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Composition of the Root Essential Oils of Several *Geum* Species and Related Members of the Subtribus Geinae (Rosaceae)*

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The root essential oils of several members of the genera *Geum, Waldsteinia* and *Coluria*, together representing the subtribus Geinae, were analysed by GC–MS. The qualitative composition of these oils was relatively similar with eugenol and some pinane derivatives, e.g. myrtanals, myrtenal, myrtanols and myrtenol, as characteristic constituents. The oils differed considerably concerning the quantitative composition, e.g. two groups of *Geum* species could be observed, one with a high (>65%) and one with a low (<5%) content of eugenol. In the root oil of *Waldsteinia ternata* Fritsch, only traces of this phenylpropanoid were found. Headspace analysis of a root extract of *W. geoides* Willd. showed a high percentage of cinnamyl alcohol.

KEY WORDS *Geum urbanum* L.; *G. fauriei* Léveillé; *G. macrophyllum* Willd.; *G. rhodopeum* Stoj. et Stefanov; *G. borisii* Kellerer ex Sündermann; *G. rivale* L.; *G. bulgaricum* Pancic; *G. chiloense* Balb.; *G.* × *heldreichii* s.s. Benth.; *Waldsteina geoides* Willd.; *W. ternata* Fritsch; *Coluria geoides* (Pall.) Ledeb.; Geinae; Rosaceae; Avens; root essential oil; GC–MS

INTRODUCTION

According to Engler,[1] the genus *Geum* belongs to the subtribus Geinae (tribus Dryadeae, subfamily Rosoideae, family Rosaceae), which is subdivided into three genera: *Geum* (59 species), *Waldsteinia* (4 species) and *Coluria* (5 species).[2]

Members of the genus *Geum* are found worldwide except in tropical and arctic regions, whereas those of *Waldsteinia*, a genus of the holarctic woodland region, only grow in scattered areas of Europe, Asia and North America. The genus *Coluria* is restricted to Asia; *C. geoides* (Pall.) Ledeb. is native to northern China and southern Siberia and is cultivated in the Ukraine because of the eugenol content of its roots.

Some *Geum* species (*G. urbanum* L., *G. rivale* L. and *G. japonicum* Thunb.) are used as medicinal plants in folk medicine and homeopathy; recently a review of the genus *Geum* predominantly dealing with the pharmaceutical aspects has appeared.[3] In this respect, *G. urbanum* (common or wood avens) is of main importance (herb and root). The roots of this plant (*Gei urbani radix*) are still used in folk medicine. The old pharmaceutical name '*Caryophyllatae radix*' for this drug is attributed to the content of clove-like smelling eugenol in its essential oil, which is set free from the glycoside gein, for example, during hydrodistillation.

Because of their content of tannins, *G. urbanum* roots have astringent properties; additionally, the occurrence of eugenol is at least partly responsible for the antiseptic effects of this drug. *Gei urbani radix* is applied internally as a remedy against diarrhoea, indigestion and loss of appetite. External application is as a gargle, against gingivitis, frostbite and haemorrhoids.[3] The herb of this plant (*Gei urbani herba, Caryophyllatae herba*), also containing tannins, is used for the same purposes. In the *German Homoeopathic Pharmacopoeia* (HAB 1), *Gei urbani radix* is represented by two monographs, one about dried underground parts of *Geum urbanum* L.[4] and the second one about an ethanolic decoction of the fresh underground parts.[5] Apart from the medicinal uses, the plant is used in industry for flavouring brandies and liqueurs, and is used in several toothpastes and mouthwashes. It is also reported to be a substitute for cloves.[3]

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The roots, and formerly also the herb (HAB 34),[6] of water avens (*G. rivale* L.) are also used medicinally, i.e. in the same way as those of *G. urbanum*. However, because of the lower content of tannins and essential oil, this drug (*Caryophyllatae aquaticae rhizoma*) is of minor importance.

