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CHEMICAL COMPOSITION OF DIFFERENT GENOTYPES OIL-BEARING ROSES

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Abstract

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Gas chromatography and gas chromatography-mass spectrometry was applied for comparison the chemical profile of the essential from three genotypes of oil-bearing roses: *Rosa damascena Mill., Rosa alba L.* and *Rosa № 836/61 (Rosa damascena Mill. x Rosa gallica L.).* The analyses identified 60 components. This study reveals that they have the same quality, but different quantitative composition. The main compounds are citronelol (8.76 – 48.24 %), geraniol (8.76 – 23.33 %), nonadecane (7.78 – 18.84 %) and nerol (4.19 – 12.09 %)

Introduction

The fragrant products obtained from oil-bearing roses find wide application in perfumery and cosmetics, pharmaceutical and food industry. Depending on the climate's and soil's characteristics in world scale only some species are grown commercially: Rosa damascena Mill., Rosa alba L., Rosa gallica L., Rosa centifolia L. and Rosa rugosa Thunb. (Bahaffi**,** 2005; Baser**,** 1992; Dobreva**,** 2010; Kovacheva**,** 2007; Shaul, 2009; Yu et al., 1994). The essential oil from Damask rose is the most highly valued on the world markets and the Bulgarian rose oil is a world standard for quality. In the past, it has been produced from Rosa damascena Mill. and Rosa alba L. (Dobreva**,** 2010; Staikov and Kalaidjiev, 1980), but the current ISO standard 9842 explicitly indicates only Rosa damascena Mill. as a raw material (ISO 9842, 2003). The white oil-bearing rose is being processed separately and its fragrant products are getting more and more popular (Dobreva**,** 2010). The innovative works with rose and rose oil production in Bulgaria have long traditions for centuries, aiming the nomination of elite rose's samples with high economical indexes, resistant to diseases and pests, frost-hardy, with high quality essential oil. The rich collection of local and introduced roses in the Institute of Rose and Aromatic Plants, situated in Kazanlak, is a good basis for such a selection - by clone selection and hybridization promising populations are created, clones, varietetes and hybrids (Kovacheva**,** 2007; Rusanov et al**.,** 2011). One of the most perspective hybrid is Rosa № 836/61(Staikov and Kalaidjiev, 1980), combining the good features of the parent forms Rosa damascena Mill. and Rosa gallica L.

Rose essential oil is a product of double distillation. It is a complex mixture of thousands of components. The development of the analytical techniques and methodology the elucidation of its composition is getting more and more comprehensive (Bahaffi, 2005; Baser**,** 1992; Baser et al**.,** 2003; Jalali-Heravi et al., 2008; Kovats, 1987; Shaul, 2009; Yu et al., 1994; Won et al**.,** 2009). Genotype is decisive for the profile of the essential oil when all other conditions are remained constant (Rusanov et al., 2011; Yu et al., 1994). Differences are observed between laboratory and industrial oils of the same material (Dobreva**,** 2011). In practice, the industrially obtained rose oils are more important. In this aspect it is important to compare the chemical profile of the industrial types of essential oils from different rose species.

The aim of the present work is a comparative investigation of the chemical composition of Rosa damascena Mill., Rosa alba L. and hybrid Rosa № 836/61 essential oils by GC/MS.

Materials and Methods

Experiments were conducted in 2006. A rose blossoms were used from the population of Rosa damascena Mill., Rosa

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alba L. and the Hybrid №836/61 (Rosa gallica L., subsp. Eriostyla Austriaca crants f. panonica X Rosa damascena Mill.) X Rosa damascena Mill. (Staikov and Kalaidjiev, 1980). The rose plants are cultivated on the experimental field of the Institute of Rose and Aromatic Plants, Kazanluk. Plantations are created and grown according to an accepted technology. The blossoms were picked in the morning (6-8 a.m.), in IV -V phase of development (semi-opened to fully open) (Staikov al., 1975). Distillation was carried out immediately after collection in a semi-industrial system with 100 L distillation apparatuses (Balinova – Tsvetkova et al., 1976), following these parameters: raw material for single time loading - 10 kg; hydromodule 1:4; distillation rate 8 – 10%; duration - 150 min; distillate temperature - 25-30°C. Cohobation of the primary distillate was done by distillation in the same apparatus. The essential oil produced from any of the rose species represents a mixture of primary and secondary oils in their natural proportion. Samples are treated with anhydrous Na_2SO_4 and filtered.

