INCREASING THE GERANIOL CONTENT OF PALMAROSA OIL BY CHEMICAL METHODS

by

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DECLARATION

I hereby declare that this thesis entitled **Increasing geraniol content of palmarosa oil by chemical methods** is a *bona fide* record of research work done by me during the course of research and that the thesis has not previously formed the basis for the award to me of any degree diploma associateship fellowship or other similar title of any other University or Society

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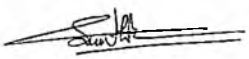

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INTRODUCTION

INTRODUCTION

India is gifted with an abundant wealth of aromatic plants The vast geographical area and varied agroclimatic conditions make it the home of a variety of aromatic and essential oil bearing crops Commercial cultivation of aromatic crops was established in the country from time immemorial It is but natural that India is one of the major producers and exporters of essential oils in the world

Among tropical essential oil crops palmarosa [*Cymbopogon martinii* (Stampf) var *motia*] occupies a foremost position This gramineaceous plant is commonly known as Rosha grass or Russa grass It is an aromatic perennial grass seen distributed in the warm humid regions of the tropics In India the crop can be grown in almost all states in the peninsular region Commercial cultivation of palmarosa prevails in the states of Madhya Pradesh Maharashtra Andhra Pradesh Karnataka Tamilnadu and Kerala The essential oil is extracted from the whole plant by steam distillation The crop yields around 70 kg essential oil per hectare annually The production of palmarosa oil in the country is estimated at 60 70 tonnes/year and the export of oil during 1994 95 was to the tune of 5 4 tonnes (Patil 1996)

Palmarosa oil finds extensive use in flavouring cosmetics and toiletry Because of its sweet rosaceous odour it is greatly demanded in perfumery Being stable to alkali it is particularly useful in blending soaps It is also used for flavouring chewing tobacco

The principal constituent of palmarosa oil is the terpene alcohol geraniol ($C_{10}H_{18}O$) It is present in the oil to the extent of 75 82% The perfumery and flavour value of the oil is attributed to this compound Separation of geraniol from palmarosa oil is the first step in its industrial utilisation Besides being a high grade perfume geraniol is the starting material for a number of synthetic aroma chemicals

Since palmarosa oil is valued for geraniol its quality is determined primarily by the geraniol content Next to geraniol the most abundant chemical component of the oil is geranyl acetate The content of geranyl acetate in palmarosa oil is highly variable Generally it ranges from 2 to 12% However there are oils which contain up to 25% of

this compound In the plant geranyl acetate is derived from geraniol by acetylation (Farooqi *et al* 1995) Probably due to this reason a reciprocal relationship exists between the geraniol and geranyl acetate content of palmarosa oil

Even today palmarosa oil produced in India is largely extracted from the wild growth in different states These natural types possess the advantages of high adaptability robust growth resistance to biotic and abiotic stress factors and fairly high oil yield But the oil from these types is inferior in terms of geraniol percentage However they contain a commensurately high level of geranyl acetate since geraniol and geranyl acetate are mutually exclusive in the plant

Several factors like the genotype season stage of harvest method of oil extraction etc influence the ratio of geraniol to geranyl acetate in the oil Although improved varieties of this crop are available which can yield more oil with high geraniol content factors like season stage of harvest and oil extraction procedure are very much critical in realising high geraniol percentage A careful regulation of these parameters is not practical under farming situations Obviously it is difficult to assure high geraniol content of palmarosa oil produced in bulk

Due to the reasons stated above at most times the geraniol content of palmarosa oil produced by cultivators fall short of requirements of the user industry According to ISI specifications palmarosa oil must contain a minimum of 90% of total alcohols calculated as geraniol Usually the traders blend such oils with high grade geraniol to tone up the geraniol content to the prescribed level The concomitantly high level of geranyl acetate in oils with low level of geraniol offers great scope for increasing the geraniol content of such oils by the conversion of the ester to alcohol The conversion is possible by the hydrolysis of the ester using a suitable chemical process The availability of an inexpensive and efficient method of hydrolysis will facilitate the farmer to undertake an on farm quality upgradation of his product which will fetch him better price

Alkalis are often used for the hydrolysis of carboxylic esters Being an ester of acetic acid and geraniol geranyl acetate can be hydrolysed with alkalis in alcoholic or aqueous medium Palmarosa is a mixture of several terpenoids which are combinedly responsible for its perfumery note Hence the conditions of the reaction will have to be

carefully chosen to ensure select vity of the reaction and quality of the product Ideally the process should satisfy the following requirements

a) The process should effect complete hydrolysis of geranyl esters present in the oil in the shortest t me under the m ldest cond t ons

b) The react on should be select ve to esters so that other chemical const tuents of the o l are not reacted upon

c) The process should have a h gh product recovery

d) It should be cheap simple and easy to perform

e) The t me and energy requ rements of the process should be low

f) The product should conform to the quality specifications and possess the perfumery characteristics of palmarosa oil

A ser es of exper ments were conducted with the following object ves

1 Standardisation of react on conditions for the hydrolysis of geranyl acetate in palmarosa oil using alcoholic alkali

2 Standard sation of react on cond tions for the hydrolysis of geranyl acetate n palmarosa oil using aqueous alkali

3 Selection of the best method for the convers on of geranyl acetate in palmarosa oil to geraniol

4 Verificat on of the effic ency of the selected method on different aromatic oils

5 Testing of the selected method on pilot plant scale

REVIEW OF LITERATURE

REVIEW OF LITERATURE

Centur es before the b rth of Chr st the techn cal basis for the production of essent al o l was well establ shed n Pers a Ind a Egypt and other parts of Orient In very olden days tself essent al oil yielding plants were cultivated extens vely in several parts of the world Palmarosa *Cymbopogon martini* Stapf var *motia* is one of the important essent al oil crops Th s grass is of perennial nature and is widely distributed in the tropics It was reported to grow in many parts of Indian subcontinent lying between the Ganges to the front er of Afghan stan It comes up well n agro cl matic conditions existing in Kerala and other south Indian sta es

Palmarosa grass is believed to be the native of the forests of Madhya Pradesh Assam and Maharastra where it s known to grow n the w ld (S ngh 1977) Many cult vars have been selected from the natural hab tat It is a hardy plant which can grow in vary ng alt tudes and s generally found n the slopes of mounta ns and in well drained soils However oil content and qual ty are very much nfluenced by the cl mate and the alt tude at which it is grown

Research efforts n the last few decades have been a med at evolv ng h gh o l y elding varieties developing agronomic practices for its cultivation improving techniques of oil d st llation and divers fying the utilisation of the product Little work has been done on mprovement of qual ty of the o l Qual ty of palmarosa o l s dec ded ma nly by the content of the terpene alcohol geran ol $C_{10}H_{18}O$ Several factors are known to influence the geran ol content of palmarosa o l

Recent l terature related to the cult vat on and ut l sat on of palmarosa w th spec al emphasis on quality of essential oil is briefly reviewed in this chapter

1 Biochemistry of essential oil synthesis

The biosynthesis of monoterpene appears to be based on the pattern of biosynthesis hypothetically rationalised on the basis of known chemical structures and reactions well before any systematic biochemical studies were available (Ruzicka 1953)

The latest findings on biosynthesis of monoterpenes have been excellently reviewed by Akhila and Ngam (1983) wherein it was pointed out that some of the work on monoterpene biosynthesis were invalidated by faulty experimental techniques as radio chemically impure biosynthetic products were used Over the last hundred years soprene has been identified as the product of thermal decomposition of natural terpenoid compounds of low molecular weight

According to Ruzicka (1953) majority of monoterpenes are formed by the head to tail linkages of soprene units and this idea was encapsulated in what is called as the isoprene rule The proposed pathways of Ruzicka has been confirmed by later work The actual reactants may be pyrophosphate esters glycosides or protein bounded species Linear combination of soprene units occurs to give geraniol isopentenyl pyrophosphate (IPP) geranyl pyrophosphate (GPP) etc which are involved in the synthesis of monoterpenes Synthesis studies have been carried out with labelled precursors and the monoterpene products have been degraded to elucidate the position of the label The results of such studies confirmed the broad correctness of Ruzicka s hypothesis

2 Essential oil biosynthesis in *Cymbopogon spp*

According to Pridham (1967) certain compounds like sugars and amino acids are translocated to the secretary cells which produce the monoterpenes He postulated that amino acids like alanine valine etc are probable precursors of monoterpene biosynthesis in plants It has also been claimed that the precursor of essential oils could be obtained through degradation of carbohydrates and proteins

Ghosh and Chatterjee (1976) reported that the essential oil content of *Cymbopogon flexuosus* and *Cymbopogon martinii* were most pronounced during the reproductive stage of development which declined thereafter Total nitrogen and protein nitrogen contents

increased apprec ably dur ng pre reproductive stage of both species and this trend cont nued dur ng the post reproduct ve stage also On the contrary total nitrogen and protein nitrogen decreased during the reproductive stage whereas soluble n trogen ncreased apprec ably dur ng this per od n both spec es Dur ng the reproduct ve stage decompos t on of prote n may occur and decomposed products may serve as substrate for essent al o l format on Decrease in total nitrogen and protein n trogen can be just f ed by an ncrease in soluble nitrogen during this period However during the pre reproductive stage a greater demand of total and protein n trogen for enhanced growth rate may result in a comparatively lesser degree of essential oil synthes s During the post reproduct ve stage as senescence approaches the nutr ents are mobilised to develop ng fru ts wh ch are l kely to d sturb the relationsh p between the decrease in total nitrogen and prote n n trogen and increase n essential o l contents

The stud es on the format on of isothujone geran ol and nerol in *Tanacetum vulgare* by Banthorpe *et al* (1978a b) have shown that GPP is first converted to neryl pyrophosphate (NPP) and subsequently to cyclic terpenes The interconvers on of geraniol and nerol via redox process involving dephosphorylat on and ster ospec fic ox dat on to the correspond ng aldehydes also has been reported

Bas c enzymat c processes in the b osynthesis of monoterpenes n palmarosa have been eluc dated by Thakur and Akh la (1993) and Farooqi *et al* (1995) Accord ng to them geran ol is synthes sed in palmarosa by dephosphor lat on of geranyl pyrophosphate and it is later acetylated to geranyl acetate

3 Physico chemical characteristics of palmarosa oil

Accord ng to Guenther (1950) the earl est research on the chem cal compos t on of palmarosa o l derived from *Cymbopogon martini* Stapf var *motia* was carr ed out by Jacobsen n the year 1871 It was he who ident f ed an alcohol $C_{10}H_{18}O$ as the ma n const tuent for which he assigned name geraniol

The presence of geran ol c tral geranyl acetate limonene farnesol citronellal methyl heptenone formaldehyde dipentene isovaleraldehyde ar d geranyl *n* caproate in palmarosa oil c ted by Guenther (1950) s attributed to d fferent workers According to h m about 3 to 15 % of geran ol present n Ind an palmarosa oil is n the form of acetic

and caproic esters He has also reported the important physical properties of geraniol as density 0 8812 optical rotation α^{D}_{20} 0 ° and refractive index n^{D}_{20} 1 4766

According to Nebney (1973) the chemical composition of Indian palmarosa oil is as follows myrcene 0 07% limonene 0 26% ocimene 0 11% methyl heptenone traces terpinene 0 35% linalool 0 59% caryophyllene 0 35% neral 0 24% geranyl acetate 6 85% geramol 88 37% and caryophyllene oxide traces

Following populansation of gas chromatography in the analysis of essential oils a number of studies have been reported on the ultimate chemical composition of palmarosa oil

Mohammed *et al* (1981) reported the results of gas chromatographic analysis of palmarosa oil conducted using Perkin Elmer Sigma 3 gas chromatograph They used a 12 feet long 1/8" i d stainless steel column packed with 6% silar 5 CP on 100 120 mesh Gaschrom Q An isothermal column temperature of 190°C was followed According to them typical palmarosa oil contained 81 7% geraniol 5 7% geranyl acetate 2 4% linalool 1% β terpineol 0 6% each of farnesene and β humulene 0 4% each of citronellol α terpineol farnesol and 0 1% each of limonene *p*-cymene methyl heptenone and 2 nonanol

Siddiqi and Garg (1990) in their chemical investigations on palmarosa oil identified fourteen constituents The main components were reported as geraniol (79 9%) geranyl acetate (9 15%) and linalool (3.6%)

Kalia *et al* (1980) in studies on the utilisation of wild growing palmarosa estimated that about 100 tonnes of herb of palmarosa is available in lower regions of Himachal Pradesh every year Composition of the oil was reported as α pinene (0 03 %) carvene (2 8%) 1 8-cineole (9 8%) carvone (29 62%) dihydrocarvone (2 31%) carveol (15 3%) caryophyllene oxide (1 65%) pnlyl alcohol (18 4%) and carveol acetate (1 2%)

Gaydou and Randnamihanosa (1987) conducted elaborate studies on the hydrocarbon fraction of palmarosa oil which represented about 5% of the weight of the oil They identified 11 monoterpenes 28 sesquiterpenes and sixteen n alkanes which accounted for 40% 50% and 1 6% of the fraction under study The major constituents

were l monene α humulene β and δ selenenes The study of the n alkanes of palmarosa revea ed the presence of all members of the homologous series C15 C30

Mohammed *et al* (1981) based on extens ve gas chromatograph c study reported the presence of trace amounts of *p* cymene nonanol l naloo c tronellol α terpenıol β humu ene and β terpenıol n palmarosa oil

In a study on terpeno ds ın essent al o ls Saxena and Maheswarı (1980) solated β caryophyllene caryophyllene epoxıde l naloo geran ol geranyl acetate geranyl n butyrate and an uncharacterised component from the hydro dıstılled oıl of palmarosa

Randr am har osa and Gaydou (1987) studıed the compos t on of palmarosa o l from Madagascar Twelve samples of essentıal oıl of palmarosa were studıed by cap llary gas chromatography The analys s us ng the comb nation of ndıces and gas chromatography mass spectrometry led to the dent f cat on of sıxty n ne components Among them n ne were determ ned for the first tıme n palmarosa oıl Statıst cal analys s showed a h gh pos t ve correlat on between some monoterpenes and a h gh negatıve correlat on between farnesyl acetate and varıous monoterpenes and between geran ol and geranıol acetate

4 Quality standards of p~lmarosa oıl

Accord ng to Ind an Standards Inst tut on (ISI 1968) Ind an palmarosa o l should comply w th the follow ng spec fıcat ons

Colour l ght yellow to yellow
Odour rosaceous w th a character stıc grassy back ground
Spec f c grav ty 0 8740 to 0 8860
Opt cal rotat on 2 ° to +3 °
Refract ve ndex 1 4690 to 1 4735
Ac d va ue max mum 3
Ester value 9 to 36 [geranyl acetate 3 1 to 12 5 %]
Ester (Sapon fıcatıon) value after acetylat on 266 to 284
Solub ıty soluble ın two volumes of 70% alcohol
Total alcohol calculated as geran ol m nımum 90%

A ıce (1982) reported that the va ues obta ned for geran ol (free alcoho) and geranyl acetate (ester content) by G L C analys s were ın conformıty w th values obtaıned by

chemical method However it was seen that GLC analysis recorded a slightly low value with regard to geraniol and geranyl acetate contents

Thappa *et al* (1982) were of the opinion that no single method for the evaluation of essential oils can be relied upon All the analytical (chemical/ spectroscopic) methods have their on advantages as well as disadvantages According to them a suitable combination of the techniques should be utilised for reproducible results

Patil and Jayappa (1986) conducted studies on palmarosa oil specification and analysis According to them palmarosa oil available in India was obtained mainly from ginger grass *Cymbopogon martini* Stapf var *sofia* Ginger grass oil being deficient in geraniol was considered inferior to palmarosa oil produced from *Cymbopogon martini* Stapf var *motia* Both the oils have different ranges for total alcohol refractive index specific gravity and optical rotation As it is difficult to distinguish a palmarosa oil admixed / adulterated with ginger grass oil based on any one analytical specification only colour reactions and TLC tests have been recommended for the detection of ginger grass oil in palmarosa oil

5 Influence of geographical and seasonal differences on quality of palmarosa oil

A few reports are available on the variation in the yield and quality of palmarosa oil from different geographical and agroclimatic regions However the reports do not specify whether the variation is due to difference in the genotypes cultivated or due to difference in environmental factors

Mohammed *et al* (1981) observed a large variation in chemical composition of palmarosa oils collected from different geographical regions in India On analysing 12 samples of oil they found that geraniol content varied from 65 to 84 9 % and geranyl acetate from 6 4 to 13 0% Some of the constituents such as limonene *p*-cymene methyl heptenone 2 nonanol farnesene β terpeniol β humulene α terpineol farnesol etc were absent in certain samples They have also reported that apart from the major constituents like geraniol limonene *p*-cymene and farnesene minor components like β terpeniol humulene α terpineol and farnesol were also of great significance in determining the real note of the Indian variety of palmarosa oil

