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CITRUS OILS

Part-II. Gas Chromatographic Analysis of the Essential Oil of *Citrus limetta* Var. Mitha

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Steam distillation of the peels of *Citrus limetta* var. Mitha afforded an essential oil [1] in 0.014% yield. Gas chromatographic analysis of the oil revealed the presence of 32 components out of which 26 could be identified. Limonene (60.17%) was the most abundant terpene present in the oil followed by γ-terpinene (11.80%), terpinolene (2.96%), β-pinene (2.08%), linalool (1.85%), *p*-cymene (1.38%), geranial (1.33%), α- terpineol (1.28%). The rest of the terpenes were present in less than 1 %.

Key words: *Citrus limetta* var. Mitha, Rutaceae, Essential oils, Terpenes, Limonene.

Introduction

Citrus limetta Var. Mitha (sweet lime) (N.O. Rutaceae) is a small evergreen tree, chiefly cultivated for its valuable fruits [2]. It is a popular citrus fruit of the subcontinent. The origin of *C. limetta* is uncertain but a variety of sweet lime grows wild and semi-wild in certain parts of Mexico. Possibily it is hybrid [3] of lime similar to Mexican and a sweet lime like *Dorshapo* or a sweet citron like *Corsican*.

The juice of *C. limetta* is reckoned as curative in ailments of the rainy season including malarial fever. The juice is cooling and refreshing but on standing in the air develops bitterness due to the presence of unstable flavonoids. The fruit is green when picked up in Jul./Sept. Unlike other citrus fruits, the composition of the juice does not change much as the maturity advances i.e. it remains largely sweet throughout its development. The surface of the green peel contain oil sacs which yield a volatile oil on steam distillation or expression.

Peel oils of various citrus fruits such as oranges, lemons, lime, grape-fruit are used as flavours for various industrial products like beverages, squashes, candies, ice creams, bakery products and pharmaceuticals. These citrus oils are presently being imported [4] annually for well over Rs.30 million. The present studies are part of our programme [5] to evaluate the peel oils of the locally available citrus fruits for developing indigenous soures of these oils.

Experimental

Extraction of the oil. The fruit was purchased from the local market in late Aug. The juice of the fruit was reemed off and the peels without rags were cut into small pieces. The cut peels (300 g) were subjected to steam distillation for 4 hrs with live steam. The distillate was extracted twice with ether (2x100 ml). The organic extract was dried over anhydrous sodium sulphate which on removal of the solvent afforded a slightly pale oil (yield 0.014%).

The oil was split into hydrocarbon and oxygenated fractions with the help of column chromatorgaphy over silica gel (60-80 mesh) using hexane and hexane: ether (1:1) eluting solvents.

Analysis of the oil. The whole oil as well as its fractions were analysed with the help of gas chromatography using two types of capillary columns; CBPI and CBP 20 (length 2.5 m x 0.2 mm inner dia) hold up column temperature of 70° for 8 min. and then rise of temperature at the rate of 4°/min., final column temperature of 170°, injection port temperature of 250°. FID was the detector and hydrogen was used as the carrier gas under split injection system (Fig. 1). The composition of the essential oil is given in Table 1.

Discussion

Peel oil of *C. limetta* (sweet lime) was analysed by gas chromatography over 2 different polarity stationery phases; a non polar (CBPI) and a polar phase (CBP 20) in order to

TABLE 1. COMPOSITION OF THE ESSENTIAL OIL OF *CITRUS LIMETTA* VAR. MITHA BY GAS CHROMATOGRAPHY (GC GRAPH).

Component	Average value (%)	Component	Average value (%)
1. α-Thujene	0.10	14. Decanal	0.06
2. α-Pinene	0.89	15. Linalyl acetate	0.15
3. Camphene	0.12	16. Linalool	1.85
4. α-Fenchene	0.10	17. Caryophyllene	0.37
5. β-pinene	2.08	18. Terpinene-4-ol	0.03
6. Octanal	0.61	19. Citronellyl acetate	0.03
7. α-Phallendrene	0.18	20. Neral	0.64
8. α-Terpinene	0.11	21. α-terpinol	1.28
9. Limonene	60.17	22. Neryl acetate	0.46
10. γ-Terpinene	11.80	23. Geranial	1.33
11. *p*-Cymene	1.38	24. Geranyl acetate	0.30
12. Terpinolene	2.96	25. Nerol	0.15
13. Citronellal	0.10	26. Geraniol	0.13

