

## Water soluble fractions of rose-scented geranium (*Pelargonium* species) essential oil

B.R. Rajeswara Rao <sup>a,\*</sup>, P.N. Kaul <sup>a</sup>, K.V. Syamasundar <sup>b</sup>, S. Ramesh <sup>b</sup>

<sup>a</sup> Central Institute of Medicinal and Aromatic Plants (CIMAP) Field Station, Boduppal, Uppal (P.O.), Hyderabad 500 039, India

<sup>b</sup> CIMAP Field Station, Allalasanra, GKVK (P.O.), Bangalore 560 065, India

Received 28 November 2001; received in revised form 21 January 2002; accepted 15 February 2002

### Abstract

The essential oil of rose-scented geranium (*Pelargonium* species, family: Geraniaceae) obtained through steam or water plus steam distillation of shoot biomass is extensively used in the fragrance industry and in aromatherapy. During distillation, a part of the essential oil becomes dissolved in the distillation water (hydrosol) and is lost as this hydrosol is discarded. In this investigation, hydrosol was shaken for 30 min with hexane (10:1 proportion) and the hexane was distilled to yield 'secondary' or 'recovered' essential oil. The chemical composition of secondary oil was compared with that of 'primary' oil (obtained directly by distilling shoot biomass of the crop). Primary oil accounted for 93.0% and secondary oil 7.0% of the total oil yield (100.2 ml from 100 kg green shoot biomass). Fifty-two compounds making up 95.0–98.5% of the primary and the secondary oils were characterized through gas chromatography (GC) and gas chromatography–mass spectroscopy (GC–MS). Primary oil was richer in hydrocarbons (8.5–9.4%), citronellyl formate (6.2–7.5%), geranyl formate (4.1–4.7%), citronellyl propionate (1.0–1.2%),  $\alpha$ -selinene (1.8–2.2%), citronellyl butyrate (1.4–1.7%), 10-*epi*- $\gamma$ -eudesmol (4.9–5.5%) and geranyl tiglate (1.8–2.1%). Recovered oil was richer in organoleptically important oxygenated compounds (88.9–93.9%), commercial rhodinol fraction (74.3–81.2%), sabinene (0.4–6.2%), *cis*-linalool oxide (furanoid) (0.7–1.2%), linalool (14.7–19.6%),  $\alpha$ -terpineol (3.3–4.8%) and geraniol (21.3–38.4%). Blending of recovered oil with primary oil is recommended to enhance the olfactory value of the primary oil of rose-scented geranium. Distillation water stripped of essential oil through hexane extraction can be recycled for distilling the next batch of rose-scented geranium. © 2002 Published by Elsevier Science Ltd.

**Keywords:** Rose-scented geranium; *Pelargonium* species; 'Primary' or 'decanted' oil; 'Secondary' or 'recovered' oil; Essential oil composition; Water soluble fractions; Linalool; Citronellol; Geraniol

### 1. Introduction

Rose-scented geranium (*Pelargonium* species, family: Geraniaceae) is a multi-harvest high value, aromatic plant cultivated for its essential oil which is widely used in the fragrance industry, in aromatherapy and for extraction of commercial rhodinol (mixture of linalool, citronellol, geraniol).

The essential oil is isolated from the shoot biomass either by steam distillation or by water plus steam distillation. This essential oil is referred to as 'primary' or 'decanted' oil. During distillation, a certain proportion of the essential oil becomes dissolved in distillation or condensate water (hydrosol). The hydrosol is discarded,

leading to loss of dissolved essential oil. Losses upto 25% were reported in Israel (Fleisher and Fleisher, 1985). This phenomenon was observed in many other aromatic crops and attempts were made to recover the dissolved oil from hydrosol. The essential oils, thus recovered are often referred to as 'secondary' or 'recovered' oils. The methods tried to recover aromatic oils from hydrosol were: cohobation (Bohra et al., 1994; Gokhale, 1959), extraction with diethyl ether (Bouزيد et al., 1997), adsorbing oil constituents on to an adsorbent followed by ethanol extraction (Bohra et al., 1994; Machale et al., 1997) and poroplast technique (Fleisher, 1991).

