cases, n_D and $[\alpha]_D$ values have been measured. It is relevant to recall that, in our laboratory experiments, samples are collected during 15, 30, .. 90 minutes or more and are analyzed. In factories, samples are collected in less than one-minute intervals from time to time. Thus, in laboratory experiments, analyses give more "global" compositions. On the other hand, in factories, they give "instantaneous" compositions.

RESULTS AND DISCUSSION

a) *White cedar oil.*

As shown in Table 1, the essential oil of *Thuja occidentalis* L. is relatively well-known. For example, in 1961, Rudloff gave a very detailed analysis of the oil extracted from eastern white cedar. The major compounds are α-thujone (51-61.5 %), fenchone (13.5-14.5 %), and β-thujone (9-10 %); 29 other products were observed among which 15 were identified [8]. More recently, Lawrence has reviewed the composition of the cedarleaf oil [9]. The reported GC-MS analysis of a lab-distilled oil grown in Japan, again, shows a very similar content (both in qualities and in quantities) [10].

The steam distillation process itself has also been given attention [11]. In each batch, 100 lbs (≈ 45 kg) of raw material were exposed to water vapor. It appears that more than 90 % of the available oil was extracted in less than two hours (> 95 % in three hours). Obviously, the time parameter is important since vapor generation is an important item of cost.

Other parameters were also studied. Vapor pressure, vapor flow rate, packing of extraction chamber, design of the vapor distribution system at the bottom of the reaction chamber, age of raw material,... have been examined. The results were evaluated in terms of the following parameters: refractive index and specific gravity. Percentage composition of ketones were also given. It is a little disturbing to see in this report that roughly half of the values fall outside the limits reported in Table 1. More particularly, the refractive index values were generally higher than the admitted value. Specific gravities were also higher in 50 % of the samples. These values, and more particularly the former ones, suggest the presence of high molecular weight compounds such as sesquiterpenes, diterpenes, and eventually oleoresins in rather high concentrations. In other words, at the pilot plant level, it is possible that the extraction time was too long. A good indication of this situation is given from time optimization experiments. In 10 different experiments, the oil fractions obtained during the first 30 minutes (yields ≈ 70 %) meet all the values given in Table 1: refractive index, specific gravity, and % of ketone. However, during the next 30-minute period, the refraction index values are higher than 1.4590 and the ketone content is in the 47-57 % range. This ketone content decreases with a further increase in hydrodistillation time.

In our study, the ketone content is generally higher than 60 % and the sum (α-thujone + β-thujone + fenchone) is found to be in the 58-70 % range (Table 2). On the other hand, the analyses of industrial white cedar oils coming from various plants of the Quebec Province show that this value generally falls within the 70-80 % range.

At least two pertinent pieces of information can be extracted from Table 2. First, the composition of the lab cedarleaf oil is in agreement with

TABLE 2

Composition of Cedarleaf Oil: Effect of Laboratory Storage of Foliage.

Chemical compound	Room temperature			0 °C	
	3 days	11 days	20 days	12 days	20 days
(E)-2-hexenal	0.36	0.26	0.10	0.27	0.33
α-thujene	0.30	0.35	0.32	0.39	0.29
α-pinene	1.47	1.74	1.46	1.96	1.69
α-fenchene	0.86	1.15	0.94	1.07	0.97
camphene	0.73	1.01	0.81	0.98	0.81
sabinene	6.60	6.31	4.87	7.64	6.97
myrcene	1.87	2.19	1.71	2.47	1.80
α-terpinene	0.42	0.38	0.52	0.40	0.33
limonene	1.26	1.30	1.31	1.48	1.37
γ-terpinene	0.83	0.73	0.95	0.75	0.63
fenchone	9.03	10.4	10.2	9.86	11.3
α-thujone	42.6	43.5	42.9	42.8	49.4
β-thujone	6.81	8.43	8.40	8.46	8.21
camphor	1.41	1.19	0.67	0.81	1.85
4-terpineol	2.29	2.02	2.25	2.02	2.11
isocarveol (?)	0.39	0.24	0.47	0.22	0.37
unknown	0.49	0.70	0.74	0.64	0.60
bornyl Acetate	2.52	3.77	4.47	3.64	2.18
unknown	0.32	0.31	0.33	0.28	0.39
unknown	1.74	1.67	1.48	1.71	1.09
caryophyllene (?)	0.97	1.28	0.98	1.56	0.78
α-humulene	0.56	0.57	0.47	0.70	0.32

what is known from literature. Moreover, the stockpiling effect has a low impact either at room temperature or in a refrigerated room (≈ 0 °C). In fact, the main observed change occurs with a very volatile compound: (E)-2-hexenal. Its concentration decreases steadily with prolonged storage, particularly at room temperature. This observation is interesting since it is known that aldehydes, and particularly this one, have interesting properties for the perfume industry.[12]

