

Isolation of Geraniol content from various essential oils

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ABSTRACT

Geraniol is a highly valuable aroma chemical and having extensive use in perfumery and flavour compounds. There are three sources to isolate this aroma chemical. Palmarosa oil *Cymbopogon martini* commonly known 'Rosha' or russa is the main source of geraniol (80 - 95%) and Jamrosa oil contains 80-89%. Another source of geraniol is *Cymbopogon winterianus* (Java citronella oil), which contains 40-45% including citronellol. This paper reports the processing of these essential oils to the recovery of geraniol content and find out the comparative study in respect of yield and cost economics.

Key words : Palmarosa oil, *Cymbopogon martini*, Citromella oil, Jamrosa oil, Essential oil

Palmarosa *Cymbopogon martini* commonly known 'Rosha' or 'Russa' is a multi harvest perennial aromatic grass. The colorless to pale (greenish) yellow essential oil obtained on distillation from the flowering tops and foliage of the herb has great commercial value in high-grade perfumery. This oil is very rich in geraniol (80-95%). The total annual world production of palmarosa oil is estimated to be 200 tones¹. Out of this, India shares for major world production 70-80 tones. India remained a major exporter of palmarosa oil to the world market.

Citronella oil is one of the industrially important essential oil obtained from different species of *Cymbopogon* belonging to family Graminae. The essential oil is volatile oil produced by steam, or water distillation of whole plant. The vapours are condensed to yield a water condensate and oil that can be separated off, usually by gravity. It is classified in trade into two types: Ceylon citronella oil, which is extracted from *Cymbopogon nardus* and java citronella oil, obtained from *Cymbopogon winterianus*. The main difference between these two oils is the proportion of geraniol and citronellal. The java type oil generally is considered to be of superior quality to the Ceylon oil. The high proportion of geraniol and citronellal in java citronella oil makes it an important source of various derivatives like Citronellol, citronellyl nitrile and hydroxycitronellal, which are extensively used in compounding high-grade perfumes. The Ceylon type citronella oil, which contains relatively low citronellal, is mainly used in cheaper products rather than for the production of derivatives.

The world consumption of citronella oil has amounted to several thousand tons annually due to the most important source of geraniol and citronellal. In 1997, the

world production of citronella oil is estimated at 5000 tons, valued at about 19 million US\$. Most citronella oil is java citronella oil; production of Ceylon citronella oil is restricted to Sri Lanka and Nepal. Citronella oil is regarded as one of the twenty most important essential oil. It had a world production of 2830 tons in 1993, valued at US\$10.8 million (Lawrence, 1993) and 3500 tons in 2005, valued at US\$ 15.0 million.

An Interspecific hybrid between *Cymbopogon nardus* var. confertiflorus and *Cymbopogon jwarancusa* was adequately evaluated and subsequently released as var. RRL-82 (jamrosa) providing an additional rich source of geraniol (Sobti *et al.*, 1981). Jamrosa contains about 80-89% geraniol content.

Due to high potential of geraniol in fragrance, flavour and essential oil industries, this study has been taken up for the production as well as cost economics of geraniol. In this study, first, saponification (hydrolysis) of the oil is carried out by using aqueous alkali solution and then fractionated the saponified oil under high vacuum. Actually, Fractionation is a process in which the oil is redistilled in vacuum so individual components, or fractions, are separated out as they evaporate one after the other. This is possible because fractions or constituent has its own rate of volatility based on time and temperature.

MATERIALS AND METHODS

The essential oils for the experiment are collected from the manufacturers and analysed by Gas Liquid Chromatograph to find out the percentage of geraniol content. The Hewlett Packard 5890 series II gas chromatograph is used and equipped with flame ionization

detector (FID) and Carbowax 20mm polar fused silica capillary column (30m x 0.32mm.). The injector and detector temperature were maintained 210c and 220 c, respectively. Nitrogen was used as carrier gas; flow rate was 1.5 ml/min. The amount of sample injected was 0.1ml (split ratio 60:1). The oven temperature was programmed as 60-210c was programmed at 3c/min.

The experiments are carried out in 5 liters capacity glass fractionation unit which is equipped with 3-neck flask capacity of 5litres, column 2"x4" with stainless steel wire sulzer packing, reflux divider 2", condenser 2"x24", receivers of 250ml, 500ml, 1000ml along with 300liters per min. capacity vacuum pump. Glass reaction unit of 5 liters capacity fitted with Teflon stirrer, thermometer pocket and condenser is also used to carry out chemical conversion of acetates into alcohols (hydrolysis purpose).

Processing of oils:

Palmarosa oil:

3 kg Palmarosa oil is charged into a glass reaction unit and added aqueous alkali solution for reflux at just boiling of the solution. After completion of the reaction saponified oil is washed with plain water and aqueous solution of sodium bicarbonate. Washed saponified oil is subjected to fractionate in a 5 liters capacity glass fractionation unit under high vacuum for the recovery of geraniol content (Table 3).