In the present investigation, a simple technique employing hexane as an extractant was used to recover essential oil of rose-scented geranium from hydrosol and the chemical composition of the recovered oil was compared with that of the primary oil.

\* Corresponding author. Tel.: +91-40-720-1131/2602.

E-mail address: cimaphyd@rediffmail.com (B.R. Rajeswara Rao).

## 2. Methods

Rose-scented geranium cv. Bourbon was grown in the Research Farm of Central Institute of Medicinal and Aromatic Plants Field Station, Hyderabad, following standard agricultural practices (Rajeswara Rao et al., 1989). Fully grown crop plants were harvested and steam distilled in a field distillation unit. The primary oil decanted from distillation water was filtered to remove extraneous particles, treated with anhydrous sodium sulphate to make it moisture-free, refiltered and measured. The distillation water mixed with hexane in 10:1 proportion was vigorously shaken for 30 min and the hexane saturated with essential oil was separated from the hydrosol. The hexane was then distilled to yield secondary oil. Three batches of distillations, each with 100 kg of rose-scented geranium green biomass were carried out to yield three samples of primary and secondary oils.

### 2.1. Gas chromatography

Gas chromatography (GC) analyses of oil samples were performed employing a Perkin–Elmer gas chromatograph (Model 8500) fitted with flame ionization detector (FID), GP-100 printer–plotter and an electronic integrator, using a bonded phase fused silica capillary column BP-1 (25 m length  $\times$  0.5 mm i.d.; film thickness 0.25  $\mu$ m) coated with polydimethylsiloxane. Nitrogen at a flow rate of 40 ml/min (linear velocity 34 cm/s) and 10 psi inlet pressure was the carrier gas employed. Temperature was programmed from 60 to 220 °C at 5 °C/min ramp rate with a final hold time of 10 min. Injector and detector were maintained at 250 and 300 °C, respectively. The oil samples (0.1–0.2  $\mu$ l) were injected neat with 1:80 split ratio.

### 2.2. Gas chromatography–mass spectroscopy

Gas chromatography–mass spectroscopy (GC–MS) analyses of oil samples were carried out on a Hewlett-Packard 5890 gas chromatograph coupled to a HP 5970 mass-selective detector (MSD) using a fused silica ultra performance cross-linked methyl silicone column (50 m length  $\times$  0.2 mm i.d.; film thickness 0.25  $\mu$ m). Temperature programming was done from 100 to 280 °C at

4 °C/min. Helium was used as the carrier gas at 1 ml/min flow rate. Mass spectra were recorded over 40–400 amu range at 1 scan/s with ionization energy 70 eV and ion source temperature 250 °C.

### 2.3. Identification of compounds

Essential oil components were identified by comparing retention times of the chromatogram peaks with those of reference compounds run under identical conditions, by comparison of retention indices (retention indices were computed from gas chromatograms by logarithmic interpolation between *n*-alkanes. The homologous series of *n*-alkanes C<sub>8</sub>–C<sub>22</sub>, Poly Science Inc., Niles, USA were used as standards) with literature data (Davies, 1990; Jennings and Shibamoto, 1980), peak enrichment on co-injection of authentic compounds and comparison of mass spectra of the peaks with those of standard compounds reported in the literature (Adams, 1989; Jennings and Shibamoto, 1980). Peak areas and retention times were measured by the electronic integrator. The relative amounts of individual constituents were computed from peak areas without FID response factor correction.

## 3. Results and discussion

### 3.1. Essential oil yield

The results are summarized in Table 1. An average of 7.0% of the total oil yield could be recovered by hexane extraction from the hydrosol. The 7.0% loss of essential oil in rose-scented geranium hydrosol in this study is much less than 15–30% losses reported in the literature for this and other crops (Fleisher and Fleisher, 1985; Fleisher, 1991). The distillation water stripped of essential oil through hexane extraction can be recycled for the next batch of distillation.