A Perkin Elmer Autosystem Gas Chromatograph equipped with a flame ionization detector at the following conditions did GC analysis:

Column 1:

- Supelcowax-10 capillary column, 30 m x 0.25 mm, 0.25 μm film thickness, inlet pressure 12 Psi;

Temperature programm:

1 min at 45°C, to 80°C with ramp rate 4°C/min, 1 min hold, elevating temperature to 190°C with ramp rate of 1.5°C/min, 10 min hold, elevating temperature to 240°C with ramp rate of 4°C/min and holding for 10 min;

injector temperature - 240°C, detector temperature - 250°C;

injected sample volume 0.2 μl through a splitter at split flow rate of 70 ml/min;

carrier gas - helium.

Column 2:

- DB-35 capillary column, 30m x 0.25mm, 0.25um film thickness, inlet pressure 15 Psi.;

Temperature programm:

2 min at 45°C, to 80°C with ramp rate 6°C/min, 1 min hold, to 190°C with ramp rate 1.5°C/min, 5 min hold, elevating temperature to 320°C with ramp rate 3°C/min and holding for 20 min;

injector temperature – 250°C, detector temperature – 320°C; Injected volume into GC: 0.3 μl through a splitter with flow rate 70 ml/min.

carrier gas - hellium.

Column 3:

- DB-35 capillary column, 60 m x 0.25 mm 0.25 μm film thickness, inlet pressure 25 Psi.;

Temperature programm:

1 min at 50°C, to 80°C with ramp rate 8°C/min, 1 min hold, to 190°C with ramp rate 2°C/min, 5min hold, elevating temperature to 320°C with an increase of 3°C/min and holding for 20 min;

injector temperature – 250°C, detector temperature – 320°C;

injected sample volume 0.2 μl through a splitter at split flow rate of 70 ml/min;

carrier gas - helium.

GC-MS analyses were performed on a Thermo-Finnigan Trace Ultra GC equipped with a Trace DSQ mass detector according GC conditions mentioned above.

Quantitative analyses were done using the peak areas without correction factor. Identification of separated components was carried out according retention times, compared with chromatograms of relevant reference substances, and by mass spectra, compared with data from the MS library NIST'2002.

Identification was finally confirmed by literature data for retention indexes for the identified components.

Results and Discussion

Results for the chemical composition of essential oils analyzed are presented in Table 1.

Data show identical qualitative results, but different proportion of the components. 60 compounds are identified. Rosa damascena Mill. oil contains 10 components in higher than 1 % concentration, Rosa alba L. oil - 11 and Rosa № 836/61 - 13. They represent respectively 83%, 80.1 % and 85.8 % from the total amount of the identified components.

Distinctive feature for the three rose species are the proportions of the main components of eleopten (terpeneols) and of stearopten (saturated hydrocarbons with carbon chains C_{17}, C_{19}, C_{21} and C_{23}).

In Rosa damascena Mill. and Rosa alba L. rose oils the amount of the majority alcohols are arranged in descending range: citronelol>geraniol>nerol. In rose oil of the hybrid, the range is geraniol>nerol>citronelol.

The first two genotypes demonstrate a "citronelol type" oil, while the hybrid has a typical "geraniol model". For Rosa damascena Mill. (Bahaffi**,** 2005; Baser**,** 1992; Gochev et al**.,** 2008; Kovacheva**,** 2007; Kovats**,** 1987; Nicolov et al., 1976; Yu et al.,1994) and Rosa № 836/61 (Rusanov et al., 2011; Staikov and Kalaidjiev, 1980) the results are in accordance with the literary sources. Rosa alba L. is the most striking example for differences in composition after production in a Clevenger apparatus, where geraniol is a majority component (Rusanov et al., 2011; Staikov and Kalaidjiev, 1980), and in

Table 1
The content of chemical components in *Rosa damascena* Mill., *Rosa alba* L. and *Rosa* № 836/61

