PART I

INTRODUCTION
HISTORICAL:

"The rose looks fair, but fairer we it deem for that sweet odour, which doth in it live......, of their sweet deaths are sweetest odours made."

William Shakespear.

Throughout the mist of ages and the span of time, the fragrance impulse has always influenced human beings. What timeless thoughts, what emotions are contained in a purposed scent? For the fragrance impulse persuades like a soundless language, speaks powerfully to our senses and moves us to action. How often the fragrance impulse, alone, tells which soap, which lotion, which spray, our reaching hand should choose. Yet to create the fragrance impulse is an art. Beauty of fragrance is elusive, indefinable, yet vital to the success of a perfume or cosmetic. It takes imagination to conceive a beautiful, original fragrance, skill and knowledge to give it exactly the right distinction and character.

Fragrant flowers and plants have attracted the attention of man from times immemorial and have focussed his mind towards the colouring of the flowers and the vegetation around him. The utilisation of plants for his food and clothing must have been the result of the desire aroused in him to know something about his surroundings. The beauty combined with fragrance and perfume in plant life has always enchanted him and has excited admiration to a point of worship. The art of perfuming, thus, seems to be coincidental with religious ceremonies and the use of incense, and
The application of X-ray diffraction methods to essential oil chemistry is very limited. The work so far reported on essential oil constituents has been confined to the determination of atomic structure. Recently, the structural problem of some of the essential oil constituents has been solved directly by the application of the above method.

Nuclear magnetic resonance spectroscopy is, at present, another powerful tool for investigating chemical problems. The widest application of this technique is in the field of structure determinations and particularly, in the terpenoid chemistry. The N.M.R. work on essential oils includes the detection and identification of double bonds, the determination of the number of rings and the analysis of the mixtures of terpenes.

The introduction of chromatography (including gas chromatography) has enriched the physical methods available and has surpassed the conventional method of distillation. The difficulties encountered in the distillation method, due to polymerisation and other factors, has made the essential oil chemist in the modern times to rely more on chromatographic technique. The technique has become more popular in recent years due to its innumerable applications in other fields of chemistry also. Separation of essential oil constituents by column chromatography, is now considered to be a standard procedure. The method has been found to be very successful for the preparation of terpeneless oil. The other chromatographic techniques in use are partition chromatography, paper chromatography, and
vapour phase chromatography\textsuperscript{75}. Thin layer chromatography, in recent years, has also been considered as a highly useful method in organic, biological and terpene chemistry\textsuperscript{76}.

Heyrovsky in 1921, introduced a new technique of polarography which has until now gained tremendous importance in the field of chemistry. It has a number of applications in the field of terpene chemistry also and has been utilised for the evaluation of many reducible compounds by Schwabe and his co-workers\textsuperscript{77,78}. Citral and cinnamaldehyde have been successfully estimated in lemon and cinnamon bark oil respectively by this technique.

Colorimetric analysis, which is only a special case of photometric chemical analysis, and has proved to be of great importance in the field of chemistry, has not been properly utilised in the field of terpene chemistry. But though, it has a vast qualitative significance due to a number of specific colour reactions available, its use for the quantitative analysis is limited. Some of the other physical methods available are viscosity and surface tension which do not seem to have been utilised so far in terpene chemistry and offer a good field of investigation in this sphere.

**PROBLEM TAKEN AND WORK DONE**

The complex nature of an essential oil and the multiplicity of components present in it has made it a difficult task to analyse and estimate the oil quantitatively. The analytical figures obtained, seldom represent actual percentages of single
constituents. The estimation for example of eugenol in clove oil or citral in lemon oil, as a single component is not possible by chemical methods which give us an idea of the total phenolic and aldehydic content respectively of the mentioned oils. This difficulty has been solved by the use of physical methods, which in fact have revolutionised the whole domain of essential oil chemistry and have placed it on a firm footing. The physical methods have made it possible to carry out the analysis with speed and accuracy. These methods have not, so far, been utilized for the quantitative estimation of the constituents present in essential oils but have been used only for the identification and determination of structure of individual compounds. The present investigation has, therefore, been undertaken in order to apply some of the physical methods for the quantitative estimation of the constituents present in essential oils and also to see whether they could prove as a substitute for the age old less accurate chemical methods, the former having an added advantage over the latter of using smaller quantities of the oil.

The physical methods tried in this connection are (i) chromatography, (ii) colorimetry, (iii) ultraviolet absorption spectroscopy, (iv) polarography, (v) viscosity and surface tension, and a summary of the work done is given below:

(i) **Chromatography**:

The chromatographic technique has proved very successful in the field of essential oils, since it affords a satisfactory separation of the constituents without causing any polymerisation or change of structure. The method has, therefore, been applied
to some artificial mixtures of terpenes and later to some essential oils. A mixture of silica gel and kieselguhr or alumina has been used as the adsorbent and petroleum ether (60° - 80°), followed by benzene, ethyl acetate, ether and alcohol have been used as the eluants. The essential oils investigated are those of (a) caraway, (b) lemongrass, (c) citronella, (d) dillseed, and (e) patchouly.