Citronella oil:

Method -I:

This was three-step method. Fractionation of oil for removal of the terpene and aldehyde under reduced pressure and the balanced portion of the oil is subjected to chemical conversion of the acetates into their corresponding alcohols. There after the chemically treated or saponified oil is washed properly and again charged into fractional distillation unit for the recovery of total alcohols. In this experiment 3kg material is taken for the purpose and results are shown in Table 6.

Method -II:

This was also three-step method. Fractionation of oil for removal of the terpene, aldehyde along with balanced part except residual part under reduced pressure and the balanced portion of the oil is subjected to chemical conversion of the acetates into their corresponding alcohols. Thereafter the chemically treated or saponified oil is washed properly and again charged into fractional distillation unit for the recovery of total alcohols. In this experiment 3kg material is taken for the purpose and the results are shown in Table 6.

Jamrosa oil:

The processing of jamrosa oil is similar to the processing of palmarosa oil. There is only difference *i.e.*, more quantity of alkali is used in the saponification of the oil due to presence of high percentage of Geranyl acetate. In this experiment also, 5kg material is taken for the purpose and the results are shown in Table 9.

RESULTS AND DISCUSSION

The composition of palmarosa oil, which is used in the processing, is displayed in Table 1 along with BIS specification in Table 2. The oil sample was analyzed by GC and found that Palmarosa oil contains 5.95 % Geranyl acetate and 82.35% geraniol. First, this oil is saponified by taking aqueous alkali solution for the conversion of all Geranyl acetate into geraniol. After saponification of the oil and proper washing that is charged into 5 liters capacity fractionation unit for the recovery of total alcohol as geraniol. Thereafter the fractionations, all possible geraniol containing fractions were blended and it was found that the recovery of the main product as geraniol was 82%. The purity was 98.3%. The losses were 8-9% during whole processing of oil.

Table 1 : Quality parameters of palmarosa oil used in the processing

Sr. No.	Quality parameters	Values
1.	Refractive index at 27 ⁰ C	1.4703
2.	Specific gravity at 27 ⁰ C	0.8815 ⁰ C
3.	Limonene	0.15%
4.	Cineol	0.18%
5.	Linalool	2.67%
6.	Citronellol	6.12
8.	Geranyl acetate	5.95%
9.	Geraniol	82.35.0%
10.	Farnesol	0.58%

Table 2 : BIS Standards for palmarosa oil (IS: 526-1988)

Properties	Specifications
Colour and appearance	Light yellow to yellow
Odor	Rosaceous with a characteristic grassy background
Specific gravity at 30 ⁰ c	0.8740 to 0.8860
Optical rotation	- 2 ⁰ to +3 ⁰
Solubility in 70% (V/V) ethanol	One (1) volume in two (2) volumes to give a clear solution
Refractive index at 30 ⁰ c	1.4690 to 1.4735
Acid value, max	3
Ester value after acetylating	266 to 280
Ester value	9 to 36
Total alcohols, calculated as geraniol, per cent, min	90.0

The sample of Java citronella oil is also analysed by GC and the composition of the oil is shown in Table 4 along with BIS specification in Table 5. The main components in processed JCO were Limonene 2.65%, Citronellal 32.12%, Citronellol 9.35%, Geraniol 24.47%, Citronellyl acetate 2.47%, Geranyl acetate 3.76%, Beta caryophyllene 1.8% and Elemol 4.58%. In the fractionation of the oil, various fractions were collected at required temperature and reduced pressure. These fractions were checked by Refractometer for knowing their respective Refractive index. Actually it is the quick and easy method of physical analysis during very sophisticated operation of fractionation unit. Vacuum was maintained 5-3mm and the processed temperature was maximum 165°C. These fractions were sent finally for Gas Liquid Chromatography analysis for purity purpose. The recovery of the main product as total geraniol content was found almost same in both the method *i.e.*, 40-43%

Table 3 : Yield of geraniol after fractionation of saponified palmarosa oil

Fractions	Boiling points at vacuum 3-5mm Hg	Percentage of geraniol content in the fractions	Refractive index n ₂₀ /D	Yield of fractions
1	67-68	0.87	1.4825	0.40
2	68-70	1.47	1.4740	1.21
3	70-74	0.27	1.4610	0.353
4	74-77	4.9	1.4620	1.71
5	77-80	42.2	1.4737	1.66
6	80-84	69.92	1.4745	2.06
7	84	95.8	1.4730	6.20
8	84	96.88	1.4730	4.28
9	84	98.2	1.4730	24.4
10	84	99.2	1.4732	20.47
11	84	98.8	1.4732	1.76
12	84	98.6	1.4732	17.90
13	84-82	99.9	1.4732	6.20

Table 4 : Quality parameters of Java citronella oil used in the processing

Sr. No.	Quality parameters	Values
1.	Refractive index at 27°C	1.4653
2.	Specific gravity at 27°C	0.8823 ⁰ C
3.	Limonene	2.65%
4.	Citronellal	32.12%
5.	Beta caryophyllene	1.8%
6.	Citronellyl acetate	2.47%
7.	Geranyl acetate	3.76%
8.	Citronellol	9.35%
9.	Geraniol	24.47%
10.	Elemol	4.58%

