CROATICA CHEMICA ACTA CCACAA **75** (1) 189–197 (2002)

ISSN-0011-1643
CCA-2792

Original Scientific Paper

Volatile Constituents from the Leaves of Young and Old *Ailanthus altissima* (Mill.) Swingle Tree

Josip Mastelić and Igor Jerković*

Department of Organic Chemistry, Faculty of Chemical Technology,
University of Split, N. Tesle 10/V, 21000 Split, Croatia

Received March 7, 2001; revised October 17, 2001; accepted October 18, 2001

The chemical composition of volatile compounds from the tree of heaven leaves (*Ailanthus altissima* (Mill.) Swingle) was analysed, for the first time, by gas chromatography-mass spectrometry (GC-MS). The volatiles were isolated from fresh as well as from dried leaves of young and old trees. Forty-nine compounds were identified, representing 88.5–96.3% of total volatiles. The main constituents were aliphatic C_6-compounds (alcohols, aldehydes, acids, esters) 30.8–59.7%, sesquiterpene compounds, especially hydrocarbons (β-caryophyllene, α-humulene, γ- and δ-cadinene, calarene) 11.3–57.4%, oxygenated monoterpenes (linalool, geraniol, α-terpineol) 3.6–9.4% and other compounds 4.5–12.0%. The stage of plant development and the air-drying of plant material have a strong influence on the qualitative and quantitative composition of ailanthus volatile compounds.

Key words: Ailanthus altissima (Mill.) Swingle, *Simaroubaceae*, volatile constituents, β-caryophyllene, γ-cadinene, (*E*)-2-hexenal, (*Z*)-3-hexene-1-ol.

INTRODUCTION

Tree of heaven (*Ailanthus altissima* (Mill.) Swingle), also known as ailanthus, is a fast-growing deciduous tree which is native to Asia. It was introduced into Europe (1751) and the United States (1784) by a Philadelphian gardener and into western states by Chinese immigrants who used it for medicinal purposes. Due to its rapid growth and prolific seed production, it quickly escaped cultivation. The tree also produces toxins in its root, bark

---

* Author to whom correspondence should be addressed. (E-mail: josip.mastelic@ktf-split.hr)

and leaves. These toxins inhibit the growth of other plants. The isolated quassinoids ailanthone and chaparrinone are so effective that they are currently being studied as a possible source of a natural herbicide.[1,2] These factors make the tree of heaven a very aggressive and invasive plant able to displace native trees and herb species. Extracts of this plant have anti-insect activity[3] and anti-tuberculosis activity.[4]

Male flowers emit a foul-smelling odour, which has been described as the smell of burnt peanut butter. The leaves produce the same smell. The aim of this study was to determine the chemical composition of volatile compounds from the leaves of ailanthus depending on the stage of plant development and on the process of air-drying. The chemical composition of ailanthus volatile compounds has not been reported to date.

EXPERIMENTAL

Plant Material

Ailanthus leaves were collected from young (two years old) and old plants (approximately twenty years old) at the beginning of September, 2000. Fresh and dried leaves (dried at room temperature, in a shaded place for ten days) were used for this investigation. Voucher specimens were deposited at the Department of Organic Chemistry, Faculty of Chemical Technology, University of Split.

Isolation of Volatile Compounds

The plant material was hydrodistilled in a Clevenger type apparatus for 3 h. One mL of pentane was added to the graduated part of the apparatus to trap volatile compounds. After hydrodistillation, the pentane layer was separated, dried over Na_2SO_4 and used for GC-MS analysis.

Gas Chromatography-Mass Spectrometry (GC-MS)

Volatile compounds were analysed by gas chromatography-mass spectrometry (Hewlett-Packard, model 5890, with a mass selective detector, model 5971A). Two columns with different polarity of stationary phases were used: column HP-20M (50 m × 0.2 mm i.d., film thickness 0.2 μm) and column HP-101 (25 m × 0.2 mm i.d., film thickness 0.2 μm). GC operating conditions were similar to those described in our previous papers.[5,6] Carrier gas (helium): flow rate 1 mL min^{-1}, injector temperature 250 °C, volume injected: 0.5 μL, split ratio 1 : 50. MS conditions: ionisation voltage 70 eV, ion source temperature 280 °C, mass range 30–300 mass units. Mass spectra were recorded in the scan mode.

