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THE GLYCOSIDICALLY BOUND VOLATILE COMPOUNDS OF *Taxus baccata*

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The steam volatiles obtained from the fresh and dried needles of Taxus baccata *(Taxaceae), collected from Turkey after enzymatic hydrolysis, were analyzed by GC/MS. Sixty-three compounds representing 88.6% of the oil obtained from the fresh needles were identified. Hexadecanoic acid (19.6%) and decanoic acid (19.5%) were the most abundant components in these oils. Sixty-five components representing 86.6% of the oil from the dried needles were characterized, with hexadecanoic acid (22.5%) and decanoic acid (12.6%) being the major components.*

Key words: *Taxus baccata*, Taxaceae, European yew, essential oil, glycosides**,** hexadecanoic acid, GC/MS analysis.

The genus *Taxus* L. (*Taxaceae*) is represented by eight species [1, 2]. *Taxus* species have been intensively investigated by several research groups since the discovery of taxol, an anticancer agent which was first isolated from the bark of *T. brevifolia* L., and many more compounds have been reported to date [3–5]. *Taxus* has only one species growing in Turkey, *Taxus baccata* L. (European yew), a poisonous plant, which is called "porsuk agaci" [6].

The essential oil and glycosidically bound volatile compounds of *Taxus canadensis* Marsh. and glycosidically bound volatile aliphatic and aromatic alcohols of *T. baccata* L. have been reported previously [7, 8]. To the best of our knowledge, this is the first detailed GC/MS study of the volatile compounds of *T. baccata* needles. Since the constituents of essential oil accumulate in the plant as glycosides [8, 9], we have investigated the oil of *T. baccata* obtained by hydrodistillation after enzymatic hydrolysis of the needles.

Due to the very low yield of essential oil in *T. baccata* needles, we have decided to carry out hydrodistillation after enzymatic hydrolysis, since volatile compounds have been observed to be glycosidically bound in Conifers [8–10]. The results of analysis of the oils are presented in Table 1. In the oil of fresh needles of *T. baccata*, sixty-three compounds representing 88.6% of the oil were identified with fatty acids: hexadecanoic acid (19.6%) and decanoic acid (19.5%) as main constituents. Sixty-five compounds, representing 86.6% of the oil of dried needles of *T. baccata*, were characterized, with hexadecanoic acid (22.5%) as the main constituent.

In the literature, there were only two reports on the volatile compounds of *Taxus* species [7, 8]. The essential oil and glycosidically bound volatile compounds of *T. canadensis* were analyzed, and 1-octen-3-ol (44.6%) and (*E*)-2-hexenal (24.1%) were reported as the major components of the essential oil from fresh needles. 1-octen-3-ol (23.1, 39.1%) and 3,5-dimethoxyphenol (48.7, 26.3%) were identified as the major aglycones in the glycosidically bound volatiles, which were extracted after hydrolysis of the dried needles using β-glucosidase and cellulase enzymes, respectively [7]. Four compounds, octanol, borneol, methyl salicylate, and geraniol, were found to be similar to the aglycone composition of *T. canadensis*.

In another study, only three glycosidically bound volatile compounds obtained by enzymatic hydrolysis with β-glucosidase in the fresh needles of *T. baccata* were reported. Among them, 1-octen-3-ol (more than 50%) was found as the major compound. The other compounds eugenol (0.5–5%) and (*Z*)-3-hexenol (less than 0.5%) were found as trace components [8]. These three compounds were also found as aglycones in the dried needles of *T. canadensis* [7].

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TABLE 1. The Composition of the Volatiles of *Taxus baccata*

