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Essential Oil of the Wood of *Thuja occidentalis* L.

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ABSTRACT: Composition of the heartwood oil of *Thuja occidentalis* L. was investigated by a combination of capillary GC (retention indices) and GC/MS. The oil was obtained by steam distillation of various lots of waste residues from cedar shingle industries. Twelve out of 20 observed compounds were identified. Monooxygenated sesquiterpene compounds are the most important components (80% of the total). Occidentalol is the main component: its relative concentration varies between 20% and 50%, depending on the isolation parameters. This concentration decreased as the isolation proceeded, typically from 40-50% to 10-20% between 1 and 5 hours of distillation. Three occidol isomers, occidenol, and α-, β-, and γ-eudesmols were also observed in relative concentrations of 4% to 12%. The monoterpene family is represented by terpinen-4-ol, and carvacrol. α-Thujaplicin, a tropolone derivative, is also among the products. The relative concentration of thujaplicin decreased from 5% to 0% between 1 and 5 hours of distillation.

KEY WORD INDEX: *Thuja occidentalis*, Cupressaceae, eastern cedar heartwood, essential oil composition, occidentalol, occidol.

INTRODUCTION: The essential oil of the leaves of *Thuja occidentalis* L. is relatively well-known (1-4). It may be regularly found as an essential oil of commerce. However, the knowledge of the wood oil of this species is limited (5). This is quite surprising since this wood has a strong and characteristic smell; it is used for its miticide properties in the storage of furs in Canada, and as will be shown, it has a high oil content (6).

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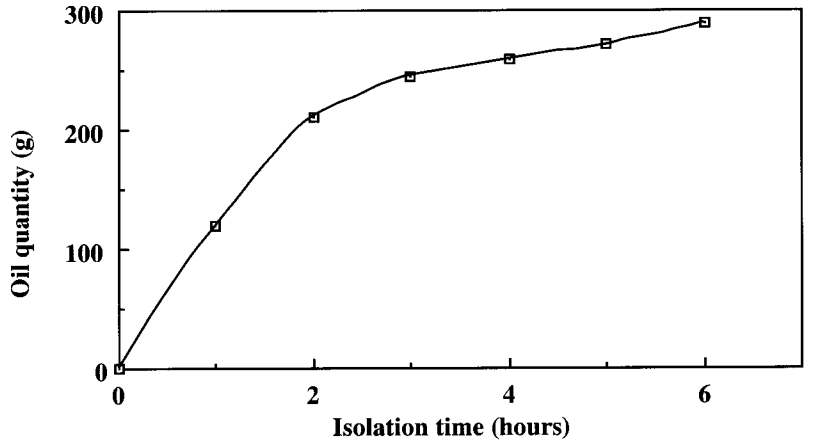

Figure 1. Quantitative production of the essential oil from 50 pounds of raw material

Table I. Chemical composition of *Thuja occidentalis* wood oil produced from different distillation times⁺

Compound	Ret. time (sec)*	K.I.** DB-5	K.I.** S-10	Distillation time (hour) 1	2	3	4
terpinen-4-ol	820	1177		0.16			
unidentified	885	1200	2142	0.13	0.07	-	-
carvacrol	1137	1309	2225	0.20	0.12	0.06	-
methyl geranate	1197	1323		0.20			
α-thujaplicin	1415	1400	2120	1.87	0.49	0.0	t
occidentalol	1756	1548	2097	50.97	48.98	31.72	19.65
unidentified	1772	1554		0.30	0.36	0.34	0.30
unidentified	1862	1591	2032 ?	1.46	1.08	0.89	0.83
C_{15} acetate ?	1881	1594		0.79	0.83	0.64	0.54
γ-eudesmol	1955	1625	2157	4.68	5.69	7.54	8.87
β-eudesmol	1996	1644	2214	7.44	7.78	8.30	7.78
α-eudesmol	2003	1647	2208	3.78	4.19	4.89	5.19
occidenol + unknown	2052	1669[a]	2328	13.64	13.15	13.67	10.97
(eudesmol type)***	2046		2308				
unidentified[a]	2091	1691		t	0.13	0.20	0.31
occidol	2396	1824	2653	11.10	12.55	23.67	34.50
occidol isom. #1	2416	1832	2658	2.46	2.81	5.32	7.59
occidol isom. #2	2468	1860	2709	0.56	0.63	1.25	1.95
occidol / occidol isom. #1				4.51	4.47	4.45	4.54
occidol isom. #1 / occidol isom. #2				4.39	4.46	4.25	3.89

