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Chemical profiles of primary and secondary essential oils of palmarosa (*Cymbopogon martinii* (Roxb.) Wats var. *motia* Burk.)

B.R. Rajeswara Rao [a,*], P.N. Kaul [a], K.V. Syamasundar [b], S. Ramesh [b]

[a] *Central Institute of Medicinal and Aromatic Plants (CIMAP) Field Station, Boduppal, Uppal (Post Office), Hyderabad 500 039, India*
[b] *CIMAP Field Station, Allalasandra, GKVK (Post Office), Bangalore 560 065, India*

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Abstract

Natural essential oils extracted from aromatic crops through steam distillation are extensively used in fragrance, flavour and pharmaceutical industries and in aromatherapy. During steam distillation, a part of the essential oil becomes dissolved in condensate or distillation water and is lost as this water is discarded. A method was developed to recover the dissolved essential oil from condensate water. Palmarosa (*Cymbopogon martinii* (Roxb.) Wats. var. *motia* Burk., family: Poaceae), an important aromatic grass was used as the test crop. The distillation water of palmarosa mixed with hexane in 10:1 proportion was thoroughly shaken for 30 min to trap the dissolved essential oil. Hexane was then distilled to yield 'secondary' or 'recovered' oil. In palmarosa, the 'primary' or 'decanted' oil (obtained directly by distilling the crop biomass) accounted for 92% and the recovered oil accounted for 8% of the total oil yield. The solvent loss in this process was 4–7%. Experiments conducted in the laboratory with the essential oil showed that the water solubility of palmarosa oil ranged from 0.12 to 0.15% at 31 °C and 0.15 to 0.20% at 80 °C. Hexane recovered up to 97% of the dissolved essential oil in water. The recovered essential oil was richer in organoleptically important oxygenated compounds linalool (2.6–3.8%), geraniol (91.8–92.8%) and geranial (1.8–2.0%) compared to the primary oil.

Keywords: Palmarosa; Distillation water; Hexane extraction; Primary or decanted oil; Secondary or recovered oil; Essential oil chemical profile

1. Introduction

Natural essential oils are extracted from different plant parts of aromatic crops. Essential oils which are also known by the names aromatic oils, fragrant oils, ethereal oils, steam-volatile oils are extensively used in fragrance, flavour and pharmaceutical industries and in aromatherapy. More than 250 types of essential oils (1,20,000 t world annual production) worth US$ 1.2 billion per annum are traded in the world market. A number of countries produce different kinds of essential oils. India ranks second in the world trade of essential oils. Essential oils are commonly extracted from aromatic crops through steam distillation. In this

* Corresponding author. Tel.: +91-40-27201131/27202602.
E-mail addresses: brrrao1@rediffmail.com, cimaphyd@rediffmail.com (B.R.R. Rao).

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method, the aromatic crop biomass is loaded into a distillation tank and steam generated either in a boiler or in the distillation tank itself is allowed to pass through the crop biomass. The essential oil present in the biomass vapourises. Steam and essential oil vapours are passed through a condenser. The condensate (mixture of water and essential oil) is collected in a receiver. The essential oil is decanted, cleaned, made moisture free and traded. During the process of steam distillation, a part of the essential oil becomes dissolved in the condensate or distillation water. Unless recovered, the essential oil is lost as the distillation water is discarded. Since organoleptically important oxygenated compounds such as alcohols, esters, aldehydes, ketones, etc. are more soluble in condensate water, the aroma of the steam distilled essential oil is incomplete or is different from the natural aroma of the plant (Fleisher, 1990, 1991). Therefore, attempts were made to recover the dissolved essential oil from distillation water employing several techniques such as cohobation or re-distillation of condensate water (Gokhale, 1959), solvent extraction with diethyl ether (Bouzid et al., 1997), poroplast technique (Fleisher, 1990) and adsorption employing commercially available synthetic polymeric adsorbents (Bohra et al., 1994; Machale et al., 1997). The recovered oil is then added to the steam distilled oil to obtain a true replica of the natural essential oil (Fleisher, 1991). In the present investigation, a method employing hexane as an extractant is described for isolation of dissolved essential oil of an important aromatic crop palmarosa from the distillation water and the chemical profile of the steam distilled and recovered oils has been compared.

