## GC-MS ANALYSIS AND ANTIOXIDANT ACTIVITIES OF ESSENTIAL OILS OF TWO CULTIVATED Artemisia SPECIES

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*Artemisia* is a fairly large genus within the family Asteraceae (*alt.* Compositae), with *ca.* 300 individual species of aromatic and medicinal plants, which are usually found as small fragrant shrubs or herbs in the northern hemisphere [1, 2]. While some of their essential oils are used in perfumery and medicine, the leaves of some species are used as culinary herbs [3]. The various pharmacological effects of *Artemisia* species, e.g., anticonvulsant [4], apoptosis [5], immunosuppressive [6], antipeptic ulcer [7], anthelmintic [8], antimalaria [9], anti-inflammatory [10], anti-HIV, antiplatelet aggregation [11], antibacterial [12] and antifungal effects [13], have previously been reported. We now report on the determination of the main constituents of the essential oils from two cultivated *Artemisia* species, *Artemisia fragrans* and *A. austriaca*, aiming at the comparison between the composition of the oils from these cultivated species with those of wild species. The free radical scavenging properties (antioxidant) of these essential oils using the DPPH assay are also reported.

The aerial parts of *A. fragrans* Willd. and *A. austriaca* Jacq., cultivated in the Botanical Garden of the Drug Applied Research Center (Tabriz University of Medical Sciences, Tabriz, Iran), were collected during August-September 2004 (flowering).

The steam distillation for 3 h of the aerial parts of two cultivated species, *Artemisia fragrans* and *A. austriaca*, yielded essential oils 0.95% and 1.1%, respectively. The percentage yield of the essential oil of *A. austriaca* was more than that of *A. fragrans*. While the total yield of essential oils of the cultivated *A. fragrans* was similar to that of this species growing wild (0.97%) [2], the yield was much higher, almost doubled, in the cultivated *A. austriaca* than its wild variety (0.59%) [14]. The identified constituents of the oils of *A. fragrans* and *A. austriaca* are listed in Table 1.

The GC-MS analysis of the aerial parts of *A. fragrans* and *A. austriaca* led to the identification and quantification of a total of 14 main compounds (Table 1), and these compounds accounted for the 88.7% and 91.5% of the total components present, respectively. Camphor (**2**), which has a bornane skeleton, and 1,8-cineole (**7**) are the main components of the essential oils of *Artemisia* species [2, 14].

According to a previously published reports [14, 15], the main components of the essential oil of *A. austriaca* were camphor (**2**, 45.5%), 1,8-cineole (**7**, 30.4%), camphene (**1**, 6.5%),  $\alpha$ -terpineol (3.2%),  $\alpha$ -pinene (3.0%), terpinen-4-ol (**8**, 2.9%), and *p*-cymene, and those of the essential oil of *A. fragrans* were camphor (**2**, 46.0%), 1,8-cineole (**7**, 23.7%), camphene (**1**, 7.9%), borneol (4.9%), and germacrene D (**14**, 1.9%) [2, 16, 17]. All these previously published reports were on the species that were collected wild. A clear variation in the profile as well as in the amounts of individual compounds present in the cultivated species (Table 1) in the present study was identified when compared with wild species. Both in the cultivated *A. fragrans* and *A. asutriaca*, the two major components were camphor (**2**, 54.92% and 40.59%, respectively) and 1,8-cineole (**7**, 11.48% and 27.97%, respectively), which accounted for ~70% of the total essential oils (Table 1). In addition to **2** and **7**, while in the cultivated *A. fragrans*,  $\alpha$ -thujone (**11**, 9.21%),  $\beta$ -thujone (**12**, 4.83%), and germacrene D (**14**, 3.57%) were identified in significant amounts, camphene (**1**, 3.95%) and *trans*-pinocarveol (**6**, 2.69%) were present in significant proportions in the cultivated *A. austriaca*.