⁺: Origin of the raw material: Gaspesia, Quebec Province.
*: Retention time measured at Baylor Univ. on DB-5 column;
**: Kovats indices measured at UQAC on the apolar DB-5 and Supelcowax 10 columns;
***: 1/3.5 < unknown/occidenol ratio < 1/5.5
[a]: M/e 218, *m/z*: 159, 59(75), 105 (39), 91 (35), 131 (25), 79 (21),...
t = trace

The purpose of this project was to study the wood oil of *T. occidentalis*, emphasizing the distillation of the waste materials from the cedar shingle industry. It should be noted that although in the eastern part of North America, the thuja tree is misleadingly called "cedar or white cedar" ("cèdre" or "cèdre blanc"), the oil is totaly different to the one obtained from the Texas cedarwood (*Juniperus ashei* Buch.) which yields mainly α- and β-cedrene, thujopsene and cedrol (7).

EXPERIMENTAL: ***Material***—*T. occidentalis* waste materials were obtained from various cedar shingle mills in Quebec as well as in New Brunswick (Canada), and in Maine (U.S.A.) during the Spring of 1992. The wood contained 35% to 45% moisture.

Oil Isolation—Twenty-five to fifty kilograms of fresh as well as aged shingle waste material (1 to 5 weeks) was hydrodistilled batchwise in a 280 L distillation vessel made of stainless steel. The water vapor rises through the material at a low pressure, typically a few pounds per square inch and at a flow rate of 0.4-0.5 L/min. The oil temperature at the oulet of the condenser was 80°-90°C. At this temperature, the oil had a deep reddish color and a density slightly lower than that of water. At a lower temperature (60°-75°C), the oil becomes a yellowish solid with a density slightly higher than that of water. An oil was also isolated from the distillation water by extraction with Et_2O.

Analysis—The oil was analyzed at University of Quebec at Chicoutimi (UQAC) by a combination of GC-capillary columns using either an apolar capillary column (DB-5, 30 m x 0.25 mm) or a polar column (Supelcowax 10M, 30 m x 0.25 mm) (8). Identification of the compounds was done by GC/MS (VG12-250). At Baylor University, a Finnigan ion trap mass spectrometer (model 800) was used with a J&W 30 m x 0.25 mm DB-5 column (9). Kovats indices and mass spectra of each compound were compared to those available from the literature or from our own data sources to confirm the mass spectral identifications.

RESULTS AND DISCUSSION: The oil obtained is a yellowish solid at room temperature which melts between 55°C and 70°C. The yields were typically 0.6-1.0% (fresh material) and 0.9-1.3% (dry material) (Figures 1 and 2). The analyses of the oils are given in Tables I and II. Although no results are given here, the origin of the raw material had no influence on the yield and the composition of the oil. The main compounds were oxygenated sesquiterpenes. Occidentalol with a relative percentage in the 20-50% range was the main product. The three α-, β-, and γ-eudesmols, occidenol and three occidol isomers were also present in lower concentrations (<15%). The ratio between occidol isomer #1/occidol isomer #2 is constant and is unaffected by changes in the working parameters. Occidentalol, occidenol and the three occidol isomers are unusual natural compounds. They have been observed in tobacco leaves in response to a virus infection (10). On the other hand, the three eudesmols are commonly found. For example, the α- and β-eudesmols occur in various eucalyptus oils (11) as well as wood oil of *Amyris balsamifera* (12) and the leaf oil of *Cryptomeria japonica* (13). In addition these sesquiterpene alcohols were also observed in *Thuja koraiensis*, the α- and β-eudesmols being the main components (14). The monoterpene family is represented by two oxygenated products: terpinen-4-ol, and carvacrol. α-Thujaplicin, a tropolone derivative, is also observed. Terpinen-4-ol is a very common compound found in many essential oils whereas carvacrol is somewhat less common except in certain Lamiaceae where it is often found (15). Carvacrol methyl ether was shown to be present in high percentage in the wood essential oils of *Cupressus sempervirens* (16).