The herb of *G. japonicum* Thunb. was applied, mainly in East Asia, against diarrhoea, as an astringent and as a diuretic.[7,8] As far as we know, there is no information concerning medicinal uses of other *Geum* species. The same holds true for the members of the two other genera of the subtribus Geinae, *Waldsteinia* and *Coluria*. However, in some regions of the former USSR, roots of *Coluria* species have been cultivated and used for several purposes, e.g. as a substitute for cloves, in cooking as a substitute for cinnamon, for the distillation of vodka, as a substitute for tea, and to flavour tobacco.[9]

Although some *Geum* species were used as drugs, and roots of *G. urbanum* are also employed in the flavour industry, very little is known about the essential oil composition of these *Geum* species. The same applies to the members of the genera *Waldsteinia* and *Coluria*. The investigation of the other *Geum* species is also of interest from a practical point of view, since sometimes adulterations of *Gei urbani radix* have been observed.[10] Thus, we investigated the essential oil composition of the roots of nine *Geum*, two *Waldsteinia* and one *Coluria* species by capillary GC and GC–MS.

EXPERIMENTAL

Plant Material and Essential Oil Isolation

Underground parts of *Geum urbanum* L. and *G. rivale* L. were collected at locations in the surroundings of Würzburg (Germany) and Hamburg (Germany). Plants of a hybrid of *G. chiloense* Balb., and plants of *Waldsteinia geoides* Willd. were grown in the Botanical Garden of Würzburg; the other *Geum* species and *Coluria geoides* (Pall.) Ledeb. were cultivated there from seeds originating from the Hortus Botanicus Arcto Alpinus, Murmansk (Russia), and the Central Republic Botanical Garden of the Ukrainian Academy of Sciences, Kiev (Ukraine), respectively. The roots of *Waldsteinia ternata* Fritsch were collected near Ratzeburg (Germany). The essential oils were obtained by hydrodistillation (6 h) from the fresh roots of flowering plants using the distillation apparatus described by Sprecher.[11] The analysis of pentane/ether extracts by dynamic headspace sampling was performed using the headspace apparatus described by Schmaus.[12]

Gas Chromatography (GC)

Capillary gas chromatograph: Varian 3700 equipped with FID (220°C), column: 30 m × 0.25 mm i.d., DB-Wax coated (film thickness 0.25 μm) fused-silica (Fisons), flow: 0.9 ml/min N_2, temperature programme 45–220°C (3°C/min), injection port: Grob-type splitter (1:17), 220°C, integrator: Hewlett-Packard 3396 A.

Gas Chromatography–Mass Spectrometry (GC–MS)

GC–MS-system: Hewlett-Packard (GC: 5890 A series II; MSD 5970 B; data system: HP-UX series 9000, Mod. 340), column: 60 m × 0.25 mm i.d., DB-Wax coated (film thickness 0.25 μm) fused-silica (Fisons), directly led into the ion source (220°C), flow: 0.9 ml/min helium, temperature programme 45–220°C (3°C/min), ionization energy: 70 eV.

The compounds were identified by computer search using the Wiley library, the TNO library of mass spectral data, and a user-generated library with the retention times and mass spectral data of authentic reference substances. Some compounds of the root oil of *G. urbanum* were isolated, and additionally NMR spectra were taken (see Table 1).

RESULTS AND DISCUSSION

Fresh minced roots of several *Geum* and *Waldsteinia* species and of *Coluria geoides* were subjected to hydrodistillation and the volatile oils obtained were analysed by capillary GC and GC–MS. The results of these investigations are given in Tables 1 and 2.

Geum urbanum L.

The root essential oil of *G. urbanum* consisted of about 60 components, 29 of which were identified, representing 99% of the oil (Table 1). Apart from the main component eugenol (67%) which has already been described by several authors, all

the other volatiles were detected for the first time in this oil. Most of them were oxygenated monoterpenes with a pinane skeleton, e.g. myrtanal and myrtanol. All these compounds were also found in a pentane/ether extract of the fresh roots (eugenol was set free from its glycoside during the mincing procedure). Altogether the oil consisted of 32% monoterpenoids, 0.1% sesquiterpenoids, 67% phenylpropanoids and 0.1% miscellaneous compounds.