### 3.2. Essential oil composition

Fifty-two compounds constituting 95.0–98.5% of the essential oil have been identified. The variations in chemical profiles of the primary and the secondary oils are shown in Table 2. Primary oil was richer in hydro-

Table 1  
Details of primary and secondary essential oil yields of rose-scented geranium and their recovery percentages in relation to total essential oil yield

Batch no.	Amount of biomass distilled (kg)	Amount of primary oil obtained (ml)	Amount of secondary oil recovered (ml)	Total oil yield (ml)	Recovery (%)	
					Primary	Secondary
1	100	120.0	10.0	130.0	92.3	7.7
2	100	80.0	6.0	86.0	93.0	7.0
3	100	79.0	5.5	84.5	93.5	6.5

Table 2  
Chemical composition of primary and secondary essential oils of rose-scented geranium

Compound	Retention index	Peak area (%)					
		Primary oil			Secondary oil		
		1	2	3	1	2	3
$\alpha$ -Pinene	934	0.3	0.4	0.2	–	–	–
Sabinene	968	0.1	0.1	0.1	1.4	0.4	6.2
Myrcene	985	0.1	0.2	0.1	0.1	–	–
$\alpha$ -Phellandrene	998	0.1	0.1	0.1	–	–	–
<i>p</i> -Cymene	1015	t <sup>a</sup>	0.1	0.1	–	–	–
Limonene	1025	0.2	0.2	0.2	0.1	0.1	0.1
( <i>Z</i> )- $\beta$ -ocimene	1028	0.2	0.2	0.2	–	–	–
( <i>E</i> )- $\beta$ -ocimene	1040	0.2	0.2	0.2	0.1	–	t
<i>cis</i> -Linalool oxide (furanoid)	1064	0.1	0.1	0.1	0.7	1.2	1.0
<i>trans</i> -Linalool oxide (furanoid)	1077	t	0.1	t	0.4	0.1	0.1
Terpinolene	1082	t	0.1	t	0.1	–	0.1
Linalool	1089	6.7	8.0	8.1	14.7	17.0	19.6
<i>cis</i> -Rose oxide	1097	0.5	0.8	0.5	0.2	0.2	0.3
<i>trans</i> -Rose oxide	1115	0.2	0.3	0.3	0.1	0.1	0.2
Menthone	1136	0.2	0.6	0.4	0.3	0.4	0.3
Isomenthone	1149	5.3	7.3	6.3	4.5	5.9	5.5
Terpinen-4-ol	1165	0.1	0.1	0.2	0.2	0.4	0.1
$\alpha$ -Terpineol	1178	1.4	0.3	0.2	3.3	4.6	4.8
Nerol	1206	0.1	0.1	0.1	0.1	0.2	0.2
Citronellol	1220	28.2	27.5	27.9	28.1	26.8	33.4
Geraniol	1247	22.1	19.4	21.0	38.4	33.6	21.3
Geranial	1250	0.8	1.0	0.9	0.7	1.7	0.5
Citronellyl formate	1262	6.3	7.5	6.2	0.2	0.3	0.2
Geranyl formate	1284	4.1	4.7	4.1	0.2	0.4	0.2
$\beta$ -Phenylethyl acetate	1304	t	t	t	–	0.1	t
Citronellyl acetate	1338	t	–	0.4	0.2	–	–
Neryl acetate	1343	0.3	0.5	0.3	–	0.3	0.2
$\alpha$ -Cubebene	1358	0.1	0.2	0.4	–	–	0.1
$\alpha$ -Ylangene	1369	0.3	0.4	0.3	0.1	–	0.1
$\alpha$ -Copaene	1379	0.5	0.2	0.4	1.6	0.6	0.1
$\beta$ -Bourbonene	1384	0.3	0.4	0.6	–	–	–
$\beta$ -Caryophyllene	1420	0.2	0.1	0.1	–	–	–
Citronellyl propionate	1428	1.2	1.0	1.0	–	–	0.1
Guaia-6,9-diene	1443	0.1	–	t	–	–	–
Geranyl propionate	1449	0.2	0.1	0.2	–	–	–
$\alpha$ -Humulene	1456	0.3	0.3	0.6	–	–	–
Germacrene D	1479	0.1	0.2	0.1	–	–	–
$\alpha$ -Salinene	1487	2.2	1.9	1.8	–	–	t
Geranyl isobutyrate	1491	0.1	0.1	0.1	–	–	–
$\alpha$ -Muurolene	1497	0.1	0.1	t	–	0.1	–
Citronellyl butyrate	1503	1.7	1.4	1.6	0.1	–	0.1
$\gamma$ -Cadinene	1512	0.1	t	0.1	–	–	–
Calamene	1519	0.3	0.1	0.1	0.1	0.1	t
Geranyl butyrate	1534	0.1	0.1	t	–	–	–
$\beta$ -Phenylethyl tiglate	1555	1.0	1.0	1.0	0.4	0.4	0.3
Geranyl isovalerate	1585	0.1	0.1	0.1	–	–	0.1
Citronellyl valerate	1600	0.2	0.2	0.2	–	–	t
10- <i>epi</i> - $\gamma$ -Eudesmol	1618	5.3	4.9	5.5	0.9	0.7	0.9
Geranyl valerate	1630	t	–	0.1	–	–	–
$\beta$ -Eudesmol	1633	0.3	0.1	0.1	–	–	0.1
Citronellyl tiglate	1645	0.6	0.7	0.7	1.1	1.0	1.2
Gernyl tiglate	1675	2.0	1.8	2.1	0.1	0.1	0.1

