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CHEMICAL EXAMINATION OF CUTICLE WAX OF ORANGE AND KINNOW FRUITS

Part I. Analysis of the Saponifiable Fraction

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Saponifiable matter of the cuticle wax from oranges and kinnow fruit peels has been analysed for its fatty acid composition. The constituent fatty acids vary from C_{12} to C_{24} with unsaturated acids ranging from 40 to 60 % of the total saponifiable matter. The neutral fraction of the wax is under examination.

INTRODUCTION

Oranges, Kinnow and Lemons are processed in the country for making beverages, squashes and many other food products. The essential oils from the peels of these fruits are the major by-products of the industry. In the process of extraction of the essential oil, the cuticle wax from the peels gets dissolved in the oil and becomes an impurity. In order to use these citrus oils as flavour in various food products the major portion of terpene hydrocarbons and dissolved wax need be removed from the oils. A process has been developed in these laboratories to dewax and deterpenate[1] the orange and kinnow oils. In the process, a dark brown jelly like residue is obtained which can be processed and clarified to a pale yellow soft wax. Some 7 to 8 tons of this soft wax can be obtained from the deterpenation of the available orange and kinnow oils annually which can find application in cosmetics, fruit-coating emulsions, and other wax compositions[2]. Chemical examination of this cuticle wax was undertaken with a view to studying its composition so that this by-product could be better utilized. The present communication describes the results so far obtained from the saponifiable fraction of the wax.

EXPERIMENTAL

Isolation of the Cuticle Wax From

i) *Commercial citrus oils.* 1 kg of the cold pressed commercial citrus oils (orange or kinnow essential oil) supplied by a local beverage industry was thoroughly steam distilled to remove all of the volatile material. The steam non-volatile residue was taken up in 100 ml of hexane and water was removed in a separating funnel. The organic layer was dried over anhydrous sodium sulphate and the solvent was removed under vacuum. A dark brown thick liquid was obtained. This material was used without further purification.

ii) *Peels.* 1 kg each of fresh kinnow and orange peels were broken in a shredding machine. The finely divided peels were packed in a wide glass column which was eluted with hexane (3x300 ml). The solvent was removed and the residue was steam distilled to remove the volatile oil. The resultant pale yellow viscous liquid was used for further analysis.

Saponification[3]. 1 g of the wax in 10 ml benzene and 20 ml 1 N methanolic potassium hydroxide was refluxed over a water bath for 3 hr. The mixture was diluted with 120 ml water and extracted with ether (5x25 ml). The ethereal extract was dried over anhydrous sodium sulphate and the solvent removed under vacuum to yield an unsaponifiable portion of the wax.

The alkaline layer was acidified with hydrochloric acid and the acid fraction was extracted with diethyl ether (5x30 ml). The organic layer was dried and the solvent removed to obtain the saponifiable fraction.

Esterification[4]. The acid fraction was dissolved in 20 ml of methanol and few drops of conc sulphuric acid were added to the solution. The mixture was refluxed on a water bath for 4 hr and then diluted with water (100 ml). The reaction product was extracted with ether (3x30 ml). The ether extract was passed through a short column of anhydrous sodium carbonate and sodium sulphate (1:10) and the solvent removed to obtain the ester fraction.

Identification of Methyl Esters. The methyl ester fraction was analysed on a GLC column of 10 % PEGS, operating at 200° and nitrogen flow rate of 40 ml/min with flame ionization detector heated to 250° against the standard methyl esters.

RESULTS AND DISCUSSION

Although orange and kinnow fruits contain small amounts of cuticle wax (Table 1) and its recovery as such is not an economic proposition yet deterpenation leads to the accumulation of substantial quantities of this wax.

Recovery and utilization of this wax thus can become feasible as a part of the deterpenation process.

The fatty acid composition of the cuticle wax from oranges and kinnows is given in Table 2. It is seen from the Table that there is an even distribution of all the commonly occurring fatty acids in nature. Wax of oranges contain C_{16} as the major fatty acid with $C_{18:1}$, $C_{18:2}$, $C_{18:3}$ and $C_{22:1}$ also occurring significantly. Kinnow wax contains $C_{22:1}$ as the major acid with C_{14} and unsaturated C_{18} acids following up. Because of the high percentage of the unsaturated fatty acids in orange wax (53.4 %, 41.4 %) and kinnows wax 60.1 %, 52.5 %), these are liquid in nature. $C_{22:0}$ acid is absent in orange wax while C_{12} acid is absent in the kinnow wax. The presence of high percentage of saponifiable matter in the wax (Table 1) of oranges and kinnows points out to the good quality of these vegetable waxes which have the potential of being utilized in food, cosmetic and polish industries.

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Table 1. Orange and kinnow wax

Wax of		Yield %	Saponifiable matter %	Unsaponiciable matter %	Unsaturated fatty acids %
Orange	Oil	2.37	47.1	49.8	41.4
	Peels	0.04	54.8	44.0	53.4
Kinnow	Oil	2.82	40.1	55.7	52.5
	Peels	0.06	48.3	50.4	60.1

Table 2. Composition of fatty acids (saponifiable portion) present in the cuticle waxes.

Acid	Oranges		Kinnows	
	Oil	Peels	Oil	Peels
C_{12}	–	5.5	–	–
C_{14}	19.1	4.1	16.5	12.2
C_{16}	16.2	22.2	12.3	9.5
$C_{16:1}$	–	8.6	9.8	9.2
$C_{18:0}$	11.7	7.6	10.9	9.9
$C_{18:1}$	11.5	11.0	9.2	9.5
$C_{18:2}$	9.1	11.4	10.1	11.0
$C_{18:3}$	5.9	8.0	9.2	10.3
$C_{22:2}$	–	–	2.6	4.5
$C_{22:1}$	10.1	14.4	14.2	20.1
$C_{24:0}$	11.0	6.7	4.5	3.7
$C_{24:1}$	4.8	–	–	–

supply of orange and kinnow peel oils for these studies.

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