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TABLE 1. Chromatographic and Spectral Data of the Components of the Essential Oil of *A. fragrans* (AF) and *A. Austriaca* (AA) at Flowering Stage Analyzed by GC-MS

Compound	Retention time t <sub>R</sub> in min	Real % Area		MS fragment ions	Mol.	Mol.
		AF	AA	(intensity)	mass	formula
Camphene (1)	14.74	1.54	3.95	41 (34.9), 67 (36.7), 79 (40.5), 93 (100), 107 (25.0), 121 (46.7), 136 (10.5)	136	$C_{10}H_{16}$
Camphor (2)	22.92	54.92	40.59	32 (0.4), 41 (75.5), 55 (44.8), 69 (47.0), 81 (80.6), 95 (100), 108 (39.4), 137 (2.7), 152 (24.8)	152	C <sub>10</sub> H <sub>16</sub> O
Pinocarvone (3)	23.56	1.80	1.84	32 (7.3), 41 (64.3), 53 (100), 69 (24.3), 81 (76.4), 91 (11.0), 108 (51.9), 122 (8.8), 135 (21.0), 150	150	C <sub>10</sub> H <sub>14</sub> O
Myrtenal (4)	24.897	2.24	0.78	(8.0) 32 (3.6), 41 (38.4), 53 (15.4), 67 (15.0), 79 (100),	150	C <sub>10</sub> H <sub>14</sub> O
Myrtenol (5)	24.891	-	1.29	91 (36.3), 107 (55.5), 117 (6.9), 135 (6.9), 150 (1.0) 31 (8.4), 32 (36.1), 55 (12.1), 67 (14.9), 79 (100),	152	C <sub>10</sub> H <sub>16</sub> O
trans-Pinocarveol (6)	22.65	2.19	2.69	91 (42.2), 108 (22.7), 119 (9.5), 135 (1.6), 152 (2.4) 31 (5.5), 41 (99.5), 55 (100), 70 (71.4), 83 (51.4),92	152	C <sub>10</sub> H <sub>16</sub> O
1,8-Cineole (7)	18.07	11.48	27.97	(81.2), 109 (20.3), 119 (30.0), 134 (13.0), 151 (0.5) 31 (2.2), 43 (100), 55 (29.3), 71 (42.1), 81 (47.8), 93	154	C <sub>10</sub> H <sub>18</sub> O
Terpineol-4 (8)	24.105	0.78	0.80	(27.2), 108 (31.1), 125 (4.7), 139 (17.3), 154 (16.1) 32 (10.4), 43 (47.1), 55 (22.4), 71 (100), 86 (14.0),	154	C <sub>10</sub> H <sub>18</sub> O
cis-Sabinene hydrate (9)	20.81	0.81	1.59	93 (43.0), 111 (32.1), 119 (2.9), 136 (10.8), 154 (6.6)	154	C <sub>10</sub> H <sub>18</sub> O
<i>trans</i> -Sabinene hydrate (10)	19.53	-	1.31	30 (1.8), 43 (100), 55 (37.5), 71 (53.9), 81 (35.4), 93 (50.1), 121 (18.6), 139 (11.9), 154 (2.3)	154	C <sub>10</sub> H <sub>18</sub> O
$\alpha$ -Thujone (11)	21.16	9.21	-	32 (1.81), 43 (100), 55 (30.9), 71 (85.7), 81 (34.4), 93 (59.4), 111 (28.3), 136 (11.7), 154 (2.6)	152	C <sub>10</sub> H <sub>16</sub> O
$\beta$ -Thujone (12)	21.60	4.83	-	41 (83.9), 55 (37.2), 67 (82.4), 81 (100), 95 (49.5), 110 (71.26), 124 (3.4), 137 (1.0), 152 (5.6)	152	C <sub>10</sub> H <sub>16</sub> O
<i>trans-<math>\beta</math></i> -Farnesene (13)	34.182	1.51	0.62	30 (0.4), 41 (88.0), 55 (43.3), 67 (83.8), 81 (100), 95 (68.8), 110 (79.7), 124 (3.6), 152 (6.1)	204	$C_{15}H_{24}$
Germacrene D (14)	35.63	3.57	2.00	41 (87.2), 55 (17.9), 69 (100), 79 (24.3), 93 (44.4), 133 (17.0), 161 (9.2), 204 (1.6) 41 (60.2), 55 (32.1), 67 (27.1), 81 (56.7), 81 (77.9), 105 (87.2), 119 (49.1), 133 (27.2), 147 (8.2), 161 (100), 183 (1.0), 204 (16.5)	204	C <sub>15</sub> H <sub>24</sub>

While thujane derivatives, e.g.,  $\alpha$ -thujone (11) and  $\beta$ -thujone (12), are well spread within the genus *Artemisia* [14], they were absent in the cultivated *A. austriaca*. This finding was consistent with the previously published report on wild *A. austriaca* [14]. Myrtenol (5, 1.29%) and *trans*-sabinene hydrate (10, 1.31%) were found in *A. austriaca*, but not in *A. fragrance*. The amount of camphor (2) present in the cultivated *A. fragrance* was much higher than previously reported amounts in wild species (54.92% as opposed to 46.0%) [2]. Interestingly, the amount of 1,8-cineole (7) in the cultivated *A. fragrance* was much lower than the previously reported amount in wild species (11.48% as opposed to 23.7%) [2]. The amounts of 1,8-cineole (7) and camphor (2) in the cultivated *A. austriaca* were slightly lower than those of the wild species (7, 27.97% as opposed to 30.4%; 2, 40.59% as opposed to 45.5%). The observed variations in the profile and amounts of individual components in the cultivated and wild species might have resulted from the variations in the growing conditions.