1, 2, 3 = distillation batch numbers.

<sup>a</sup> t: traces (< 0.1%).

carbons, whereas secondary oil was richer in oxygenated components and commercial rhodinol (linalool + citronellol + geraniol) fraction (74.3–81.2% of essential oil). The relative abundance of hydrocarbons in the

primary oil is due to their low solubility in distillation water (Machale et al., 1997). Oxygenated components contribute to the richness and fullness of the organoleptic profile of an essential oil (Fleisher, 1991). In

rose-scented geranium, the loss of oxygenated constituents in distillation water makes the aroma of primary oil incomplete in terms of organoleptic richness and fullness. When the recovered oil was blended with the primary oil, the olfactory evaluation of the blended oil indicated that it had a much more natural and richer aroma than the primary oil.

#### 4. Conclusions

In this investigation, a simple procedure using hexane as an extractant has been described to recover dissolved essential oil from distillation water (hydrosol) of rose-scented geranium. Employing this method, 7.0% of total oil yield was recovered from the hydrosol. The recovered oil was rich in organoleptically important oxygenated compounds. The distillation water stripped of essential oil can be recycled for the next batch of distillation.

#### Acknowledgements

The authors thank the Director, CIMAP, Lucknow and the Scientist-in-Charge, CIMAP Field Station, Hyderabad for facilities.

#### References

- Adams, R.P., 1989. Identification of Essential Oil Components by Ion Trap Mass Spectrometry. Academic Press, New York.
- Bohra, P., Vaze, A.S., Pangarkar, V.G., Taskar, A., 1994. Adsorptive recovery of water soluble essential oil components. *J. Chem. Tech. Biotechnol.* 66, 97–102.
- Bouzid, N., Toulgouate, K., Villarem, G., Gaset, A., 1997. Analyse quantitative des fractions d'huile essentielle pouvant co-exister lors d'hydrodistillation de plants aromatiques. *Rivista Ital Eppos* 79, 15–25.
- Davies, N.W., 1990. Gas chromatographic retention indices of monoterpenes and sesquiterpenes on methyl silicone and carbowax 20 M phases. *J. Chromatogr.* 503, 1–24.
- Fleisher, A., 1991. Water-soluble fractions of the essential oils. *Perfum Flavor* 16 (3), 37–41.
- Fleisher, A., Fleisher, Z., 1985. Yield and quality of essential oil from *Pelargonium graveolens* cultivated in Israel. *J. Sci. Food. Agric.* 36, 1047–1050.
- Gokhale, N.N., 1959. The distillation waters. *Indian Pefum* 3 (2), 95–97.
- Machale, K.W., Niranjana, K., Pangarkar, V.G., 1997. Recovery of dissolved essential oils from condensate waters of basil and *Mentha arvensis* distillation. *J. Chem. Tech. Biotechnol.* 69, 362–366.
- Jennings, W., Shibamoto, T., 1980. Qualitative Analysis of Flavor and Fragrance Volatiles by Glass Capillary Gas Chromatography. Academic Press, New York.
- Rajeswara Rao, B.R., Prakasa Rao, E.V.S., Narayana, M.R., 1989. Rose geranium: an economical crop in the South Indian plains. *Indian Hortic.* 36 (2), 14–17.