α-Thujaplicin, which is known for its fungicidal properties, has been found in various Cupressaceae together with β- and γ-thujaplicin (16), particularly in *Thuja plicata* (17). It was identified in *T. occidentalis* by early workers (18). These fungicidal properties may promote the use of eastern white cedar wood in fur storage. It should be noted that old

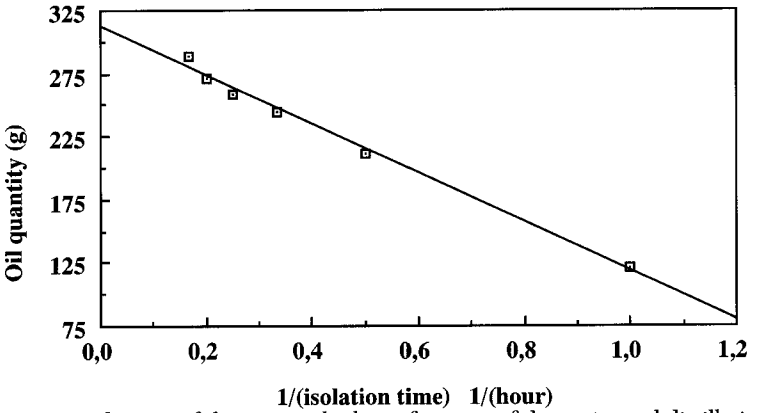

Figure 2. Production of the essential oil as a function of the reciprocal distillation time (see Figure 1); $y = 310 - 192\ x$; $r^2 = 0.998$

Table II. Composition of the accumulated samples of *Thuja occidentalis* wood oil produced over 5 hours+

	Collecting period (hour)				
Compound	1	2	3	4	5
terpinen-4 ol	0.47	0.13	0.07	0.07	0.05
29.64 (1200)*, [a]	0.57	0.18	0.09	0.10	0.10
31.43 (1229)[b]	0.78	0.61	0.68	0.27	0.36
carvacrol	0.47	0.23	0.14	0.12	0.13
38.13 (1331)[c]	0.34	0.08	0.05	0.06	0.06
α-thujaplicin	12.32	5.13	2.01	1.97	1.25
occidentalol	50.57	40.29	31.61	28.26	23.94
52.81 (1554)[d]	0.17	0.20	0.19	0.18	0.16
55.30 (1591)[e]	1.49	1.05	0.94	0.92	0.88
55.52 (1593)[f]	0.88	1.06	0.90	0.79	0.64
γ-eudesmol	3.91	5.73	6.89	7.57	8.48
β-eudesmol	6.24	10.01	9.92	9.13	8.06
α-eudesmol	2.93	4.73	5.11	5.04	4.95
occidenol + unknown **	9.75	17.60	18.37	16.38	13.33
60.87 (1691)	t	t	0.16	0.16	0.23
occidol	6.21	9.13	16.66	21.28	27.52
occidol isom. #1	1.56	2.17	3.99	5.12	6.67
occidol isom. #2	0.34	0.46	0.86	1.11	1.49
occidol / occidol isom. #1	3.98	4.21	4.17	4.16	4.13
occidol isom. #1 / occidol isom. #2	4.59	4.72	4.64	4.61	4.48

+ Origin of the sample: Maine State;
*: Kovats indices on apolar DB-5 column; **: 1/3.5 < unknown/occidenol ratio < 1/5.5
[a]: M/e 136?, *m/z*: 121, 77(32), 136(30), 91(27), 103(23), 51(16),...
[b]: M/e >163?, *m/z*: 121, 77(95), 91(68), 149(66), 41(57), 51(51),...
[c]: M/e >151?, *m/z*: 69, 41(82), 114(20), 83(15), 53(13),...
[d]: M/e 218, *m/z*: 95, 41(82), 43(56), 131(45), 91(38), 56(33),...
[e]: M/e 218, *m/z*: 43, 41(96), 59(91), 91(75), 157(63), 145(61),...
[f]: M/e 220, *m/z*: 59, 43(88), 131(72), 41(70), 91(60), 107(57),...
t = trace

