CHEMICAL COMPOSITION OF THE NEEDLES OIL OF Pinus canariensis FROM ALGERIA

T. Dob, ^{1,2} T. Berramdane, ¹ D. Dahmane, ¹ and C. Chelghoum ²

UDC 547.913

The essential oil of the needles of Pinus canariensis, cultivated in the Algiers region (Algeria), was obtained by hydrodistillation in a yield of 0.3% and analyzed by capillary GC and GC/MS. More than 46 compounds were identified amounting to ca 92.6% of the total oil. The more important constituents were β -selinene (63.7%), β -caryophyllene (9.9%), and limonene (3.5%).

Key words: *Pinus canariensis*, Pinaceae, essential oil composition, GC, GC/MS, β -selinene.

Pinus canariensis, an endemic tree of the Canary Islands, was planted extensively for timber in several Mediterranean countries where it escaped cultivation and became domesticated [1, 2].

Extensive studies have concentrated on the composition of turpentine from *Pinus* species, whereas a few reports on the constituents of the needle oils are available [3–7].

Very little is known about the chemical composition of the volatile metabolites of *P. canariensis* in the world and it is not described in Algeria. In this paper we have oriented our investigation toward the chemical composition of the oil from the needles of this species cultivated in Algeria.

More than 46 oil components were detected, characterized, and quantified. The list of the compounds, in order of elution on DB-1, and the quantitative data, expressed as area percentage, are reported in Table 1 and amounting to 92.6% of the total oil. GC and GC/MS analysis revealed the identity of the components as mainly monoterpene groups (6.0%), while the sesquiterpene hydrocarbons were the highest (79.6%), this fraction being dominated by the presence of the chemotype β -selinene (63.7%).

The main compounds of our oil were β -selinene (63.7%), β -caryophyllene (9.9%), and limonene (3.5%). As reported it in our tabulated results, we have found traces of sabinene, *trans-\beta*-terpineol, bornyl acetate, and β -gurjunene (Table 1).

This result agrees with the literature data, which show that the sesquiterpenes constituted the predominant class in oil of the same species found in Morocco (91.60%) with an elevated amount of germacrene D (62.5%) followed by β -caryophyllene (16.8%) [6], and in Canary Island constituents, 52.1% of which were characterized by germacrene D (35.7%) and α -pinene (23.1%) [8]; in addition, other investigations have shown the highest levels of sesquiterpenes (60.34%), while germacrene D (50.55%) and α -pinene (14.01%) were the major constituents in the oil [1]. Originating from different geographical regions, the chemical differences between these three oils reflect mainly environmental and not genotypic influences [6].

¹⁾ Laboratoire de Molecules Bio-actives et Valorisation de la Biomasse, Ecole Normale Superieure Kouba-Alger, B. P. 92-Kouba-Alger. Algerie, fax: (213) 21 28 20 67, e-mail: t_dob2010@yahoo.co.uk; 2) Laboratoire de Chromatographie, Faculte de Chimie USTHB Alger, Algerie. Published in Khimiya Prirodnykh Soedinenii, No. 2, pp. 134-135, March-April, 2005. Original article submitted August 16, 2004.

TABLE 1. Chemical Composition of the Needles Oil of Pinus canariensis

RRI	Compound	%	RRI	Compound	%
831	trans-2-Hexenal	Tr.	1355	Geranyl acetate	Tr.
920	Tricyclene	Tr.	1358	lpha-Yalangene	0.1
924	α-Pinene	1.0	1376	eta-Bourbonene	0.3
934	Camphene	Tr.	1381	eta-Cubebene	Tr.
956	Sabinene	Tr.	1408	eta-Caryophyllene	9.9
961	eta-Pinene	0.1	1423	eta-Gurjunene	Tr.
979	β -Myrcene	1.3	1427	$trans-\alpha$ -Bergamotene	0.1
1003	lpha-Phellandrene	Tr.	1437	lpha-Humulene	1.9
1017	Limonene	3.5	1449	<i>trans-</i> β -Farnesene	0.3
1026	cis - β -Ocimene	Tr.	1482	eta-Selinene	63.7
1042	γ-Terpinene	Tr.	1487	lpha-Muurolene	1.1
1071	trans-Linalol oxide	Tr.	1492	eta-Bisabolene	0.8
1077	lpha-Terpinolene	Tr.	1498	δ -Cadinene	1.3
1112	exo-Fenchol	Tr.	1509	cis-Nerolidol	3.3
1118	Camphor	Tr.	1553	Caryophyllene oxide	0.9
1127	lpha-Terpineol	Tr.	1565	Longipinene epoxide	0.2
1136	trans -Pinocamphone	Tr.	1603	γ-Eudesmol	Tr.
1151	$trans$ - β -Terpineol	Tr.	1622	<i>epi</i> -α-Cadinol	0.6
1163	Terpinen-4-ol	0.1	1631	α -Cadinol	0.1
1168	Myrtenal	Tr.	1650	lpha-Eudesmol	0.6
1252	Bornyl acetate	Tr.	1765	Benzyl benzoate	Tr.
1316	α -Terpinyl acetate	Tr.	1924	Cembrene	0.1
1332	Citronellyl acetate	Tr.	1970	Sandracopimara-8-(14), 15-diene	0.7