2. Material and methods

2.1. Efficiency of field distillation unit

Freshly harvested flowering biomass (500 g per sample) of palmarosa (*Cymbopogon martinii*) (Roxb.) Wats var. *motia*) was hydrodistilled in Clevenger (1928) trap for 3 h and the essential oil samples were collected. They were dried over anhydrous sodium sulphate to make them moisture free, weighed and the essential oil concentration (%) in the plant tissue samples were calculated:

$$\text{essential oil concentration (\%)} = \frac{\text{amount of essential oil recovered (g)}}{\text{amount of crop biomass distilled (g)}} \times 100$$

2.2. Field distillation of aromatic crops

A plantation of palmarosa was maintained at the Research Farm of Central Institute of Medicinal and Aromatic Plants, Field Station, Hyderabad, India following standard agricultural practices. The crop was harvested at flowering stage. One hundred kilograms of crop biomass was distilled in the field distillation unit. Three replications of distillations were carried out. The essential oil decanted from the receiver was filtered to remove extraneous matter, allowed to settle overnight by adding 30 g anhydrous sodium sulphate per litre of oil for removing the moisture, re-filtered, weighed and recorded as 'primary' or 'decanted' oil. The percentage recovery from the crop biomass was computed as shown earlier.

2.3. Recovery of dissolved essential oil

The condensate or distillation water from each distillation was collected (three samples in total). These were divided into 10 l sub-samples. Each 10 l of distillation water was mixed with 1000 ml of hexane to trap the dissolved essential oil and was thoroughly shaken in a mechanical shaker for 30 min at room temperature (31 °C). The mixture was then allowed to settle and the hexane layer was separated using a separating funnel. The distillation water stripped of essential oil through hexane treatment was discarded. The hexane from the sub-samples was mixed and distilled for 1 h to yield 'secondary' or 'recovered' essential oil. Three samples of secondary oils were obtained. They were treated with anhydrous sodium sulphate, filtered and weighed. In this process, the solvent loss ranged from 4 to 7%. The essential oil samples were stored in airtight containers at 0 °C until analysed for their chemical profile.

2.4. Solubility of essential oil in water and efficiency of hexane extraction

Two sets of experiments were conducted. In the first set, 2000 ml of water was heated in a round bottom

flask to 80 °C and 20 ml of essential oil was added, stoppered immediately and the mixture was vigorously shaken in a shaker for 30 min, the mixture was allowed to stand for 30 min, the un-dissolved essential oil was separated employing a separating funnel, the water with dissolved essential oil was distilled in Clevenger trap and the essential oil recovered from the water was treated with anhydrous sodium sulphate, filtered and measured. In the second set, the experiment was repeated and after the separation of un-dissolved essential oil, the water with dissolved essential oil was mixed with 200 ml of hexane, vigorously shaken for 30 min, the hexane was separated and distilled to yield trapped essential oil. The essential oil was treated with anhydrous sodium sulphate, filtered and measured. The two sets of experiments were repeated with cold water (31 °C). All the treatments were replicated thrice (12 samples in total). The efficiencies of the two methods for isolation of dissolved essential oil from distillation water were compared:

$$\text{efficiency of the extraction process (\%)} = \frac{\text{amount of oil (ml) recovered from water}}{\text{amount of oil (ml) dissolved in water}} \times 100$$

2.5. Gas chromatography (GC) of essential oils

Gas chromatography analyses of essential oil samples were carried out with a Perkin-Elmer gas chromatograph (Model 8500) equipped with flame ionization detector (FID), GP-100 printer-plotter and an electronic integrator, employing a bonded phase fused silica capillary column BP-1 (30 m × 0.32 mm i.d.; 0.25 μm film thickness) coated with polydimethylsiloxane. Nitrogen was used as the carrier gas at 0.4 ml/min flow rate (linear velocity 14 cm/s) and 10 psi inlet pressure. Temperature was programmed from 60 to 245 °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 μl) were injected neat with 1: 80 split ratio.