The stockpiling effect may be more pronounced in industrial facilities. Particularly, during the summer time, several days of stockpiling may induce a beginning of fermentation and the resulting cedar oil is said to have a "burnt" character. This fermentation process seems more pronounced in piles higher than three feet [13]. Thus, as a rule, long storage time must be avoided.

Typical oil compositions produced in a plant appear in Table 3. From these values, in all samples, the ketone contents were higher than 60 %. However, except for a maximum value registered after 30 minutes, there was a decrease from 80 to 60 % for the ketone content (Fig. 1). At the same time, the pinenes concentrations reached minimum values at 30 minutes and increased slowly with a further increase in extraction time (Table 3). Other compounds had a different behavior. At first sight, three different considerations may be proposed to explain this behavior. First, a physical one: more volatile compounds are easier to extract. Second, a biological one: the extraction rate depends on the cohesion of the biological matrix containing terpenoid compounds. Finally, in some cases, a compound may be chemically linked to a substrate. In that case, the decomposition rate of the chemical bond involved may be the limiting rate parameter.

Thus, taking into account the variation of the ketone content with time, it appears that the steam distillation of ca. 80 % of the available oil is a good target since the cost of energy is kept at a minimum, the ketone content is maintained at a sufficient value, and the concentration of high molecular sesquiterpenes,... and eventually oleoresins are also inside reasonable limits.

TABLE 3

Analyses of Cedarleaf Oil During the Distillation Process (Plant Production, Main Products %).

Time (minutes)	0	30	60	90	120	180	300
n_D^{20}	1.4561	1.4563	1.4570	1.4584	1.4605	1.4605	1.4606
α-thujone	51.57	55.55	53.80	49.83	43.93	42.95	42.22
fenchone	17.23	16.63	14.15	10.88	9.49	11.59	10.94
ß-thujone	7.45	8.37	8.35	8.44	7.75	6.77	7.12
α-pinene	9.04	3.06	5.09	3.80	4.345	7.11	7.75
sabinene	2.86	2.92	2.88	2.74	2.35	2.64	1.63
camphor	1.70	2.18	2.55	2.93	2.91	1.92	1.72
bornyl acetate	1.26	1.27	2.00	3.82	5.46	4.75	4.11
limonene + ß-phellandrene	1.16	1.22	1.39	1.63	1.90	1.94	2.43
camphene	1.16	1.28	1.49	1.85	2.04	2.00	2.73
α-fenchene + α-thujene	1.05	1.14	1.33	1.70	1.87	1.83	2.46
myrcene	0.96	0.70	0.85	0.81	0.93	1.12	1.24
γ-terpinene	0.87	1.00	1.02	1.21	1.50	1.63	2.17
4-terpineol	0.71	0.93	1.28	2.25	2.95	2.34	2.09
p-cymene	0.61	0.68	0.72	0.77	0.89	0.94	1.05
α-terpinene	0.60	0.74	0.66	0.74	0.95	1.04	1.42
ß-pinene	0.41	0.18	0.26	0.24	0.34	0.42	0.52
cumene	0.23	0.28	0.38	0.58	0.72	0.69	1.19
(E)-2-hexenal	0.28	0.067	0.097	0.078	0.090	0.12	0.20

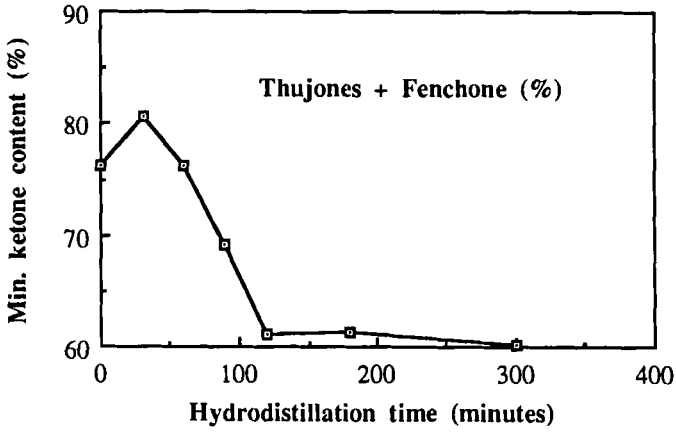

Figure 1. The variation of the (α-thujone + β-thujone + fenchone) % *versus* the hydrodistillation time of cedarleaf oil.

