DETERPENATION OF PAKISTANI LEMON AND ORANGE OILS

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Various processes for the deterpenation of Pakistani lemon and orange oils have been studied with regard to their efficiency. Silica gel and fuller's earth as adsorbents have been found most efficient. It has been shown that the deterpenation of the oils is quite feasible and about 4% of the more valuable oxygenated products can be recovered.

Citrus fruits consisting of lemon, orange, grape fruit and lime are available in both East and West Pakistan. It has been estimated that the total quantity of the fruit produced including lemon and orange alone, in West Pakistan was about 1,12,990 tons in 1953.[1] Industrial production of citrus products such as juice, concentrates, marmalades, jellies, pectins and essential oils is being carried out at one or two places. Most of the fruit is consumed locally and so far no substantial industry based on the utilization of citrus fruit wastes and/or by-product exists in the country.

The fruit is rather a valuable commodity of considerable commercial importance, particularly for Pakistan which has a great potential for the production of citrus fruits. On the evidence that our major citrus fruit yields about 4 % of essential oils, it is calculated that 10,16,960 lbs. of lemon oil and 91,06,944 lbs. of orange oil can be produced in the country.[1] Although essential oils find extensive application in various industries as such yet their further preferred part is the one which constitutes oxygenated compounds. This fraction is the principal odour carrier and contains open chain alcohols, aldehydes, ketones, esters and terpene alcohols, such as D-α-terpineol. Different citrus oils contain different quantities of these oxygenated products and their composition is also variable. But, by and large, the oils contain about 4% of oxygenated components. The rest of the oils consists of terpenes and sesquiterpenes mainly.

The importance of the oxygenated fraction can be judged from the fact, that whereas, on the average, one pound of the oil costs from Rs. 10 to 15 in Pakistan, the price of the fraction free from the relatively less important terpenes varies[2] from Rs. 165.6 to 324.9 [3] in the U. K.

The oil freed from the oxygenated compunds mainly contains terpene hydrocarbons, in which limonene predominates to the extent of 90%. Limonene, after the removal of the oxygenated components from the oils can still be employed for perfuming cosmetics and pharmaceuticals.[4] Furthermore, limonene can also be used for the production of terpinyl acetate, when its equimolecular quantities are reacted upon with acetic acid in the presence of certain clays as a condensing agent.[5]

The process for the removal of the terpenes and sesquiterpenes and less important materials from the oils is referred to as 'deterpenation'. The process is valuable because not only it yields terpeneless and sesquiterpeneless highly priced oxygenated fraction but also because the removal of the terpenes from the main bulk of the oil, renders a substantial decrease in the volume of the oil with the result that transport and freight charges for export purposes are far less. In veiw of Pakistan's large potential for the production of citrus essential oils, the development of deterpenation process, largely based on the indigenous deterpenating agents, was, therefore, considered of vital importance from the commercial point of view.

Our studies show that the deterpenation of citrus essential oils is quite feasible in the country as the materials required for the process are easily available.

In the present investigations the separation of oxygenated constituents has been tried by different techniques such as fractional distillation under reduced pressure, liquid-liquid extraction[6] and adsorption.[7] In the adsorption method, different adsorbents such as cellulose, starch, sucrose, glucose, silica gel, anhydrous calcium chloride and fuller's earth have been tried.

These studies have revealed that the complete deterpenation of the oils is best accomplished by adsorption of the oxygenated compounds on silica gel and fuller's earth. However, for the sake of comparison, other absorbents have also been studied.

Deterpenation of the oils was assessed by determining the percentage of alcohols, aldehydes, ester numbers and the refractive indices of the oils from which the oxygenated constituents had been removed.[8]

Method

Materials.—Orange and lemon oils were procured from Mitchell's Fruit Farm, Renala, Khurd, District Montgomery. Silica gel was made from sodium silicate which is available locally. Ethyl alcohol was of commercial quality. Petroleum ether of commercial quality was secured from Burmah Shell. Other reagents used for analysis are already listed in analytical methods discussed by Guenther.[8]

