Chemical Composition of Hips Essential Oils of Some *Rosa* L. Species

Renata Nowak

Chair and Department of Pharmaceutical Botany, Skubiszewski Medical University of Lublin, 20-093 Lublin, Chodźki 1 Str., Poland. E-mail: renata.nowak@am.lublin.pl

Z. Naturforsch. 60 c, 369-378 (2005); received November 11/December 13, 2004

The chemical composition of the hips essential oils of 9 taxa of *Rosa* L. was analyzed and compared using the standardized analytical GC and GC/MS methods. The volatile hips oil compositions for these species are presented. All oil samples were dominated by following components: vitispiran (isomer), α -*E*-acaridial, dodecanoic acid, hexadecanoic acid, docosane (C22), β -ionone, 6-methyl-5-hepten-2-one, 2-heptanone, heptanal, myristic acid and linolic acid. Statistical analyses of 97 GC peaks of these oils were used to distinguish compositional patterns. There appeared to be correlation between the essential oil patterns and the classification within *Rosa* L. Cluster analysis of the composition of main components clearly showed two groups, one constituted by *R. rugosa* Thunb. from the Cinnamomea section, and the other constituted by the remaining taxa from the Caninae section.

Key words: GC-MS, Essential Oils, Rosa L.

Introduction

The genus Rosa L. (Rosaceae) consists of approx. 150 wild species, all of which grow in the northern hemisphere of Europe, Asia, the Middle East and North America. The genus is divided into four subgenera. Three of them, Hulthemia, Platyrhodon and Hesperhodos, have only one species each. The fourth subgenus, Eurosa, contains more species grouped into ten sections (Rehder, 1940). Most Polish wild species belong to the Caninae section of the subgenus Eurosa, whose nomenclature is extremely confused. The majority of species became a source of Polish Pharmacopeial material Fructus Rosae (FP IV). Rose hips have long been used as a herbal tea, vitamin supplement or food product in many European countries, since they are rich in vitamin C, phenolics and carotenoids (Nowak and Krzaczek, 1994; Hvattum, 2002). There is growing evidence that rose hips possess important pharmacological properties, e.g. anti-inflammatory and antioxidant (Winther, 1999; Gao et al., 2000). Roses are economically the most important ornamental crop because of their popularity as garden, landscape and pot plants or cut flowers, and their use as a source of aromatic oils for the perfume industry, too (Gudin, 2000). Their petals are the main source of fragrance compounds. There are some literature data about pharmacological activity of rose oil from flower, e.g. antimicrobial and anxiolitic (Basim and Basim, 2003; Aridogan et al., 2002; Umezu et al., 2002; Almeida et al., 2004).

Essential oils are complex mixtures of phenylpropanoids (including benzenoids), fatty acid derivatives, and terpenoids. They create the specific smell of plants and show multitude of pharmacological properties, such as bactericidal, fungicidal, antiviral, cytotoxic, immunostimulative and antioxidative (Aridogan *et al.*, 2002; Haze *et al.*, 2002).

The examinations of essential oils in roses were so far concentrated on recognition of the compounds of oil coming from petals or flowers, mainly of various rose cultivars. It is known that the mixture consists of approx. 400 components. These compounds have been classified into several chemical groups including hydrocarbons (mostly sesquiterpenes such as β -caryophyllene), alcohols (monoterpenes such as geraniol, nerol, citronellol and aromatic alcohols, e.g. phenethyl alcohol), esters (mainly acetates, e.g. hexylacetate, geranyl acetate, and phenethyl acetate), aromatic ethers (such as orcinol dimethyl ether, benzyl methyl ether, estragole, and methyl-eugenol), and "others" (e.g. aldehydes such as geranial and nonanal, rose oxide, and norisoprenes such as β -ionone) (Ohloff and Demole, 1987; Kim et al., 2000). The main compounds, which are emitted by flowers, are 2-phenylethyl, geranyl, and citronellyl acetates (Dobson et al., 1987; Shalit et al., 2003). The composition of oil obtained by hydrodistillation showed some differences (Knudsen and Tollsten, 1993).

The components of essential oil from rose hips are not well-known and the Polish roses have never been investigated from this point of view.

0939-5075/2005/0500-0369 \$ 06.00 © 2005 Verlag der Zeitschrift für Naturforschung, Tübingen · http://www.znaturforsch.com · D

Experimental

Plant material

The material comprised hips of 9 taxa of roses, which are classified by Flora of Poland into 6 species (Zieliński, 1987; Popek, 1996).

The fruits were collected in September 2002 near Lublin and Zamość (Table I) in the same stage of development and from the same region with similar environmental factors to diminish their influence on essential oil composition. The plants were confirmed by Prof. T. Krzaczek and voucher specimens are deposited in the Department of Pharmaceutical Botany of Medical University in Lublin (Poland).

In the research 100 g of frozen and crushed fruits were used.

Analysis of volatile compounds

The essential oils were obtained by means of hydrodistillation with m-xylene in a Derynge apparatus for 3 h. The composition of oils was analyzed using the methods of gas chromatography (GC) and gas chromatography connected with mass spectrometry (GC/MS).

