Studies on the Essential Oils of Cymbopogon martini, var. Motia and var. Sofia

Genesis of the investigation

Gingergrass and palmarosa oils are obtained by the hydrodistillation of two varieties of Cymbopogon martini — sofia and matia which are morphologically indistinguishable. At many places, they grow contiguously and get mixed up during collection for distillation. Palmarosa oil is in great demand because of its high geraniol content, but is often contaminated with gingergrass oil due to intended or accidental adulteration.

In Andhra Pradesh, both these varieties are abundantly available. The geraniol content of the palmarosa oil obtained from these areas is, however, relatively low (50-80 per cent); the commercially acceptable oils are required to contain 90 to 95 per cent of geraniol. The lower geraniol content of the palmarosa oil may either be due to its admixture with gingergrass oil which has a much lower alcohol content or because of the hybridisation of the motia variety of grass. While investigating some geraniol-containing oils, the present author came across a sample of gingergrass oil which had no geraniol (reported geraniol content for gingergrass oil, 36-75 per cent). Oils from other authentic sources also showed absence of geraniol.

A study of available literature revealed that the results obtained by different workers on the chemical composition of the gingergrass oil show considerable divergence. It seemed likely that these studies were carried out on impure samples of
the oil. A critical examination of pure gingergrass oil was, therefore, thought necessary.

Palmarosa oil distilled in Andhra Pradesh is of low quality. The distillers, therefore, raise the geraniol content to the desired 90-95 per cent by a subsequent distillation, usually fractional hydrodistillation. This, however, impairs the floral quality of the oil. It was, therefore, considered advantageous to study the deterpenation of low-grade palmarosa oils by an improved technique. Hydrotropic extraction which has been employed to produce geraniol-rich oils has been applied to the field of essential oils for the first time.

Since the palmarosa oil is often found adulterated with gingergrass oil and also because the need of authenticity of the two oils required for the present studies, it was necessary to find methods to assess the purity of the two oils as also to enable the detection of admixture of one oil in the other.

The present investigations were, therefore, divided into three parts.

1. Chemical examination of gingergrass oil;

2. Deterpenation of palmarosa oil by hydrotropic extraction; and


1. **Chemical examination of gingergrass oil**

The gingergrass oil used for this study was distilled from grass growing at Bhongir, a place about thirty miles from Hyderabad. The collection of the grass and the distillation of the oil were conducted under the personal supervision of the author.
For the isolation and identification of the constituents, techniques like fractional distillation, paper, thin-layer, column and gas-liquid chromatography and ultraviolet and infrared spectroscopy were employed.

Free acids in the oil were first extracted and were found to be acetic, n-caproic and levulinic acids (total acids, 0.1 per cent). Phenols (0.8 per cent) were resolved in ten spots on a paper chromatogram.

The main portion of the oil consisted of hydrocarbons, alcohols and carbonyl compounds. (-)-Limonene (I) was shown to be the only hydrocarbon constituent. (+)-α-Phellandrene, reported by earlier workers to be present in gingergrass oil was not detected.

Three alcohols were identified. These are i) (-)-cis-p-Mentha-1,8-dien-3-ol (Isopiperitenol) (II), ii) (-)-cis-p-Mentha-1(7),8-dien-2-ol (Isoperillyl alcohol*) (III), and iii) (+)-Perillyl alcohol (IV).

* In consultation with Dr. Naves, alcohol III has been given the trivial name of isoperillyl alcohol.
Geraniol, which was considered to be the main constituent of gingergrass oil by previous workers, was found to be completely absent.

The isolation of alcohols II and III, which have been isolated for the first time and for which the structures have been established was of particular interest and they were studied in detail.

Among the carbonyl constituents, (+)-carvone (V) was identified. An aldehyde was also present in trace quantities, but it could not be identified. The analysis of its 2,4-dinitrophenylhydrazone showed it to have a molecular formula of C_{10}H_{16}O.

While this work was in progress, Naves and Grampoloff published results of the chemical examination of two essential oils, viz. Cymbopogon densiflorus and Cymbopogon martini, var. sofia. The oil from Cymbopogon densiflorus was studied in detail and besides (-)-perillyl alcohol, the presence of three new alcohols, namely, (+)-cis- and trans-p-mentha-2,8-dien-1-ols and (+)-cis-p-mentha-1(7),8-dien-2-ol, is reported. The presence of these constituents in gingergrass oil was shown by the comparison of gas-liquid chromatographic and fractional distillation data. The alcohols, cis- and trans-p-mentha-2,8-dien-1-ols were not found by the present author.