Other Geum Species

As follows from Table 1, the qualitative pattern of all other *Geum* root oils investigated was similar to that of *G. urbanum*. However, in some cases considerable differences were found concerning the quantitative composition. Obviously the *Geum* species can be divided into two groups according to the eugenol content of their root oils. This has already been postulated in earlier investigations, first mainly based on organoleptic tests and later also on chemical analyses, which were summarized and critically commented on by Hegnauer.[13] One group with *G. urbanum*, *G. fauriei* Léveillé and *G. macrophyllum* Willd. is rich in eugenol (66–92%) and possesses a clearly lower content of derivatives with a pinane skeleton, whereas the second group consisting of *G. rivale* L., *G. rhodopeum* Stoj. et Stefanov (not accepted by all authors as a clearly defined species), *G. bulgaricum* Pancic, *G. borisii* Kellerer ex Sündermann and a hybrid of *Geum chiloense* Balb. is characterized by a high percentage of these pinane derivatives and is poor in eugenol (0.3–4.1%). A particular situation exists concerning the eugenol content of the root oil of *G.* × *heldreichii* s.s. Benth. which amounted to 11.6%. Perhaps this also reflects the hybrid character of this species, that originates from a crossing between one parent with a root oil rich in eugenol (*G. macrophyllum*) and the second one with a root oil with a low eugenol content (*G. rivale*). However, crossing experiments performed in the early 1950s between a *Geum* species with a high (*G. urbanum*) and a low (*G. rivale*) eugenol content revealed no clear picture concerning the heredity of this feature.[13,14]

Genus Waldsteinia

The genus *Waldsteinia* that also belongs to the subtribus Geinae of the Rosaceae family, comprises four species, two of which, *W. geoides* Willd. and *W. ternata* Fritsch were investigated regarding the essential oil composition of their roots. It can be gathered from Table 2 that the volatiles from the roots of *W. geoides* are to a large extent similar to those of the members of the *G. rivale* group, the oils of which are also characterized by a low content of eugenol and a remarkable amount of myrtanals, myrtenal, myrtenol and myrtanols.

It is noteworthy, however, that the dynamic headspace analysis of a pentane/ether extract from *W. geoides* roots showed quite a different composition compared with that of the root oil isolated by hydrodistillation. The headspace 'extract' was surprisingly dominated by cinnamyl alcohol, that amounted to 59% of the total volatiles. This difference can be explained by the fact that because of its polarity this compound is soluble in water to a considerable extent and thus is extracted from the pentane phase during hydrodistillation.

To sum up, the root essential oil of *W. geoides* is on the one hand largely similar in composition to those of members of the *G. rivale* group (rich in pinane derivatives, poor in eugenol), but on the other hand there are two remarkable differences. Firstly, cinnamyl alcohol, the main component found by headspace analysis of the roots of *W. geoides* is absent in the oils of the *Geum* species. The alcohol could also not be detected in the corresponding headspace 'extracts'. Secondly, eugenol, being present in the root oils of all *Geum* species investigated, was not found in that of *W. geoides*.

The root essential oil of *W. ternata* showed one remarkable difference. In contrast to the analysis of the root oil of *W. geoides*, we could not detect cinnamyl alcohol in the oil of *W. ternata*. Apart from that, the qualitative composition of the two oils was similar.

Genus Coluria

The root essential oil of *Coluria geoides* (Pall.) Ledeb. a member of the third genus within the subtribus Geinae, was also analysed. This oil was strongly dominated by the phenylpropanoid eugenol, amounting to 98% of the oil. Concerning the trace compounds, the oil resembled that of *G. urbanum*.

To conclude, our studies have shown that the root essential oils of several members of the three

Table 1. Composition of the root essential oils of several *Geum* species.