The GC analyses were performed using a gas chromatograph Carlo-Erba Instruments typ HRGC 5300 Mega (Milan, Italy) with a flame ionization detector (FID) and a SSL injector (both 320 °C). The compounds were separated on a CP sil-5CB capillary column (30 m \times 0.32 mm i.d.; film thickness: 0.25 μ m). The temperature programme was from 50 °C to 300 °C (30 min isothermal) at a rate of 4 °C/min. The flow of carrier gas (N₂) was 1 ml/min.

GC/MS analyses were carried out using a gas chromatograph Fisons Instruments typ GC 8000 (Milan, Italy) with a CP sil-5CB capillary column (30 m \times 0.32 mm i.d.; film thickness: 0.25 μ m) coupled to a mass spectrometer. The analytical conditions for GC and GC/MS analyses were similar. Helium was used as a carrier gas at a flow rate of 0.8 ml/min. The ionization energy was 70 eV.

The components of oils were identified by comparing the mass spectra with a computer databank (National Institute for Standard Technology, NIST, library) and literature data, as well as by comparison of their retention indices with literature data (McLafferty and Stanffer, 1989; Adams, 1995).

Retention indices (RI) were determined according to Kovats (1958) and calculated with respect to a set of co-injected standard hydrocarbons (C5–C26).

The amount of separate components was determined in percentages of the GLC peak area to the whole fraction composition.

Species		Section	Data and place of collection	Abbreviation
R. rugosa Thunb.		Cinnamomea	02.09.19. Lublin	R.r
R. canina L.		Caninae	02.09.21. Szczebrzeszyn	R.c
R. vosagiaca Desportes			02.09.21. Szczebrzeszyn	R.v
<i>R. caryophyllaceae</i> Besser pro parte	R. dumalis		02.09.21. Szczebrzeszyn	R.car
R. coriifolia Fries	Bechst.		02.09.21.	R.cor
<i>R. subcanina</i> (Christ) Dalla Torre et Sarnath.		Caninae	Szczebrzeszyn 02.09.19. Lublin	R.sub
R. eglanteria $L. = R.$ rubiginosa $L.$			02.09.21. Szczebrzeszyn	R.e
R. villosa L.			02.09.19. Lublin	R.vil
R. tomentosa Sm.			02.09.21. Szczebrzeszyn	R.t

Table I. Description of the plant taxa used in the study.

Statistical analysis

Statistical analyses of GC peaks in the rose oils were used to distinguish compositional patterns. The software Metlab 6.5 and Statistica 6.0 were used for the analyses.

Firstly, all variables were checked if they differentiate species between groups. Secondly, only variables which differentiate species were chosen. In order to eliminate affection of distances by differences in scale among the dimensions from which the distances are computed, standardization was processed. After all these steps cluster analysis was computed. The silhouette value and single linkage method was used. In this method the distance between two clusters was determined by the distance of the two closest objects (nearest neighbors) in the different clusters.

The determination of overall chemical similarity between taxa was calculated using a correlation coefficient. Statistically significant coefficients are higher than $R^* = 0.197$.

Results and Discussion

The performed analyses showed that essential oils of rose hips are a complex mixture of about 100 compounds including a wide range of aldehydes, acids and esters. Table II lists all compounds isolated from the nine taxa sampled. Most of the components were identified. All these components have not earlier been reported as rose hips fragrances. However, several of the aromatics detected in rose hips have been found in flower fragrances. Flowers contained predominantly terpenoids and aromatics, present as alcohols, *e.g.* citronellol, nerol, and geraniol (Ohloff and Demole, 1987; Kim *et al.*, 2000; Babu *et al.*, 2002). In contrast to flowers, hips showed large amounts of al-dehydes, ketones, and acids.

The main compounds of rose hips essential oil, occurring in the majority of taxa are: vitispiran (isomer) (No. 58) (1.8–17.38%), *a-E*-acaridial (No. 57) (0–13.55%), hexadecanoic acid (No. 87) (2.45–14.26%), β -ionone (No. 70) (0.11–10.97%), dodecanoic acid (No. 75) (0.62–11.98%), 6-methyl-5-hepten-2-one (No. 18) (to 14.49%), myristic acid (No. 80) (0.52–4.05%), linolic acid (No. 90) (0–21.95%), docosane (C22) (No. 91) (0–13.29%).

All the investigated oils differed noticeably in their quantitative composition and proportions of separated compounds. There were more than 20 typical substances which appear in all oils in significant amounts. Their occurrence and the analysis of characteristic components of rose hips oil in each of the investigated taxa are shown in Table III.

Apparently some of the compounds are characteristic for each taxa. So, the presence of cis-3-hexenal (No. 2) was noted only in four taxa and in R. rugosa its amount was dominant reaching 27.5% whereas in *R. eglanteria* it stated 1.5%. There was no α -E-acaridial (No. 57) in the oil of R. subcani*na*, while this substance was dominant in the rest of the samples. Rose hips oils from R. canina and R. vosagiaca possess the similar composition and the highest similarity value of 0.98 for these species was obtained (Table IV). The essential oil from R. rugosa mostly differed from the composition of others. The similarity value obtained between this species and the others ranged only from 0.02 to 0.29. This fact was in accordance with the systematic distance of this species belonging to the Cinnamomea section from the others representing the Caninae section. Cluster analysis of the composition of main components clearly showed two groups, one constituted by R. rugosa Thunb. from the Cinnamomea section, and the other constituted by the remaining taxa from the Caninae section.