Qualitative Analyses

Individual peaks were identified by comparison of their retention indices with those of authentic samples, as well as by comparison of their mass spectra with those stored in a data base (Wiley library) and also spectra published by Adams.[7]

Quantitative Analyses

Relative component concentrations were obtained directly from GC peak areas by the normalisation method without correction factors. Total contents of volatiles were determined by two methods: by calculation from the GC-peak areas related to the GC-peak area of an internal standard[5] (menthol; a preliminary GC-MS analysis showed the absence of menthol in ailanthus volatiles) and by weighing after careful remove of pentane by fractional distillation (gravimetric method). All yields were calculated as the mean values of the above methods (in duplicate analysis) with respect to the mass of the starting fresh plant material. This mode of representing the results makes it possible to determine the impact of drying on the content and composition of ailanthus volatiles.

RESULTS AND DISCUSSION

The content and chemical composition of the volatile compounds of ailanthus are given in Table I. Forty-nine compounds were identified, representing 88.5–96.3% of total volatiles. The yields of volatile compounds in fresh leaves were 210.5 mg kg^{-1} for the young plant and 120.6 mg kg^{-1} for the old plant. After drying, the yields were several times smaller, 51.3 mg kg^{-1} for the young and 60.2 mg kg^{-1} for the old plant. A good agreement between the two methods applied for the determination of yields was noted. Significant differences in the chemical composition of ailanthus volatiles from the leaves of the young and the old tree were observed, accounting for their different smells.

After air-drying of the plant materials, additional differences in the volatiles chemical composition were observed and they will be discussed in the following paragraphs. As it is known, the losses and changes of volatile compounds in herbs, during drying of plant material, mainly depend on the drying parameters, biological characteristics of the plants as well as on the physical and chemical characteristics of the investigated compounds. During the drying process, the plant material indicates atrophy of metabolism, but the enzymes are still active for some time. The action of these enzymes is not a normal living cell process.

The ailanthus volatiles are characterised by a high content of oxygenated aliphatic compounds (alcohols, aldehydes, ketones, acids and esters), especially C_6-compounds (Table I). Twenty-four compounds were identified in this group. From young plants, the contents of aliphatic volatile compounds were 58.5% for fresh and 59.7% for dried leaves; the contents from old plants were 30.8% for fresh and 54.0% for dried leaves. The main components of aliphatic compounds were: (*Z*)-3-hexen-1-ol, (*E*)-2-hexenal, (*Z*)-3-hexen-1-ol esters (butanoate, acetate and hexanoate) and hexadecanoic acid for fresh young plant material; (*E*)-2-hexenal, 6-methyl-5-hepten-2-on, esters

TABLE I

Composition of volatile compounds from the leaves of *Ailanthus altissima* (Mill.) Swingle[a]