Gupta *et al* (1981) analysed essential oil of palmarosa collected from different tracts n Madhya Pradesh and Maharastra They found that there was much variability with regard to the r geran ol and geranyl acetate contents and that the tracts having a cooler cl mate at harvest t me produced oil of superior qual ty They concluded that palmarosa y eld ng more herbage with h gher o l content of super or qual ty occurred in forest ranges where so l was comparat vely med um n texture rich in nutrients and where climate was cool at harvest time They also found that the o l from these tracts showed much variab l ty w th regard to the r phys cal and chem cal propert es The ranges obta ned n the phys co chem cal properties were specif c gravity 0 8702 to 0 9174 refractive ndex 1 4712 to 1 4787 opt cal rotat on 0 05 ° to +0 60° linalool 1 0 to 5 1 % geran ol acetate 2 0 to 24 5 % and geraniol 59 6 to 93 4%

Maheswar and Sethi (1987) also observed that in general palmarosa oil from winter harvest possessed h gher percentage of geran ol

Kal a *et al* (1980) conducted studies on the cultivat on of palmarosa grass ava lable in the w ld n lower regions of H machal Pradesh They observed that harvest ng and d st llat on done dur ng September October yielded more essent al o l of superior qual ty

Ol varo (1989) conducted elaborate stud es on the essent al oil of palmarosa in Phil ppines He recorded that palmarosa leaves yielded 1 75 % essential oil by hydrod st llation By us ng kovats index gas liquid chromatography and gas liqu d chromatography mass spectroscopy us ng BP 1 column he dent f ed the components of o l as c tronellol geran ol geranyl acetate β elemene δ cad nene c tronellyl acetate limonene sopulegol l nalool and eugenol Bes des the presence of geraniol gua ene γ murolene and β selenene were tentatively dentif ed Leaves collected from Sanbernado Bulusan Sorsogon and Ph l pp nes types gave the highest percentage of essent al o l Among the plants from one geographical or gin c tronellol (30%) geran ol (21%) and c tronellal (10%) were ma n components of the o l

6 Influence of planting density on the quality of palmarosa oil

Pareek *et al* (1983) stud ed the effect of planting density on y eld and quality of palmarosa o l They found that all the five spac ng treatments ncluded in the study produced good quality essent al o l with low amount of terpene and geranyl acetate but

higher content of free geraniol Plant densities 14 81 and 22 2 numbers per sq m gave oil yield of 152 1 and 154 2 kg per ha respectively

7 Influence of plant nutrients on the quality of palmarosa oil

A large number of reports are available on the effect of nitrogen phosphorus and potassium fertiliser application on the yield and quality of palmarosa oil

Hazarika *et al* (1978) studied the effect of 16 NPK combinations on yield and quality of palmarosa oil at Jorhat Assam The geraniol content in the different treatments varied between 66 1% and 75 4% They reported that higher geraniol containing oil (75 4 %) was obtained for the N (120) P(0) and K (40) treatment However the oil yield for the aforesaid nutrient combination was low In their study maximum oil yield with fairly high geraniol content (74 8%) was obtained for an N P K combination of 60 40 40 which was considered to be the optimum dose to get highest yield of good quality oil

Another study has been reported from Jorhat Assam by Singh *et al* (1981) in which it was observed that though N had no significant effect on geraniol content application of P & K brought about positive significant difference in geraniol over control The geraniol content with different levels of application N P & K varied from 64 1 65 0% 62 9 65 5% and 63 8 65 1% respectively

According to Muns and Mukherj (1982) the total alcohol content of oil is influenced by N & P They observed a gradual increase in total alcohol content with increasing doses of N and P Application of N & P_2O_5 at 60 kg per hectare recorded the highest geraniol content of 90 5% as against 90 3% in the control However Pareek *et al* (1981) reported that the quality of oil neither improved nor deteriorated by N P & K treatments either when applied singly or in combination According to them the specific gravity of the oil varied from 0 8643 to 0 8914 optical rotation ranged from +0 04 to +0 54^0 and acid value from 0 7 to 6 6 Variation in the contents of geraniol geranyl acetate and total alcohol calculated as geraniol were from 78 8 92 7% 4 5 14 21% and 86 5 99 9 % respectively

Chinnamma and Aiyer (1988) reported similar results from a study conducted in Kerala They found that application of different levels of N P and K fertilisers had no

significant influence on most of the physico chemical properties of palmarosa oil The quality of oil improved with increase in the interval of harvest up to 95th day or beyond

Geetha and Thomas (1993) studied the effect of soil and foliar applied micronutrients on the yield and quality of palmarosa They observed that the oil yield and geraniol content were increased by foliar spraying of 0 1% manganese sulphate

Thus it is seen from various reports that the influence of the major nutrients viz N P & K on the quality of palmarosa is not consistent

8 Influence of variety on the quality of palmarosa oil

Shahoo *et al* (1987) evaluated improved palmarosa selections RRL(B)-49 RRL(B) 65 RRL(B) 17 along with improved stains IW 312445 IW 31262 for herb yield oil yield and geraniol content The study was aimed to observe the growth performance oil yield and geraniol content of these selections and to select better biogenotypes for commercial cultivation Out of these selections three improved stains IW 31245 RRL(B) IW 3630 had been recommended for commercial cultivation

Punia (1986) conducted studies on breeding methods for the improvement of palmarosa grass Through clonal selection mutation breeding polyploidy etc they could obtain improved genotypes yielding essential with 90% geraniol

Maheswari and Sethi (1987) conducted a series of experiments on selection and improvement in palmarosa Selection from germplasm resulted in identification of the superior type IC 31245 Hybridisation of genetic stock from different regions led to development of ten cultures with high yield and increased geraniol content

Gupta *et al* (1981) conducted studies on the effect of gamma radiation during the growth period of plants on the physico chemical properties of oil They found that acid value and total alcohol content increased while geranol content decreased in the case of oil of plants subjected to somatic gamma radiation

Srivastava and Thyagi (1986) studied the oil quality of mutant progeny of palmarosa They found that herbage yield per plant and leaf area index in palmarosa increased with

gamma radiation at 5 Kr which was attributed to micro level mutation The yield and quality of the oil were enhanced significantly by 10 Kr and 15 Kr radiation treatments

9 Influence of harvesting stage and plant part on the quality of palmarosa oil

Studies on the content and quality of essential oil in different parts of palmarosa plant started very early in India

Lal (1935) reported that stalks and flowers yielded an oil of sub normal quality

Gupta and Jain (1978) observed that the oil of leaf contained higher percentage of free alcohol calculated as geraniol than flower crop and composite of leaf and flower crop According to them the oil obtained from flower contained more ester than that from the leaf

According to Karira and Beri (1966) the quality of oil obtained at flowering stage was better than that at late flowering stage Refractive index density of oil and acid value were high at flowering stage that at late flowering stage Ester value after acetylation was low during flowering stage when compared to that at the late flowering stage Also total alcohol and geraniol contents were high during flowering stage than in the late flowering stage

Virman *et al* (1967) based on studies conducted at Haldwani reported that refractive index specific gravity optical rotation and acid value of palmarosa oil decreased after sixty weeks of planting whereas saponification value of unacetylated oil ester value and free alcohol content increased within this period

Corroboratory results have been obtained by Pareek *et al* (1981) in a study conducted on the effect of growth stage on the physico chemical properties of palmarosa oil They found that geranyl acetate was higher at the commencement of flowering than other growth stages When the plants reached the late seeding stage the ester content decreased progressively and became minimum During this period the geraniol content increased progressively and reached maximum The odour of the oil at the commencement of the flowering was poor than at other stages Content of terpenes and linalool were highes n oil at the commencement of flowering which impaired the odour

Akhila *et al* (1984) conducted studies on the variation of essential oil constituents of palmarosa at different developmental stages showed that the total oil content of palmarosa reached its maximum (1 18%) towards the end blooming The oil present was maximum in flowers at full bloom stage The percentage of geraniol the most useful constituent in the oil was also maximum (81 88%) in the aerial parts at the end of blooming

Contrary to these reports Nair *et al* (1980) found that in case of the cultivated variety ODP 2 grown at AMPRS Odakkaly the ester content was high (16 3%) in oil distilled at the late flowering stage than at earlier stages and they reasoned this as a varietal character

According to Chinnamma and Aiyer (1988) the palmarosa variety ODP 2 yielded oil conforming fully to ISI specifications when the successive cuttings were spaced at more than 95 days

The essential oil extracted from different parts of palmarosa grass showed large differences in the quality parameters Alice (1982) found that oil obtained from the bottom portion of the plant recorded the lowest ester content and the highest saponification value free alcohol and total alcohol whereas the flower top contained the highest combined alcohol

10 Influence of oil extraction method on the quality of palmarosa oil

According to Guenther (1950) the ester content of Indian palmarosa is low and this was reasoned to the hydrolysis of ester taking place during the crude method of distillation employed by the farmers of the country He also reported that the oil produced in Java from grass introduced from India was different from the usual commercial oil produced in India itself Javanese oil contained a much higher ester content He attributed this to both differences in the environment under which the grasses were grown and superior and clear methods of distillation followed in Java

11 Influence of plant disease on the quality of palmarosa oil

Janardhan *et al* (1980) conducted studies on the effect of *Curvularia* leaf blotch disease on the essential oil content of palmarosa They found that healthy and infected

leaves of palmarosa conta ned 22 9% and 2 0% essential oil respectively The disease caused a reduct on of oil content by 31% and geraniol content by 11 8%

12 Utilisation of palmarosa oil

Stud es conducted by Balas and Gupta (1988) on the contr but on of 2 trans 3 7 d methyl 1 2 octadien 1 ol to the perfumery and cosmet c industry have shown that geraniol (2 trans 3 7 dimethyl 1 2 octadien 1 ol) is the main component of palmarosa oil and s used in perfumery and cosmetic industry Its various reactions like hydrogenat on condensation oxidation cycl zation ester fication etc were reported Odour character stics and utilisation of products have been reviewed They have identified about thirty n ne synthetic and semi synthetic products obtained from geraniol having appl cation in aroma industry

13 Production of geramol from palmarosa oil

Few reports are available on the methods of separation of geraniol from palmarosa

N gam *et al* (1985) undertook the hydrolysis of esters present in palmarosa oil using alcoholic alkal to increase the free geraniol content of the oil The product was subjected to fractional dist llation under vacuum to separate 98 99% pure geraniol in about 70% yield

Aggarwal *et al* (1986) attempted aqueous sodium hydroxide treatment for undertak ng ester hydrolysis By fract onal d stillation of the hydrolyt c product they could recover h gh grade geran ol of 94 to 95% purity and high perfumery value in an overall recovery of 70 72% on the bas s of palmarosa oil

The rev ew of l terature clearly brings out the fact that very little att=mpt has been made to evolve methods and procedures for increasing the content of geraniol in palmarosa o l wh ch determines the industr al util ty of the o l

MATERIALS AND METHODS

MATERIALS AND METHODS

The study was carried out at the Regional Analytical Laboratory Aromatic & Medic nal Plants Research Station Odakkaly Kerala during 1994 1996

1 Materials

1 1 Essential oils

The following essential oils which contain h gh total geraniol but do not possess the spec fied level of free geraniol were selected for the study All the plants were high essential oil yielding *Cymbopogon* types The plants were maintained at the Aromatic & Medicinal Plants Research Stat on Odakkaly and essential oil was extracted from them by steam d stillation

a ODP 1 (*Cymbopogon martinii* var *motia*) The type was a selection made at the Aromat c & Medicinal Plants Research Station Odakkaly

b ODP 3 (*Cymbopogon martinii* var *motia*) The type was collected from cultivated field at Coimbatore Tamilnadu

c OD-455 (Thathimalangatha II) The type is an unidentified species of *Cymbopogon* maintained in the germplasm at the Aromatic & Medicinal Plants Research Station Odakkaly

d C 3 (*Cymbopogon martinii* var *motia*) The type was a selection made at the Aromatic & Medicinal Plants Research Station Odakkaly

e Jamrosa The plant is an interspecific hybrid between *Cymbopogon nardus* var *confortiflorus* and *C jwarancusa* developed at the Regional Research Laboratory (CSIR) Jammu India

1 2 Chemicals

1 2 1 Standard geraniol The chemical of 98% purity was purchased from Aldrich Chemical Co Milwaukee USA

1 2 2 Standard geranyl acetate This was prepared by the acetylation of standard geraniol To 10 ml geran ol taken in a 100 ml round bottom flask was added 20 ml acet c anhydr de and 2 g sodium acetate The contents were refluxed on a water bath for 2 hours Heating was cont nued at 40 to 45°C for 15 to 20 m nutes after add ng about 50 ml distilled water The product was cooled and transferred to a 125 ml separating funnel with 50 ml brine The separating funnel was shaken vigorously for 3 to 5 minutes and the lower aqueous layer was dra ned off The o l n the separating funnel was washed with 50 ml of brine containing 2 g sodium carbonate followed by 50 ml of br ne and finally with 20 ml of water The product was dried by passing through sodium sulphate and preserved in coloured glass bottle at 4°C The identity of the product was established by chromatography and FTIR spectroscopy

1 2 3 Reagent chemicals All the reagents used n the study were prepared from analytical grade (A R) chemicals

2 Methods

2 1 Physico chemical characteristics of essential oil

2 1 1 Colour

The colour of the oil was compared w th standard colour chart and reported

2 1 2 Specific grav ty

The spec fic grav ty of the o l was expressed as the rat o of the we ght of the o l to that of an equal volume of water The spec f c grav ty of the samples was determined at 25°C using a standard specif c grav ty bottle

2 1 3 Optical rotation

Opt cal rotation of the o l s the angle in degrees through which the plane of polar sed light is turned when plane polarised sodium l ght s passed though a layer of oil 10 cm n thickness This was measured us ng a polarimeter model 22A1 (Advanced Research Instruments Co Pune India) following standard procedure

2 1 4 Refractive index

Refract ve ndex of the o l s the ratio of the sine of the angle of incidence to that of the angle refraction when a ray of light of wave length 5893°A passes from air to the o l It was measured us ng a refractometer model Focus AR 204 (Advanced Research Instruments Co Pune Ind a) us ng standard procedure

2 1 5 Solub lity in 70% alcohol

Solub lity in 70% alcohol is defined as the number of volumes of 70% ethyl alcohol requ red for the complete solub l ty of one volume of o l One ml of the oil was taken n a bo ling tube and t trated aga nst 70% ethyl alcohol from a burette shaking the contents thoroughly after each addition When a clear solution was obtained the volume of alcohol titrated was noted and reported as the solubil ty n 70% alcohol

2 1 6 Ac d value

Ac d value is defined as the number of m ll grams of potass um hydroxide required to neutralise free ac ds present in 1 g of o l It was determ ned by titrating 2 5 g of oil n presence of 15 ml of 95% alcohol against 0 1 *N* aqueous potassium hydroxide

2 1 7 Ester value

The ester value s given by the number of mill grams of potass um hydrox de requ red to sapon fy the esters present in 1 g of o l It was determined by refluxing 2 5 g of prev ously neutralised o l w th 10 cc of 0 5 *N* alcoholic sodium hydrox de for 1 hour and back t trat ng the unreacted alkali with standard acid

2 1 8 Ester value after acetylation

The essential oil was acetylated by refluxing 10 ml of the oil with 20 ml of acetic anhydr de and 2 g of sod um acetate The acetylated material was hydrolysed w th alcohol c potass um hydrox de and the we ght of potass um hydrox de requ red to neutral se the ac ds liberated in the process was calculated and expressed as ester value after acetylat on

2 1 9 Saponification value

Saponification value is defined as the number of milligrams of potassium hydroxide required to saponify esters and neutralise the acids liberated from one gram of oil It is equivalent to the ester value plus acid value

2 1 10 Free alcohol content

The percentage of free alcohol in the essential oil was calculated from the following equation

$$\text{Free alcohol (\%)} \quad \frac{(A - E) \times M}{(561 - 0.42A)}$$

where A = ester value after acetylation E = ester value of the original material and M = molecular weight of the specified alcohol viz geraniol

2 1 11 Combined alcohol content

Combined alcohol content is the content of alcohols combined as esters in the oil It is an estimate of esters present in the oil It was calculated as

$$\text{Combined alcohol (\%)} = \frac{E \times M}{561}$$

where E = ester value of the original material and M = molecular weight of the specified alcohol viz geraniol

2 1 12 Total alcohol

Percentage of total alcohol was given by the sum of the percentages of free alcohol and combined alcohol