The analyzed taxa R. vosagiaca, R. coriifolia, R. subcanina, and R. caryophyllaceae are classified by Flora Europaea as distinct species (Klášterský, 1968). However, Polish Flora joined these taxa into one species called R. dumalis (Zieliński, 1987). The essential oils obtained from their fruits showed vital differences, mainly in quantitative, but also in qualitative composition. A high similarity value was obtained between R. vosagiaca and R. coriifolia, and R. vosagiaca and R. subcanina (0.78 and 0.77, respectively), but the similarity coefficient of R. caryophyllaceae to these three species ranged only from 0.34 to 0.47. This species differs morphologically from the others including to R. dumalis because it possesses (among other things) plenty of glands on the leaves and the characteristic strong smell. Fig. 1 shows the results of the cluster analysis in the Caninae section species using the standardized Euclidean distance.

The differences observed in the composition of oils may be the result of systematic and evolutionary position of the analyzed taxa. It is known that the plant scent is highly species specific, and al-

Table II. Chemical composition of the essential oils of Rosa L. hips and their retention indices.

No.	Compound	Identi- fication	RI	R.r	R.c	R.v	R.car	R.cor	R.sub	R.e	R.vil	R.t
1	3-Methyl-3-hexen- 2-ol	MS	832	0.80	tr	tr	_	_	_	-	tr	_
2	cis-3-Hexenal	MS, RI	835	27.50	0.4	0.13	_	tr	tr	1.5	-	_
3	5-Methyl-3- hexanone and 2-heptanone	MS, RI	844	0.52	7.45	6.47	_	4.69	0.27	2.03	_	7.43
4	Styrene	MS	845	0.35	0.22	0.16	_	tr	tr	0.36	_	_
5	5-Methylhexanal	MS	857	2.32	-	_	-	-	-	-	-	-
6	4,4'-Dimethyl- hexanal	MS	871	0.25	-	_	-	-	-	_	_	-
7	Hydrocarbon	MS	881	0.65	-	_	-	-	-	-	_	-
8 9	Methyl caproate	MS, RI	889 896	0.17	-	-0.80	-	0.27	_ **	-0.09	-	_ 8.98
10	Heptanal α -Thujene	MS MS, RI	890 913	_	0.89 tr	0.80 tr	_	0.27 tr	tr tr	0.09 tr	3.65	0.90 1.84
11	Benzaldehyde and α -pinene	MS, RI	923	0.31	1.80	1.49	-	0.90	0.45	0.33	0.57	2.41
12	2-Heptenol	MS	927	0.61	1.12	0.98	1.00	1.40	2.05	0.39	_	-
13 14	Camphene β -Methoxy-2-	MS, RI MS	935 939	0.35	0.79 _	0.67	tr –	0.40 _	0.28	0.15	0.18	0.15
15	furanethanol <i>n</i> -Amyl propionate or <i>iso</i> -amyl propionate and	MS	942	0.19	0.46	0.36	1.36	0.65	tr	0.38	0.98	2.54
16 17	1,5-octadiene deriv. 4-Octen-3-one 2-Hexenoic acid	MS MS	948 952	0.12	0.66	0.53	0.45	0.46	0.12	0.24	0.18	_
	methyl ester											
18	6-Methyl-5-hepten- 2-one	MS, RI	960	14.49	3.58	3.06	tr	3.10	1.26	3.26	0.35	0.21
19 20	β -Pinene 2,4-Heptadienal	MS, RI	975	0.30	_	_	tr	_	0.11	tr	_	_
	and 2-pentylfuran	MS, RI	981	0.14	1.69	1.40	1.07	1.09	0.44	0.81	0.77	0.82
21	Octanal	MS, RI	984	0.29	-	-	-	-	tr	-	-	-
22	β -Myrcene	MS, RI	989	0.07	_	_	_	_	tr	_	-	_
23 24		MS, RI MS	993 1004	tr 0.68	$0.57 \\ 0.44$	0.48 0.38	0.10 0.43	0.30 0.24	0.16 tr	$\begin{array}{c} 0.18\\ 0.12\end{array}$	tr 0.28	0.05 0.51
25	acetaldehyde Salicylaldehyde	MS, RI	1007	0.87	1.23	1.02	1.01	2.06	0.31	0.72	0.62	0.83
26	<i>p</i> -Cymene	MS, RI	1011	0.92	0.77	-	1.17	0.02	0.57	0.87	0.47	0.00
27	1,4-Epoxy- <i>p</i> - menthane	MS	1015	-	1.49	1.24	1.85	1.15	0.16	0.70	0.92	1.13
28	2,2'-Bifuran	MS	1020	0.50	-	_	-	-	_	_	-	_
29	1,8-Cineole	MS, RI	1026	tr	0.1	tr	-	—	tr		_	_
	Limonene 2-Octenal (isomer)	MS, RI	1026	0.15	0.05	tr	_	_	tr	tr	_	_
51	and methylbenzal- dehyde	MS	1030	0.55	0.36	0.32	-	0.35	0.30	0.25	-	-
32	Acetophenone	MS, RI	1034	_	0.18	0.15	_	tr	0.10	0.16	tr	tr
33	2-Octenal (isomer) and β - <i>E</i> -ocimene	MS, RI	1037	0.24	0.35	0.27	1.0	0.29	-	0.15	0.42	0.16
34	Butyric acid	MS, RI	1042	0.10	0.14	0.11	tr	0.10	tr	tr	tr	tr
35	isopentyl ester γ-Terpinene	MS, RI	1045	0.05	tr	tr	_	tr	tr	tr		_
35 36	γ-terpinene Linalool oxide A	MS, RI MS, RI	1043	0.05	tr 0.54	tr 0.48	0.24	tr 0.65	tr 0.36	tr 0.32	– tr	- tr
37	Linalool oxide B	MS, RI	1061	_	0.11	-	_	-	tr	0.06	0.14	0.05