Identified compounds	Content / mg kg^{-1}			
	Young plant		Old plant	
	A	B	A	B
Aliphatic oxygenated compounds				
1. n-hexanal	—	tr	—	0.30
2. (*E*)-2-hexenal	8.21	10.36	0.36	9.03
3. (*Z*)-3-hexenal	1.05	—	0.12	1.02
4. (*Z*)-3-hexen-1-yl acetate	21.89	—	2.29	—
5. 6-methyl-5-hepten-2-one	tr	1.64	—	2.23
6. (*Z*)-3-hexen-1-ol	40.63	0.46	12.18	0.78
7. nonanal	1.68	1.39	1.81	1.81
8. (*Z*)-3-hexen-1-yl butanoate	22.52	1.49	—	0.30
9. (*Z*)-3-hexen-1-yl methyl butanoate	1.05	1.49	—	0.36
10. 1-octanol	—	0.15	0.24	0.30
11. (*Z*)-3-hexen-1-yl hexanoate	4.42	0.77	tr	0.96
12. (*Z*)-3-hexen-1-yl tiglate	0.42	0.41	—	0.12
13. hexanoic acid	—	—	0.96	0.36
14. octanoic acid	—	1.13	—	0.36
15. undecanoic acid	—	0.10	—	—
16. dodecanoic acid	2.74	1.28	1.45	2.35
17. tetradecanal	—	0.98	2.77	1.81
18. hexadecanal	—	—	1.09	—
19. 1-hexadecanol	—	0.98	9.53	1.81
20. octadecanal	—	—	2.41	—
21. tetradecanoic acid	2.95	1.23	1.45	2.05
22. pentadecanoic acid	tr	0.15	0.48	0.24
23. hexadecanoic acid	13.05	6.62	tr	6.26
24. 9-octadecenoic acid[b]	2.53	—	—	0.06
Total (1–24)	123.14 (58.5%)	30.63 (59.7%)	37.14 (30.8%)	32.51 (54.0%)
Sesquiterpene compounds				
1. α-cubebene	0.63	—	0.48	—
2. α-copaene	—	—	2.53	0.36
3. β-bourbonene	—	—	—	0.42
4. calarene	5.26	0.98	4.70	1.08
5. β-caryophyllene	19.37	1.64	24.60	2.77
6. α-humulene	3.34	0.62	7.48	1.20
7. γ-cadinene	20.00	2.41	25.33	1.38
8. δ-cadinene	3.79	—	3.26	—
9. α-sinesal	—	—	—	3.37

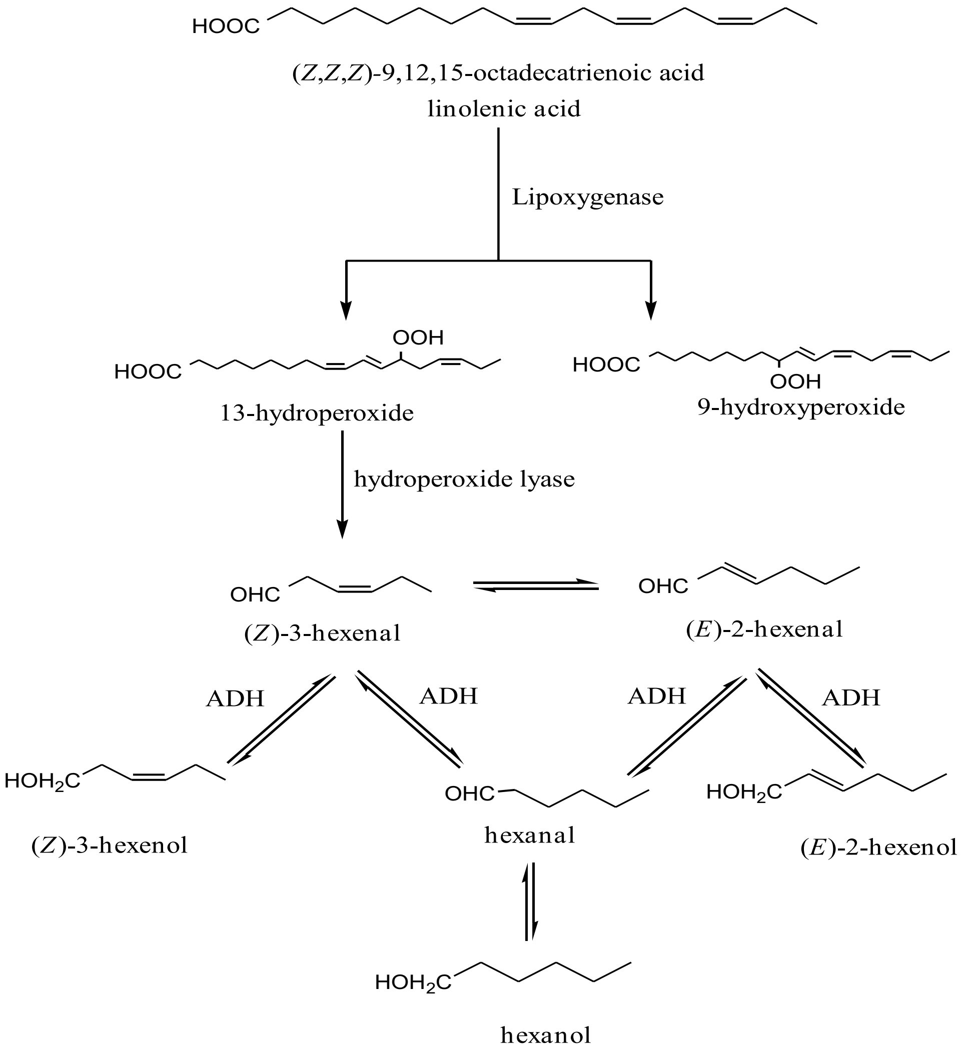
TABLE I (cont.)