2 1 13 Gas chromatographic analysis

Gas chromatographic analysis of oil was performed using a gas chromatograph Chemito model 8510 [Chemito Instruments (Pvt) Limited Madras India] The chromatographic conditions were as follows

Column 5% OV 225 on 80 100 mesh chromosorb W packed in 12 long stainless steel tube of 1/8 internal diameter

Detector Flame ionisation detector

Carrier gas (nitrogen) flow rate 30 ml/min

Hydrogen gas flow rate 30ml/min

Auxiliary gas (air) flow rate 100ml/min

Attenuation 4

Sample volume 1 µl

Column temperature A temperature programme as given below was followed

Initial temp (°C)	Hold time (min)	Rate of heating (°C/min)	Final temp (°C)	Hold time (min)
110	0 5	4	225	10

Detector temperature 270 °C

Injector temperature 250 °C

Peak data were integrated and analysed by a computer using Class LC10 chromatographic software (Shimadzu Corporation Kyoto Japan) Peaks were identified by coincidence of retention times with authentic standards The content of each component in the oil was estimated by the area normalisation method

2 2 Standardisation of method for the conversion of geranyl acetate to geraniol

A method for conversion of geranyl acetate in palmarosa oil to geraniol was standardised using a sample of palmarosa oil containing a high percentage of geranyl acetate (14 35%) The oil was distilled from the palmarosa type ODP 3 collected from Coimbatore Tamilnadu

2 2 1 Hydrolysis using methanolic alkali

The method involved hydrolysis of geranyl acetate in palmarosa oil with methanolic alkali solution

2 2 1 1 Treatments

The treatments comprised of combinations of the following parameters

2 2 1 1 1 Alkalis NaOH and Na_2CO_3

2 2 1 1 2 Concentration of alkali 1 0% 2 5% 5% 7 5% 10% and 15% This denotes the concentration of alkali (w/v) in the methanolic alkali reagent The calculated amount of A R grade alkali was dissolved in a very small volume of water and diluted to the required volume with methanol

2 2 1 1 3 Temperature Ambient and reflux temperatures (88°C)

2 2 1 1 4 Agitation The reaction mixture was e ther left undisturbed or stirred at 200 rpm us ng a magnetic stirrer

2 2 1 1 5 Time of reaction 0 0 5 1 0 1 5 2 0 and 2 5 h

The reaction was stopped at the end of a specified time and the product was worked up

2 2 1 2 Method

Method reported by Nigam *et al* (1985) was followed w th suitable modifications Weighed quantity of palmarosa oil (5 10 g) and the measured quantity of methanolic alkali reagent in the rat o 1 4 were taken in a 100 ml round bottom flask In exper ments conducted at reflux conditions the flask was fitted w th a water condenser and refluxed on a heat ng mantle The temperature of the reaction mixture under these cond t ons was found to be 88°C In other cases the flask was placed on a temperature controlled water bath whose temperature was monitored using a thermometer

At the close of the react on about 80% of the methanol in the reaction mixture was recovered by distillation over a water bath The left over was transferred into a separating fun nel diluted w th tw ce the volume of 10% sodium chloride solution and left undisturbed for 10 20 min for separat on of layers The upper layer which consisted of the essential oil was drawn into a previously weighed beaker and weight noted

2 2 2 Hydrolys s w th aqueous alkal

Th s involved the hydrolysis of geranyl esters present in the oil using aqueous alkal

2 2 2 1 Treatments The treatments in the experiment comprised of combinations of the following parameters

2 2 2 1 1 Alkalis NaOH and Na_2CO_3

2 2 2 1 2 Ratio of reactants 1 4 1 2 1 1 and 2 1

This denotes the ratio (w/v) of oil to the aqueous alkali reagent

2 2 2 1 3 Concentration of alkal in the aqueous alkali reagent 0% 10% 20% and 40%

This denotes the percentage (w/v) of alkali in the aqueous solution The reagent was prepared by dissolv ng the calculated amount of alkali in measured amount of distilled water

2 2 2 1 4 Temperature Ambient 60 70°C and reflux (102 105°C)

2 2 2 1 5 Time of react on 0 0 5 1 0 1 50 and 2 0 h

The experiment was stopped at the end of a specified time and product worked up

2 2 2 2 Method

The we ghed quant ty of palmarosa oil (5 10 g) and the measured quantity of aqueous alkali reagent were taken in a 100 ml round bottom flask In experiments conducted at reflux cond t ons the flask was f tted w th a water condenser and refluxed on a heating mantle The temperature of the reaction m xture under these conditions was found to be 102 105°C In other cases the flask was placed on a temperature controlled water bath

At the close of the reaction the m xture was transferred into a separating funnel and allowed to stand for 0 5 h for the layers to separate The upper layer comprising of the essential oil was removed washed 3 times with twice the volume saturated brine tw ce w th dist lled water transferred into a beaker and weighed

2 2 3 Ammonolysis

In this method geranyl ester was attempted to be hydrolysed with ammon a solut on Ammonolysis was carried out in the presence of 95% NH_4OH

2 2 3 1 Treatments

2 2 3 1 1 Stirring time 10 m n and 30 min

This is the time for which reaction m xture was stirred

2 2 3 1 2 Keeping time 24 38 & 48 h

This is the time for which the reaction mixture was kept undisturbed after stirring

2 2 3 2 Method

Palmarosa oil (10 g) was transferred into a 100 ml round bottom flask into which 50 ml of ammonium hydroxide (95% A R) was added and the contents stirred vigorously at 200 rpm using a magnetic stirrer for the specified period of time The mixture was left undisturbed for the specified length of time The mixture was transferred into a separating funnel and the upper oil layer was collected and washed 3 times with twice the volume saturated brine solution twice with distilled water transferred into a beaker and weighed

2 2 4 Quality improvement of essential oils by aqueous NaOH hydrolysis

Efficiency of the aqueous sodium hydroxide reflux method for the hydrolysis of geraniol acetate was verified using five d fferent essent al oils The essential oils were high in total geraniol but did not possess the specified level of free geraniol A sample of 100 g oil was taken in a 250 ml round bottomed flask and 100 ml of 20% aqueous solution was added The flask was attached with an air condenser and was refluxed for 0 5 h while being stirred at 200 rpm with a magnetic stirrer At the close of the period the flask was cooled and the oil and reagent layers were allowed to separate The reagent was removed and the oil was washed repeatedly with saturated brine solution to remove all the residual alkali The weight of product obta ned was recorded

2 2 5 Pilot plant scale quality improvement of oil of palmarosa var ODP 3

The aqueous sodium hydroxide reflux method was employed in pilot plant scale for the quality improvement of palmarosa oil of cultivated type ODP 3 One kg oil was taken in a three-litre round bottomed flask and 1 litre of 20% aqueous NaOH solution was added The mixture was refluxed for 0 5 h while being stirred at 200 rpm with the help of a magnetic stirrer At the close of the period the flask was cooled and the oil and reagent layers were allowed to separate The reagent was removed and the oil was washed repeatedly with saturated brine solution to remove all the residual alkali

The weight of product obtained was recorded The alkali reagent separated out was used in the subsequent batch process

2 2 6 Geraniol content The geraniol content of essential oil samples were determined by gas chromatographic analysis as described under 2 1 13 The peak of geraniol was identified by coincidence of the retention time with that in the case of standard geraniol The gravimetric percentage of geraniol in the sample was calculated by area normalisation method

2 2 7 Recovery of oil From the weight of oil initially taken for the experiment and the weight of product obtained after the reaction the percentage recovery of essential oil in the experiment was calculated as

$$\text{Recovery of oil (\%)} = \frac{\text{(Weight of oil recovered after reaction)} \times 100}{\text{Weight of oil taken for reaction}}$$

2 2 8 Yield of geraniol The process yield of geraniol is the quantity of geraniol obtained by the process expressed as percentage of the quantity of palmarosa oil taken for processing

It was calculated as

$$\text{Yield of geraniol (\%)} \quad \text{Recovery of oil (\%)} \times \frac{\text{Geraniol content (\%)}}{100}$$

2 2 9 Replications Each experiment was repeated three times and the mean vlaue was worked out

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

1 Synthesis of geranyl acetate

Geranyl acetate was prepared by the acetylation of geraniol as described n sect on 1 2 2 of chapter Materials and Methods" The product was obtained in 93% y eld The gas chromatogram of the product is shown in Fig 1 The major peak which accounted for 98 9% of the product by area normalisation was identified as geranyl acetate by coincidence chromatography The FTIR spectrum of the product is shown in Fig 2 The strong carbonyl stretch at 1741 cm the strong COO stretch at 1232 cm^{1} and weak O CH_2 stretch at 1024 cm^{1} confirmed the product as geranyl acetate It was used as a reference in gas chromatographic analysis of samples

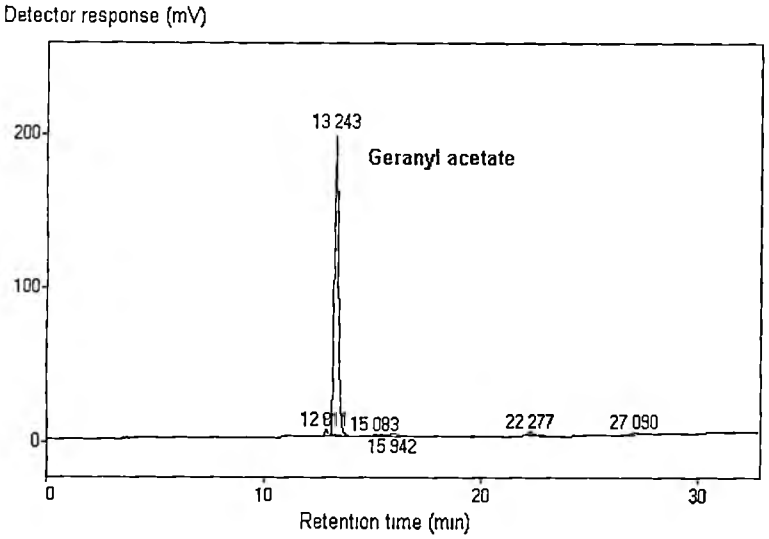

Fig 1 Gas chromatogram of geranyl acetate

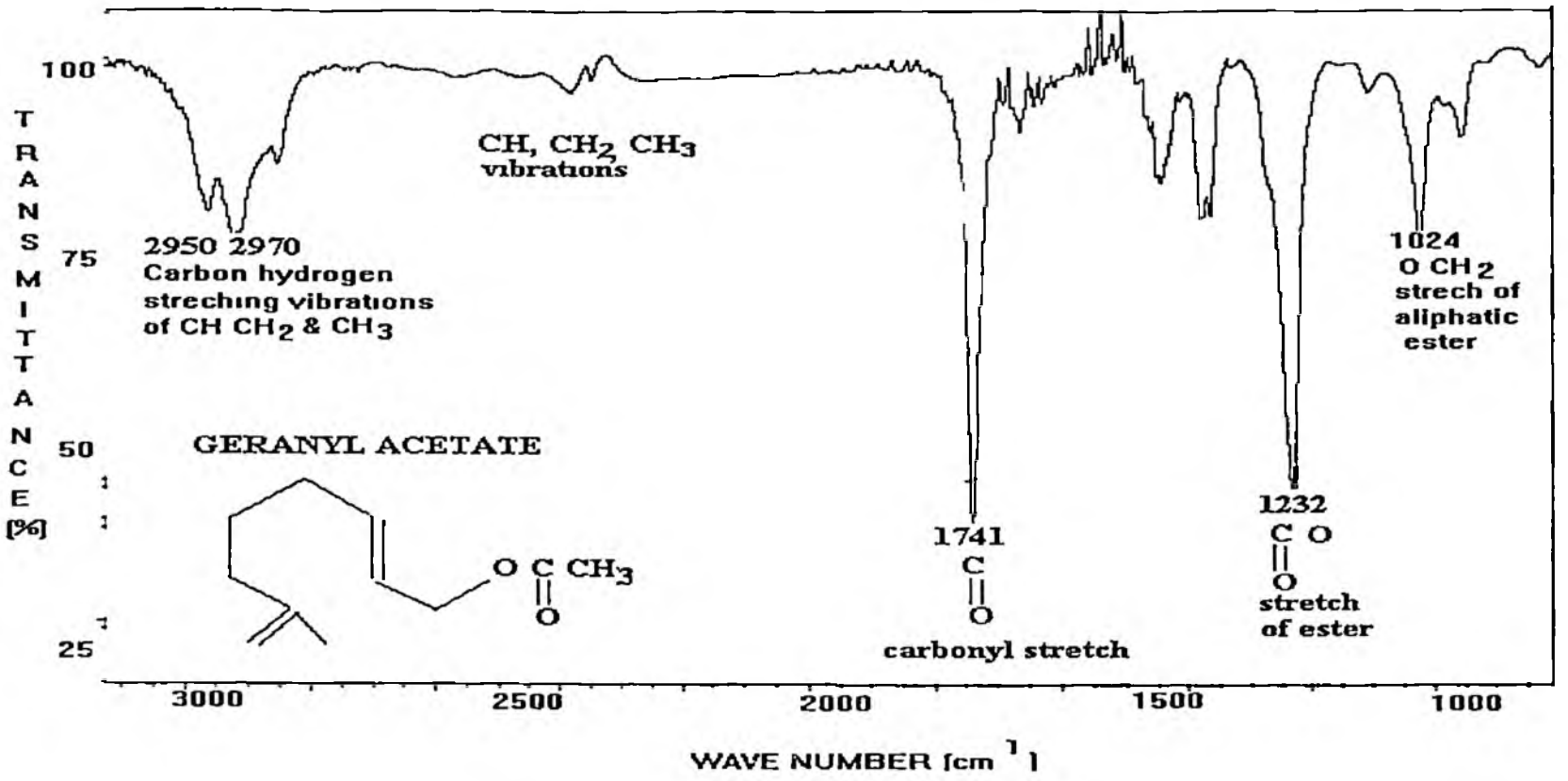

Fig 2 FTIR spectrum of geranyl acetate

2. Standardisation of method for chemical conversion of geranyl acetate in oil to geraniol

Different methods for the chemical conversion of geranyl acetate in palmarosa oil to geraniol were tried using the palmarosa oil ODP 3 as the test material The physico chemical characteristics of the oil are shown in Table 1 The gas chromatographic data are presented in Fig 3

Table 1 Physico-chemical characteristics of palmarosa oil ODP 3

Sl No	Characteristic	ODP 3	ISI specification
1	Colour	Light yellow	Light yellow to yellow
2	Specific gravity (at 30° C)	0 9903	0 8740 to 0 8860
3	Optical rotation (degrees at 30° C)	+2 0	2 to +3
4	Refractive index (at 30° C)	1 4745	1 4690 to 1 4735
5	Solubility in 70% alcohol	1 30	less than 2 00
6	Acid value	0 6003	< 3 00
7	Ester value	49 67	9 to 36
8	Ester value after acetylation	300	266 to 280
9	Saponification value	51 67	–
10	Free alcohol content as geraniol (%)	88 62	–
11	Combined alcohol content as geraniol (%)	13 63	–
12	Total alcohols as geraniol (%)	102 25	> 90 0
13	Geraniol by GC (%)	76 25	
14	Geranyl acetate by GC (%)	14 35	