(ii) Colorimetry:

Although a number of colour reactions are known for the qualitative analysis of the constituents of essential oils, their quantitative estimations do not seem to have been studied by the method so far. The present approach has, therefore, been made to estimate quantitatively some of the constituents present in essential oils, directly by the colorimetric method. The quantitative estimation of lemonene, eugenol, citral, geraniol, and cineole have thus been attempted in certain essential oils. The results obtained are quite encouraging.

(iii) Ultraviolet absorption spectroscopy:

The ultraviolet absorption spectroscopy coupled with a number of physical characteristics, have provided methods for the structural investigations of an unknown terpene. It has, however, not been utilized much for the qualitative and quantitative estimations of the terpenic compounds. An attempt has, therefore, been made to estimate quantitatively some terpenes by spectrophotometry. As for example the percentages of citral in the essential oil of
lemongrass and lemon have been estimated by observing the absorption maxima. The results obtained are in close agreement with the chemical values. Similarly the percentages of eugenol in cinnamon leaf oil, anethole in anise oil have been estimated fairly accurately. Spectrophotometry has also been used with the help of the method of Fearn for the correct estimation of mixtures of known composition of two terpenes e.g., citral and anethole; eugenol and anethole; and eugenol acetate and pulegone; eugenol and methyl anthranilate.

(iv) Polarography:

Polarography has proved quite useful in a number of fields in organic chemistry, and terpenes are no exception. The scope of the technique has, however, been limited so far. The present investigation has been carried out to widen the field with the collection of more data. Thus some aromatic aldehydes and ketones and their 2:4-dinitrophenylhydrazones and nitrosoclorides of hydrocarbons and alcohols have been studied and the polarograms of these compounds recorded. The half wave potentials of the above mentioned compounds have been determined at different pH values using different buffer solutions. In all the cases the number of electrons involved in each state of reduction have been calculated and found to fit in reasonably with the expected mode of reduction, for example the 2:4-dinitrophenylhydrazones of aldehydes and ketones give two irreversible reduction steps, pointing to the reduction of nitro-groups.

(v) Viscosity and surface tension:

In the first instance, viscosity and surface tension of a number of essential oils have been determined. Secondly, the
viscosity and surface tension of a number of terpenes have been found out and the property used for their quantitative estimations in solutions of known composition consisting either of individual terpenes or mixtures of two. The value of some of the constants, like 'm', the viscosity - density constant and I/P (where I is the viscosity constitutional constant and P is the parachor) have been determined and seems to be characteristic of the terpenes studied. Further, it has been observed that, whereas in the case of aliphatic alcohols, the viscosities are higher than those of their acetates, the aromatic aldehydes have viscosities lower than their acetates.

**Importance of the present work:**

Due to the multiplicity of components present in essential oils, it has become of primary importance to evaluate them before they are put to any use. So far the chemical methods were the only tools in the hands of essential oil chemist for the identification and structural investigation of the components. This procedure, however, required large quantities of the oil for analysis and sometimes even gave misleading results due to changes in the structure, polymerisation or molecular rearrangement of the components present consequent upon the chemical manipulation and thus seldom represented the actual percentages of single constituents present. The important factor in the analysis of an essential oil is to judge its quality. The odour or flavour which is always
present in it, plays an important role in the day to day life of an essential oil dealer. He is always craving for improving the odour or flavour of his oil so that it is acceptable to the public. These essential oils contain some major components which are responsible for their odour or flavour and sometimes the beauty of its odour is also due to some traces of substances present and here it is important to know the amount of this constituent present correctly so as to compare it with the standards laid down for the particular oil and eliminate any chances of adulteration, the possibility of which is always there. It is this gross adulteration that has polluted the perfume industry in particular and the development of the country in general and has been responsible for the downfall of this industry in which India had a flourishing trade for many centuries. During the last few years the Indian perfume industry has, to some extent, regained its old position. The credit of this achievement goes to the Indian Standard Institution which has successfully checked this gross adulteration by laying down some of the standards for the various indigenous essential oils. The following table shows the present position of India's import and export trade in the field of essential oils.
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A glance at the above table shows that as yet the trade in essential oils is not commensurate with the natural resources of the country. Hence there is a need for proper standardisation of the natural resources as well as the essential oils produced from them. It is hoped that the physical methods used by the present author would help in quick identification and estimation of the important constituents of the existing essential oils in the country, as well as those that may be produced in future. This would thus lead to a better market abroad for Indian essential oils and thus a source of national wealth. It would also give an impetus to the research workers in the country and abroad by providing useful data for the identification of the investigated terpenic constituents when present in hitherto unworked essential oils and thus facilitate research work in this field.
REFERENCES

2. Sadgopal, Indian oil and soap J., 1959, 25, No. 1, p. 3; Perfumery Essential Oil Record, 1927, 18, 285.
37. de-Mayo, Loc. Cit.
38. Surve, Chakravarti & Bhattacharya, Perfumery Essential Oil Record, 1958, 49, 724.
57. Robertson & Todd, Chem. & Ind., 1953, 437.
58. Moffet and Rogers, Chem. & Ind., 1953, 916.
71. N.M.R. at work, No. 60, Varian Associate, Palo Alto, Calif.
74. Lederer & Lederer, ibid.