Table 5 : BIS Standards for Java citronella oil (IS: 512-1988)

Properties	Specifications
Colour and appearance	Pale yellow to light tan Clear liquid
Odour	Characteristic citrus grassy with rose undertone
Relatively density at 27 ⁰ C	Minimum: 0.8743 Maximum: 0.8893
Refractive index	Minimum: 1.4624 Maximum: 1.4714
Optical rotation	Range: -0.5 ⁰ to -5 ⁰
Solubility in 80% (V/V) ethanol	One (1) Volume in two (2) volumes to give a clear solution
Total acetylizable matter calculated as geraniol, % by mass, Min	85
Total carbonyl compounds calculated as citronellal % by mass, Min	35-45
Mineral oil	No readable separation of mineral oil
Steam distillation residue % by mass, Max	3

is given Table 6. The losses were 6-7% during whole processing of oil.

In case of Jamrosa oil, the sample contains Geranyl acetate 36.6%, geraniol 45.4% and shown in Table 8 along with BIS specification in Table 7. After saponification, the oil was fractionated under vacuum 3-5 mm Hg at process temperature 160-175°C. The results are shown in Table 9 with the recovery of geraniol content 60-65%, which is having 89% purity.

The cost economics for the isolation of geraniol

Table 6 : Yield of geraniol after fractionation of saponified citronella oil (after removal of 35% citronellal)

Sr. No.	Boiling points at vacuum 3-5mm Hg	Percentage of geraniol + citronellol contents in the fractions	Refractive index n ₂₀ /D	Yield of fractions (%)
1.	72-79	8.6+26.3	1.4668	1.15
2.	79-80	12.5+34.5	1.4683	3.25
3.	80	15.2+43.5	1.4650	3.15
4.	80-81	32.2+49.7	1.4650	3.30
5.	81-82	32.3+49.7	1.4655	5.30
6.	82-83	57.2+30.8	1.4715	22.1
7.	83	62.8+23.0	1.4725	20.3
8.	83	65.2+17.7	1.4730	8.35
9.	83	52.7+8.2	1.4745	2.50
10.	83-85	22.0+7.8	1.4745	1.35
11.	85-93	12.0+3.5	1.4810	7.0

Table 7 : BIS Standards for jamrosa oil (IS: 14508:1998)	
Properties	Specifications
Colour and appearance	Colorless to Pale yellow liquid
Odour	Sweet floral rosy, with citrusy, minty top-note appreciation
Relatively density at 27 ⁰ C	Minimum: 0.8830 Maximum: 0.8890
Refractive index	Minimum: 1.4680 Maximum: 1.4745
Optical Rotation	Range: -2 ⁰ to +2 ⁰
Solubility in 80% (V/V) ethanol	One (1) volume in one (1) volume to give a clear solution
Total alcohols calculated as geraniol, % by mass	80-90
Total esters calculated as Geranyl acetate % by mass	19-33
Total carbonyl compounds calculated as Citral, % by mass	2-5
Free alcohols as geraniol, % by mass,	52-60

Table 8 : Quality parameters of jamrosa oil used in the processing		
Sr. No.	Quality parameters	Values
1.	Refractive index at 27 ⁰ C	1.4715
2.	Specific gravity at 27 ⁰ C	0.8860 ⁰ C
3.	Limonene	2.45
4.	Geranyl acetate	36.6%
5.	Geraniol	45.4%

Table 9 : Yield of geraniol after fractionation of saponified jamrosa oil				
Fractions	Boiling points at vacuum 3-5mm Hg	Percentage of geraniol content in the fractions	Refractive index n ₂₀ /D	Yield of fractions
1	64-80	1.05	1.4623	3.0
2	80-84	24.0	1.4655	1.8
3	84	65.0	1.4666	2.0
4	84	76.0	1.4710	5.0
5	84	89.0	1.4739	30.0
6	84-85	92.0	1.4745	25.0
7	85-94	58.0	1.4735	5.0

Table 10 : Cost economics for isolation of geraniol							
Name of oil	Current market rates of oils (Rs.)	Processing charges @ Rs. 55.5 per kg	Miscellaneous expenses @ 5 % of oil cost (Rs.)	Total cost of process material (Rs.)	Yield of geraniol	Current market price of geraniol (Rs.)	Cost of geraniol after processing (Rs.)
Palmarosa	800.00	55.50	40.00	895.50	82%	1400.00	1092.00
Citronella	425.00	55.50	21.50	502.00	42%	700.00	611.00
Jamrosa	425.00	55.50	21.50	502.00	65%	850.00	772.00

content was calculated on the basis of commercial charges and market price of these oils and their geraniol (Table 10). The commercial charges were taken from Fragrance and Flavour Development Centre, A Govt. of India autonomous body, ministry of MSME, Kannauj, U.P. India. In the cost of geraniol, the cost of the other byproducts was not calculated due to minor profit. It means if we calculate the cost of geraniol only, the profit comes about 10-25% after processing. In case of citronella oil, the cost of citronella as 35% @Rs 700 per kg was calculated from the cost of original oil and finally the cost of geraniol was found out.

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