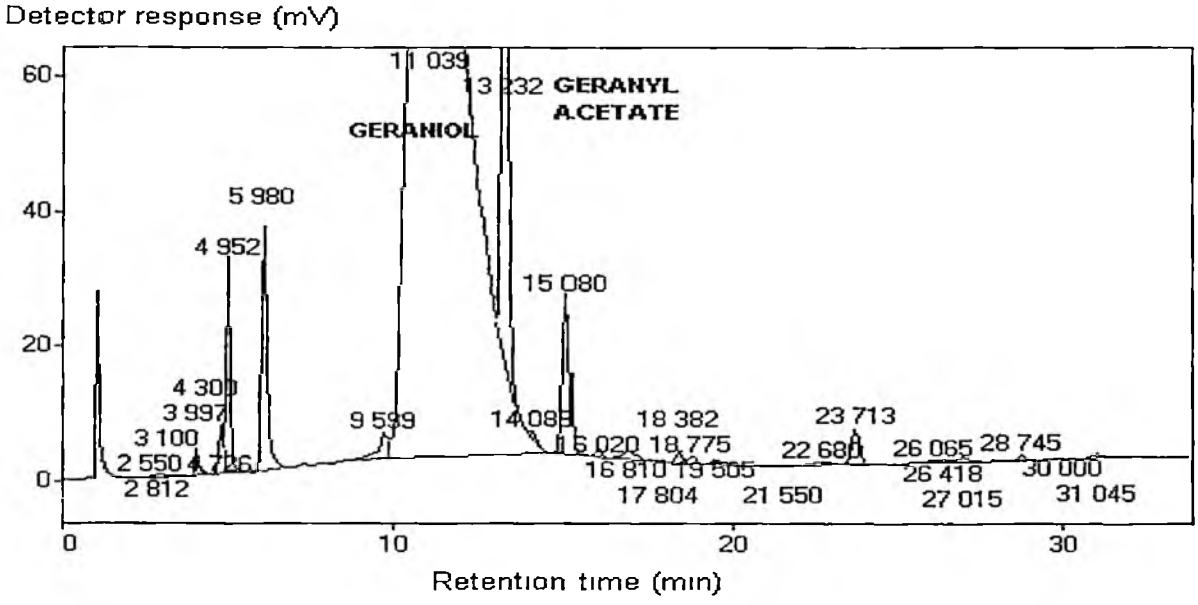

Fig 3 Gas chromatogram of palmarosa oil ODP-3

Peak Report

Peak No	T me	A ea	Concent at on (%)	Name
1	2 550	2163	0 0142	
2	2 812	7340	0 0482	
3	3 100	2185	0 0144	
4	3 997	34573	0 2271	Myrcene
5	4 300	1618	0 0106	
6	4 726	59360	0 3899	
7	4 952	262737	1 7258	L monene
8	5 980	424531	2 7885	
9	9 599	75818	0 4980	
10	11 039	11575216	76 2506	Ge an ol
11	13 232	2178410	14 3507	Ce any acetate
12	14 088	10330	0 0679	
13	15 080	319310	2 0974	
14	16 020	15286	0 1004	Ge any p op onate
15	16 810	34558	0 2270	
16	17 804	4136	0 0272	
17	18 382	24094	0 1583	Ce any butyrate
18	18 775	18879	0 1240	
19	19 505	17219	0 1131	
20	21 550	2230	0 0146	
21	22 680	23799	0 1563	
22	23 713	74800	0 4913	Ge anyl cap oate
23	26 065	6212	0 0408	
24	26 418	8292	0 0545	
25	27 015	17066	0 1121	
26	28 745	11884	0 0781	
27	30 000	3040	0 0200	

Results of gas chromatographic analysis of the oil showed that the oil contained 76 25% geraniol and 14 35% geranyl acetate Besides minor amounts of other esters (geranyl caproate 0 49% geranyl butyrate 0 16% and geranyl propionate 0 10%) were also detected Even though the total alcohol content of the oil estimated by the volumetr c method prescribed in ISI specif cations was high (102 25%) the free alcohol content was low (88 62%) with a relatively h gh content of combined alcohol (13 63%) The absolute levels of geraniol (76 25%) and geranyl acetate (14 35%) estimated by gas chromatography also demonstrated that the oil had a relatively low level of geraniol and h gh level of geranyl acetate This characteristic feature renders the oil unsuitable for industrial utilisation

The hydrolysis of geranyl acetate in the oil to geraniol was followed up by gas chromatographic analysis of the product The efficiency of conversion was assessed in terms of increase in the level of geraniol and decrease in that of geranyl acetate in the product However hydrolysis of esters of geraniol other than acetate which are present in the oil in minor amounts (propionate butyrate caproate etc) can also contribute to increase in the geraniol content of the hydrolysate Hence increase in geraniol content of the product was selected as the criterion for evaluating the efficiency of the conversion method

The treatment of geraniol with aqueous or methanolic reagents can be expected to render a portion of the oil water miscible This portion is liable to be lost during the subsequent washing of the product with water thereby resulting in decreased recovery of geraniol Hence mass recovery of oil after the reaction was also taken as a parameter for evaluating the method

The third parameter worked out to evaluate the efficiency of the conversion process was the geraniol yield The process yield of geraniol is the quantity of geraniol obtained by the process expressed as the percentage of quantity of palmarosa oil taken for processing It takes into consideration both oil recovery and geraniol content of the conversion product It was calculated as the product of oil recovery and geraniol content

3 1 Hydrolysis of geranyl acetate in palmarosa oil using methanolic sodium hydroxide

3 1 1 Effect of temperature

Palmarosa oil and 10% methanolic sodium hydroxide were taken in the ratio 1 4 and the mixture stirred at ambient conditions In another set of studies the mixture was refluxed on a water bath at 90°C while being stirred At the end of specified periods of time the samples were worked up as described in section 2 2 1 2 of chapter "Materials and Methods and recovery of oil calculated The product was subjected to gas chromatographic analysis to determine the content of geraniol and geranyl acetate The yield of geraniol in the process was expressed as percentage of the initial quantity of palmarosa oil taken for the process The results of the experiments are given in Table 2 and depicted graphically in Fig 4

In case of methanolic alkali hydrolysis at ambient temperature geraniol content of the essential oil increased abruptly from the initial value of 76 25% to 90 08% in a short period of 0 25 h The level remained almost steady even on prolonged treatment Simultaneously geranyl acetate content of the product declined sharply from the original level of 14 35% to less than 0 10% When the reaction mixture was heated at reflux the geraniol content increased steadily and reached peak value of 92 02% in a period of 0 75 h Thereafter it declined marginally From the results it is inferred that the increase in geraniol content is attributed mainly to the hydrolysis of geranyl acetate by sodium hydroxide in the methanolic medium

Table 2 Effect of temperature on the hydrolysis of geranyl acetate in palmarosa oil by alcoholic NaOH

Temp	Time (h)	Geraniol (%)	Geranyl acetate (%)	Recovery (%)	Geraniol yield (%)
Ambient	0 00	76 25	14 35	100 00	76 25
	0 25	90 08	0 10	84 60	76 21
	0 50	90 17	0 11	88 20	79 53
	0 75	90 72	0 11	87 20	79 11
	1 00	90 82	0 12	85 50	77 65
	1 50	90 97	0 10	84 60	76 96
	2 00	90 08	0 09	83 20	74 95
Reflux	0 00	76 25	14 35	100 00	76 25
	0 25	85 96	0 06	85 00	73 06
	0 50	91 98	0 01	87 50	80 48
	0 75	92 02	0 10	87 00	80 05
	1 00	90 48	0 13	88 20	79 80
	1 50	90 50	0 06	87 30	79 01
	2 00	90 63	0 00	83 40	75 59

The geraniol content reached a maximum of 90 82 to 90 97% when the reaction mixture was stirred at ambient temperature for 1 0 to 1 5 h Alternatively the peak geraniol content of 92 02% was obtained in a shorter period of 0 75 h when the mixture was heated under reflux conditions Thus it has been demonstrated that heating under reflux accelerated the methanolic alkali hydrolysis of geranyl acetate

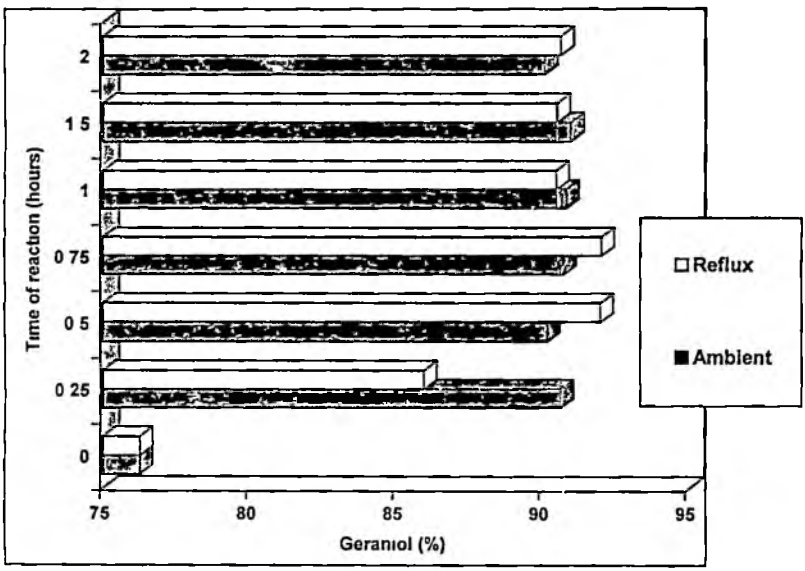

Fig 4 Effect of temperature on geraniol content

(Alcoholic NaOH method)

The effect of methanolic alkali treatment on recovery of oil is shown in Fig 5 The recovery of oil after the process n the different treatments was rather low (83 2 to 88 2%) The low recovery is attributed to loss of volat le oil in various steps of the process

The loss of oil is considered to have occurred in three ways

(a) by co dist llation of volatile components w th methanol when the mixture is refluxed

(b) by co distillation of volatile components with methanol during removal of methanol from

the product mixture by distillation and (c) as solution/suspension in water when the product is partitioned with water in the working up process

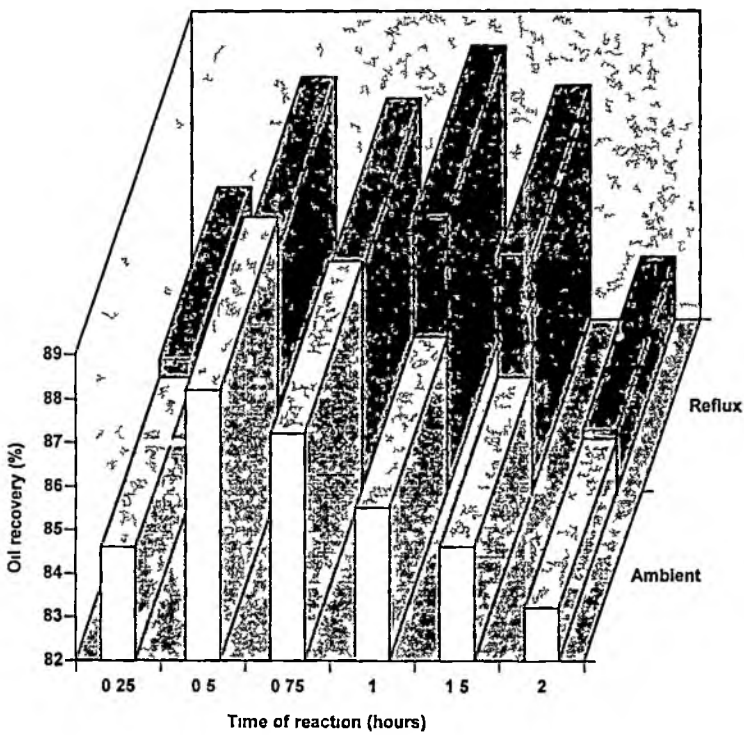

Fig 5 Effect of temperature on the recovery of oil

(Alcoholic NaOH method)

The loss by the first process was not considerable in this experiment because the recoveries in the refluxing treatment paralleled those in the non refluxing treatment On the contrary during certain periods of time the recovery values in the reflux treatment were higher than those in the non refluxing treatment

Hence the second and third processes are considered to be more important in explaining the loss of oil After the treatment period 80% of methanol was removed by distillation Some portion of the volatile oil would have been lost by co distillation with methanol Gas chromatographic analysis of the recovered methanol showed presence of volatile oil components Methanol that remained in the product was partitioned into water when the product was washed repeatedly with water Exhaustive partitioning of the wash water with hexane and gas chromatographic analysis of the hexane extract revealed the presence of palmarosa oil components The residual amount of methanol would have acted as a bridge solvent between water and oil resulting in the carrying of around 10 15% oil into water

In a similar study Nigam *et al* (1985) attempted hydrolysis of geranyl esters with alcoholic sodium hydroxide and separation of geraniol by vacuum fractional distillation They could recover only 70% of the total geraniol present in the oil in 98 99% purity which also indicated a loss of geraniol during the process However these figures cannot as such be compared with the recoveries obtained in this study as recovery of geranoil by fractional distillation was not attempted

Data on the process yield of geraniol are available in Table 2 and the results are depicted graphically in Fig 6 The process yield of geraniol is a measure of the overall efficiency of the process This in fact is determined by the geraniol content and process recovery of essential oil In this experiment geraniol yield reached maximum at 0 5 h and slowly declined thereafter The increase in geraniol yield in the first half an hour was due to the fast hydrolysis of geranyl acetate and its subsequent decline was due to decrease in oil recovery The trend was similar in both refluxed and unrefluxed treatments When the reaction was carried out at ambient temperature condition the product recorded 90 17% geraniol and the geranoil yield was 79 53% Under reflux condition the geraniol content of product was 91 98% and the geraniol yield was 80 48% Thus a marginally higher geraniol percentage and yield was obtained when the reaction mixture was refluxed at 88°C

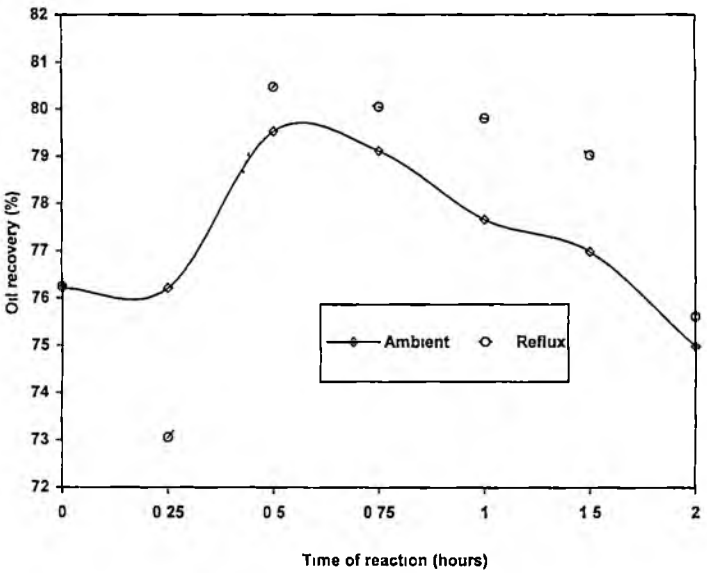

Fig 6 Effect of temperature on the geraniol yield

(Alcoholic NaOH method)

3 1 2 Effect of agitation on the hydrolysis of geranyl acetate in palmarosa oil

In order to study the effect of stirring on the hydrolysis of geranyl acetate by methanolic alkali palmarosa oil was mixed with methanolic sodium hydroxide and kept at laboratory conditions In one set of experiments the mixture was continuously stirred at 200 rpm using a magnetic stirrer Another set was left undisturbed Samples were worked up and analysed for chemical composition after specified periods of time The results are shown in Table 3 and represented graphically in Fig 7

Table 3 Effect of agitation on the hydrolysis of geranyl acetate in palmarosa oil by alcoholic NaOH

Agitation	Time (h)	Geraniol (%)	Geranyl acetate (%)	Oil recovery (%)	Geraniol yield (%)
Stirred	0 00	76 25	14 35	100 0	76 21
	0 25	81 81	0 10	88 6	72 48
	0 50	90 17	0 11	88 2	79 53
	1 00	90 82	0 12	85 5	77 65
	1 50	90 97	0 10	84 6	76 96
	2 00	90 08	0 09	83 2	74 95
Not stirred	0 00	76 25	14 35	100 0	76 21
	0 25	90 08	0 10	84 6	76 21
	0 50	90 17	0 11	88 2	79 53
	1 00	90 72	0 11	87 2	79 11
	1 50	90 97	0 01	84 6	76 96
	2 00	90 08	0 09	83 2	74 95

Geran ol content and consequently the geraniol yield were slightly less in samples wh ch were st rred n comparison to those which were left undisturbed This effect was evident only up to 0 25 h From 0 5 h onwards the geraniol content and geraniol yield in the two treatments were alike

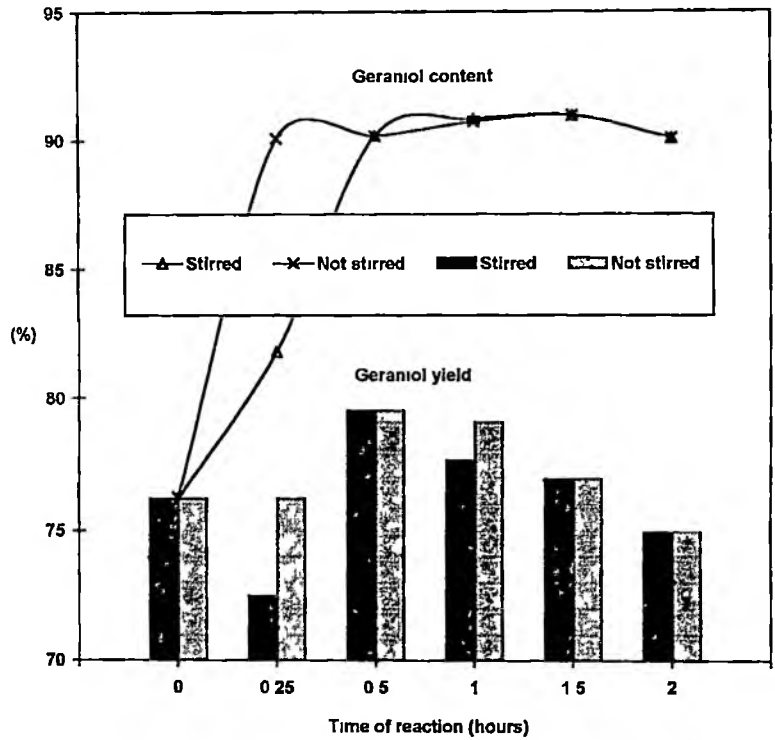

Fig 7 Effect of agitation on geraniol content and geraniol yield (Alcoholic NaOH method)