The essential oils of *A. fragrans* and *A. austriaca* displayed weak antioxidant activities in the DPPH assay [18, 19]. The RC<sub>50</sub> values of the extracts were 7.86 mg/mL and 8.06 mg/mL, respectively. The RC<sub>50</sub> value of the positive control, Trolox, was  $3.07 \times 10^{-3}$  mg/mL.

- 1. GRIN Database, USDA, ARS, National Genetic Resources Program, Germplasm Resources Information Network, Beltsville, Maryland, USA (2007). Available on-line at: http://www.ars-grin.gov/cgi-bin/npgs/html/genform.pl.
- 2. K. Mortez-Semnani, M. Akbarzadeh, and K. Moshiri, Fravour Fragrance J., 20, 330 (2005).
- 3. Dr. Duke's, *Phytochemical and Ethnobotanical Databases (2007)*, Available on-line at: http://www.ars-grin.gov/cgi-bin/duke/ethnobot.pl.
- 4. M. Sayyah, L. Nadjafnia, and M. Kamalinejad, J. Ethnopharmacol., 94, 283 (2004).
- 5. Y. Li, M. Y. Li, L. Wang, Z. H. Jiang, W. Y. Li, and H. Li, Sichuan Da Xue Xue Bao Yi Xue Ban., 35, 337 (2004).
- 6. S. Noori, G. A. Naderi, Z. M. Hassan, Z. Habibi, S. Z. Bathaie, and S. M. Hashemi, *Int. Immunopharmacol*, **4**, 301 (2004).
- 7. P. C. Dias, M. A. Foglio, A. Possenti, D. C. Nogueira, and J. E. de Carvalho, *Phytother. Res.*, 15, 670 (2001).
- 8. Z. Iqbal, M. Lateef, M. Ashraf, and A. Jabbar, J. Ethnopharmacol.,93, 265 (2004).
- 9. H. Van der Meersch, J. Pharm. Belg., 60, 23 (2005).
- 10. S. Jang, Y. J. Kim, W. Y. Lee, K. C. Kwak, S. H. Baek, G. B. Kwak, Y. G. Yun, T. O. Kwon, H. T. Chung, and K. Y. Chai, *Arch Pharm Res.*, **28**, 203 (2005).
- 11. T. S. Wu, Z. J. Tsang, P. L. Wu, F. W. Lin, C. Y. Li, C. M. Teng, and K. H. Lee, *Bioorg. Med. Chem.*, **9**, 77 (2001).
- 12. H. H. Yu, Y. H. Kim, B. S. Kil, K. J. Kim, S. I. Jeong, and Y. O. You, *Planta Med.*, 69, 1159 (2003).
- 13. S. Kordali, A. Cakir, A. Mavi, H. Kilic, and A. Yildirim, J. Agric. Food Chem., 53, 1408 (2005).
- 14. V. P. Papageorgiou, M. M. Bakola-Christianopoulou, K. K. Apazidou, and E. E. Psarros, *J. Chromatogr. A*, **769**, 263 (1997).
- 15. Z. Guvenalp, A. Cakir, M. Harmandar, and H. Gleispach, *Flavour Fragr. J.*, **13**, 26 (1998).
- 16. R. K. Christopher, A. M. Duffield, B. J. Ralph, and J. J. Simes, Aust. J. Biol. Sci., 34, 115 (1981).
- 17. R. P. Adams (ed), *Identification of Essential Oil Components by Gas Chromatography/Mass Spectroscopy*, Allured Publishing Co., Carol Stream, pp. 18–43, 57–332 (1995).
- 18. T. Takao, N. Watanabe, I. Yagi, and K. Sakata, *Biosci. Biotech.Biochem*, 58, 1780 (1994).
- 19. Y. Kumarasamy, M. Fergusson, L. Nahar, and S. D. Sarker, *Pharm. Biol.*, 40, 307 (2002).