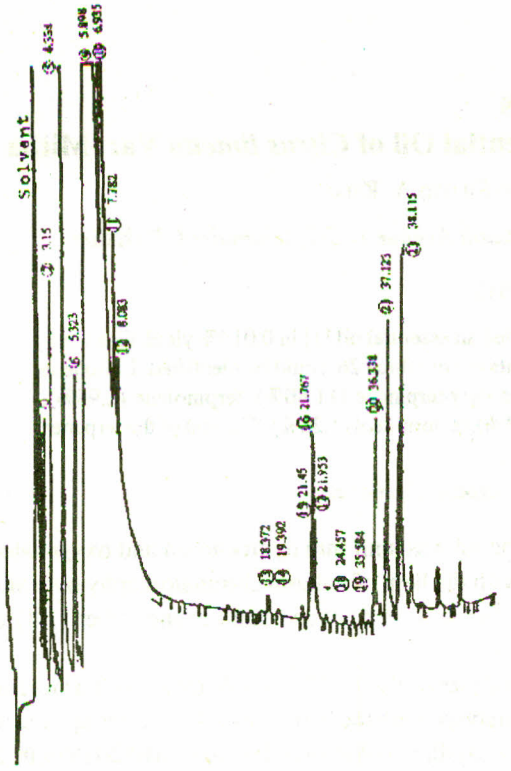

Fig. 1. *Citrus limetta* var. Mitha oil on CBP 20 column.

resolve various peaks. The whole oil as well as its hydrocarbon and oxygenated fractions were subjected to GC for detecting the various components. Retention time indices were used for identification of components and confirmation was made by coinjection of standard samples. The percentage composition of the essential oil was obtained with the help of linked computing integrator, Shimazu model C-R6A.

Limonene was the largest single hydrocarbon (60.17%) of the oil but it was present in lower quantities compared to its presence in other major citrus oils, where it ranges from 85-95%. It was more close to lemon oils (55-76%).

γ-terpinene (11.80%), terpinolene (2.96%), β-pinene (2.08%) and *p*-cymene (1.38%) were other hydrocarbons present in significant quantities. α-Thujene, α-pinene, camphene, α-phallendrene, α-terpinene and caryophyllene were present in less than 1%.

The terpene alcohols amounting to 3.44% that have been identified were; linalool, terpinene-4-ol, α-terpineol, nerol and geraniol. Among these, linalool (1.85%) was the major alcohol present in the oil followed by α-terpineol (1.28%). The rest were less than 1%.

The amount of aldehydes in citrus oils is very important to the oil quality and flavour. The total aldehydes present in sweet lime oil were 2.74%. Geranial (1.33%) was the major aldehyde followed by neral (0.64%), the 2 isomeric components of citral. Octanal (0.61%) and decanal (0.06%) were the aliphatic aldehydes present in the oil.

Other oxygenated compounds identified included citronellyl acetate (0.03%), neryl acetate (0.46%) and geranyl acetate (0.30%) with linalyl acetate in trace amounts.

From the results of the analysis, it can be concluded that the essential oil of the *Citrus limetta* var. 'Mitha' (sweet lime) differs from that of *Citrus limetta* var. Nimbu (acid lime) as to not only from the flavour point of view but also in quantitation of individual components. Amounts of β-pinene (2.08%), γ-terpinene (11.80%), geranial and neral (1.97%), geranyl acetate (0.30%) and neryl acetate (0.46%) present in the sweet lime oil make it more comparable to lemon oil and cold pressed lime oil [6].

References

1. Abdul Sattar, Shahid Mahmud and Shafiq A. Khan, Pak. j. sci. ind. res., **29**, 196 (1986).
2. E. Nasir and A. I. Ali, *Flora of West Pakistan* (Stewart Herbarium Gordon College, Rawalpindi, 1972), pp. 436.
3. E. Guenther, *The Essential Oils* (D. Van Nostrand, Co. Inc., New York, 1952), Vol. III, pp.332.
4. *Statistical Bulletin of Pakistan*, (Federal Bureau of Statistics, Govt. of Pakistan, 1989-90).
5. (a). Abdul Sattar, Shahid Mahmud and Shafiq A. Khan, J. Sci. Res., **16**, 25 (1987).
   (b). Shahid Mahmud and A. Sattar, Proceeding of the First National Symposium on Essential Oils, Perfumes and Flavours, March, (1989), pp.44-49.
   (c). A. Sattar, Shahid Mahmud and S. A. Khan, Pak. Pat. No.130331 (1988).
6. (a). J. F. Kefford and B. V. Chandler, *The Chemical Constituents of Citrus Fruits* (Academic Press, New York, 1970), pp.85.
   (b). Philip E. Shaw, J. Agric. Fd. Chem., 27, 246 (1979).