No.	Compound	Identi- fication	RI	R.r	R.c	R.v	R.car	R.cor	R.sub	R.e	R.vil	R.t
38	2,2'-Methylenedi- furan	MS	1062	0.42	_	0.15	0.32	0.08	tr	-	_	-
39	Benzoic acid methyl ester	MS,RI	1069	-	0.32	0.32	0.32	0.38	0.19	0.15	0.13	tr
40	Terpinolene and guaiacol	MS, RI	1073	0.05	0.28	0.26	0.71	0.14	0.07	0.11	0.25	0.12
41	Nonanal	MS, RI	1079	2.51	0.91	0.76	3.79	0.3	0.21	0.41	0.35	0.4
12	Linalool	MS, RI	1082	0.95	1.11	1.01	_	0.66	0.26	1.65	1.00	0.5
13	Perrylene	MS, RI	1092	0.05	0.1	tr	0.3	tr	tr	tr	0.08	tr
4	Caprylic acid methyl ester	MS, RI	1107	0.05	_	_	_	_	_	_	_	_
5	7-Methyl-3-octen-2- one	MS	1116	0.31	-	-	-	_	-	-	-	-
16	<i>n</i> -Amyl isovalerate and	MS, RI	1144	0.25	0.15	0.12	0.47	0.09	0.05	0.09	0.23	tr
	acetic acid benzyl ester and <i>trans</i> -2-undecenal											
47	Benzoic acid ethyl ester	MS, RI	1154	-	0.25	0.24	0.30	0.20	0.09	0.05	0.1	tr
18	Safranol	MS, RI	1160	0.40	_	_	_	_	_	_	tr	tr
49	Methyl salicylate	MS, RI	1172	0.31	0.47	0.42	0.75	0.93	0.16	0.42	0.23	0.0
50	Eucarvone	MS	1176	tr	0.24	0.24	tr	0.17	0.1	0.08	tr	_
51	Bicyclo-[3.3.1]- nonan-2-one and	MS, RI	1184	0.64	1.02	0.88	0.40	0.63	0.51	0.60	0.14	0.2
-0	decanal	MO DI	1100	0.17	0.1	0.00			0.00			
	β -Cyclocitrol	MS, RI	1190	0.17	0.1	0.08	tr	tr	0.08	tr	tr	tr
53	Unknown	MS	1197	1.16	0.11	0.11	0.34	0.09	tr	0.31	0.06	0.0
94	Neral and benzyl methyl ketone	MS, RI	1216	0.91	0.35	0.25	0.60	1.09	0.11	0.37	0.88	0.2
55	Geraniol	MS, RI	1240	0.67	tr	0.05	_	0.14	0.16	0.17	0.07	_
56	Geranial	MS, RI	1240	1.01	0.29	0.00	0.30	0.14	0.10	0.17	0.26	tr
57	α -E-Acaridial	MS, KI MS	1247	0.75	5.14	3.98	2.44	12.69	-	3.36	13.55	13.0
58												
59 59	Vitispiran (isomer) Undecanal and phenylacetic acid propyl ester or	MS MS, RI	1264 1271	5.84 0,27	10.31 0.21	9.30 0.32	3.89 0.39	13.38 0.15	16.10 0.05	17.38 0.17	1.80 0.69	5.4 tr
	butanoic acid											
50	phenylmethyl ester (E,E) -2,4-	MS, RI	1285	0.76	0.07	0.07	0.26	0.29	0.40	tr	0.56	0.3
51	Decadienal	MS DI	1201	0.22	0.14	0.10	0.06	0.10	tr	0.22	t+	+ ••
51	Edulan Mathyl caprate	MS, RI	1291 1303	0.22	0.14	0.18 tr	0.06 tr	0.18	tr	0.22 tr	tr	tr
52	Methyl caprate	MS, RI		0.22	0.05	tr 0.65	tr 0.74	- 0.37	- 30	tr 0.51	- 1 74	tr
53 54	α -Damascenone	MS DI	1351	0.17	0.42	0.65	0.74	0.37	0.39	0.51	1.74	0.0
	Decanoic acid	MS, RI		1.99	0.29	0.26	0.61	0.46	0.69	1.37	0.69	0.0
	Asterisca-3(15)-6- diene	MS, RI	1395	0.51	0.05	tr	0.07	0.11	0.16	0.27	0.25	tr
56 57	Unknown trans-Geranyl-	MS MS, RI	1412 1426	0.55 1.96	0.41 0.29	0.37 0.24	1.50 0.82	2.25 0.51	$0.85 \\ 0.19$	$1.95 \\ 0.57$	0.88 0.73	0.7 tr
68	acetone 2,3-Dehydro-4-oxo-	MS	1437	0.14	tr	tr	tr	tr	tr	tr	0.19	_
<i>c c</i>	β -ionol	10 5-		<i>.</i>						0.01		
	α -Cadinene	MS, RI	1443	0.14	-	-	tr	-	_	0.86	tr	0.2
	β -Ionone	MS, RI	1455	0.80	5.49	5.66	2.82	10.97	0.11	2.40	7.90	4.2
71	α -Farnesene	MS, RI	1490	0.23	tr	tr	tr	0.15	0.08	0.87	0.24	tr
72	cis-Psi-ionone	MS	1495	0.16	0.29	0.33	1.59	0.16	0.10	0.36	0.24	tr
73	Lauric acid methyl ester	MS, RI	1505	0.45	_	_	-	-	tr	0.41	0.13	tr