2.6. Gas chromatography–mass spectroscopy of essential oils

Gas chromatography–mass spectroscopy (GC–MS) analyses of essential 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 × 0.2 mm i.d.; 0.25 μm film thickness) at 4 °C/min ramp rate. Helium was 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.

2.7. Identification of essential oil constituents

Essential oil constituents were identified by comparing retention times of the chromatogram peaks with those of reference compounds run under identical conditions, by comparison of retention indices (Kovats, 1965) (retention indices were computed from gas chromatograms by logarithmic interpolation between *n*-alkanes. The homologous series of *n*-alkanes C_8–C_{22}, Poly Science Inc., Niles, USA were used as standards) with literature data (Jennings and Shibamoto, 1980; Davies, 1990), peak enrichment on co-injection of authentic compounds and comparison of mass spectra of the peaks with those of standard compounds reported in literature (Jennings and Shibamoto, 1980; Adams, 1989). 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. Comparison of Clevenger and field distillation methods

Due to continuous re-distillation or cohobation of condensate water and more controlled distillation of crop biomass, the Clevenger distillations produced higher yields compared to field distillations (Table 1). The lower recoveries in field distillations were because of the following two major reasons:

1. Incomplete recovery of essential oil from the crop biomass.
2. Loss of dissolved essential oil in condensate or distillation water.

As a result, the field distillation efficiency ranged from 64.0 to 65.0% compared to Clevenger distil-

Table 1
Comparison of Clevenger and field distillation methods for essential oil recovery from palmarosa

Sample no.	Oil recovery in Clevenger apparatus (g/100 g)	Oil recovery in field distillation unit (g/100 g)	Efficiency of field distillation unit in comparison to Clevenger apparatus (%)
1	0.80	0.52	65.0
2	0.75	0.48	64.0
3	0.50	0.32	64.0

Table 2
Details of primary and secondary essential oil yields of palmarosa and their recovery percentages with relation to total essential oil yield

Sample no.	Yield of primary oil obtained (g/100 kg)	Yield of secondary oil recovered (g/100 kg)	Total oil yield (g/100 kg)	Recovery (%)	
				Primary oil	Secondary oil
1	525.2	44.1	569.3	92.3	7.7
2	476.9	39.5	516.4	92.4	7.6
3	320.0	27.1	347.1	92.2	7.8

lation. These results confirm the earlier reports that steam/field distillation of aromatic crops leads to incomplete recovery of essential oils from aromatic crops (Gokhale, 1959; Fleisher, 1990, 1991; Bouzid et al., 1997).

3.2. Primary and secondary essential oil yields

The essential oil of palmarosa is widely used as a perfumery raw material in soaps, floral rose-like perfumes, cosmetics preparations, for masking the odour of botanical pesticides and in the manufacture of mosquito repellent products. It is used for flavouring tobacco products, foods and non-alcoholic beverages. In medicine, the volatile oil is used as a remedy for lumbago, stiff joints, skin diseases and for bilious complaints. In aromatherapy, it is used as an aphrodisiac for elevating the senses. Field distillation of flowering biomass produced 92% of the total oil yield (Table 2). Hexane treatment of the distillation water yielded 8% of the total oil yield. Unless recovered, the secondary oil dissolved in distillation water would have been lost. The loss of oil in distillation water in palmarosa is less than the loss reported for other crops (Fleisher, 1990, 1991). The differences among the replicates was due to the differential flowering behaviour of palmarosa. Palmarosa tillers (side shoots) within and among the plants in a population flower at different times. The oil recovery depends on the amount of flowering panicles (which contain more oil than other plant parts) in the distilled biomass.