№	Component	Formula	Peak area, %		
			Rosa damascena Mill.	*Rosa alba* L.	*Rosa* 836/61
1	Ethanol	C_2H_6O	0.10	0.04	0.56
2	α-Pinene	$C_{10}H_{16}$	1.13	0.04	0.21
3	β-Pinene	$C_{10}H_{16}$	0.45	0.02	0.06
4	Δ-3-carene	$C_{10}H_{16}$	0.05	0.04	0.03
5	Ocimene	$C_{10}H_{16}$	0.02	0.04	0.06
6	Linalool	$C_{10}H_{18}O$	0.95	0.74	0.96
7	Cis-rose oxide	$C_{10}H_{18}O$	0.36	0.24	0.10
8	Nonanal	$C_9H_{18}O$	0.05	0.08	0.05
9	Trans - rose oxide	$C_{10}H_{18}O$	0.16	0.13	0.05
10	Phenyl ethyl alcohol	$C_8H_{10}O$	0.87	0.26	1.31
11	α-Terpineol	$C_{10}H_{18}O$	0.18	0.16	0.25
12	Citronellol	$C_{10}H_{20}O$	48.24	30.94	8.12
13	Nerol	$C_{10}H_{18}O$	4.19	4.96	12.09
14	iso-geraniol	$C_{10}H_{18}O$	0.26	0.23	0.26
15	iso-geraniol 2	$C_{10}H_{18}O$	0.18	0.14	0.11
16	Geraniol	$C_{10}H_{18}O$	13.06	8.76	23.33
17	Citral 1	$C_{10}H_{16}O$	0.43	0.48	2.35
18	Citral 2	$C_{10}H_{16}O$	0.57	0.63	2.77
19	Methyl geranate	$C_{11}H_{18}O_2$	0.13	0.21	0.09
20	β-Bourbonene	$C_{15}H_{24}$	0.10	0.08	0.07
21	Citronellyl acetate	$C_{12}H_{22}O_2$	0.12	0.35	0.02
22	β-Elemene	$C_{15}H_{24}$	0.16	0.16	0.35
23	Caryophyllene	$C_{15}H_{24}$	0.55	3.76	2.56
24	Geranyl acetate	$C_{12}H_{20}O_2$	0.88	0.65	0.61
25	α-Humulene	$C_{15}H_{30}$	0.31	0.29	0.03
26	τ - Muurolene	$C_{15}H_{24}$	0.02	0.25	0.01
27	β-Cubebene	$C_{15}H_{24}$	0.54	0.15	0.04
28	α - Muurolene	$C_{15}H_{24}$	0.07	0.20	*
29	Methyl eugenole	$C_{11}H_{14}O_2$	1.29	*	0.05
30	Δ-Guaijene	$C_{15}H_{24}$	0.26	*	0.01
31	β - Cadinene	$C_{15}H_{24}$	0.18	0.46	0.11
32	Elemol	$C_{15}H_{25}O$	0.10	0.43	0.07
33	Benzyltiglate	$C_{12}H_{14}O_2$	0.08	0.01	0.14
34	Caryophyllene oxide	$C_{15}H_{24}O$	1.79	0.39	0.05
35	Heptadecene	$C_{17}H_{34}$	0.21	0.58	0.68
36	γ - Eudesmol	$C_{15}H_{26}O$	0.14	0.09	0.07
37	α - Eudesmol	$C_{15}H_{26}O$	0.08	*	0.03
38	β - Eudesmol	$C_{15}H_{26}O$	0.30	0.23	0.68
39	Cadinol	$C_{15}H_{26}O$	0.55	0.45	1.43
40	Z,E - Farnesol	$C_{15}H_{26}O$	0.14	0.77	0.17
41	Octadecane	$C_{18}H_{38}$	0.40	*	0.19
42	E,E - Farnesol	$C_{15}H_{26}O$	1.56	2.32	1.35
43	Nonadecene	$C_{19}H_{38}$	2.23	5.92	1.79