As far as hydrodistillation time in the plant is concerned, we have observed variations among factories. Of course, several parameters such as preparation of branches, vapor pressure and flow rate,... are important factors. However a three to four hour hydrodistillation period is usual for a reactor containing 1 to 2 tons of raw material.

Essential oil from the foliage of *Abies balsamea* (L.) Mill. is also well documented (Table 1). In 1982, Rudloff and Granat published a paper on the seasonal variations of the terpenes in leaves, buds, and twigs of balsam fir from Saskatchewan [14]. The main product reported is β-pinene (43-55 %). The relative importance of various monoterpenes and bornyl acetate depended on the anatomical origin of the oil (Table 4). There were also important seasonal variations, particularly for new buds. As far as bornyl acetate is concerned -the chemical whose concentration must be in the 8-16 % range- the anatomical origin of oil and the harvesting season were also important for new buds. Since, on an industrial basis, there is no discrimination between leaves, buds, and twigs, these parameters have not been considered.

TABLE 4

Essential Oil from Western Balsam Fir: Laboratory Scale, Main Products.

Compound	Leaves	Twigs	Buds
β-pinene	54.2 ± 1.0	52.6 ± 1.8	42.8 ± 1.6
α-pinene	7.0 ± 1.0	10.6 ± 0.5	9.1 ± 0.5
limonene	3.1 ± 0.2	15.6 ± 1.5	21.8 ± 0.9
β-phellandrene	6.5 ± 0.2	6.3 ± 0.3	5.6 ± 0.4
camphene	6.1 ± 0.3	1.9 ± 0.3	1.9 ± 0.5
bornyl acetate	12.8 ± 0.3	4.1 ± 0.4	4.6 ± 0.3
Total oil % yield	2.8 ± 0.6	1.8 ± 0.5	3.2 ± 0.5

Samples collected during Winter (see ref 14).

b) *balsam fir oil*

The extraction process has also been studied in details at the prepilot plant level [11]. These results are similar to those reported above for cedarleaf oil. Again more than 92 % of the available oil was extracted in less than three hours (97 % in four hours). Moreover, half of the samples had refractive index values lower than 1.4730 and 40 % had specific gravities higher than 0.878. Much better values were obtained for the ester content: this value was generally in the 8-16 % range, except for the "old trees" where the ester content was lower than 8 % (8 out of 13 samples). From our own experience, this last value is often close to the minimum 8 % value, and sometimes it may be much lower in industrial production.

Typical analyses of oil fractions collected during an industrial hydrodistillation process are given in Table 5. A decrease in the β-pinene concentration was observed during the process (Fig. 2). On the other hand, α-pinene concentration passed through a minimum value and that of bornyl

TABLE 5

Analyses of Balsam Fir Oil During the Hydrodistillation Process: (Industrial Scale, Main Products %)

Time (min.)	0	35	65	320	375	440
n_D^{20}	1.4744	1.4740	1.4742	1.4743	1.4742	1.4741
β-pinene	38.07	36.78	35.42	25.40	22.84	24.34
Δ^3-carene	14.91	14.78	15.74	20.73	14.44	16.18
α-pinene	15.87	12.44	10.58	11.05	11.17	12.44
bornyl acetate	3.59	9.02	8.10	12.96	15.13	12.04
limonene	6.94	5.19	7.26	7.97	6.16	7.21
β-phellandrene	6.61	5.01	7.28	6.98	4.76	5.19
camphene	6.83	3.57	5.88	4.97	4.18	4.43

