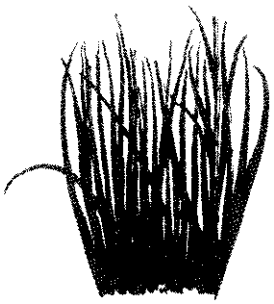

A New Method of Separation of Citral from Lemongrass Oil

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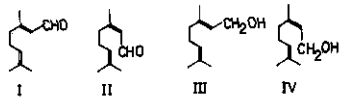
Although many methods are known for the separation of citral from lemongrass (*Cymbopogen flexuosus*) oil, like fractional distillation, adduct formation and regeneration, the purity and the yield of citral as separated are not satisfactory. A new method for separation of citral in pure form and in near quantitative yield uses the column chromatographic technique. This method may also be adapted for large scale separation of citral and hence can be of commercial importance.

Citral, a mixture of geranial (I) and neral (II) roughly in the ratio 5:3, is present in lemongrass oil generally to the extent of 70-80%. Citral has been separated from lemongrass oil by vacuum fractionation of the oil or by sodium bisulphite,[1,2] and neutral sulphite adducting[3] methods. In vacuum fractionation the enrichment of citral happens and citral of 95% purity is generally obtained. Moreover removal of components like geraniol (III), nerol (IV) which have boiling points differing only by a few °C from that of citral is found to be difficult even when high efficiency fractionating columns are used. Being a mixture of α, β unsaturated aldehydes, citral is heat labile, and excessive heat treatment is likely to lead to rearrangements, polymerisation and eventual destruction of the material.



I II III IV

The other method of separation of citral, namely bisulphite adducting, also suffers from disadvantages.[4-6] In this process, the oil is shaken with a sodium bisulphite solution. The resulting crystalline solid is separated and purified by washing with alcohol or ether. The citral is regenerated by decomposition of the adduct with sodium carbonate, sodium hydroxide or hydrochloric acid. Even though the normal adduct is formed quantitatively and can be easily decomposed, quantitative regeneration of citral is difficult—usually a loss of about 10-15% is encountered. The loss is reported to be due to the formation of a cyclic bisulphite compound in the presence of alkali from which the recovery of citral is found to be difficult.[7]

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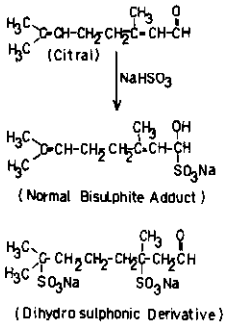
Acid initiated decomposition of the adduct usually leads to cyclisation and polymerisation of the product which is undesirable. The presence of unsaturation and the aldehydic group makes the reaction of citral with sodium bisulphite complicated.

In addition to the normal bisulphite adduct, adducts containing 2 moles of sodium bisulphite are also reported, i.e., sodium bisulphite adding to the ethylinic double bonds as shown below.



This dihydrosulphonic acid derivative is reported to exist in a labile form and a stable form.[7] Citral can no longer be regenerated from the stable form showing that a slight change in the reaction parameters can lead to the formation of unwanted stable adducts. Even in this method pure citral is obtained only after vacuum distillation since other aldehydes and methyl ketones present in lemongrass oil also form adducts with sodium bisulphite. Thus the purity of citral isolated by this method is poor.

In 1985 we reported a simple method for the estimation of citral in lemongrass oil by column chromatography.[8] In this method pure citral in near quantitative yield is isolated from lemongrass oil using hexane and ether as eluents.

Now we describe a modification of our earlier process which is developed with a view to commercialising the separation of pure citral—purity 99+% by GLC (see figure 1) and TLC (see figure 2)—in near quantitative yield from lemongrass oil. This process makes use of hexane and isopropanol as eluents. Being a physical process, it does not involve use of chemicals and hence the possibility of rearrangements during separation of citral is minimised. This process also excludes excessive heat treatment which is undesirable in the case of thermally liable molecules like citral.