10. α-muurolene	0.42	—	0.36	—
11. (*E,E*)-farnesal	—	0.15	0.48	0.24
12. farnesol[*]	—	—	—	0.12
Total (1–12)	52.81	5.80	69.22	10.94
	(25.1%)	(11.3%)	(57.4%)	(18.2%)
Oxygenated monoterpene compounds				
1. linalool oxide	0.42	0.10	—	—
2. linalool	5.26	1.39	0.60	1.87
3. β-cyclocitral	3.58	0.92	2.53	0.84
4. sabinyl acetate	—	1.13	0.84	0.24
5. α-terpineol	2.11	0.36	tr	—
6. (*E*)-citral	—	0.10	—	0.72
7. geraniol	1.05	0.82	0.36	0.18
Total (1–7)	12.42	4.82	4.33	3.85
	(5.9%)	(9.4%)	(3.6%)	(6.4%)
Other compounds				
1. benzaldehyde	—	0.10	—	0.24
2. phenylmethyl benzoate	—	0.31	—	0.12
3. phenylacetaldehyde	0.63	1.90	0.36	1.81
4. cis-jasmone	2.53	1.23	2.41	1.51
5. geranyl acetone	—	1.90	—	2.05
6. neophytadiene	7.58	0.72	2.65	0.24
Total (1–6)	10.74	6.16	5.42	5.97
	(5.1%)	(12.0%)	(4.5%)	(9.9%)
Total identified volatile compounds	199.1	47.41	116.11	53.27
	(94.6%)	(92.4%)	(96.3%)	(88.5%)
Yield of volatiles mg kg^{-1} fresh material	210.5	51.3	120.6	60.2

[a] A, fresh plant material; B, dried plant material; —, not detected; tr, trace (< 0.05 mg).

[b] The isomer was not identified.

of (*Z*)-3-hexen-1-ol (butanoate and methylbutanoate), nonanal and hexadecanoic acid for dried young plant material; (*Z*)-3-hexen-1-ol, (*Z*)-3-hexen-1-yl acetate, 1-hexadecanol, tetradecanal, octadecanal for fresh old plant; (*E*)-2-hexenal, 6-metil-5-hepten-2-on, hexadecanoic, dodecanoic and tetradecanoic acid for dried old plant. The highest contents of (*Z*)-3-hexen-1-ol, and its esters (acetate, butanoate and hexanoate) were found in the fresh material of young plants. (*Z*)-3-hexen-1-yl acetate was not identified in dried (young and old) materials. On the other hand, dried plant materials contained several times higher amounts of (*E*)-2-hexenal and 6-methyl-5-hepten-2-one than the fresh ones. (*Z*)-3-Hexen-1-yl acetate is probably hydrolysed (during drying) to (*Z*)-3-hexen-1-ol, which is in equilibrium with (*Z*)-3-hexenal, as well as with (*E*)-2-hexenal and hexanal, according to Scheme 1. In a similar manner, the hydrolysis of native glycosides, during the drying process, was already reported.[8] Hexadecanoic, dodecanoic, tetradecanoic and 9-octadecenoic acids were most abundant in the fresh leaves of young plants. Furthermore,