Deterpenation of Citrus Oils by Adsorption Method.—Seventy-eight g. active granulated silica gel (100 mesh) was made into a slurry with pure *n*-hexane. The slurry was poured into a column, which had 45 mm. length and 3.5 mm. diameter. A slight suction was applied from below and the slurry was allowed to settle uniformly. When the excess of *n*-hexane was removed from the adsorbent, 40 g. of the citrus oil was passed through the column and drawn over the adsorbent by washing with *n*-hexane. Various fractions of the eluate were tested for hydrocarbons by taking them over chromatostrips and applying the fluorescein bromine test.[9] The column was washed with 250 ml. of *n*-hexane in all, which removed all the hydrocarbons. As soon as the eluate gave negative tests for hydrocarbons, the *n*-hexane was replaced on the top of the column by ethyl acetate. Development with ethyl acetate was continued till the eluate gave negative fluorescein bromine test. For complete elution of oxygenated components, 250 ml. of ethyl acetate were used. The ethyl acetate was removed from the oxygenated components by evaporating the solvent at room temperature under diminished pressure. After the complete removal of ethyl acetate, 3.9% of the oxygenated constituents were obtained.

The results of the adsorptive capacity of different adsorbents for oxygenated components are summarised in Table 1.

Discussion and Conclusion

Lemon and orange oils from Mitchell's Fruit Farm (Renala, Khurd) have been found to contain about 4% of oxygenated constituents. The rest of the oils contains hydrocarbons in which limonene predominates to the extent of 90%. Free acids, coumarin derivatives, camphene and α- pinene have been detected in small amounts in lemon and orange oils.

It has also been found (Table 2) in these investigations that the required valuable oxygenated constituents can be obtained in concentrated form when lemon and orange oils are fractionated at low temperature and under reduced pressure. But it has been noticed that the application of heat during fractionation of lemon and orange oils has a deleterious effect on the flavour and odour of the oils. Furthermore, because of the complicated nature of the oil components and their similarity of boiling points, the terpenes are not removed quantitatively. On the other hand, as is evident from the study of Table 2, some of the oxygenated compounds are also removed during fractional distillation. The concen-

TABLE 1.—PHYSICO-CHEMICAL CHARACTERISTICS OF ORANGE AND LEMON OILS BEFORE AND AFTER PASSING THROUGH DIFFERENT ADSORBENTS.

Values	Oils	Oils as such	Adsorbents							
			Cellulose	Starch	Sucrose	Glucose	Silica gel	Activated charcoal	Anhydrous $CaCl_2$	Fuller's earth
Ester No. ..	Orange	11.5	3.8	7.9	1.3	4.26	0.0	8.3	2.7	0.0
	Lemon	16.19	4.14	8.2	8.6	2.04	0.0	11.66	8.6	0.0
% of aldehyde calculated as citral ..	Orange	0.56	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Lemon	0.64	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
% of primary alcohol calculated as geraniol	Orange	0.61	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Lemon	0.71	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Refractive index at 34.0 C. ..	Orange	1.5300	1.3163	1.3164	1.3163	1.3157	1.3200	1.3160	1.3166	1.3152
	Lemon	1.4645	1.4628	1.4632	1.4649	1.4600	1.4630	1.4610	1.4605	1.4643

TABLE 2.—PHYSICO-CHEMICAL VALUES OF FRACTIONS OF ORANGE AND LEMON OILS OBTAINED AFTER DISTILLATION THROUGH YOUNG AND THOMAS COLUMN.

Oils	Fractions	Ester No.	% of aldehyde calculated as citral	% of primary alcohol calculated as geraniol	Refractive index at 33.5°C.
Orange ..	Ist at 84-85°C./44 mm. ..	0.417	0.036	0.609	1.4649
	2nd at 90–91°C./49 mm. ..	16.6	1.52	0.062	1.4706
	Residue ..	45.4	1.81	0.66	1.4747
Lemon ..	1st at 99-100°C./118 mm.	4.14	0.05	0.0	1.4629
	2nd at 98-100°C./55 mm. ..	2.1	0.061	0.89	1.4634
	Residue	28.3	0.59	6.51	1.4682

trated oils so obtained do not have the same refreshing and pleasant odour as the original oils.

The finest quality of oxygenated compounds were, however, obtained by the liquid-liquid extraction method,[10] (using 50-70°C. petroleum ether and 70% ethyl alcohol) although the yield recorded is only 2%. These compounds resemble the natural peels in olfactory characteristics.

The highest percentage of oxygenated constituents was best obtained by adsorption of the oxygenated components on silica gel and fuller's earth. It was observed that silica gel and fuller's earth adsorb all the oxygenated constituents from lemon and orange oils, including oxygenated compounds of coumarin type. The yield of these terpene- and sesquiterpene-free constituents without the inclusion of coumarin derivatives was 4%.

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