Table II. (cont.)

No.	Compound	Identi- fication	RI	R.r	R.c	R.v	R.car	R.cor	R.sub	R.e	R.vil	R.t
74	Z-Nerolidol	MS, RI	1521	0.06	0.07	0.07	0.07	0.08	tr	-	tr	0.08
75	Dodecanoic acid	MS	1576	5.01	5.01	5.60	11.98	4.95	6.08	5.15	3.36	0.62
76	Unknown	MS	1595	0.49	5.31	5.64	2.34	9.09	0.21	2.29	6.80	2.94
77	α -Copaenal	MS, RI	1693	0.19	-	-	-	-	-	0.73	-	-
78	Myristic acid methyl ester	MS, RI	1700	0.20	0.16	0.12	0.23	0.13	0.13	0.18	0.39	0.24
79	Unknown	MS	1722	0.35	3.77	3.02	_	0.06	0.22	0.79	tr	_
80	Myristic acid	MS	1754	0.86	2.68	2.51	4.05	1.19	2.73	1.90	1.37	0.52
81	Octadecane	MS, RI	1792	0.06	-	-	0.36	0.03	0.12	tr	0.11	0.11
82	?-Phthalate	MS	1811	0.11	0.45	0.94	0.45	1.17	0.18	0.33	1.05	0.49
83	Hexahydrofarnesyl acetone	MS, RI	1822	0.12	0.24	0.35	0.80	0.17	0.24	0.32	0.46	0.33
84	Farnesyl acetone	MS	1886	0.06	0.05	0.07	0.18	0.13	0.11	0.18	0.05	tr
85	Palmitic acid methyl ester		1903	0.07	tr	tr	0.09	0.06	tr	0.05	tr	tr
86	Dibutyl phthalate	MS, RI	1912	0.17	0.61	0.73	1.52	0.49	0.52	0.36	0.65	0.92
87	Hexadecanoic acid	MS	1953	2.45	7.28	9.47	8.40	4.06	14.26	6.53	9.62	11.65
88	Linolenic acid methyl ester	MS, RI	2067	0.17	0.75	0.21	0.87	0.28	0.31	0.80	0.24	0.22
89	Heneicosane (C21)	MS, RI	2090	0.07	0.07	0.07	1.02	tr	tr	0.16	0.23	tr
90	Linolic acid	MŚ	2113	0.8	5.93	7.78	_	1.68	21.95	_	4.52	1.43
91	Docosane (C22)	MS, RI	2190	tr	0.06	0.07	13.29	tr	_	5.54	0.34	0.05
92	Tricosane (C23)	MS, RI	2290	0.08	0.37	0.42	0.60	0.07	0.08	0.30	0.47	0.30
93	Tetracosene	MS	2382	0.07	0.19	0.22	0.48	0.06	0.40	0.88	1.49	0.62
94	Tetracosane	MS, RI	2390	tr	0.13	0.15	0.12	tr	0.07	0.13	0.62	0,17
95	Pentacosane	MS, RI	2490	0.09	0.76	0.84	0.35	tr	0.12	0.25	0.91	0.76
96	Unsaturated hydrocarbon	MS	2785	0.25	0.41	0.46	0.74	0.22	1.07	0.70	1.80	3.73
97	Hydrocarbon	MS, RI	3076	0.22	0.52	0.67	1.19	0.25	1.15	1.03	1.74	7.68

Contents below 0.01% are marked as "-" and those between 0.01 and 0.04% as "tr" (traces).

most no two species produce identical mixtures of scent compounds. Even within species, often there is a great deal of variability in floral scent production, e.g. many cultivars of roses produce little or no scent, and among those that do, is considerable variability in the type of scent produced (Guterman et al., 2002). Some genetic and biochemical studies have confirmed that the ability to produce floral scent is easily acquired and easily altered or lost in natural populations as well as among cultivated species (Dudarewa and Pichersky, 2000). Some genetic and biosynthetic studies of rose flowers scent have been reported, too (Guterman et al., 2002). Helsper et al. (1998) proved that the emission of volatile compounds of rose flowers displays a circadian rhythm pattern. Kim et al. (2000) demonstrated that floral fragrances of Rosa hybrida differ between rose taxa and from sample to sample within a single taxa.