Tr.: Trace (<0.05%).

RRI: Retention Indices calculated against *n*-alkanes.

EXPERIMENTAL

Plant Material. The needles of *Pinus canariensis* were collected in May 2002, at the forest of Sidi Fradj (Algiers, Algeria).

Oil Isolation. The needles (100 g) were cut into small pieces and separately hydrodistilled for 2 h in a modified Clevenger apparatus with a water-cooled receiver in order to reduce hydrodistillation overheating artifacts. The essential oils were taken up in diethyl ether and dried over sodium sulfhate and stored at $+4^{\circ}$ C in a refrigerator.

GC and GC/MS Analysis. GC analysis was performed on a Chrompack CP 9002 chromatograph using fused silica capillary columns with stationary phase DB-1. The various parameters fixed for DB-1 column are: $30 \text{ m} \times 0.32 \text{ mm}$ i.d., 0.25 mm film thickness column; temp. prog., 50° C for 3 min then 2° C/min to 260° for 5 min; detector heaters 280° C; injector heaters 250° C; nitrogen was used as carrier gas at a flow rate of 1 mL/min in the split mode, with injection volume 0.2 mL.

Mass spectra were obtained from GC/MS analysis on a Trace MS Finnigan chromatograph equipped with a $30 \text{ m} \times 0.32 \text{ mm}$. i.d., 0.25 mm film thickness column; DB-1 capillary column programmed from 50°C (3 min) to 260°C (5 min) at 2°C/min with helium carrier gas at a flow rate of 1 mL/min and injector heater 250°C . The mass spectrometer was operated in the EI-mode at 70 eV.

Component Identification. The identification of the chemical constituents was based on comparisons of their retention Indices and mass spectra with those obtained from the NIST/NBS library spectra and literature data [7, 9–12].

REFERENCES

- 1. R. Vassilios, V. P. Panos, O. Antonio, and E. M. Basilis, *Phytochemistry*, **39**, 357 (1995).
- 2. R. Vassilios, K. Papadogianni, C. Vagias, C. Harvala, V. P. Panas, and O. Antonio, *J. Essent. Oil Res.*, **13**, 118 (2001).
- 3. O. Ekundayo, Flav. Frag. J., 3, 1 (1988).
- 4. K. H. Kubeczka and W. Schultze, *Flav. Frag. J.*, **2**, 137 (1987).
- 5. G. Shiller, M. T. Conkle, and C. Grunwold, Silvae Genet., 35, 11 (1986).
- 6. H. Hmamouchi, J. Hmamouchi, and M. Zouhdi, J. Essent. Oil Res., 13, 298 (2001).
- 7. C. Tsitsmpikou, P. V. Petrakis, A. Ortiz, C. Havala, and R. Vassilios, J. Essent. Oil Res., 13, 174 (2001).
- 8. W. P. Hartwig, Flav. Frag. J., 15, 266 (2000).
- 9. P. V. Petrakis, C. Tsitsimpikou, O. Tzakou, M. Kouladis, C. Vagias, and R. Vassilios, *Flav. Frag. J.*, **16**, 249 (2001).
- 10. H. van den Dool and P. D. Kratz, *J. Chromatogr.*, **11**, 463 (1963).
- 11. N. W. Davies, J. Chromatogr., **503**, 1 (1990).
- 12. R. P. Adams, *Identification of Essential Oils by Ion Trap Mass Spetroscopy*, Allured Publishing Corporation Co., Carol Stream IL, 1995.