3.3. Comparison of Clevenger distillation and hexane extraction at different temperatures

The water solubility of palmarosa oil ranged from 0.12 to 0.15% at 31 °C and 0.15 to 0.20% at 80 °C (Tables 3 and 4). Through Clevenger distillation or co-

Table 3
Comparison of Clevenger and hexane extraction methods for isolation of dissolved palmarosa oil in hot water (80 °C)

Factor	Clevenger distillation			Hexane extraction		
	1	2	3	1	2	3
1. Amount of oil (ml) dissolved in water	4.0	3.0	3.0	3.2	3.0	3.0
2. Amount of oil (ml) recovered from water	2.4	2.0	2.0	3.1	2.7	2.8
3. Efficiency of extraction process (%)	60.0	66.7	66.7	96.9	90.0	93.3

1, 2, 3: replications.

Table 4
Comparison of Clevenger and hexane extraction methods for isolation of dissolved palmarosa oil in cold water (31 °C)

Factor	Clevenger distillation			Hexane extraction		
	1	2	3	1	2	3
1. Amount of oil (ml) dissolved in water	2.8	2.5	2.6	3.0	2.4	2.5
2. Amount of oil (ml) recovered from water	2.3	2.1	2.0	2.9	2.2	2.3
3. Efficiency of extraction process (%)	82.1	84.0	76.9	96.7	91.7	92.0

1, 2, 3: replications.

hobation 60–67% of the dissolved essential oil in water at 80 °C and 77–84% of the oil dissolved in water at 31 °C could be recovered. Hexane extraction, on the other hand, recovered 90–97% of the water dissolved oil both at 31 and 80 °C. Hexane extraction, therefore is much superior to cohobation technique. These results corroborate the findings of earlier researchers that cohobation is not an efficient technique for recovering dissolved essential oils from distillation waters (Fleisher, 1990, 1991). This experiment has also demonstrated the efficiency of hexane for trapping the dissolved essential oil. The recoveries reported in this study with hexane are higher than those reported with synthetic polymer adsorbents (Machale et al., 1997).