3 1 3 Effect of NaOH concentration on the hydrolysis of geranyl acetate in palmarosa oil

In order to determine the effect of NaOH concentration on the hydrolysis of geranyl acetate a series of experiments were conducted in which palmarosa oil and methanolic NaOH reagent of the specified concentration were mixed in 1 4 ratio and allowed to react

Table 4 Effect of NaOH concentration and reaction time on the hydrolysis of geraniol acetate in palmarosa oil by alcoholic NaOH

NaOH concen (%)	T me of eact on (h)	Geran ol content (%)	Geranyl acetate content (%)	O l recovery (%)	Geran ol y eld (%)
15 0	0 00	76 25	14 35	100 0	76 25
15 0	0 50	85 23	5 29	89 5	76 28
15 0	1 00	89 78	0 02	81 4	73 10
15 0	1 50	90 00	0 02	81 1	72 99
15 0	2 00	90 00	0 02	79 3	71 37
15 0	2 50	90 05	0 06	78 0	70 24
10 0	0 50	85 90	0 12	82 0	70 44
10 0	1 00	88 12	0 14	79 9	70 41
10 0	1 50	90 22	0 11	78 5	70 82
10 0	2 00	91 15	0 09	74 5	67 91
10 0	2 50	91 22	0 06	73 2	66 77
7 5	0 50	85 57	0 00	77 8	66 57
7 5	1 00	87 37	0 00	77 0	67 27
7 5	1 50	89 93	0 11	78 0	70 15
7 5	2 00	89 96	0 11	75 0	67 47
7 5	2 [illegible]	89 89	0 00	72 0	64 72
5 0	0 50	90 50	0 00	87 0	78 74
5 0	1 00	91 65	0 31	84 0	76 99
5 0	1 50	90 76	0 02	78 0	70 79
5 0	2 00	91 05	0 01	76 0	69 20
5 0	2 50	90 85	0 10	72 0	65 41
2 5	0 50	90 01	0 00	80 0	72 01
2 5	1 00	91 87	0 00	80 0	73 50
2 5	1 50	90 30	0 00	76 0	68 63
2 5	2 00	90 76	0 02	73 2	66 64
2 5	2 50	90 88	0 02	72 0	65 43
1 0	0 50	89 32	0 00	7o 0	69 67
1 0	1 00	89 04	0 00	77 0	68 56
1 0	1 50	89 40	0 00	77 5	69 29
1 0	2 00	89 53	0 00	74 6	66 79
1 0	2 50	90 29	0 00	3 2	66 09

Data on the effect of sodium hydrox de concentration on the geraniol content of palmarosa o l is depicted graphically in Fig 8 The pattern of hydrolysis of geraniol

acetate to geraniol was similar at all concentrations of NaOH The hydrolysis was fast with major portion of the conversion taking place in the initial 0 5 h In all treatments geraniol content of the product reached maximum at 1h and thereafter it showed a marginal decline Maximum geraniol was recorded in treatments containing 2 5% and 5% NaOH (91 87% and 91 65% respectively) after 1h of reaction

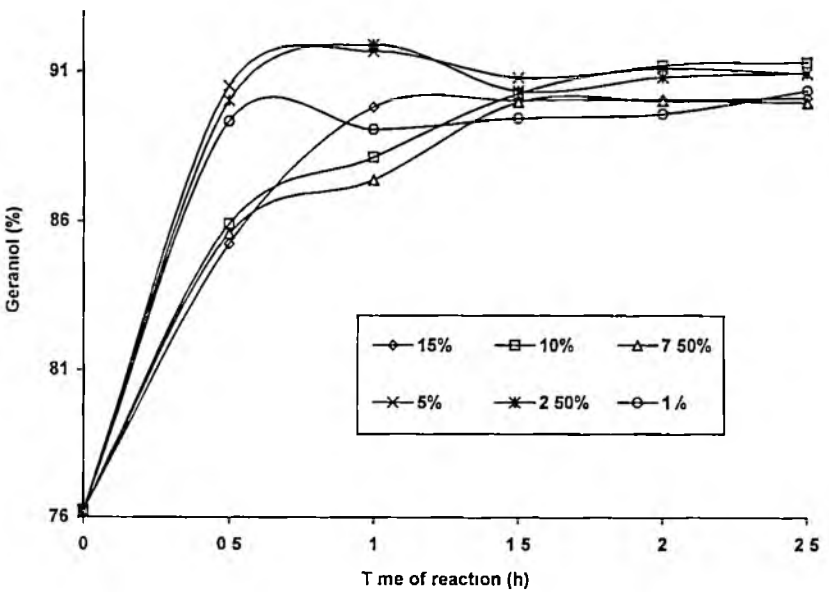

Fig 8 Effect of NaOH concentration on geraniol content

(Alcoholic NaOH method)

Fig 9 depicts the effect of NaOH concentration on the hydrolysis of geraniol esters with respect to geraniol yield In general the process yield of geraniol increased up to 0 5 1 0 h of treatment and thereafter it showed a progressive decline The highest geraniol yield was obtained by treatment with 5% NaOH for 0 5 h

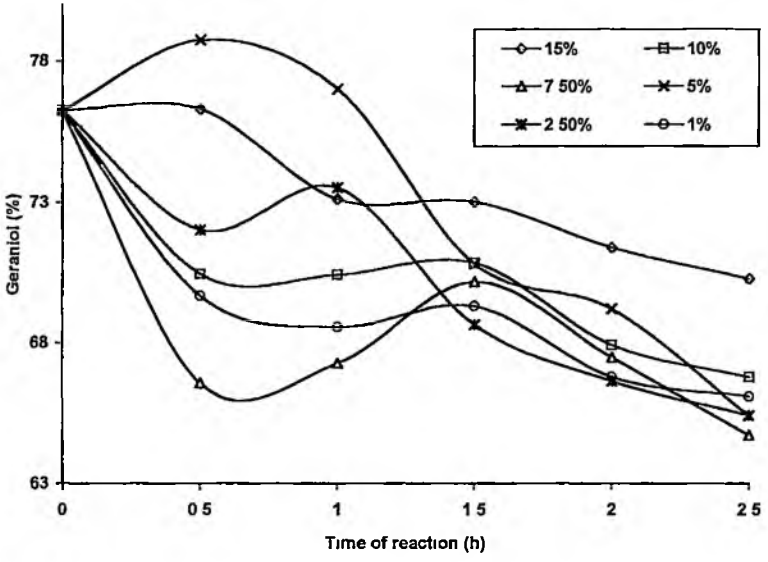

Fig 9 Effect of NaOH concentration on geraniol yield

(Alcoholic NaOH method)

It may thus be concluded that the following conditions are most optimum for the methanolic alkali hydrolysis of geranyl acetate in palmarosa oil to get high percentage and yield of geraniol

Oil alkali reagent ratio	1 4
Concentration of NaOH in methanolic alkali reagent	5%
Conditions	Ambient undisturbed
Time of reaction	0 5 h

In similar studies conducted by Nigam *et al* (1985) treatment of palmarosa oil with four times the volume 10% methanolic sodium hydroxide for 1 hour under reflux resulted in increased geraniol content of oil However in this study geraniol acetate to geraniol conversion was achieved under milder conditions of temperature and NaOH concentration and in a shorter period of time

3.2 Hydrolysis of geranyl acetate in palmarosa oil using methanolic sodium carbonate

Another set of experiments was conducted to study the effect of methanolic sodium carbonate in converting geranyl acetate in palmarosa oil to geranol The essential oil was mixed with methanolic sodium carbonate in the ratio 1 4 and refluxed for 2 hours The product was worked up as described in section 2 2 1 2 of chapter Materials and Methods" and subjected to gas chromatographic analysis The data are presented in Table 5 and results depicted graphically in Fig 10

Methanolic sodium carbonate at three concentrations (5 10 and 15%) were tried for hydrolysing geranyl acetate The results showed that even prolonged treatment for 3 hours could not bring about any appreciable increase in the content of geraniol

The yield of geraniol showed a progressive decrease with time This decrease was attributed to decrease in oil recovery

Table 5 Effect of methanolic sodium carbonate on the hydrolysis of geranyl acetate in palmarosa oil

Na_2CO_3 (%)	T me (h)	Geran ol (%)	Geranyl acetate (%)	O l recovery (%)	Geran ol y eld (%)
5	0 00	76 25	14 35	100 0	76 25
5	1 00	76 43	14 23	95 5	72 99
5	2 00	77 44	13 87	89 0	68 92
5	3 00	77 32	13 57	85 5	66 11
10	1 00	76 14	13 91	89 8	68 37
10	2 00	75 32	14 56	88 5	66 65
10	3 00	76 99	13 96	83 2	64 05
15	1 00	75 23	14 25	96 5	72 60
15	2 00	77 26	14 56	90 5	69 92
15	3 00	77 42	13 65	85 4	66 12

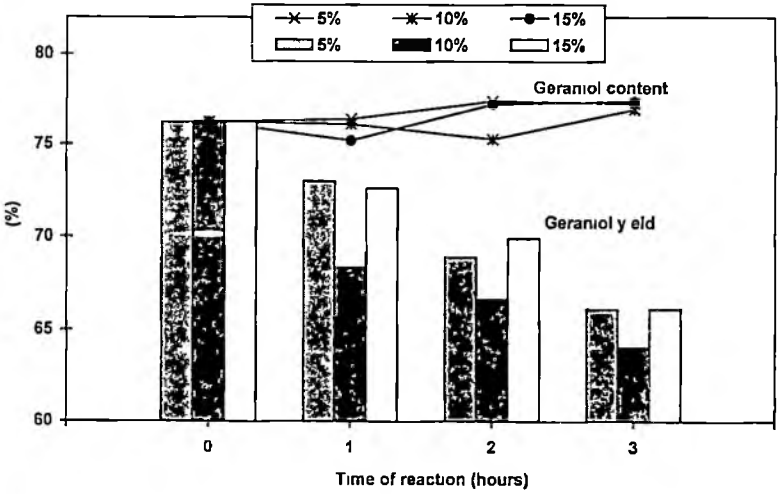

Fig 10 Effect of sodium carbonate concentration on geraniol content and yield (Alcoholic Na_2CO_3 method)

In summary treatment with methanolic sodium carbonate did not produce satisfactory results in the hydrolytic conversion of geranyl acetate in palmarosa oil to geraniol

3 3 Hydrolysis of geranyl acetate in palmarosa oil using ammonia

In this experiment ammonia was employed to effect the hydrolysis of geranyl acetate in palmarosa oil The essential oil was mixed with concentrated ammonia solution in the ratio 1 5 and the mixture stirred at room temperature for specified periods of time using a magnetic stirrer At the end of the period the oil layer was separated washed and analysed by gas chromatography The results of the trials are shown in Table 6

Table 6 Effect of ammonia on the hydrolysis of geranyl acetate in palmarosa oil

Time (h)	Geraniol (%)	Geranyl acetate (%)	Oil recovery (%)	Geraniol yield (%)
0 00	76 25	14 35	100 0	76 25
1 00	76 25	14 22	99 3	75 72
2 00	76 24	14 01	98 7	75 25
3 00	75 89	14 81	98 3	74 60
4 00	76 14	14 25	99 1	75 45
5 00	76 22	14 01	98 3	74 92

Level of geranyl acetate and geraniol were unaffected by the treatments The results indicated that stirring with ammonia solution did not effect the hydrolysis of geranyl acetate

3 4 Hydrolysis of geranyl acetate in palmarosa oil using aqueous sodium hydroxide

Palmarosa oil from the type ODP 3 and aqueous sodium hydroxide of the specified concentration were mixed in the specified ratio and stirred under reflux or ambient condition for the specified periods of time At the close of the period the oil layer was separated washed free of alkali and analysed by gas chromatography The results of the studies are presented and discussed below

3 4 1 Effect of essential oil reagent ratio

In separate experiments palmarosa oil and 20% aqueous sodium hydroxide solution were mixed at 1 4 1 2 1 1 and 2 1 ratio and stirred under reflux on a water bath for different periods of time At the end of the period the oil layer was separated worked up as described in section 2 2 2 2 of chapter Materials and Methods and analysed by gas chromatography The results of the studies are presented in Table 7

Table 7 Effect of oil reagent ratio on the hydrolysis of geranyl acetate in palmarosa oil by aqueous NaOH

O Reagent	Time (h)	Geraniol (%)	Geranyl acetate (%)	Recovery (%)	Geraniol yield (%)
1 4	0 0	76 25	14 35	100 0	76 25
4	0 5	80 15	3 17	90 5	72 54
1 4	1 0	82 24	1 51	89 3	73 44
1 4	1 5	85 39	0 95	87 7	74 89
1 4	2 0	88 35	0 00	88 8	78 45
1 2	0 0	76 25	4 35	100 0	76 25
1 2	0 5	82 94	3 05	93 5	77 55
1 2	1 0	84 15	0 02	92 8	78 09
2	1 5	85 39	0 00	92 0	78 59
1 2	2 0	89 35	0 00	91 7	81 93
1 1	0 0	76 25	14 35	100 0	76 25
	0 5	89 35	0 00	97 0	86 67
1 1	1 0	89 52	0 00	96 3	86 21
1 1	1 5	89 96	0 00	96 7	86 99
1 1	2 0	89 75	0 00	95 4	85 60
2 1	0 0	76 25	14 35	100 0	76 25
2 1	0 5	78 15	7 19	97 0	75 81
2 1	1 0	88 90	1 52	96 5	85 79
2 1	1 5	89 15	0 00	97 3	86 74
2	2 0	89 30	0 00	96 4	86 09

The results presented graphically in Fig 11 showed that in all the treatments the hydrolysis of geranyl acetate started immediately on commencement of the treatment This was evidenced by a sharp increase in the content of geraniol and a sharp decrease in that of geranyl acetate during the initial phase of treatment In case of oil reagent ratios 1 4 1 2 and 1 1 the rise in geraniol content was steep up to 0 5 h and thereafter the increase was gradual However in case of 2 1 ratio the formation of geraniol was slow in the 0 0 5 h period But the rise was steep during the 0 5 1 h period and thereafter the level remained unchanged

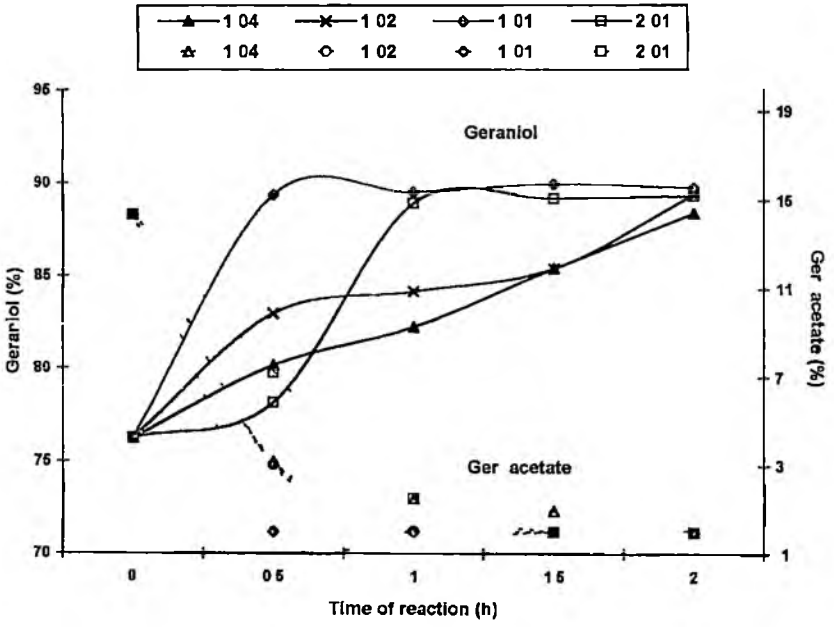

Fig 11 Effect of oil reagent ratio on geraniol and geranyl acetate content (Aqueous NaOH method)