So, I think, one should be careful in formulating the taxonomic conclusions only on the basis of fragrance compound variation.

Fragrance compounds play numerous important roles in the interactions between plants and their surroundings, a major one is to attract pollinators, although their importance seems to be limited by the lability of composition, depending on such environmental conditions as sunlight, humidity, temperature, time of the day and also the stage of the ontogenetic development of a plant. The way of preparation of the material and the conditions of its extraction seem to be crucial, too.

The significant quantitive and qualitive diversity of essential oils composition in one gender or even species, which is often noted, may be a consequence of the fact that metabolic pathways leading to their production are not the main ones in plants and thus they are less strongly established by evolution.

Species	Main compounds	Other characteristic compounds	Notice
R. rugosa	<i>cis</i> -3-hexenal (2), 27.5%; this compound occurred in large amount only in oil from <i>R.</i> <i>rubiginosa</i> hips; 6-methyl-5-hepten-2-one (18), 14.5%; it is found in another rosehips oil but only in this species in such large quantity	 vitispiran (isomer) (58); dodecanoic acid (75), 5%; nonanal (41) and hexadecanoic acid (87) about 2.5%; 5-methylhexanal (5) 2.3% occurred only in <i>R. rugosa</i> 	 decanoic acid (64) and <i>trans</i>- geranylacetone (67) occurred in large amount in this species; there is lack of benzoic acid ethyl ester (47), camphene (13) and 1,4-epoxy-<i>p</i>-menthane (27); compounds: 4,4'- dimethylhexanal (6), hydrocarbon (7), methyl caproate (8), β-methoxy-2- furanethanol (14), 2,2'-bifuran (28) occurred only in <i>R. rugosa</i>
R. canina	vitispiran (isomer) (58), 10.3%; this compound is dominant in hips oils from <i>R. rubiginosa, R. subcanina</i> and <i>R. coriifolia</i>	- 5-methyl-3-hexanone and 2-heptanone (3) and hexadecanoic acid (87), > 7%; - α - <i>E</i> -acaridial (57), β - ionone (70), dodecanoic acid (75), linolic acid (90), > 5%; - 6-methyl-5-hepten-2-one (18), > 2%	-very complicated mixture
R. vosagiaca	hexadecanoic acid (87), 9.5%; vitispiran (isomer) (58), 9.3%	- linolic acid (90), 2- heptanone (3), b-ionone (70), dodecanoic acid (75), unknown (76), > 9%; - 6-methyl-5-hepten-2-one (18), α - <i>E</i> -acaridial (57), myristic acid (80), > 2%	–very similar composition with hips oil from <i>R. canina</i>
R. caryophyll- aceae	docosane (C22) (91), 13.3%; this compound occurred in large amount only in hips oil from <i>R. rubiginosa</i> ; dodecanoic acid (75), 12%	 hexadecanoic acid (87), 8.4%; myristic acid (80), > 4%; β-ionone (70), > 2% 	 there is lack of compounds 1-11; there is only trace amount of 6-methyl-5-hepten-2-one (18), characteristic compound of the others hips oils; extreme amount of 1,4-epoxy- <i>p</i>-menthane (27), 1.9%, in the investigated rosehips oils; little amount of <i>a</i>-<i>E</i>-acaridial (57), 2.5%, and vitispiran (isomer) (58), 3.9%, however these compounds were dominant in the rest of investigated oils; there is lack of hydrocarbon (97), similar to hips oil from <i>R.</i> <i>rubiginosa</i>

Table III. Characteristic and comparison of rose hips oils from investigated species.

