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CITRUS OILS

Part I. Composition of the Monoterpenes of the Peel Oils of Oranges, Kinnows and Lemons

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Peel oils of oranges, kinnows and lemons of Pakistani origin were analysed. The yield of oils on the basis of peels were 0.43, 0.68 and 0.53% and the monoterpene fractions of the oils were 91.89, 91.29 and 89.11% respectively. The GLC analysis of the monoterpene fractions showed limonene to be the predominant constituent occurring to the extent of 94.21, 95.41 and 81.20% respectively. The other monoterpenes present in small quantities were α-pinene, β-pinene, sabinene, myrcene γ-terpinene, *p*-cymene and terpinolene.

INTRODUCTION

A variety of citrus fruits, such as oranges, kinnows and lemons (N.O. Rutaceae) are available in Pakistan. The fruits are generally processed for fruit juices and squashes and their peels which are a by-product/waste of the citrus processing industry, are sources for various essential citrus oils [1]. The peel oils of these fruits are widely used as flavours alone or in combination with other oils in beverages, ice creams, baked foods, pharmaceutical emulsions, confectionery and other such products. These essential oils are popular for their pleasant and refreshing odours.

Among the citrus oils, orange, lemon and lime peel oils are produced and traded on large scale in world market. In Pakistan orange and lemon oils are produced on a limited scale by the citrus processing industry. Locally produced orange oil is used only in substandard products but for quality products. Terpeneless orange oil is imported. All these citrus oils are being imported presently and their annual direct import runs into over Rs. 25 millions. These are also being imported indirectly for millions of rupees as beverage concentrates, ice cream mixes and other allied products, where these are important ingredients.

Although extensive research work has been carried out on the citrus oils in the outside world [2], no serious research and development studies have been undertaken in Pakistan. Our country is rich with respect to citrus fruits and this availability can be enhanced manifold provided industrial utilisation of these fruits is shown. Recently a process has been developed on pilot plant scale as an ADP project in the PCSIR Lahore for the deterpenation of the locally produced orange oil.

The present studies are a part of a systematic programme whereby the physical and chemical properties of the oils obtained from the local citrus fruits are being examined with a view to producing them locally and reducing or completely stopping their direct or indirect imports. This communication describes the physico-chemical characteristics of the essential oils from the fruit peels of oranges, kinnows and lemons along with the oil yield. The terpene fractions of the three oils are also described and their composition on the basis of determination given.

EXPERIMENTAL

Extraction of peel oils. About 2 kg peels of a citrus fruit were crushed finely and the semi-solid material was transferred along with washings with two litres of water to a 5-litre flask. The whole mass was subjected to steam distillation for 4 hrs. The oily layer was separated from the distillate and the aqueous layer was extracted twice with pure hexane (2 x 100 ml). The extracts and the oily layer were combined and dried over anhydrous sodium sulphate. Most of the solvent was distilled from the extract on a water bath and last traces were removed at low temperature under vacuum. The residue gave the oil from the peels. The percentage yield of oils from different fruits has been reported in Table 1.

Separation of the monoterpenes. The oils, one g. each, were separately absorbed on active silica gel (50 g) and eluted with hexane (200 ml). The combined hexane extracts were freed from the solvent by rotary evaporator to yield oily residues. TLC examination of these residues showed that they were single spot materials. The columns

were later eluted with ether to yield the oxygenated fractions which are being investigated.

Analysis of the monoterpene fractions. The monoterpene fractions were analysed on a Pye Unicam 204 model gas chromatograph using flame ionisation detector (FID). Two different types of GLC packed columns, 1.5 m long x 4 mm dia were tried; 5% SE-30 on 80-100 mesh celite support and 15% OV-275 on chromosorb in order to resolve the different peaks. The retention times of various peaks in the mixture were compared with those of standard commercial monoterpenes and also by their conection with the monoterpene fractions. The GLC operating conditions were: injection port temperature, 140°; detector temperature, 150°; flow rate of nitrogen as carrier gas, 40 ml/min; column temperature for SE-30, 75° and for OV-275 it was 110°

DISCUSSION

The peels of locally available varieties of citrus fruits, oranges (*Citrus sinensis*), kinnows (a hybrid) and lemons (*Citrus lemon*), were investigated for their essential oils. These fruits were purchased from the local market in their high season (March/April) when fully mature. Their peel oils were extracted and examined according to standard methods [3]. The percentage yield of oils on the basis of peels and the physical and chemical properties of these oils are reported in Table 1. The aldehyde values of orange and kinnow peel oils were calculated as decylaldehyde and that of lemon oil was based on citral. The physical and chemical values of these oils were comparable [4], with good quality citrus oils of their respective category.

The IR spectra of the peel oils were recorded and all of these showed identical absorptions at 2910, 2850, 1640, 1440, 1380, 1160, 910, 890 and 810 cm^{-1}.

The oils were separated into monoterpenes and oxygenated terpenoid fractions through their column chromatography on active silica gel. The hexane elution of the column gave the monoterpenes of the oils leaving behind the oxygenated components absorbed on the column. These were later removed by eluting the column with diethyl ether. The yields of monoterpene portion of the oil of oranges, kinnows and lemons were 91.89, 91.29 and 89.11% respectively. (Table 2).

The composition of the monoterpene fractions of the oils were found by gas chromatography. Two different types of GLC columns, SE-30 and OV-275, were used for the resolution of the different peaks. The retention times of various peaks in the mixture were compared with peaks obtained from authentic samples of individual compounds. Co-injection of individual monoterpenes with the terpene mixture was also carried out in order to confirm the presence or absence of a component.

The chemical composition of the monoterpene fraction of the various oils is reported in Table 2. It is evident from analysis that limonene was the predominant monoterpene and it occurred in more than 90% in the monoterpene fraction of orange and kinnow oils. The percentage of limonene in lemon oil was, however, well below the 90% mark as compared to other citrus oils, although the total monoterpene fraction of the oil was nearly 90%. The second major monoterpene in lemon oil was γ-terpinene (9.27%) followed by β-pinene (4.87%). The other more common but minor in amount momoterpenes present in all the oils were γ-pinene, sabinene, β-pinene, γ-terpine, *p*-cymene and terpinolene.

Table 1. Physico-chemical properties of citrus oils.

Properties	Oranges	Kinnows	Lemons
Yield (%)	0.43	0.68	0.53
Colour	Light yellow	Dark yellow	Pale yellow
Specific gravity at 28°	0.842	0.847	0.850
Ref. Index at 28°	1.4714	1.4734	1.4720
Acid value (%)	2.24	3.34	1.68
Aldehyde value (%)	0.58	0.81	1.87

Table 2. Percentage composition of the monoterpene hydrocarbon fraction of the peel oils.

Monoterpenes	Oranges	Kinnows	Lemons
Monoterpene fraction	91.89	91.29	89.11
α-Pinene	0.02	0.20	0.13
Camphene	0.32	0.34	0.98
β-pinene	0.52	0.09	4.87
Sabinene	1.11	0.23	–
Myrcene	3.10	1.42	1.53
Limonene	94.21	95.41	81.20
γ-terpinene	–	1.31	9.27
p-cymene	–	–	1.27
Terpinolene	–	0.72	0.25

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