Table 1 continued

№	Component	Formula	Peak area, %		
			Rosa damascena Mill.	*Rosa alba* L.	*Rosa* 836/61
44	Nonadecane	$C_{19}H_{40}$	7.78	11.83	18.84
45	Benzyl benzoate	$C_{14}H_{12}O_2$	0.06	0.26	0.03
46	Eicosene	$C_{20}H_{40}$	0.07	0.18	0.05
47	Eicosane	$C_{20}H_{42}$	0.51	1.22	0.84
48	Methylbenzoate	$C_8H_8O_2$	0.02	0.06	0.02
49	Phenylethylbenzoate	$C_{15}H_{14}O_2$	0.02	0.23	0.02
50	Heneicosene	$C_{21}H_{42}$	0.14	0.04	0.11
51	Heneicosane	$C_{21}H_{44}$	1.77	8.08	7.73
52	Docosane	$C_{22}H_{46}$	0.03	0.19	0.19
53	Tricosene	$C_{23}H_{46}$	0.05	0.05	0.12
54	Tricosane	$C_{23}H_{48}$	0.20	1.22	2.17
55	Tetracosane	$C_{24}H_{50}$	0.03	0.12	0.19
56	Pentacosane	$C_{25}H_{52}$	0.07	0.64	0.56
57	Hexacosane	$C_{26}H_{54}$	0.02	0.13	0.05
58	Heptacosane	$C_{27}H_{56}$	0.15	0.68	0.39
59	Nonacosane	$C_{29}H_{60}$	0.05	0.14	0.09
60	Triacontane	$C_{30}H_{62}$	0.01	0.03	0.03

* - undetected component

industrial conditions, where dominating terpene is citronelol (Dobreva, 2010). Obviously, the essential oil produced from this rose is most dynamic and the storage period is of utmost importance.

The citronelol/geraniol ratio is significant for the aroma quality. Oils with variation limits of 2.5-4.3 (Nicolov et al., 1976) and 1.25-1.30 (Baser**,** 1992) are preferred. In our study values for this ratio regarding Rosa damascena Mill. and Rosa alba L. are respectively 4.01 and 4.09 - i.e. the Rosa alba L. oil fail into the characteristic of a high quality rose fragrance. For Rosa № 836/61 the value is 0.35, i.e. this rose oil should be considered as another kind. The other components with decisive role for the scent of rose oils are rose oxides, aldehydes and esters of terpeneols (Baser**,** 1992). The three species of roses are with near values regarding these substances, with some exceptions for the hybrid (for example - citral). Metyleugenol has a definitely positive effect in rose scent erection (Baser**,** 1992) and antibactericide properties of rose oil (Gochev et al., 2008), but on the other hand, its presence is connected with some allergic reactions. It is limited for cosmetic products with directive 76/768/EEC and its reduction in essential oils is desirable. For Rosa damascena Mill. this phenol derivate is varying between 0.90 – 4.00 % (Bahaffi**,** 2005; Baser et al., 2003; ISO 9842, 2003; Jalali-Heravi et al.**,** 2008; Kovats**,** 1987; Shaul**,** 2009), and in our study it is 1.29 %.

Literature data for methyleugenol in other two species of roses show either absence or ten times lower concentrations (Dobreva**,** 2010; Rusanov et al., 2011). This fact is confirmed also in our analyses - in oils of Rosa alba L. it is not detected and in Rosa № 836/61 it is 0.05%. Results display a big potential for use in products for direct contact with skin.

As for the components of stearopten Rosa alba L. and Rosa № 836/61 show identical type of distribution, while Rosa damascena Mill. differs from them. Besides the total content of paraffins is lower in it, the structure of their profile is different.

In Rosa damascena Mill. the main hydrocarbons are with C_{17}, C_{19}, and C_{21} skeleton (Bahaffi**,** 2005; Baser, 1992; ISO 9842. 2003; Kovats, 1987; Shaul, 2009) which is confirmed in our research too. For Rosa N836/61 and Rosa alba L. the quantities of paraffins are moved to the next homologues C_{19}, C_{21} и $C_{23.}$

A major for the three species of roses are the saturated and unsaturated hydrocarbons with a C_{19} structure.

The distribution of main groups of essential oil components is shown on Figures 1, 2 and 3.

Data show that the three genotypes have different odor structure.

Monoterpene oxygen-containing substances cover the biggest part of the ingredients complex in Rosa damascena Mill. – 70% followed by Rosa № 836/61 and Rosa alba L.

These components are responsible for the character, strength and intensity of rose odor - the Damask Rose is unsurpassed in this respect.