Naves and Grampoloff have postulated that gingergrass oil contains only (-)-perillyl alcohol and the (+)-enantiomer reported by earlier authors is the result of the allylic isomerisation of (+)-cis-p-mentha-1(7),8-dien-2-ol (III) during the decomposition of geraniol by formic acid treatment to isolate perillyl alcohol (IV). It is interesting to note that in the present studies, the perillyl alcohol (IV) has been obtained in the
dextrorotatory form. Since there was no geraniol in the
gingergrass oil, heating with formic acid to eliminate it was
not carried out. Also, the cis-\(\pi\)-mentha-1(7),8-dien-2-ol (III)
has been obtained as the (-)-enantiomer and its isomerisation
by any other means is not likely to lead to (+)-perillyl
alcohol. It is, therefore, concluded that (+)-perillyl alcohol
(IV) does occur in gingergrass oil as an independent constituent.

cis-\(\pi\)-Mentha-1,8-dien-3-ol (II) is believed to be isolated
for the first time from a natural source. The identification is
based on its hydrogenation to neoisomenthol and oxidation to
isopiperitenone (probably mixed with piperitenone).

The cis-\(\pi\)-mentha-1(7),8-dien-2-ol (III) has also been
obtained for the first time. The alcohol gave carvomenthol on
hydrogenation. Its oxidation by Beckmann mixture gave perill-
aldehyde among its reaction products, and its infrared spectrum
and the results of ozonolysis indicated the presence of two
end methylene groups.

Naves and Grampoloff\(^5\) have isolated the (+)-enantiomer
of III and on its catalytic hydrogenation have obtained iso-
carvomenthol. In the present studies, carvomenthol has been
obtained as the major product of the catalytic hydrogenation.

The present author has purified the alcohol III from its
crystalline 3,5-dinitrobenzoate and recorded its physical charac-
teristics, which are different from those reported by Naves and
Grampoloff\(^5\). The melting points of the 3,5-dinitrobenzoates of
the two samples are also different. It appears that Naves and
Grampoloff\(^5\) isolated the trans isomer, which they designated
as cis. This contention has recently been supported\(^7,8\).
2. Deterpenation of palmarosa oil by hydrotropic extraction

Palmarosa oils of 90-95 per cent geraniol content are commercially important for the isolation of geraniol and their use in perfumes. A very large quantity of the palmarosa oil is produced by Andhra Pradesh which, however, is of a low geraniol content (50-75 per cent). The acceptability of the higher geraniol content oils, as also the general advantages of the terpeneless essential oils, make the deterpenation of this oil profitable. The common methods of deterpenation, viz., fractionation, steam distillation, solvent extraction and chromatographic separation suffer from one drawback or the other. In commercial practice, fractional hydrodistillation is carried out.

The present studies describe a new method for the deterpenation of the essential oils based on the principle of hydrotropy. Hydrotropy is the phenomenon in which certain organic acid salts are known to increase the solubility of the water-insoluble compounds in their aqueous solutions. It is also known that the polar compounds have a preferential solubility in such solutions.

A number of hydrotropic salts have been used to extract the geraniol and other oxygenated constituents from the low-grade palmarosa oils. Optimum conditions have been worked out and a number of general conclusions drawn. Sodium salicylate has been found to give the best results. These results have been compared with steam distillation, which is the common process for the deterpenation of this oil. The extracted oil can be quantitatively recovered by dilution of the hydrotropic solution. No heat treatment is thus involved, and the floral quality is retained by the oil. The technique of hydrotropic extraction for deterpenation
of palmarosa oils is therefore superior to the existing methods.

3. **Distinguishing tests for palmarosa and gingergrass oils**

Palmarosa oil, obtained from *Cymbopogon martini* var. motia has a considerable demand in the perfumery industry on account of its geraniol content. Its adulteration with gingergrass oil is common in the trade. The evaluation of the palmarosa oil is primarily carried out by the determination of its alcohol content (acetyl value). The presence of gingergrass oil which also has a substantial quantity of alcohols (other than geraniol) often remains undetected. Studies were, therefore, undertaken to develop methods, both chemical and physical, to detect the presence of one oil in the other. These tests were also utilised in checking the purity of the palmarosa and used gingergrass oils in the present studies. Three reagents have been developed, which give specific colours with the two oils. By their use, not only the palmarosa and gingergrass oils are distinguished from one another, but also an adulteration of one in the other can be detected. Thus, the presence of as low as 0.25 per cent gingergrass oil in palmarosa oil could be easily detected.

The above work has been extended and the specific constituents responsible for these colour differentiation have been found out.

The chemical tests are now being studied by different laboratories under the aegis of Indian Standards Institution on synthetic mixtures of palmarosa and gingergrass oils to incorporate these in their specifications for the two oils.
Gas-liquid chromatography and infrared spectroscopy were found to give information as regards the purity of the two oils. Since the two oils differ in their chemical composition\textsuperscript{3,5} and the separation of their constituents could be achieved by gas-liquid chromatography, this technique could be used to detect even the slightest adulteration of one oil in the other.

In infrared spectroscopy, the intensity of the band at about 890 cm\textsuperscript{-1} in gingergrass oil was found to be about three times that of palmarosa oil. Other characteristic bands were also found to be of use in distinguishing one oil from the other.

The physical methods are, however, being further studied for a quantitative estimation of the adulteration.
8. S. Schroeter, *Personal communication.*
11. W.R. Littlejohn, *Flavours,* 3, 7 (1940)