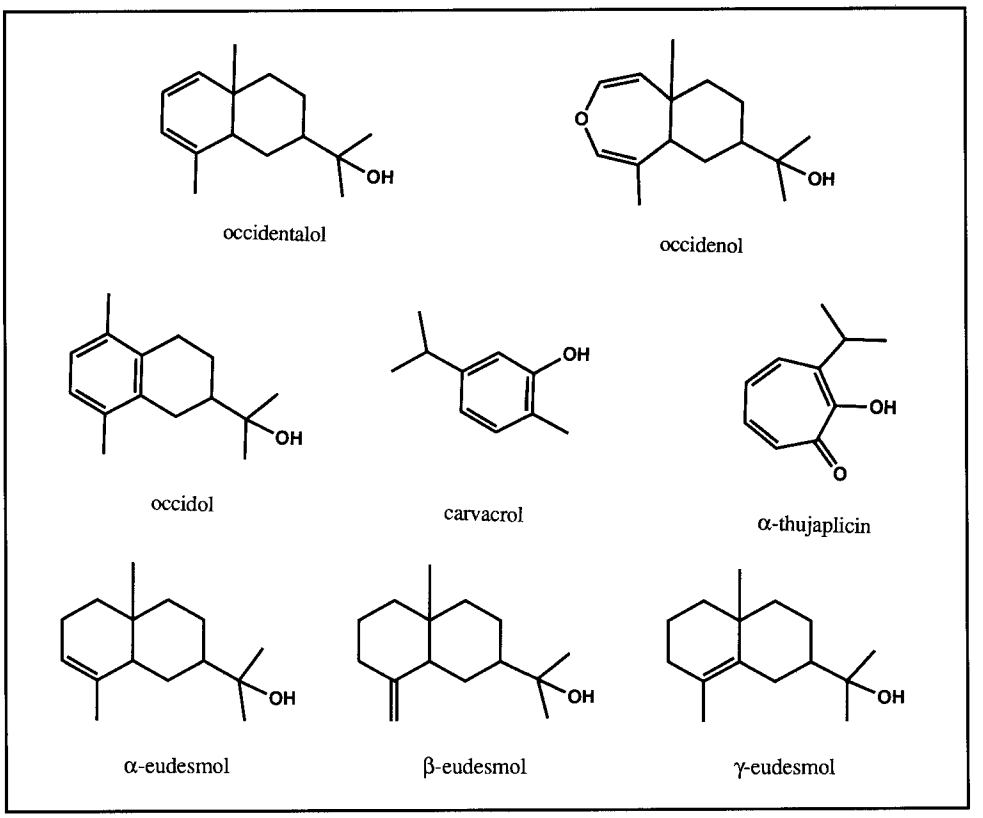

Table III. Composition of the distillation water obtained over four sampling periods during the production of *Thuja occidentalis* wood oil*

Compound	Time of extraction (hour)			
	1	2	3	4
29.69	1.15	0.07	t	-
31.47	3.79	8.69	2.51	1.37
α-thujaplicin	46.61	t	1.35	t
occidentalol	5.96	12.39	9.17	8.03
55.34	0.91	1.08	0.63	0.30
γ-eudesmol	1.54	1.83	3.00	3.36
β-eudesmol	1.95	3.06	3.02	2.81
α-eudesmol	0.91	1.45	1.58	1.72
occidenol + unknown	7.35	12.25	11.31	8.52
64.30	0.59	2.55	1.87	1.85
65.01	1.12	3.36	2.50	2.62
66.82	1.08	2.49	1.92	2.36
67.12	2.67	5.07	2.39	1.75
occidol	12.18	35.24	45.07	50.46
occidol isom. #1	2.79	8.36	10.42	11.77
occidol isom. #2	0.52	1.37	2.18	2.34

*: Results are obtained in the same set of experiments reported in Table I; t = trace

living *T. occidentalis* trees undergo a peculiar ageing process. In the center of the trunk, the wood becomes reddish and, eventually, this central part starts decaying and becomes rotten. A similar decay process has been described in Incense cedar (19). The oil obtained from this reddish portion of wood does not contain α-thujaplicin although relative concentrations of the other compounds are similar to those obtained from the isolated unaffected wood. The oil content of this reddish part may be as much as two to three times lower than that obtained from the undecayed part. Other minor compounds were also observed in the oil. Their mass spectra are reported as a footnote in Tables I and II.

The relative concentrations of all the products are very dependent on the isolation times (Tables I and II). The relative concentration of the main product, occidentalol, decreases very quickly during the distillation (see Table II). On the other hand, the relative concentration of the three occidol isomers increases. Taking into account the total yield, the isolation of occidentalol is much faster than that of the occidols. The same is true for α-thujaplicin.

The distillation water was also found to contain a fraction of the oil, although the amount was very small (<1.0%). The composition of the solvent extraction of this fraction (Table III) is quite different from the oil (Table I). The differences are probably the result of different solubilities of the oil components. α-Thujaplicin, occidol and its isomers are the main components of this water soluble fraction.

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