Scheme 1.

twelve sesquiterpene compounds were identified, representing the second significant group of ailanthus volatiles. Among them, γ-cadinene, β-caryophyllene, α-humulene and calarene were the main components. These are sesquiterpene hydrocarbons. Their contents were many times higher in fresh plant materials than in the dried ones. The smaller part of sesquiterpene compounds were oxygenated sesquiterpenes, such as α-sinesal, (E,E)-farnesal and farnesol.

Oxygenated monoterpenes were the third group of ailanthus volatile compounds. Seven oxygenated monoterpenes were identified, linalool and β-cyclocitral being the most representative. Unlike most aromatic plants, monoterpene hydrocarbons were not identified among the ailanthus volatile compounds.

The last group (Table I) contains a variety of compounds, such as neophytadiene, *cis*-jasmone, phenylacetaldehyde and geranylacetone. Aromatic compounds were represented by phenylacetaldehyde, phenylmethylbenzoate and benzaldehyde. The latter two compounds were identified only in dried plant material. The content of phenylacetaldehyde was approximately 3 to 5 times higher in dried than in fresh materials. Although geranylacetone was identified (1.90–2.05 mg kg^{-1}) in dried plant materials, it was not found in fresh plants. Neophytadiene was identified in all samples. Its content was several times higher in fresh than in dried plant materials.

The components identified in all ailanthus samples were (*Z*)-2-hexenal, (*Z*)-3-hexen-1-ol, β-caryophyllene, γ-cadinene, linalool, calarene, α-humulene, *cis*-jasmone, neophytadiene, phenylacetaldehyde, β-cyclocitral, nonanal, geraniol, as well as dodecanoic, tetradecanoic and hexadecanoic acids. Therefore, these compounds may be considered as common among ailanthus volatiles.

Aliphatic volatiles (alcohols, carbonyls, esters) may originate from fatty acid catabolism.[9] This type of reaction involves lipoxygenase, hydroperoxide lyase, alcohol dehydrogenase and other enzymes. C_6-volatile alcohols and aldehydes can originate from linolenic acid [(*Z,Z,Z*)-9,12,15-octadecatrienoic acid] and linoleic acid [(*Z,Z*)-9,12-octadecadienoic acid]. The enzymatic cleavage of 13-hydroperoxide leads to the formation of (*Z*)-3-hexenal and other nonvolatile compounds. The (*Z*)-3-double bond in aldehydes is often isomerised to a conjugated (*E*)-2-double bond, either by isomerase activity or nonenzymatically. These compounds can be reduced to (*Z*)-3-hexen-1-ol, (*E*)-2-hexen-1-ol, hexenal and n-hexanol by alcohol dehydrogenase (ADH), according to Scheme 1. These compounds are the major ones in Table I.

Primary and secondary alcohols, formed by this reduction of the corresponding aldehydes or ketones were also found to be easily esterified.[10] The volatile products from the 9-hydroperoxides of linoleic acid and linolenic acid are (*Z*)-3-nonenal and (*Z,Z*)-3,6-nonadienal, respectively, which represent the two main volatile components with a characteristic cucumber odour.[11] Aromatic plants and essential oils mainly contain monoterpene and sesquiterpene compounds. Mevalonic acid, geranyl and farnesyl diphosphate are the biosynthetic precursors of monoterpenes and sesquiterpenes.[12,13] On the other hand, fruit and vegetable aromas are composed of aliphatic oxygenated compounds. Ailanthus volatiles comprise representatives of both groups of these compounds in both numerousness and quantity.