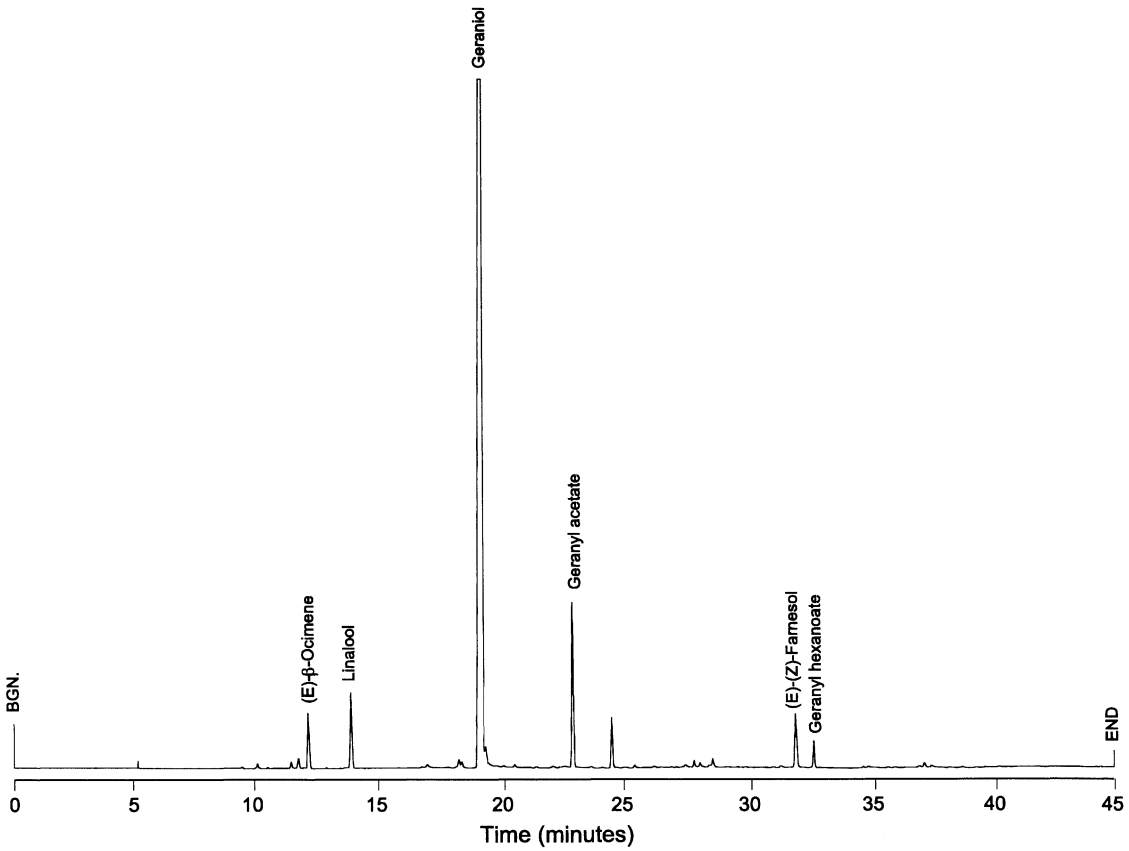

Fig. 1. Gas chromatogram of the primary essential oil of palmarosa.