In respect of geraniol content the best treatments were oil reagent ratios 2 1 and 1 1 In case of 2 1 ratio peak values of geraniol content (88 9 89 3%) were observed at 1 2 h of treatment But in case of 1 1 ratio peak values of 89 35 89 96% were attained in a shorter period of 0 5 1 h This showed that an oil NaOH reagent ratio of 1 1 is the best treatment for getting a product of high geraniol content in a shorter period of treatment

Results of oil recovery are shown in Fig 12 All the treatments recorded high oil recovery levels (87 97%) From the figure it is evident that 1 1 and 2 1 ratios were superior to the others in respect of oil recovery

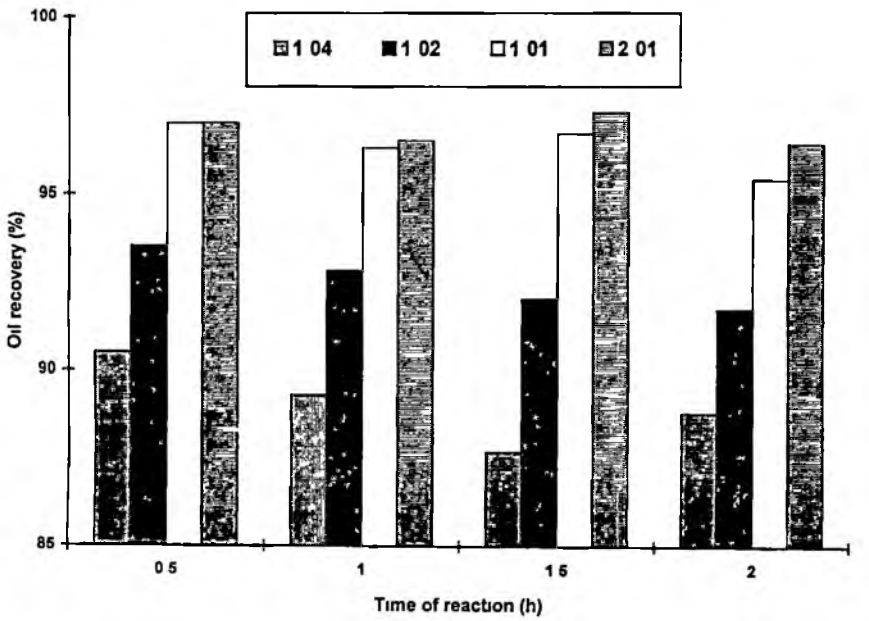

Fig 12 Effect of oil reagent ratio on oil recovery

(Aqueous NaOH method)

Results on the effect of oil aqueous sodium hydroxide reagent on the process yield of geraniol is represented graphically in Fig 13

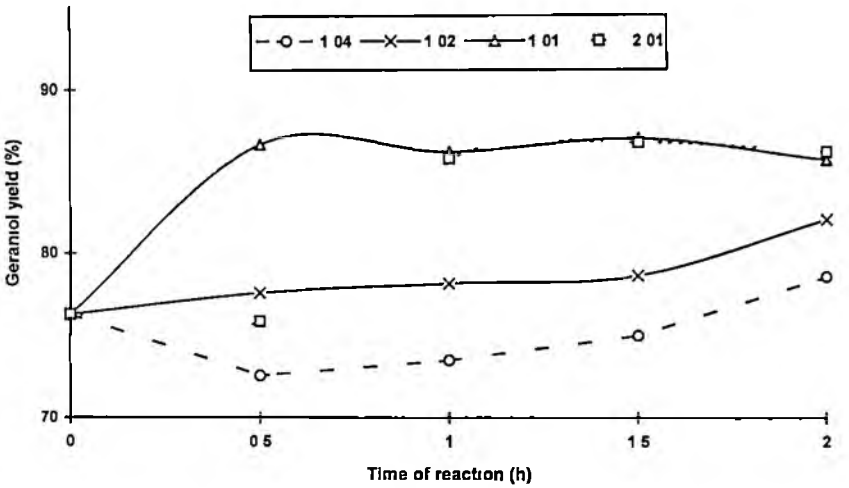

Fig 13 Effect of oil reagent ratio on geraniol yield

(Aqueous NaOH method)

The ratios 2 1 and 1 1 were superior to the other ratios in respect of geraniol yield In case of the ratio 2 1 the maximum geraniol yields were obtained in 1 1 5 h after treatment However in case of 1 1 ratio peak yield levels were obtained in an earlier period of 0 5 1 h

In conclusion it was found that oil aqueous NaOH ratio 1 1 was the best for obtaining a product of maximum geraniol content and maximum geraniol yield

3 4 2 Effect of temperature

In separate experiments palmarosa oil and 20% aqueous sodium hydroxide solution were mixed in 1 1 ratio and stirred for different periods of time at the following temperature conditions ambient 60 70°C and reflux At the end of the period the oil

layer was separated worked up as described in section 2 2 2 2 of chapter "Materials and Methods and analysed by gas chromatography The results of the studies are presented in Table 8 Data on the geraniol and geranyl acetate contents of reaction products involving different temperatures are presented in Fig 14

Table 8 Effect of temperature on the hydrolysis of geranyl acetate in palmarosa oil by aqueous NaOH

Temp (°C)	Time (h)	Geraniol (%)	Geranyl acetate (%)	Recovery (%)	Geraniol yield (%)
Ambient	0 0	76 25	14 35	100 0	76 25
	0 5	75 21	14 39	98 5	74 08
	1 0	73 32	14 50	97 3	71 34
	1 5	72 15	14 21	96 5	69 62
	2 0	73 97	14 25	95 2	70 42
60 70°C	0 0	76 25	14 35	100 0	76 25
	0 5	80 39	9 32	99 3	79 83
	1 0	85 32	3 56	98 5	84 04
	1 5	87 57	1 93	98 2	85 99
	2 0	89 65	0 00	97 9	87 77
Reflux	0 0	76 25	14 35	100 0	76 25
	0 5	89 35	0 00	97 0	86 67
	1 0	89 52	0 00	96 3	86 21
	1 5	89 96	0 00	96 7	86 99
	2 0	89 75	0 00	95 4	85 60

The geraniol content of samples that were heated increased progressively with a corresponding decrease in geranyl acetate content Thus the rise in geraniol content is attributed to the hydrolytic release of geran ol from geranyl acetate The effect was much pronounced in case of refluxed samples In case of these samples the geraniol content showed an abrupt rise to maximum values in a period of 0 5 1 h Thereafter the level remained unaltered In case of samples heated at 60 70°C the evel increased

Data on oil recovery plotted graphically in Fig 15 showed that the oil recovery values were not much influenced by the treatments The recovery values remained in the range of 95 100%

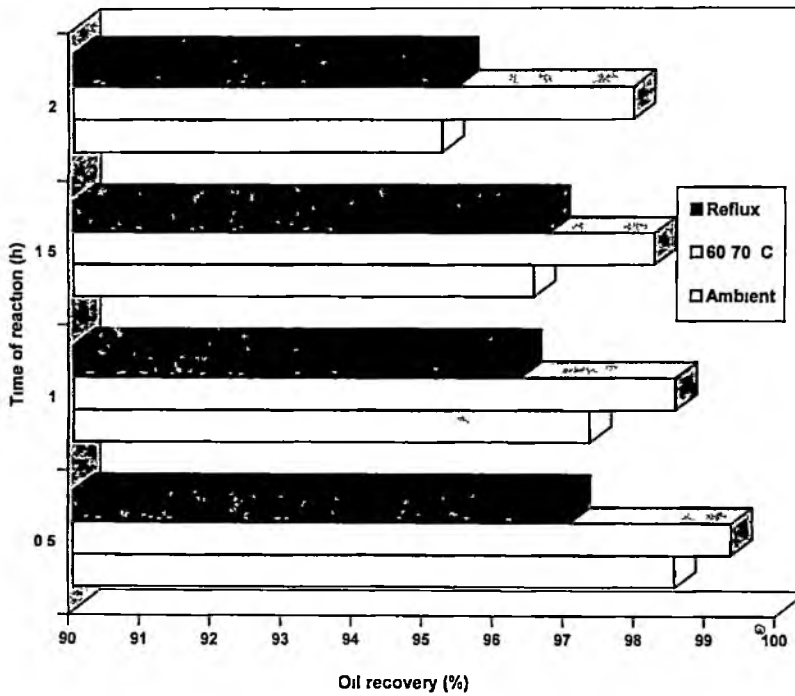

Fig 15 Effect of temperature on oil recovery

(Aqueous NaOH method)

Data on the geraniol yield is plotted in Fig 16 The process yield of geraniol under reflux condition increased abruptly and attained the maximum value of 86 67% in 0 5 h of treatment Thereafter the geraniol yield remained somewhat steady When the reaction temperature was maintained at 60 70°C the geraniol yield showed a gradual but steady ncrease throughout the experimental period to reach the maximum value of 87 77% in 2 h Contrary to this the geraniol yield values showed a marginal decline in the ambient temperature treatment Highest geraniol yields were registered by 60 70°C 2 h (87 77%) reflux 1 5 h (86 99%) and reflux 0 5 h (86 67%) treatments However the reflux 0 5 h treatment assumes mer t of high geraniol yield in the shortest time

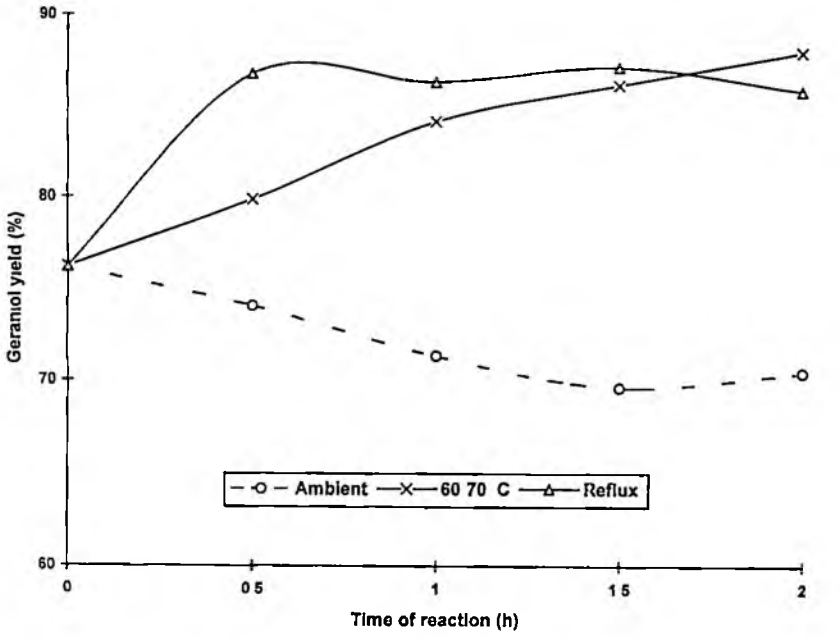

Fig 16 Effect of temperature on geraniol yield

(Aqueous NaOH method)

3 4 3 Effect of concentration of sodium hydroxide

In separate experiments palmarosa oil and aqueous sodium hydroxide solution of the specified concentration were mixed in 1 1 ratio and stirred for different periods of time under reflux At the end of the period the oil layer was separated worked up as described in section 2 2 2 2 of chapter Materials and Methods and analysed by gas chromatography The results of the studies are presented in Table 9

Table 9 Effect of sodium hydroxide concentration on the hydrolysis of geranyl acetate in palmarosa oil

NaOH (%)	Time (h)	Geraniol (%)	Geranyl acetate (%)	Recovery (%)	Geraniol yield (%)
0	0 0	76 25	14 35	100 0	76 25
0	0 5	75 21	14 39	93 5	70 32
0	1 0	72 32	14 50	89 3	64 58
0	1 5	71 15	15 01	78 5	55 85
0	2 0	70 97	14 21	72 2	51 25
10	0 0	76 25	14 35	100 0	76 25
10	0 5	79 65	9 39	98 5	78 46
10	1 0	83 29	6 54	98 9	82 37
10	1 5	85 65	0 59	97 5	83 51
10	2 0	87 39	0 07	96 4	84 24
20	0 0	76 25	14 35	100 0	76 25
20	0 5	89 35	0 00	97 0	86 67
20	1 0	89 52	0 00	96 3	86 21
20	1 5	89 96	0 00	96 7	86 99
20	2 0	89 75	0 00	95 4	85 62
40	0 0	76 25	14 35	100 0	76 25
40	0 5	88 59	2 19	95 5	84 69
40	1 0	89 32	1 16	93 2	83 25
40	1 5	89 65	0 15	89 6	80 33
40	2 0	90 05	0 00	85 5	76 99

Data on the geraniol and geranyl acetate contents of reaction products involving different concentrations of NaOH are presented in Fig 17

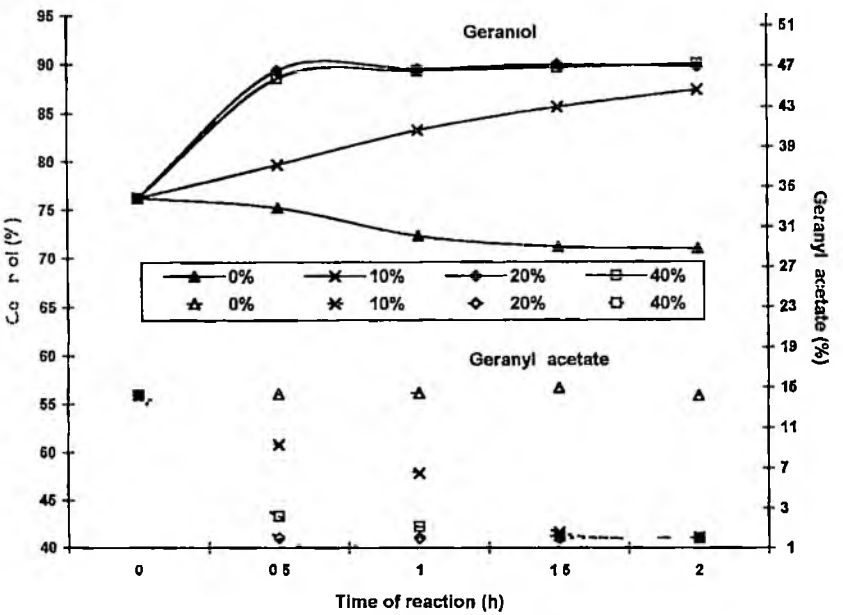

Fig 17 Effect of NaOH concentration on geraniol and geranyl acetate content (Aqueous NaOH method)

All levels of NaOH increased the concentration of geraniol and correspondingly decreased that of geranyl acetate over control The concomitant decrease in the level of geranyl acetate with increase in that of geraniol suggests the hydrolysis of the ester by NaOH Hydrolysis of geranyl acetate was not noticed in control (0% NaOH) On the contrary there was a slight decrease in the level of geraniol and a marginal increase in that of geranyl acetate Hydrolysis of acetate and accumulation of geraniol was noticed in 10% NaOH treatment The conversion was still faster in 20% and 40% NaOH treatments which in turn were on par In a similar study Aggarwal *et al* (1986) found an NaOH concentration of 12% to be optimum for the hydrolysis of geranyl esters in palmarosa oil

They have tried reaction times in the range of 2 to 9 hours only Rate of hydrolysis in periods less than 2 hours is not available in the report In this study however geraniol content as high as 89 35 89 52% was obtained in a period as short as 0 5 to 1 hour on treatment with 20% NaOH

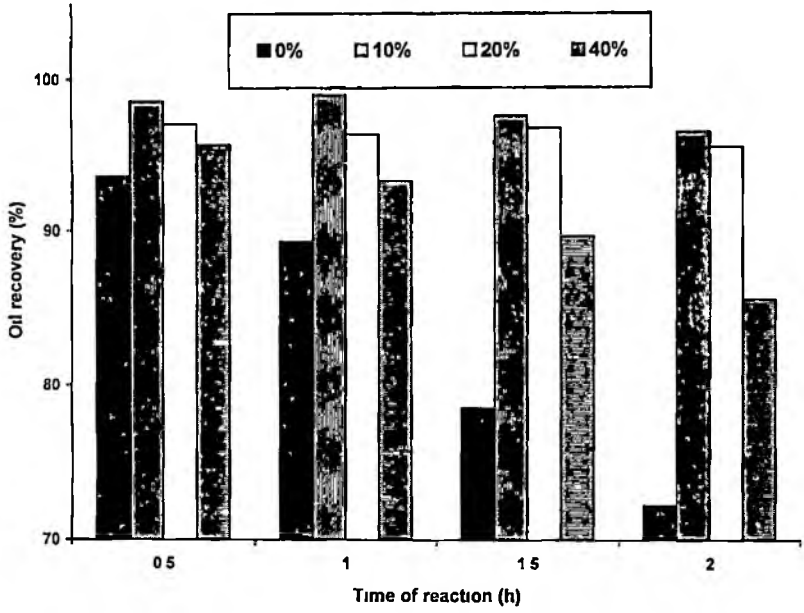

Fig 18 Effect of NaOH concentration on oil recovery

(Aqueous NaOH method)