Compound	RI[a]	Identification from	*G. urbanum* L. Area %	*G. fauriei* Léveillé Area %	*G. macrophyllum* Willd. Area %	*G. rhodopeum* Stoj. et Stefanov Area %	*G. borisii* Kellereri ex Sündermann Area %	*G. rivale* L. Area %	*G. bulgaricum* Pancic Area %	*G. chiloense* Balb.-hybrid Area %	*G.* × *heldreichii.* s.s. Benth. Area %
Oct-1-en-3-ol	1455	RT, MS	0.1	trace[b]	trace	0.1	0.1	0.4	0.1	0.1	0.7
Cymenene isomer (tent.)	1497	MS	trace	trace	trace	0.1	trace	trace	trace	0.1	0.2
α-Copaene	1498	RT, MS	trace	trace	trace	0.1	trace	trace	trace	0.1	trace
Benzaldehyde	1528	RT, MS	trace	trace	trace	trace	trace	trace	trace	trace	trace
Linalol	1552	RT, MS	trace	trace	trace	trace	–	1.7	trace	5.7	trace
cis-Myrtanal	1562	RT, MS, NMR	17.5	2.7	1.6	36.5	34.1	38.2	33.9	16.3	31.5
trans-Myrtanal	1577	RT, MS, NMR	7.7	0.8	0.3	12.8	12.5	12.7	12.2	3.7	10.9
Nopinone	1589	RT, MS, NMR	0.2	0.5	0.2	1.2	2.4	0.6	1.1	0.9	0.9
β-Gurjunene	1601	RT, MS	0.1	–	–	–	–	trace	–	0.3	–
Myrtenal	1638	RT, MS, NMR	1.2	2.1	0.7	10.7	12.9	11.3	11.8	4.8	16.7
trans-Pinocarveol	1665	RT, MS	0.4	0.2	0.1	2.2	1.6	1.7	2.6	1.9	1.5
α-Terpineol	1705	RT, MS	0.2	0.1	0.1	0.8	0.7	0.8	1.4	7.1	3.9
Oxygenated monoterpene	1717	MS	0.1	trace	trace	trace	trace	0.3	0.2	0.1	trace
α-Guaiene	1725	RT, MS	trace	–	–	–	–	trace	–	0.5	trace
Phellandral	1731	RT, MS	0.3	0.2	0.1	1.5	1.5	1.6	1.7	1.4	3.0
δ-Cadinene	1766	RT, MS	trace	–	–	–	–	–	–	–	–
Citronellol	1773	RT, MS	trace	–	–	–	–	–	–	–	–
Methyl salicylate	1785	RT, MS	trace	–	–	–	–	–	–	–	–
Cumin aldehyde	1790	RT, MS	trace	trace	trace	trace	trace	0.1	0.1	0.2	trace
Perilla aldehyde	1795	RT, MS	0.1	0.1	0.4	0.5	0.6	0.6	0.4	–	0.5
Myrtenol	1805	RT, MS, NMR	1.8	0.9	0.6	7.1	8.6	10.5	7.5	22.9	3.3
Nerol	1808	RT, MS	trace	trace	trace	trace	trace	0.1	trace	0.1	trace
trans-Anethol	1834	RT, MS	trace	–	–	–	–	trace	–	–	–
Geraniol	1855	RT, MS	0.1	trace	trace	0.1	0.1	0.3	0.2	0.5	trace
Guaiacol	1868	RT, MS	trace	trace	trace	–	–	–	–	–	trace
cis-Myrtanol	1875	RT, MS, NMR	0.2	0.8	0.4	5.4	3.8	3.2	6.8	11.5	1.3
trans-Myrtanol	1886	RT, MS, NMR	2.4	1.6	1.3	17.3	12.7	6.5	9.2	15.0	3.0
Perilla alcohol	2018	RT, MS	0.1	0.1	0.1	0.2	0.3	0.1	0.1	0.4	trace
trans-Cinnamic aldehyde	2052	RT, MS	trace	–	–	–	–	–	–	–	–
1-(4-Methoxyphenyl)-acetone	2169	RT, MS	trace	–	–	–	–	–	–	–	–
Eugenol	2180	RT, MS, NMR	67.1	88.3	91.8	0.3	0.9	3.2	4.1	2.3	11.6
2-Methoxy-6-vinylphenol	2207	RT, MS	trace	trace	0.1	trace	–	trace	trace	0.2	trace
Isoeugenol isomer	2361	MS	trace	trace	trace	0.1	–	0.2	0.4	–	–
Total			99.6	98.4	97.8	97.0	92.8	94.1	93.8	96.1	89.0