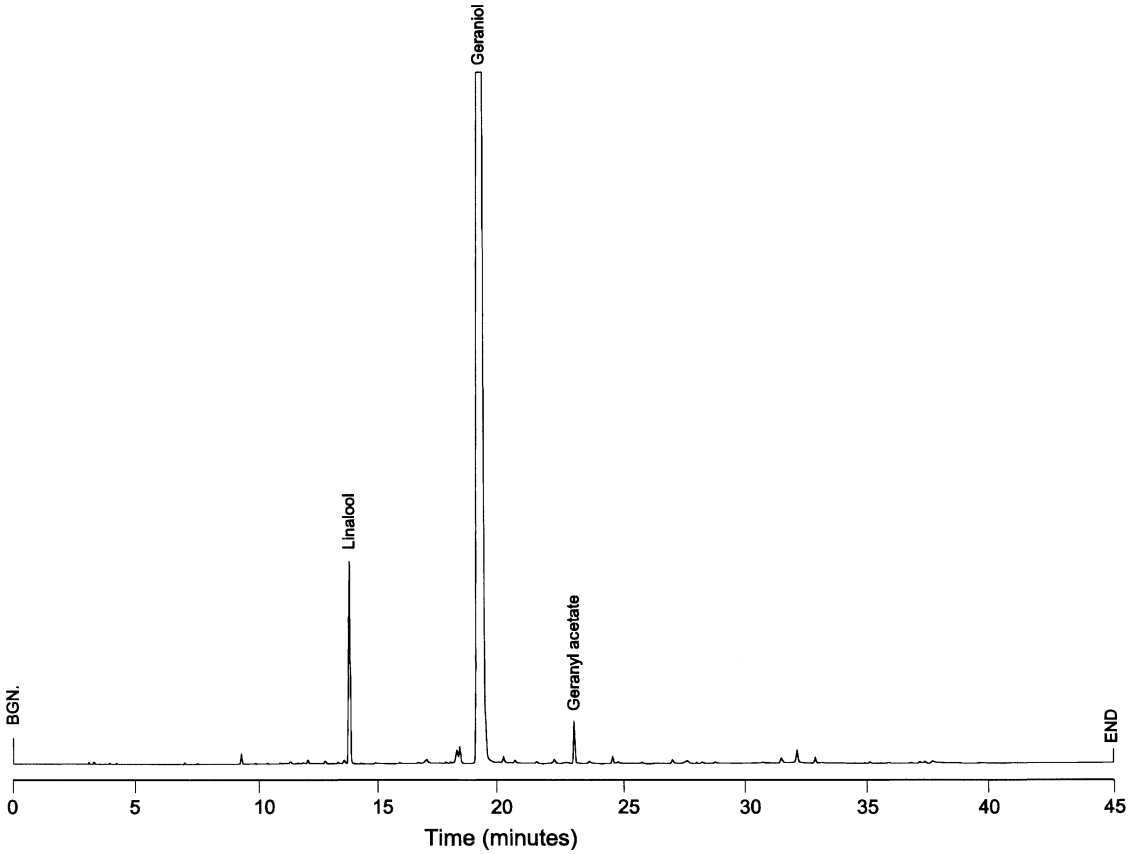

Fig. 2. Gas chromatogram of the secondary essential oil of palmarosa.

Table 5
Volatile constituents (%) of Clevenger distilled, primary and secondary essential oils of palmarosa

Constituent	Retention index	Clevenger distilled oil	Primary oil			Secondary oil		
			1	2	3	1	2	3
Sabinene	967	t	0.1	0.1	0.1	–	0.1	–
Myrcene	983	0.1	0.2	0.1	0.2	t	t	t
Limonene	1022	0.1	0.3	0.1	0.5	0.1	t	0.2
(*Z*)-β-Ocimene	1031	0.1	0.3	0.3	0.4	t	t	t
(*E*)-β-Ocimene	1042	0.7	1.5	1.3	1.6	0.1	t	t
Linalool	1085	2.3	2.2	2.4	2.3	3.1	3.8	2.6
Citronellol	1211	0.1	0.1	0.1	0.2	0.1	0.1	0.3
Geraniol	1238	84.0	83.8	78.0	85.7	92.1	92.8	91.8
Geranial	1243	–	–	–	–	1.8	1.8	2.0
Geranyl acetate	1356	5.3	4.7	12.0	2.9	0.6	0.4	0.3
Geranyl butyrate	1531	0.2	0.2	0.2	0.1	–	–	–
Geranyl isovalerate	1582	0.1	0.1	0.1	t	–	–	–
(*E*,*Z*)-Farnesol	1693	1.9	1.8	1.5	0.8	0.2	0.2	0.1
Geranyl hexanoate	1723	0.8	0.8	0.7	0.4	0.1	0.1	–

1, 2, 3: distillation batch numbers, t: traces (<0.1%).

3.4. Chemical profile of the essential oil

Fourteen peaks accounting for 95.2–99.3% of the primary (Fig. 1) and the secondary (Fig. 2) essential oils were identified and listed in Table 5. The secondary oil isolated through hexane extraction was richer in organoleptically important oxygenated compounds linalool, geraniol and geranial and was poorer in terpene components. This is due to the high solubility of oxygenated compounds (owing to their polar nature) than terpene hydrocarbons in condensate waters (Fleisher, 1991; Bohra et al., 1994; Machale et al., 1997). The essential oil of palmarosa is valued for its geraniol concentration. Palmarosa oil rich in geraniol is priced higher. Geraniol separated through fractional distillation from palmarosa oil is a high value aroma chemical widely used in the fragrance industry. The essential oil is priced at Rs. 560 kg^{-1} and geraniol at Rs. 1200 kg^{-1} (US$ 1 = Rs. 48.50) in the Indian market (Anonymous, 2002). The prices for these products are much higher in the international market (palmarosa oil Rs. 1075 kg^{-1}) (Anonymous, 2002).

4. Conclusion

Steam distillation is not an efficient method for complete extraction of essential oils from aromatic crops. During steam distillation, a part of the essential oil becomes dissolved in the distillation water. In this investigation, a method has been described for recovering the dissolved essential oil from distillation water of palmarosa employing hexane as a solvent to trap the essential oil. Through this method 8% of total oil yield could be recovered from the distillation water. The recovered oil was rich in geraniol, the main constituent of palmarosa oil.

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