Data on oil recovery presented in Fig 18 also has depicted that in the zero NaOH treatment there was a progress ve decline in oil recovery This is assumed to be due to the dissolut on of small amount of geraniol in the aqueous reagent dunng the treatment period The aqueous reagent was separated and collected at the close of 2 hour treatment period and partitioned with hexane and the extract analysed by gas chromatography The gas chromatogram is shown in Fig 19

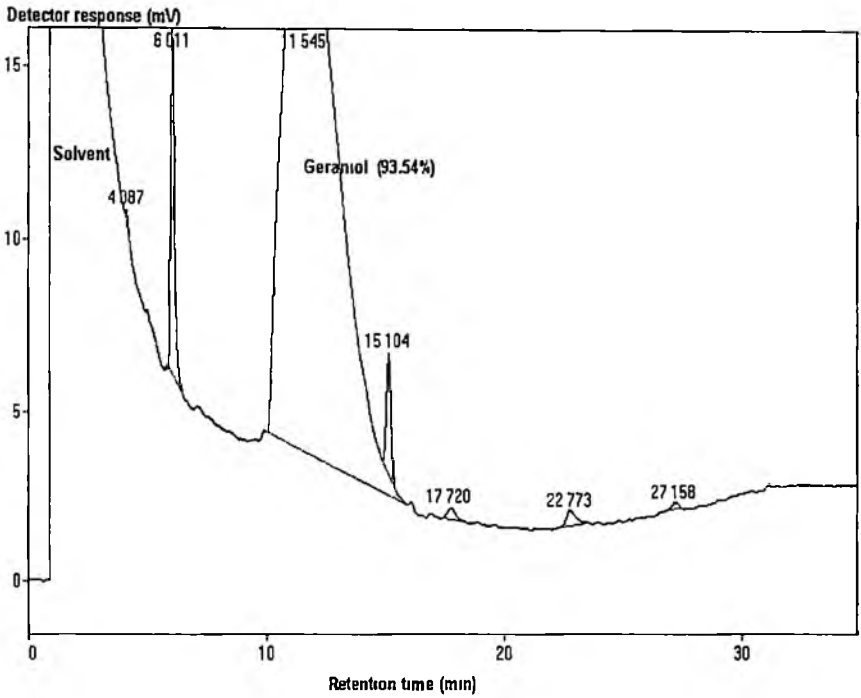

Fig 19 Gas liquid chromatogram of extract of aqueous NaOH reagent

The essential oil extracted by the solvent from the aqueous reagent contained 93 54% geraniol This has clearly demonstrated that the aqueous reagent has dissolved components of the essential oil mainly geraniol This selective removal of geraniol by the reagent would have resulted the decline in geraniol content of the product and so also in the increase in the relative percentage of geranyl acetate

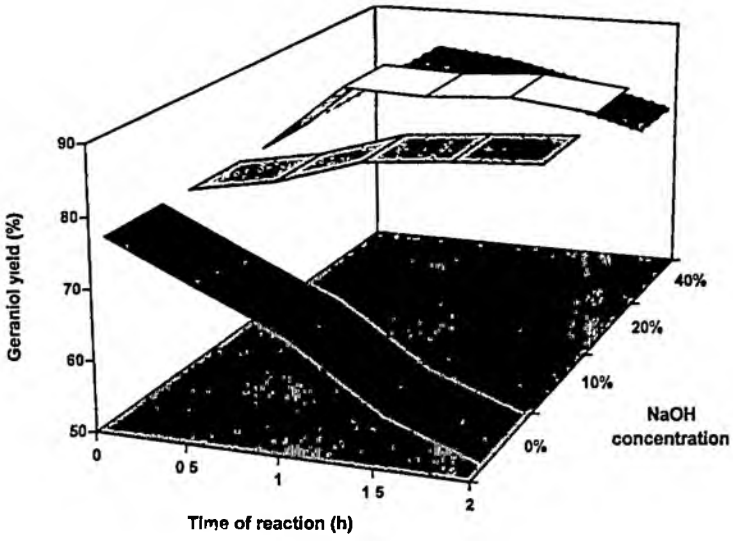

Fig 20 Effect of NaOH concentration on geraniol yield

(Aqueous NaOH method)

Data on the geraniol yield as influenced by NaOH concentration are plotted in Fig 20 The process yield of geraniol was maximum in case of 20% NaOH treatment The geraniol yield increased suddenly and attained a high value of 88 59% in 0 5 h of treatment Thereafter the geraniol yield remained almost steady In case of 40% level the yield reached the maximum value of 84 69% in 0 5 h and declined thereafter The geraniol yield in 10% NaOH treatment increased steadily but reached the maximum of 84 24% only after 2 hours On the contrary the geraniol yield showed a steep decline in case of control where NaOH was not included

3 4 4 Summary of experiments using aqueous sodium hydro ide

In trials to determine the optimum ratio of oil and sodium hydroxide it was found that 1 1 ratio resulted in product of maximum geraniol content and geraniol yield In the

second set of experiments where different temperatures were tried at an oil reagent ratio of 1 1 it was seen that reflux temperature yielded product of highest geraniol content and yield in the shortest time In the final series of experiment to standardise the optimum NaOH concentration at an oil reagent ratio of 1 1 under reflux conditions it was established that sodium hydroxide concentration of 20% was optimum for getting high geraniol content (89 35%) and geraniol yield (86 67%) in the shortest time (0 5 h)

3 5 Comparison of methanolic NaOH and aqueous NaOH methods of hydrolysis of geranyl acetate in palmarosa oil

A summary of reaction conditions and results obtained in the two methods studied for the hydrolysis of geraniol acetate in palmarosa oil for obtaining maximum oil yield and geran ol recovery is given below

Reaction conditions	Characteristics of the product
1 *Methanolic NaOH hydrolysis* O l alkali reagent ratio 1 4 Concentration of NaOH in the methanolic alkali reagent 5% Conditions Ambient undisturbed Reaction time 30 min	Geraniol 90 50% Geranyl acetate nil Oil yield 87 0% Geraniol yield 78 74%
2 *Aqueous NaOH hydrolysis* Oil alkali reagent ratio 1 1 Concentration of NaOH in the aqueous alkali reagent 20% Conditions Refluxing Reaction time 30 min	Geraniol 89 35% Geranyl acetate nil Oil yield 96 30% Geraniol yield 86 67%

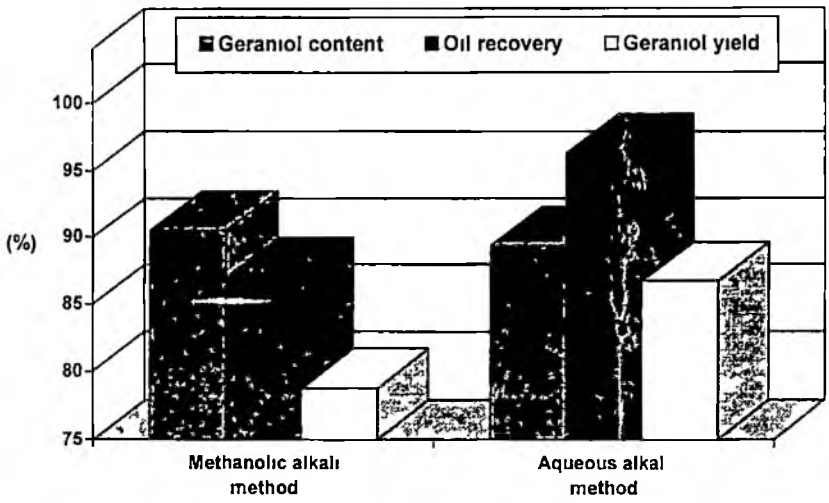

Fıg 21 Comparıson of methods for the hydrolysıs of geranyl acetate ın palmarosa oıl

A close observat on of the results ın Fıg 21 show that both methods y elded products of very hıgh geran ol content (89 35 90 5%) However aqueous NaOH hydrolysıs method was superıor ın respect of o l yıeld and process yıeld of geranıol The latter method was sımpler and easıer In the methanolic alkalı method the reactıon phase was eas er to perform The oıl and the reagent were mıxed and kept undısturbed for 0 5 h at room temperature for the reactıon to take place However n case of the aqueous hydrolysıs method the mıxture had to be stırred vıgorously and refluxed for 0 5 h for fac tatıng the react on The process ng of the product was more cumbersome ın the former method The product was dıstılled on water bath to recover most of the methanol It was then dıluted wıth water and partıtıoned several tımes wıth water to remove traces of methanol The workup process was much easy n case of aqueous alkalı process At the end of the reactıon the oıl layer separated ıtself from the aqueous layer whıch was clar f ed by repeated washıng w th water

In the light of the high process yield of geraniol and ease in the processing of the product it was established that the aqueous alkali method was the best method for the hydrolytic conversion for geranyl acetate in palmarosa oil to geraniol

3 6 Quality improvement of essential oils by hydrolytic conversion of geranyl acetate to geraniol

The aqueous NaOH hydrolysis method was employed to increase the geraniol content of essential oil of different plant types belonging to the genus *Cymbopogon* For the purpose four plant types which are important geraniol sources were selected Physico chemical properties of these essential oils as well as the conversion products are given n Table 10

The essential oil of cultivated palmarosa type ODP 3 did not conform to the specifications laid down by ISI for palmarosa oil in respect of specific gravity refractive index ester value and ester value after acetylation Eventhough the oil contained the specified level of total alcohols (free alcohol + combined alcohol) the level of free alcohol the most important component was low (71 27%) Results of gas chromatographic analysis also revealed that the oil had a low level of geraniol (76 25%) and high level of geranyl acetate (14 35%) The non conformity of the oil to the physical parameters mentioned above might be due to low content of geraniol and high content of geranyl acetate Aqueous sodium hydroxide treatment brought about a significant change in the quality of this oil It increased the geraniol content from 76 25% to 89 35% thereby increasing the geraniol per cent by 13 12% The product of treatment fully agreed with ISI specifications for palmarosa oil

The essent al oil of palmarosa cultivated type ODP 1 contained only 64 72% free alcohols The oil analysed 64 44% geraniol and 12 65% geranyl acetate by GC The hydrolysis treatment brought about an increase in the quality of the hydrolytic product The free alcohol content increased to 77 86% equivalent to 76 56% geraniol Eventhough the process could bring about an increase in geraniol content of the oil by 12 12% the product did not satisfy the requirements of palmarosa oil in respect of free alcohol and total alcohols This demonstrated that the possibility of increasing the geraniol content of the product is limited to the amount of combined alcohol present in the oil

Table 10 Physico-chemical characteristics of oils used for the evaluation of the method for quality improvement of palmarosa oil

Sl No	Characteristic	ISI specifications	ODP-3		ODP 1		C-3		OD-455		Jamrosa	
			Starting material	Conversion product	Starting Conversion product	material	Starting material	Conversion product	Starting Conversion material product		Starting material	Conversion product
1	Colour	Light yellow to yellow	Light yellow	Light yellow	Light yellow	Light yellow	Light yellow	Light yellow	Yellow	Yellow	Light yellow	Light yellow
2	Specific gravity (at 30° C)	0 8740 to 0 8860	0 9903	0 8851	0 7852	0 864	0 8840	0 7977	0 7852	0 7659	0 886	0 864
3	Optical rotation (degrees at 30° C)	2 to +3	+2 0	+1 0	+5 0	+3 0	+1 0	+2 0	+2 0	+3 0	+2 0	+1 0
4	Refractive index (at 30° C)	1 4690 to 1 4735	1 4745	1 475	1 455	1 4887	1 435	1 4799	1 455	1 5088	1 4682	1 489
5	Solubility in 70% alcohol	< 2 00	1 30	1 10	0 90	1 20	1 20	0 80	0 90	1 00	1 20	1 05
6	Acid value	3 00 (max)	0 6003	0 75	0 9171	1 20	0 259	1 05	0 853	1 34	3 08	1 51
7	Ester value	9 to 36	49 67	11 22	50 71	8 237	46 096	9 558	36 749	10 47	45 92	9 35
8	Ester value after acetylation	266 to 280	300	302 94	243 52	240 755	254 88 3	262 701	261 68 9	266 494	261 80	270 50
9	Saponification value		51 67	11 97	51 63	9 437	46 24	10 608	36 50	11 81	49 00	10 86
10	Free alcohol content as geraniol (%)	84 88	88 62	103 73	64 72	77 86	70 945	8o 50	76 918	87 80	73 71	89 87
11	Combined alcohol content as geraniol (%)	2 5-10	13 63	3 085	13 92	2 957	12 676	2 624	10 104	2 548	12 61	2 572
12	Total alcohols as geraniol (%)	90 0 (min)	102 25	106 815	78 64	80 81	83 619	89 13	87 022	90 34	86 32	92 46
13	Geraniol by GC (%)		76 25	89 35	64 44	76 56	52 90	71 92	59 51	77 52	64 365	80 17
14	Geranyl acetate by GC (%)		14 35	0 00	12 65	0 00	17 49	0 00	12 15	0 00	17 658	0 00
15	Increase in percentage geraniol in the product			13 12		12 12		19 02		18 01		15 80

The oil of ODP 1 contained 13 92% combined alcohol In palmarosa bulk of the combined alcohol is geranyl acetate GC analysis too revealed the presence of geranyl acetate to the extent of 12 65% The hydrolysis treatment effected complete conversion of the ester with a commensurate increase in the level of the alcohol In the case of this oil though the ester hydrolysis process proved to be fully efficient the objective of upgrading the oil to the specifications of palmarosa oil did not succeed for want of suffic ent amount of free and combined geraniol in the oil

The oil of palmarosa type C 3 contained only 70 95% free 12 68% combined and 83 62% total alcohols Gas chromatographic analysis showed the presence of 52 9% geraniol The rest of about 18% of the oil may be constituted by other alcohols than geraniol Examination of data on GC analysis of oil before and after hydrolysis showed that geranyl acetate present in the oil to the extent of 17 49% was converted to geraniol by the treatment However as in the case of ODP 1 the upgradation of the oil to standard palmarosa oil was precluded by limited amount of total geraniol in the oil

In case of *Cymbopogon* type OD-455 also most or the physico chemical parameters were not in conformity w th the specifications for palmarosa oil Treatment of the oil with alkali increased the geraniol content from 59 51% to 77 52% an increase through 18% Still the product fell short of ISI requirements of palmarosa oil in terms of free alcohol content

The quality of jamrosa oil also was substantially increased by alkali treatment The level of free alcohols increased from 73 71% to 89 89% crossing the minimum requirement laid down in the specifications for standard palmarosa oil The corresponding ncrease in the level of geraniol was from 64 37% to 80 17% In short the treatment of jamrosa oil with aqueous NaOH yielded essential oil which can be traded as palmarosa o l

In general aqueous sodium hydrox de treatment of essential oil resulted in a decrease in the level of combined alcohol (geranyl acetate) w th a commensurate increase in the level of free alcohol (geraniol) The increase in geraniol percentage was subject to the level of combined alcohol in the oil The process was greatly relevant in the case of ODP 3 and jamrosa wherein the oil was converted into a product that fully complied w th ISI spec fications for palmarosa oil However it is noteworthy that the aqueous sodium hydrox de treatment of essential oils vastly improved the free geraniol content of all the

above oils This has great significance since free geraniol is isolated from the oil for its industrial utilisation

3 7 Pilot plant scale quality upgradation of palmarosa oil

The aqueous sodium hydroxide reflux method was employed in pilot plant scale for the quality improvement of palmarosa oil of cultivated type ODP 3 as described in section 2 2 5 of chapter "Materials and Methods" The alkali reagent separated out after treatment was reused in the subsequent batch processes Four batches of 1 kg oil each were processed by the method

The results obtained are given in Table 11 A comparison of the gas chromatographic traces of the oil and the product is presented in Fig 22

Table 11 Batch processing of palmarosa oil by aqueous NaOH method

Batch No	Weight of oil taken (kg)	Weight of product (kg)	Recovery (%)	Geraniol content of product (%)
1	1 00	0 953	95 3	89 91
2	1 00	0 978	97 8	89 25
3	1 00	0 973	97 3	89 15
4	1 00	0 971	97 1	89 22

Examinat on of the gas chromatographic traces of the oil before and after hydrolysis showed that the peaks of geranyl acetate and geranyl caproate vanished as a result of the treatment Besides the peaks of other chemical components were unaffected by the process This demonstrated that the treatment resulted in the selective hydrolysis of geranyl esters