Species	Main compounds	Other characteristic compounds	Notice
R. coriifolia	vitispiran (isomer) (58), 13.4%; α - <i>E</i> -acaridial (57), 12.7% and β -ionone (70), 11%, they occurred in extreme amount in this oil in comparison with other investigated oils	 unknown (76), > 9%; 5-methyl-3-hexanone and 2-heptanone (3), dodecanoic acid (75), hexadecanoic acid (87), > 4%; 6-methyl-5-hepten-2-one (18), salicylaldehyde (25), unknown (66), > 2% 	– rich and diverse composition
R. subcanina	linolic acid (90), 22%, in the largest amount of investigated oils; vitispiran (isomer) (58), 16.1%; hexadecanoic acid (87), 14.3%, the largest amount of investigated oils, too	 dodecanoic acid (75), 6%; myristic acid (80) and 2-heptenol (12), > 2% 	 lack of α-E-acaridial (57), commonly occurring in the rest of oils; there are five main compounds and the rest of components in small amounts
R. rubiginosa	vitispiran (isomer) (58), 17.4%;	- hexadecanoic acid (87), dodecanoic acid (75), docosane (C22) (91), > 5%; - α - <i>E</i> -acaridial (57), 6- methyl-5-hepten-2-one (18), β -ionone (70), unknown (76), 5-methyl-3-hexanone and 2- heptanone (3), > 2%	 lack of linolic acid (90); large amount of docosane (C22) (91) comparing with the rest of oils
R. villosa	α - <i>E</i> -acaridial (57), 13.6%, in the largest amount of investigated oils	 β-ionone (70), unknown (76), hexadecanoic acid (87), > 6%; - heptanal (9), dodecanoic acid (75), linolic acid (90), > 3% 	 little amount of vitispiran (isomer) (58), only 1.8%, comparing with the rest of oils; lack of 5-methyl-3-hexanone and 2-heptanone (3); characteristic large amount of heptanal (9); α-damascenone (63), 1.7%, extreme amount among investigated oils
R. tomentosaa	<i>α-E</i> -acaridial (57), 3%, like in <i>R. villosa</i> ; hexadecanoic acid (87), 11.7%; heptanal (9), 9%, in the largest amount of investigated oils	 5-methyl-3-hexanone and 2-heptanone (3), vitispiran (isomer) (58), hydrocarbon (97), > 5%; benzaldehyde and α-pinene (11), β-ionone (70), unknown (76), unsaturated hydrocarbon (96), > 2% 	 little amount of dodecanoic acid (75); -extreme amounts of compounds: <i>n</i>-amyl propionate or <i>iso</i>-amyl propionate and 1,5-octadiene deriv. (15), benzaldehyde and α-pinene (11), α-thujene (10) among investigated oils

Table III. (cont.)

The chemistry of volatile compounds has been proven particularly helpful in assessing taxonomic relationships of several genera and species. This group of compounds is often examined in the chemotaxonomic investigations of different species, lately in *Betula* gender (Isidorov *et al.*, 2004; Santos *et al.*, 2001; Skaltsa *et al.*, 2003). There are also publications concerning high correlation of essential oils composition and the genetic profile of a plant, *e.g.* in *Juniperus* gender (and some successful attempts), implement it as taxonomic markers (Adams, 1999).

These findings explain my interest in this group of compounds. However, the high diversity of oil

Species	R.r	R.c	R.v	R.car	R.cor	R.sub	R.e	R.vil	R.t
R.r	1.00	0.21	0.18	0.08	0.15	0.14	0.29	0.03	0.02
R.c	0.21	1.00	0.98	0.43	0.83	0.69	0.75	0.64	0.63
R.v	0.18	0.98	1.00	0.47	0.78	0.77	0.70	0.67	0.62
R.car	0.08	0.43	0.47	1.00	0.37	0.34	0.59	0.41	0.29
R.cor	0.15	0.83	0.78	0.37	1.00	0.40	0.72	0.75	0.63
R.sub	0.14	0.69	0.77	0.34	0.40	1.00	0.59	0.39	0.35
R.e	0.29	0.75	0.70	0.59	0.72	0.59	1.00	0.38	0.44
R.vil	0.03	0.64	0.67	0.41	0.75	0.39	0.38	1.00	0.79
R.t	0.02	0.02	0.62	0.29	0.63	0.44	0.44	0.79	1.00

Table IV. The correlation coefficients of the investigated rose taxa. The names of species are given in Table I.

Correlations, N = 97.

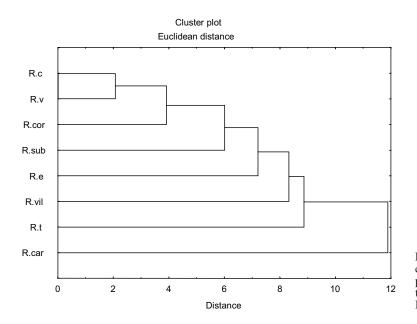


Fig. 1. Dendrogram obtained by the cluster analysis of the percentage composition of essential oils from *Rosa* L. taxa of Caninae section, based on the Euclidean distance.

composition depending on environmental conditions and ontogenetic development decreases their importance in taxonomy, in spite of the same conditions of collection and analysis of the material.

Acknowledgements

The author wish to thank Professor Tadeusz Krzaczek (Chair and Department of Pharmaceutical Botany, Medical University of Lublin) for the help in collection and identification of the plant material.