Experimental

Materials.—Silica gel (SISCO, Bombay, Mesh size 100-200) was used as such after activation at a temperature of 100°C for 1 hour. Solvent grade hexane and isopropanol (Merck-India) were used as eluents after drying. Glass columns (125 cm x 5 cm ID) were used for the separation. Fractions were analysed by TLC and GLC. For TLC Silica gel G (Merck India) was used. All gas chromatographic analysis [6 ft. 10% SE-30 on chromosorb column; oven temperature 150°C—isothermal, injection port temperature 200°C—detector temperature 250°C, FID detector, N_2 flow rate (40 ml/min)] were done on a Hewlett-Packard 5730 A gas chromatograph with a Hewlett-Packard 3390 A Reporting Integrator.

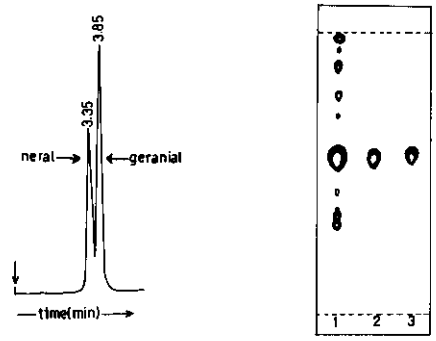


Figure 1. GLC of Citral Separated from Commercial Lemongrass oil

Figure 2. TLC of (1) Commercial Lemongrass oil (2) Citral Separated from Commercial Lemongrass oil (3) Authentic Sample of Citral-purified from 97% Citral (Aldrich). Solvent system—isopropanol: Hexane—1:19.

Solvents were removed under reduced pressure, at temperatures not exceeding 40°C using Buchi EL 130 Rotavapor.

Column packing and chromatographic conditions. Silica gel was packed by the slurry packing method using hexane as the suspending medium. The height of the adsorbant in the column after packing was 100cm. Suction was applied at the bottom to get uniform packing. A column elution rate of 12ml/min. was maintained using a constant pressure head, the length of solvent head being 16 cm and the ratio of substance to adsorbant 1:10. The experiment was done on a 25 gm scale using a typical commercial sample of lemongrass oil (obtained from M/s. Esthappanose & Sons Alwaye, Kerala, India) having 78% citral content (by adducting method).

Method

The separation was done in a single stretch at room temperature (28°C). Fractions of 50 ml were collected and analysed using TLC and GLC.

Fractions having the same R_f values in TLC and same retention time in GLC were combined and solvent removed at temperatures not exceeding 40°C under reduced pressure. When the minor components (hydrocarbon, geranyl acetate and carbonyl compounds other than citral) were eluted out (as seen by TLC and GLC), polarity of the eluent was increased by adding isopropanol. When citral fractions were over (checked by TLC and GLC), the rest of the components of alcohols were eluted in a single lot. The column elution details are given in Table I.

Conclusion

A simple and rapid method has been developed for the quantitative separation of citral from lemongrass oil in pure form (purity 99+% by GLC). Since this is a physical separation procedure using no chemicals, possibility of rearrangements are minimised; moreover, the solvents used can be recovered and recycled. The adsorbant can also be regenerated and used after proper cleaning and activation. Because of these advantages this method is far superior to other existing physical and chemical methods available for the separation of citral of high purity in near quantitative yield. Since the regeneration and recycling of materials used is possible, this process can also be of commercial importance and hence will be the subject of a future patent. Efforts are under way to separate in pure form and analyse all the other components of lemongrass oil.

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Table I. Experimental Results of Column Chromatographic Separation of Lemongrass Oil

Experiment	Solvent	Volume of Solvent (ml)	Weight of Lemongrass Oil (gm)	Remarks	%
1	Hexane	3000	5.22	Hydrocarbons	7
2	98% hexane + 2% isopropanol	500	6.01	Geranylacetate and carbonyl compounds other than citral	8
3	95% hexane + 5% isopropanol	1400	54.03	Citral	72
4	75% hexane + 25% isopropanol	500	8.98	Alcohols	12
Total		6400	74.24		99

Procedure

Column height = 125 cm
Column diameter (ID) = 5 cm
Column absorbant height = 100 cm
Height of solvent head = 16 cm
Rate of elution = 12 ml/min
Time required = 8 hrs

Amount of lemongrass oil used = 75.00 gm

Method of Analysis - TLC and GLC