RRI	Compounds	A (%)	B (%)	RRI	Compounds	A (%)	B (%)
1194	Heptanal	Tr.	-	2025	2-Pentadecanone	-	0.2
1298	1-Octen-3-one	0.2	-	2041	Pentedecanal	0.3	-
1393	3-Octanol	-	0.5	2050	(E)-Nerolidol	0.1	-
1400	Tetradecane	0.1	Tr.	2057	Ethyl tetradecanoate	0.4	0.4
1441	(E)-2-Octenal	Tr.	-		(=Ethyl myristate)		
1452	1-Octen-3-ol	-	1.3	2084	Octanoic acid	0.4	0.6
1479	(E,Z)-2,4-Hetadienal	Tr.	-	2096	(E)-Methyl cinnamate	-	0.1
1483	Octyl acetate	-	0.1	2100	Heneicosane	0.4	0.4
1500	Pentadecane	0.4	0.2	2131	Hexahydrofarnesyl acetone	4.7	1.6
1521	2-Nonanol	-	0.4	2157	(E)-Ethyl cinnamate	0.3	1.3
1553	Linalool	-	0.5	2192	Nonanoic acid	0.8	0.5
1562	Octanol	0.2	2.0	2196	4-Ethyl phenol	-	0.2
1584	Nonyl acetate	-	Tr.	2200	Docosane	0.2	0.2
1587	Longifolene (=Junipene)	0.1	-	2218	4-Vinyl guaiacol	0.1	-
1588	Bornyl formate	-	Tr.	2218	Decyl decanoate	0.1	0.1
1600	Hexadecane	0.5	0.2	2226	Methyl hexadecanoate	0.7	0.5
1604	2-Undecanone	-	0.1		(=Methyl palmitate)		
1612	β-Caryophyllene	0.1	-	2245	2-Heptadecanone	-	0.3
1647	Ethyl decanoate	0.2	0.6	2262	Ethyl hexadecanate	3.7	3.1
1664	Nonanol	1.0	0.7		(=Ethyl palmitate)		
1687	α-Humulene	0.1	-	2296	Isophytol	0.4	0.3
1687	Decyl acetate	-	0.4	2300	Decanoic acid	12.6	19.5
1700	Heptadecane	0.7	0.2	2300	Tricosane	0.5	0.5
1706	α-Terpineol	0.1	0.3	2337	Geranic acid	-	0.1
1719	Borneol	0.1	0.5	2369	(2E, 6E)-Farnesol	0.4	0.8
1722	2-Undecanol	-	0.3	2380	Dihydroactinolide	0.1	-
1741	β-Bisabolene	0.1	-	2384	Hexadecanol	-	0.9
1766	Decanol	3.6	5.4	2386	Farnesyl acetone	0.5	-
1784	(E)-α-Bisabolene	0.3	-	2401	Undecanoic acid	0.2	-
1798	Methyl salicylate	-	0.1	2400	Tetracosane	0.2	0.3
1800	Octadecane	0.8	-	2467	Ethyl octadecanoate	-	0.2
1808	Nerol	0.2	0.3		(=Ethyl stearate)		
1815	Methyl dodecanoate	-	Tr.	2493	Ethyl oleate	0.4	0.7
	(=Methyl laurate)			2500	Pentacosane	0.5	0.6
1815	2-Tridecanone	-	0.3	2503	Dodecanoic acid	5.9	8.1
1819	(E)-2-Decen-1-ol	0.4	-	2524	Abietatriene	0.6	0.2
1834	Ethyl salicylate	-	0.1	2538	Ethyl octadecadienoate	0.9	2.0
1838	β-Damascenone	0.5	0.3		(=Ethyl linoleate)		
1857	Geraniol	0.6	1.2	2583	Methyl linolenate	0.6	0.3
1868	(E)-Geranyl acetone	1.6	-	2613	Ethyl linolenate	3.2	4.2
1900	Nonadecane	0.3	0.1	2622	Phytol	1.8	1.9
1902	Benzyl isovalerate	0.1	-	2670	Ethyl arachidate	-	0.3
1933	Teradecanal	0.2	-	2713	Tetradecanoic acid	8.0	2.1
1958	β-Ionone	1.2	-	2822	Pentadecanoic acid	0.4	0.3
1973	Dodecanol	Tr.	-	2883	Ethyl docosanoate	-	0.1
2000	Eicosane	0.4	-	2931	Hexadecanoic acid	22.5	19.6
2008	Caryophyllene oxide	0.4	-				
2020	Methyl tetradecanoate	0.3	-				
	(=Methyl myristate)				**Total:**	**86.6**	**88.6**

RRI: Relative retention indices on a polar column.

Tr.: trace (< 0.1%).

TABLE 2. The Main Groups of Volatiles in *Taxus baccata*

Major groups	A (%)	B (%)
Monoterpenes	2.6	2.9
Sesquiterpenes	1.6	0.8
Diterpenes	3.3	2.4
Tetraterpenes	1.8	0.3
Aliphatic compounds	6.1	13.6
Alkane+alkenes	5.0	2.7
Fatty acid+esters	61.0	62.5
Others	5.2	3.4
Total	**86.6**	**88.6**

A: Oil obtained from dried T. baccata needles after hydrolysis.
B: Oil obtained from fresh T. baccata needles after hydrolysis.

As shown in Table 2, both sample A and sample B were found to be similar with respect to the major groups of volatile compounds; 61–63% of the steam volatiles consisted of fatty acids and their esters and 6–14% comprised aliphatic compounds. Terpenoids made up only 6.4–9.3% of the oils. Regarding fatty acids, hexadecanoic acid was found as the main compound of dried (22.5%) and fresh (19.6%) needles of *T. baccata*. Moreover, another fatty acid, decanoic acid, was also determined as the second most abundant compound in sample A (12.6%) and sample B (19.5%). Among the monoterpenes detected in previous studies, only 1-octen-3-ol (1.3%) was found as a minor aglycone in fresh needles of *T. baccata*.

EXPERIMENTAL

Plant Material. The needles of *Taxus baccata* L. (*Taxaceae*) were collected from Rize, Turkey: Maçka-Meryemana, at an altitude of 1100 m, in November 1999. Some of the needles were air-dried and then chopped (Sample A). The rest of the needles were used as fresh after chopped (Sample B). Voucher specimen (GUE 1562) was kept in the Herbarium of the Faculty of Pharmacy, Gazi University, Ankara.

Extraction. 300 ml of water was added to samples A (250 g) and B (400 g). Then, emulsin (25 mg for sample A and 40 mg for sample B) was added for enzymatic hydrolysis. The aqueous solutions were shaken for 48 h in an incubator at 37°C. Samples A and B were subjected to hydrodistillation using a Clevenger-type apparatus for 4 h to yield 0.04% (v/w) and 0.025% (v/w) of yellowish oils for samples A and B, respectively. The oils were then submitted to GC/MS analysis.

Identification of Components. The oils were analyzed by GC/MS using a Hewlett Packard GCD system. An HP-Innowax FSC column (60 m × 0.25 mm ∅, with 0.25 mm film thickness) was used with helium as a carrier gas (1 ml/min). The GC oven temperature was kept at 60°C for 10 min and programmed to 220°C at a rate of 4°C/min, then kept constant at 220°C for 10 min and then programmed to 240°C at a rate of 1°C/min. Alkanes were used as reference points in the calculation of relative retention indices (RRI). The split ratio was adjusted at 50:1. The injector temperature was at 250°C. MS were taken at 70 eV. Mass range was from 35 to 425 *m/z*. Library search was carried out using the Wiley GC/MS Library and the Baser Library of Essential Oil Constituents. The Relative percentage amounts were calculated from TIC by the computer. The identified compounds in the oil are shown in Table 1.

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