[a] Retention index relative to *n*-alkanes on the DB-Wax column. [b] Trace: <0.05%. tent. = tentative identification.

Table 2. Composition of the root essential oil of *Waldsteinia geoides* Willd.

Compound	RI[a]	Area %[b]	Identification
Propan-2-one	883	trace	RT, MS
Butan-2-one	902	trace	RT, MS
Toluene	1037	trace	RT, MS
Butylfuran	1052	0.5	RT, MS
n-Hexanal	1079	0.1	RT, MS
Limonene	1197	0.1	RT, MS
Hex-2-enal	1216	trace	RT, MS
Octan-3-one	1252	trace	RT, MS
p-Cymene	1268	trace	RT, MS
Hexan-1-ol	1352	0.1	RT, MS
p-Cymenene	1434	trace	RT, MS
Oct-1-en-3-ol	1449	0.1	RT, MS
Benzaldehyde	1521	0.1	RT, MS
Linalol	1546	0.2	RT, MS
cis-Myrtanal	1557	29.2	RT, MS
trans-Myrtanal	1571	3.1	RT, MS
Nopinone	1585	7.3	RT, MS
Myrtenal	1635	22.9	RT, MS
Menthadienol derivative	1661	0.2	MS
Neral	1688	0.1	RT, MS
α-Terpineol + unknown	1699	0.4	RT, MS
Geranyl formate	1703	trace	RT,[c] MS
Borneol	1705	trace	RT, MS
Oxygenated monoterpene	1710	0.4	MS
Oxygenated monoterpene	1713	0.3	MS
Phellandral	1726	5.2	RT, MS
Geranial	1732	0.1	RT, MS
Dihydrocarveol	1760	0.1	RT, MS
Citronellol	1767	0.2	RT, MS
iso-Dihydrocarveol	1779	trace	RT, MS
Oxygenated monoterpene	1782	0.7	MS
Perilla aldehyde	1788	0.8	RT, MS
Myrtenol	1799	10.8	RT, MS
Nerol	1801	trace	RT, MS
Isogeraniol	1812	0.2	RT,[d] MS
trans-Carveol	1837	0.2	RT, MS
Geraniol	1848	1.2	RT, MS
Guaiacol	1860	trace	RT, MS
cis-Myrtanol	1868	4.1	RT, MS
trans-Myrtanol	1878	3.8	RT, MS
p-Menth-2-en-7-ol (tent.)	1937	trace	MS
Perilla alcohol	2011	0.2	RT, MS
subst. Phenol (M+ 150) + unknown	2165	trace	MS
Myristicin	2267	0.1	RT, MS
Cinnamyl alcohol	2288	0.1	RT, MS, IR
Nerolic acid	2299	trace	RT, MS
Geranic acid	2343	trace	RT, MS
Oxygenated monoterpene	2377	0.2	MS
Hexadecanoic acid	2912	0.4	RT, MS
Total		93.5	

[a] Retention index relative to *n*-alkanes on the DB-Wax column.
[b] trace: <0.05%.
[c] No reference compound available; retention time according to: W. Jennings and T. Shibamoto, *Qualitative Analysis of Flavour and Fragrance Volatiles by Glass Capillary Chromatography*, Academic Press, New York (1980).
[d] No reference compound available; retention time according to: R. Ter Heide, *J Chromatogr.*, **139**, 143 (1976).
tent. = tentative identification.

genera of the subtribus Geinae exhibit a similar qualitative pattern. However, marked differences concerning the eugenol content of the oils of various species were found.

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