The data showed that results obtained in laboratory scale process with 5 10g oil was obtained in pilot plant scale (1 kg) also The overall recovery of oil was in the range of 95 3 to 97 8% The recovery was slightly low (95 3%) in the first batch This is due to removal of small amount of oil by the aqueous reagent in solution However when the same reagent was reused in the subsequent batches the recovery remained high in the

order of 97 1 to 97 8% The geraniol content of the products obtained in the four batches was very high (89 15 89 91%)

It was thus demonstrated that the aqueous sodium hydroxide hydrolysis method can be used in large scale for the quality improvement of palmarosa oils which contain appreciable amount of geranyl acetate

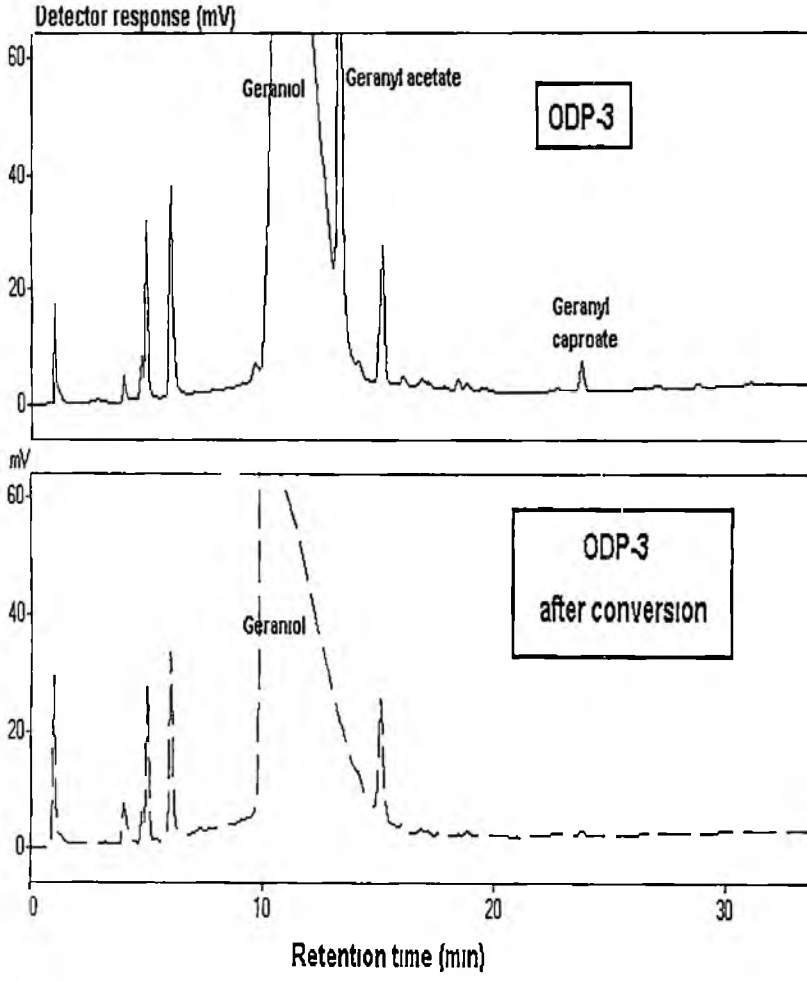

Fig 22 Gas chromatographic traces of palmarosa oil ODP 3 and its conversion product

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSION

A laboratory investigation was carried out at the Aromatic and Medicinal Plants Research Station Odakkali Kerala during 1994 96 to develop a method for upgrading the quality of palmarosa oil by the conversion of geranyl acetate in the oil to geraniol The results of the study are summarised in this chapter

1 Conditions for the hydrolysis of geranyl acetate in palmarosa oil in ODP 3 using methanolic sodium hydroxide were standardised The conditions were optimised for complete hydrolysis of geranyl acetate for getting high geraniol content as well as geraniol yield in the shortest time The essential oil was mixed with 5% methanolic NaOH reagent in the ratio of 1 4 and kept undisturbed at ambient conditions for 30 min The product analysed 90 5% geraniol A geraniol yield of 78 74% on the basis of oil taken for processing was obtained

2 Treatment of palmarosa oil with methanolic sodium carbonate under reflux at concentrations ranging from 5 to 15% for a period of up to 3 h did not bring about hydrolysis of geranyl acetate in the oil

3 Treatment of palmarosa oil with ammonia for periods up to 5 h did not result in hydrolysis of geranyl acetate in the oil

4 Conditions for the hydrolysis of geranyl acetate in palmarosa oil in ODP 3 by treatment with aqueous sodium hydroxide were standardised Refluxing essential oil with an equal volume of 20% aqueous NaOH solution for 30 min resulted in complete hydrolysis of geranyl acetate in the oil The product contained 89 35% geraniol The quantity of geraniol yielded by the process was estimated at 86 67% of the oil taken for processing

5 Efficiency of methods for effecting the hydrolysis of geranyl acetate in palmarosa oil were compared on the basis of geraniol content of the product geraniol yield from the process and time required for the reaction The aqueous sodium hydroxide method was found to be the best

6 Detailed chemical and gas chromatographic analysis of the essential oils of *Cymbopogon* types ODP 1 ODP 3 C 3 OD-455 and Jamrosa reveled that none of the types conformed with ISI specifications for palmarosa oil All the oils were character sed by low level of geraniol and high level of geranyl acetate

7 Essential oils of *Cymbopogon* types ODP 1 ODP 3 C 3 OD-455 and Jamrosa were subjected to aqueous sodium hydroxide hydrolysis In case of all the oils the treatment brought about complete conversion of geranyl acetate to geraniol with commensurate increase in the level of geraniol By the process oils of ODP 3 and Jamrosa were upgraded to meet the specifications for palmarosa oil The free geraniol content of all the oils were substantially increased thereby enhancing their industrial value

8 Verification of the sodium hydroxide hydrolysis method on pilot plant scale showed that the method can be employed on a large scale for the quality improvement of palmarosa oils which contain appreciable amount of geranyl acetate As the process is simple and economical the method can be utilised by farmers for upgrading the oil quality in palmarosa for realising higher returns

REFERENCES

REFERENCES

Aggarawal K K Naqvi A A and Kahol 1986 Production of geraniol from palmarosa oil *Res Ind* **31** 132 135

Akh la A and Nigam M C 1983 Biosynthesis of monoterpenes *Indian Perfumer* **27** 174 196

Akhila A Thyagi B R and Naqv A 1984 Variations of essential oil constituents in *Cymbopogon martini* Wats var *motia* at different stages of growth *Indian Perfumer* **28** 126 128

Al ce K 1982 *Studies on the variation in quantity and quality of oil in different parts of palmarosa in different seasons* M Sc (Ag) thesis Kerala Agricultural Un vers ty Vellan kkara Thr ssur

Balas R K and Gupta B 1988 Contribut on of 2 *trans* 3 7 dimethyl 1 2 octadien 1 ol to perfumery and cosmetic industry *Indian Perfumer* **32** 251 265

Banthorpe D V Fkunday O and Rowan M G 1978a Evidence of geraniol as an obl gatory precursor of sothujone *Phytochemistry* **17** 1111 1114

Banthorpe D V Maun J Modawi B M Poots I and Rowan M G 1978b Redox inter conversion of geraniol and nerol in higher plants *Phytochemistry* **17** 1115 1118

Ch nnamma N P and Aiyer R S 1988 Effect of fert lisers and harvests on palmarosa oil quality *Indian Perfumer* **32** 220 224

Farooqi A H A Luthra R Bansal R P and Singh N 1995 *Cympopogons The Aromatic Grasses A Monograph* CIMAP Lucknow p 112 129

Gaydou E M and Randrimihar osa R P 1987 Hydrocarbons from the essentials o l of *Cymbopogon martini Phytochemistry* **26** 183 185

Geetha K and Thomas J 1993 Effect of micronutrients on o l yield and quality of palmarosa (*Cymbopogon martinii* var *motia*) *Indian Perfumer* **37**(1) **45** 47

Ghosh M L and Chatterjee S K 1976 Pattern of essential oil formation n relation to nitrogen contents of two species of *Cymbopogon* *Indian Perfumer* **20** 71 73

Guenther E 1950 *The Essential Oils* Vol IV D Van Nostrand Co Inc Toranto pp 752

Gupta B K and Jain N 1978 Cultivation and utilisation of the grass *Cymbopogon* in India *Indian Perfumer* **22** 155 168

Gupta R S Verma S and Trived K C 1981 Improvement of *Cymbopogon martini* var *motia* by low dose gamma radiations *Pafai J* **3** 18 20

Hazarika J N Barua A and Barua A K S 1978 Effect of N P and K fertilisers on the yield and quality of oil of palmarosa under the influence of seasonal variat ons *Indian Perfumer* **22** 36 39

I S I 1968 *Specification for oil of palmarosa* IS 526 Ind an Standards Institution New Delh

Janardhan K K Gupta M L and Hussa n A 1980 Effect of *Curvularia* leaf blotch disease on the essential o l content of palmarosa *Indian J Exp Biol* **18** (4) 439 440

Kalia N K Sood R P Patha C D and Jamwal R K 1980 Ut l zation of w ld grow ng *Cybopogon martini* var *sofia* *Indian Perfumer* **24** 126 128

Karra G V and Beri R M 1966 Studies on cultivat on and explo tat on of rosha grass *Indian Forester* **92** 127 131

Lal G 1935 Some observations on essential oil content of rosha grass *Cymbopogon martini* Stapf var *motia J Agric Sci* **5** 415-421

Maheswar M L and Seth K L 1987 Selection and improvement in palmarosa *Indian Perfumer* **31** 17 31

Mohammed F Nigam M C and Rehman W 1981 Essential oil of *Cymbopogan martini* var *motia* Detect on of new trace constituents *Pafai J* **3** 11 13

Muns P K and Mukherji S K 1982 Fertil ser treatments on yield and economics of cultivation of mentha citronella and palmarosa *Indian Perfumer* **26** 74 80

Nabney J 1973 Essential oil constituents of mint and palmarosa *Phytochemistry* **12** 1511 1515

Nair E V G Chinnamma N P and Pushpakumari R 1980 Influence of varieties on the grass oil yield and quality of oil of palmarosa *Indian Perfumer* **24** 22 24

Nair E V G and Mar am K A 1978 Palmarosa the new promising aromat c plant of Kerala *Indian Perfumer* **22** 300 301

Nigam M C Akhila A Sen T and Sidd qui M S 1985 Development of new parametes for production of isolates of potental value *Indian Perfumer* **29** 57 60

Olivaro 1989 Leaf essential oil of w ld *Cymbopogon martinii* (Rox) Wats from Sorsogon Philippines *Philippine J Sci* **8** 31 58

Pareek S K Maheswari M L and Gupta R 1981 Effect of N P and K fert l zers on yield and quality of palmarosa grass under cultivation *Indian J Agron* **26** 123 129

Pareek S K Maheswari M L S ngh K D and Gupta R 1983 Nutrient uptake and dry matter production of palmarosa oil grass under different levels of N P and K fertil sers *Intern J Trop Agri* **1** 203 209

Patil K B 1996 Natural essent al oils of India A perspective *Pafai J* **18**(2) 19 24

Patil K B and Jayappa V 1986 Palmarosa o l specification and analysis *Indian Perfumer* **30** 286 292

Pr dham J B 1967 *Terpenoids in plants* Academic Press London and New York pp 425

Punia M S Verma P K and Sharma G D 1986 Ideal type co ncept in palmarosa A b ochemical approach *Indian Perfumer* **30** 240 246

Randr am har osa R P and Gaydou E M 1987 Compos tion of palmarosa (*Cymbopogon martini* Stapf var *motia*) essential oil from Madagascar *J Agric Food Chem* **35** 62 66

Ruz cka L 1953 Isoprene rule and b ogenesis of terpene compounds *Experimentia* **9** 357 367

Saxena D B and Maheswen M L 1980 Terpenoids from palmarosa grass (*Cymbopogon martini* var *motia*) *Indian Perfumer* **24** 115 120

Shahoo S Kanungo S P Babuji M and Dutta P K 1987 Herb o l yield and geraniol content of improved palmarosa selections at Bhuvaneswar *Indian Perfumer* **31** 240 244

Siddiqui N and Garg S C 1990 Chemical composition of *Cymbopogon martini* var *motia* *J essential Oil Res* 2(2) 93 94

Singh R 1977 *Cultivation and utilisation of medicinal and aromatic plants* Publicat on and Information D rectorate Council of Sc entific and Industrial Research New Delhi pp 185

S ngh R S Pathak M G and Bardolai D N 1981 Studies on NPK requirement of palmarosa under conditions of Jorhat *Pafai J* **3** 32 34

Srivastava H K and Thyagi B R 1986 Effect of seed irradiation on yield and qual ty of essential oil in palmarosa (*Cymbopogon martini* Stapf var *motia*) *Euphytica* **35** 369 380

Thakur R S and Akhila A 1993 Biosynthet c studies of some isoprenoid compounds of perfumery and flavour values from the plants cult vated in CIMAP In *Newer trends in Essential oils and Flavours* K L Dhar R K Thappa and S G Aggarwal (Eds) p 25 32

Thappa R K Aggarwal S G Dhar K L and Atal C K 1982 *Cultivation and utilisation of medicinal and aromatic plants* Publ cation and Informat on D rectorate Counc l of Scient fic and Industrial Research New Delhi pp 185

Virman O P Gulati B C and Dutta S C 1967 Product on of o l of palmarosa *Perfum essent oil Rec* **58** 294 295

INCREASING THE GERANIOL CONTENT OF PALMAROSA OIL BY CHEMICAL METHODS

by

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ABSTRACT OF THE THESIS

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ABSTRACT

Palmarosa *Cymbopogon martinii* (Stampf) var *motia* is an important essential oil crop grown commercially in various states of peninsular India Palmarosa oil finds extensive use in flavouring cosmetics and toiletry The oil is valued for the principal constituent geraniol present in the oil to the extent of 75 82% Besides being a high grade perfume geraniol is the starting material for a number of synthetic aroma chemicals Next to geraniol the most abundant chemical component of the oil is geranyl esters predominantly geranyl acetate Most oils contain about 2 12% geranyl acetate Several factors like the genotype season harvest stage method of oil extraction etc influence the ratio of geraniol to geranyl acetate in the oil and it is found that a reciprocal relationship exists between the geraniol and geranyl acetate content of the oil At most times the geraniol content of palmarosa oil produced by cultivators fall short of requirements of the user industry The availability of an inexpensive and efficient method of hydrolytic conversion of geranyl acetate to geraniol will facilitate the farmer to undertake an on farm quality upgradation of his product which will fetch him better price A laboratory investigation was carried out at the Aromatic and Medicinal Plants Research Station Odakkali Kerala during 1994 96 to develop a method for upgrading the quality of palmarosa oil by the conversion of geranyl acetate in the oil to geraniol

Four treatments were tried for the hydrolysis of geranyl acetate with essential oil of palmarosa type ODP 3 as the test material viz methanolic sodium hydroxide methanolic sodium carbonate ammonia and aqueous sodium hydroxide

Mixing of essential oil with 5% methanolic NaOH reagent in the ratio of 1 4 and keeping undisturbed at ambient conditions for 30 min were the optimum conditions for the complete hydrolysis of geranyl acetate in the oil The product of reaction analysed 90 5% geraniol and the process yielded geraniol to the extent of 78 74% of the oil

taken for processing However treatment of the oil with methanolic sodium carbonate or ammonia did not result in hydrolysis of geranyl acetate

In the case of aqueous sodium hydroxide method of hydrolysis refluxing the essential oil with an equal volume of 20% aqueous NaOH solution for 30 min was optimum for the complete hydrolysis of geranyl acetate in the oil The product contained 89 35% geraniol and the quantity of geraniol yielded by the process was estimated at 86 67% of the oil taken for processing

Comparison of the methods of hydrolysis studied revealed that in terms of geraniol content of the product geraniol yield from the process and time required for the reaction the aqueous sodium hydroxide method was found to be the best The efficiency of the method for quality upgradation was tested on essential oils of different *Cymbopogon* types viz ODP 1 ODP 3 C 3 OD-455 and Jamrosa All the oils were characterised by low level of geraniol and high level of geranyl acetate and none of them conformed with ISI specifications for palmarosa oil In case of all the oils the treatment resulted in complete conversion of geranyl acetate to geraniol with commensurate increase in the level of geraniol bringing about a vast increase in their quality By the process oils of ODP 3 and Jamrosa were upgraded to meet the specifications for palmarosa oil

Verification of the sodium hydroxide hydrolysis method on pilot plant scale showed that it can be employed on large scale for the quality improvement of palmarosa oils which contain appreciable amount of geranyl acetate