Finally, we concluded from these results that the qualitative and quantitative composition of the volatile compounds of ailanthus strongly depends on the stage of plant development as well as on the drying process. The foul-smelling odour of ailanthus mainly originates from aliphatic aldehydes and alcohols. The young plant has a more unpleasant smell than the mature plant, due to their different percentage compositions. Namely, aliphatic oxygenated compounds (58.5%) predominate in the volatiles of young plant material, while, sesquiterpene compounds prevail in old plants (57.4%), especially the sesquiterpene hydrocarbons, β-caryophyllene and γ-cadinene. Furthermore, the leaflets of the leaves of young plants are sharper compared to the old plant. Therefore, the volatiles of this plant merit further investigations.

Acknowledgements. – We are grateful to Dr. Jure Kamenjarin for identification of the plant material. This work was financially supported by the Croatian National Grant, Project 011–003.

REFERENCES

1. R. M. Heisey, *Am. J. Bot.* **83** (1996) 192–200.
2. LJ. Lin, G. Peiser, B. P. Ying, K. Mathias, F. Karasina, Z. Wang, J. Itatani, L. Green, and Y. S. Hawang, *J. Agric. Food Chem.* **438** (1995) 1708–1711.
3. M. J. Pascualvillalobos and A. Robledo, *Industrial Crops & Products* **8** (1998) 183–194.
4. S. Rahman, N. Fukamiya, M. Okano, K. Tagahara, K. H. Lee, *Chem. Pharm. Bull.* **49** (1997) 1527–1529.
5. J. Mastelić, M. Miloš, and D. Kuštrak, *Croat. Chem. Acta* **73** (2000) 781–784.
6. J. Mastelić, M. Miloš, and I. Jerković, *Flavour Fragrance J.* **15** (2000) 190–194.
7. R. P. Adams, *Identification of Essential Oil Components by Gas Chromatography / Mass Spectroscopy,* Allured Publishing Corp., Illinois, 1995.
8. I. Jerković, J. Mastelić, and M. Miloš, *Nahrung* **451** (2001) 47–49.
9. P. Schreier, *Chromatographic Studies of Biogenesis of Plant Volatiles*, Hüthig, Heidelberg, Basel, New York, 1984, p. 52.
10. I. Yamashita, K. Iino, Y. Nemoto, and S. Yoshikawa, *J. Agric. Food Chem.* **25** (1977) 1165–1168.
11. T. R. Kemp, D. E. Knavel, and L. P. Stoltz, *J. Agric. Food Chem.* **22** (1974) 717–720.
12. P. M. Dewick, *Medicinal Natural Products, a Biosynthetic Approach*, John Wiley & Sons, New York, 1997, pp. 152–162, 172–174.

13. D. V. Banthorpe, in: J. Mann, R. S. Davidson, J. B. Hobbs, D. V. Banthrope, and J. B. Harborne (Eds.), *Natural Products: Their Chemistry and Biological Significance*, Longman, Essex, 1996, pp. 290–325.

SAŽETAK

Hlapljivi spojevi listova mladog i odraslog drveta *Ailanthus altissima* (Mill.) Swingle

Josip Mastelić i Igor Jerković

Hlapljivi spojevi lišća pajasena (*Ailanthus altissima* (Mill.) Swingle), po prvi put su analizirani vezanim sustavom plinska kromatografija-spektrometrija mase (GC-MS). Hlapljivi spojevi su izolirani iz svježih, kao i iz sušenih listova mlade i stare biljke. Identificirano je 49 spojeva, što predstavlja 88,5–96,3% ukupnih hlapljivih spojeva. Glavni sastojci bili su alifatski C_6-spojevi (alkoholi, aldehidi, kiseline, esteri) 30,8–59,7%, seskviterpenski ugljikovodici (β-kariofilen, α-humulen, γ- i δ-kadinen, kalaren) 11,3–57,4%, oksidirani monoterpeni (linalol, geraniol, α-terpineol) 3,6–9,4% i ostali spojevi 4,5–12,0%. Stupanj razvitka biljke i sušenje biljnog materijala imaju veliki utjecaj na kvalitativni i kvantitativni sastav hlapljivih spojeva pajasena.