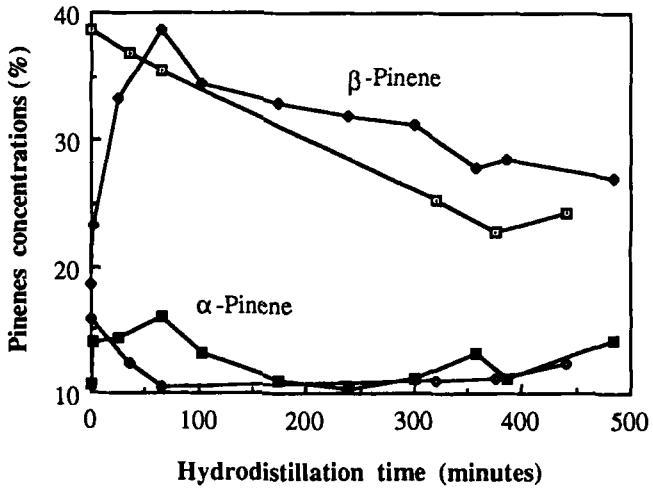

Figure 2. The variation of the β-pinene and α-pinene concentrations during the extraction process of balsam fir oil in two different plants: see table 5 and figure 3. Open dots: plant 1; closed dots: plant 2.

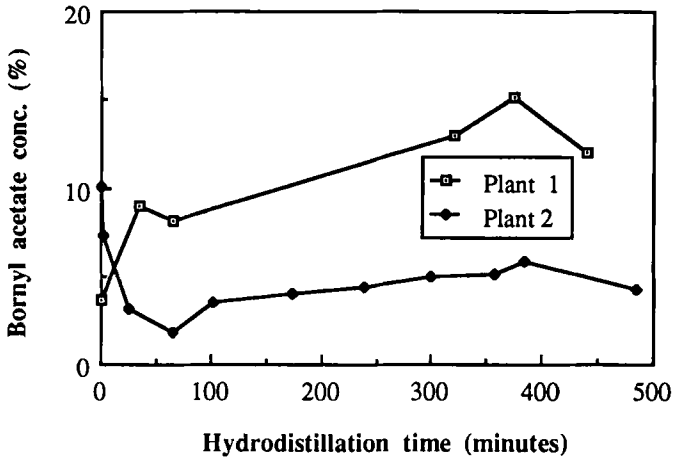

Figure 3. The variation of the bornyl acetate percentage during the hydrodistillation process of balsam fir oil in two different plants: see table 5 and figure 2.

acetate, on the contrary, seems to have reached a maximum value after six hours (Fig. 3). The most important feature is the presence of a high percentage of Δ^3-carene, a compound not reported in the Saskatchewan balsam fir oil [15] as shown in Tables 4 and 5. As far as norms are concerned, this bornyl acetate concentration is important. Since the rate of distillation decreased very quickly with an increase in hydrodistillation time, the first half hour is important. In fact, the fractions recovered after the first 30 minutes must be sufficient in order to get a global bornyl acetate concentration higher than 8 %. Finally, the 440-minute hydrodistillation time shown in Table 5 is much higher than the previously indicated three to four hours [11]. Local producers generally consider that 7 hours is necessary to get a good product. On one occasion, we observed how difficult it may be to extract balsam fir oil. In that case, fresh foliage, harvested less than 48 hours before, was submitted to steam distillation (Fig. 4 - plant 2). Even after 7 hours, the extraction did not seem to be complete. Although the concentration versus time profiles for various components were similar to what is reported above

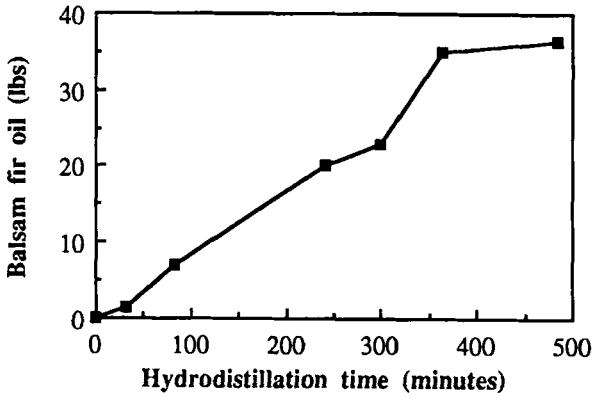

Figure 4. The quantities of balsam fir oil extracted *versus* time.

(Fig. 3), the extraction rate is more linear with time than it was expected from data obtained at pilot plant level.

It must be added that this oil composition is relatively different from that given in Table 4. Obviously, the origin of the foliage and its processing are crucial parameters.

Finally, as concluding remarks, it must be added that other parameters could be very important as far as the quantity and the quality of the oil are concerned. For example, we have observed that quality is deeply dependent on trees. Thus, genetics cannot be ignored. At other level, different grindings may improve the yield *and* either increase or decrease the quality of given oil... Other studies are planned to get more light on these parameters.

ACKNOWLEDGMENTS

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