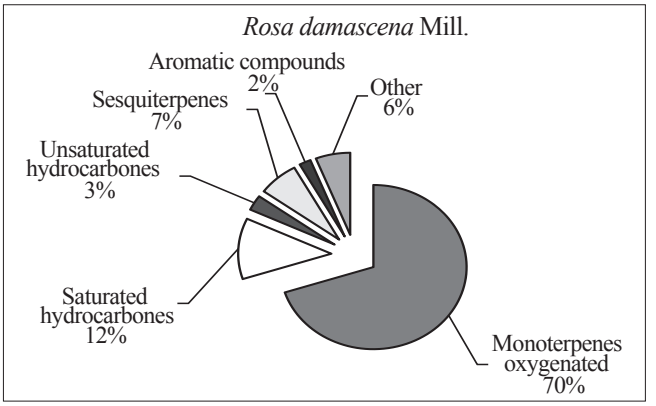

Fig. 1. Distribution of the main groups of odor substances in the essential oil of *Rosa damascena* Mill.

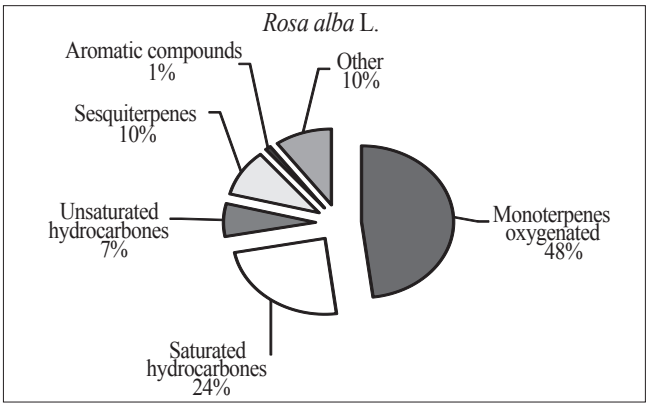

Fig. 2. Distribution of the main groups of odor substances in the essential oil of *Rosa alba* L.

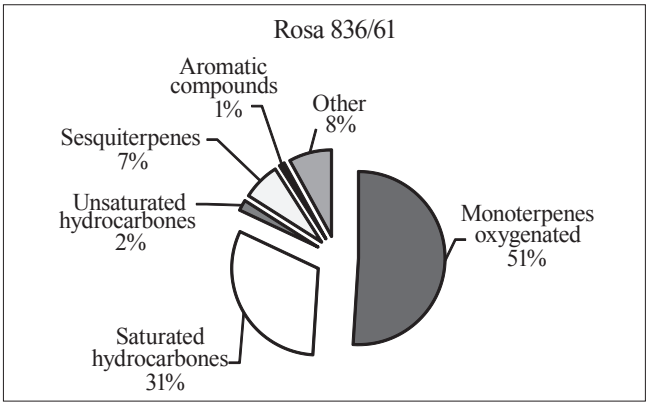

Fig. 3. Distribution of the main groups of odor substances in the essential oil of *Rosa* № 836/61

Saturated hydrocarbons are the main part of stearopten. Their presence is a guarantee for the durability of the scent (Nicolov et al., 1976). They are in highest concentration in the rose oil from the hybrid (31%) and in lowest concentration (12%) in oil from Rosa damascena Mill.

Olephines have strongest attendance in the oil from the white rose. In this oil is reported also the highest percentage of sesquiterpenes.

Components with aromatic structure are double in the Rosa damascena Mill's oil. In the column "others" fall all other ingredient substances. Their amount could be also indication for differences in the rose oils studied. It is obvious that the biggest variety of components is observed in the Rosa alba L. essential oil, less in Rosa № 836/61 and Rosa damascena Mill. This is an indirect indication for the complexity and abundance of their aroma and supposes that the advanced analytical techniques will reveal their potential in this direction.

Conclusion

A comparative characterization is made by GC-MS of a commercial type of essential oil produced from three different genotypes of oil-bearing roses - Rosa damascena Mill., Rosa alba L. and Rosa № 836/61. It was established identical qualitative composition, but the structures of their chromatographic profiles are different. 60 components are identified, from which the main ones are citronelol (8.76 – 48.24), geraniol (8.76 – 23.33 %), nonadecane (7.78 -18.84 %) and nerol (4.19-12.09 %).

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