- Adams R. (1995), Identification of Essential Oil Components by Gas Chromatography/Mass Spectrometry. Allured Publishing, Carol Stream, Illinois, USA.
- Adams R. P. (1999), Systematics of multi-seeded eastern hemisphere *Juniperus* based on leaf essential oils and RAPD DNA fingerprinting. Biochem. Syst. Ecol. 27, 709–725.
- Almeida R. N., Motta S. C., Brito Faturi C., Catallani B., and Leite J. R. (2004), Anxiolitic-like effects of rose oil inhalation on the elevated plus-maze test in rats. Pharmacol. Biochem. Behav. 77, 361–364.
- Aridogan B. C., Baydar H., Kaya S., Demirci M., Ozbasar D., and Mumcu E. (2002), Antimicrobial activity and chemical composition of some essential oils. Arch. Pharm. Res. 25, 860–864.
- Babu K. G. D., Singh B., Joshi V. P., and Singh V. (2002), Essential oil composition of Damask rose (*Rosa da-mascena* Mill.) distilled under different pressures and temperatures. Flavour Fragr. J. **17**, 136–140.
- Basim E. and Basim H. (2003), Antibacterial activity of *Rosa damascena* essential oil. Fitoterapia 74, 394–396.
- Dobson H. E. M., Bergström J., Bergström G., and Groth I. (1987), Pollen and flower volatiles in two *Rosa* species. Phytochemistry 26, 3171–3173.
- Dudareva N. and Pichersky E. (2000), Biochemical and molecular genetic aspects of floral scents. Plant Physiol. 122, 627–633.
- Gao X., Björk L., Trajkovski V., and Uggla M. (2000), Evaluation of antioxidant activities of rosehip ethanol extracts in different test systems. J. Sci. Food Agric. 80, 2021–2027.
- Gudin S. (2000), Rose: genetics and breeding. Plant Breed Rev. 17, 159–189.
- Guterman I., Shalit M., Menda M., Piestun D., Dafny-Yelin M., Shalev G., Bar E., Davydov O., Ovadis M., Emanuel M., Wang J., Adam Z., Pichersky E., Lewinsohn D., Zamir D., Vainstein A., and Weiss D. (2002), Rose scent: Genomics approach to discovering novel floral fragrance-related genes. Plant Cell. 14, 2325–2338.
- Haze S., Sakai K., and Gozu Y. (2002), Effects of fragrance inhalation on sympathetic activity in normal adults. Jpn. J. Pharmacol. 90, 247–253.
- Helsper J. P. F., Davies J. A., Bouwmeester H. J., Krol A. F., and van Kampen M. H. (1998), Circadian rhythmicity in emission of volatile compounds by flowers of *Rosa hybrida* L. cv. Honesty. Planta **207**, 88–95.
- Hvattum E. (2002), Determination of phenolic compounds in rose hip (*Rosa canina*) using liquid chromatography coupled to electrospray ionization tandem mass spectrometry and diode-array detection. Rapid Commun. Mass. 16, 665.
- Isidorov V. A., Krajewska U., Vinogorova V. T., Vetchinnikova L. V., Fuksman I. L., and Bal K. (2004), Gas chromatographic analysis of essential oil from buds of different birch species with preliminary partition of components. Biochem. Syst. Ecol. 32, 1–13.

- Kim H.-J., Kim K., Kim N.-S., and Lee D.-S. (2000), Determination of floral fragrances of *Rosa* hybrida using solid-phase trapping-solvent extraction and gas chromatography-mass spectrometry. J. Chromatogr. A 902, 389–404.
- Klášterský I. (1968), *Rosa* L. In: Flora Europaea, Vol. 2. Cambridge University Press, pp. 25–32.
- Knudsen J. T. and Tollsten L. (1993), Trends in floral scent chemistry in pollination syndromes: floral scent composition in moth-pollinated taxa. Bot. J. Linn. Soc. **113**, 263–284.
- Kovats E. (1958), Gaschromatographische Charakterisierung organischer Verbindungen. Teil I: Retentions-Indices aliphatischer Halogenide, Alkaloide, Aldehyde und Ketone. Helv. Chim. Acta 41, 1915– 1932.
- McLafferty F. W. and Stanffer D. B. (1989), Registry of Mass Spectral Data, Vol. I–II. Wiley–Interscience, New York.
- Nowak R. and Krzaczek T. (1994), Flavonoids from *Rosa pomifera* var. *ciliato-petala* Bess. (Chrshan.). Acta Pol. Pharm. **51**, 407.
- Ohloff G. and Demole E. (1987), Importance of the odoriferous principle of Bulgarian rose oil in flavour and fragrance chemistry. J. Chromatogr. **406**, 181–183.
- Popek R. (1996), Biosystematyczne studia nad rodzajem Rosa L. w Polsce i krajach ościennych. Wydawnictwo Naukowe WSP, Kraków.
- Rehder A. (1940), Manual of Cultivated Trees and Shrubs, 2nd ed. Macmillan, New York.
- Santos P. R. D., de Lima Moreira D., Guimarães E. F., and Kaplan M. A. C. (2001), Essential oil analysis of 10 Piperaceae species from the Brazilian Atlantic forest. Phytochemistry 58, 547–551.
- Shalit M., Guterman I., Volpin H., Bar E., Tamari T., Menda N., Adam Z., Zamir D., Vainstein A., Weiss D., Pichersky E., and Lewinsohn E. (2003), Volatile ester formation in roses. Identification of an acetyl-coenzyme A geraniol/citronellol acetyltransferase in developing rose petals. Plant Physiol. 131, 1868– 1876.
- Skaltsa H. D., Demetzos C., Lazari D., and Sokovic M. (2003), Essential oil analysis and microbial activity of eight *Stachys* species from Greece. Phytochemistry 64, 743–752.
- Umezu T., Ito H., Nagano K., Yamakoshi M., Oouchi H., Sakaniwa M., and Morita M. (2002), Anticonflict effects of rose oil and identification of its active constituents. Life Sci. **72**, 91–102.
- Winther K., Rein E., and Kharazami A. (1999), The antiinflammatory properties of rose-hip. Inflammopharmacology **7**, 63.
- Zieliński J. (1987), *Rosa* L. In: Flora Polski. PWN, Kraków.