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CAROTENOIDS CONTENT OF CITRUS FRUITS

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Carotenoid content of peels, flesh and juices of eight citrus fruits have been determined. Feutrell's Early has been found to be the richest source. Higher percentage of carotenoids resides in the peels than in the flesh, which contains carotenes either in equal or greater amounts than the former. Peels posses more saponifiable carotenoids (xanthophyll esters) than flesh. The distinct redder appearance of red blood is due to pigments other than carotenoids as its carotenoid content is less than that of others. The spectra of the carotenoids of peels and flesh of all varieties except lemon and grape-fruit are similar but different from those of pure β-carotene.

Investigations on the carotenoid content of green plants, dehydration of alfalfa and preparation of carotenoid and chlorophyll concentrates have been reported earlier.[1–3] The yellow-orange colour of citrus fruits[4–7] is also due to carotenoids. Many of these compounds, in addition to being useful and desirable food colours, are precursors of vitamin A. Pakistan produces about 4.7 lakh tons of citrus fruits per year.[8] Citrus peels—an industrial waste—may be a rich source of carotenoids, pectin and oil due to their abundant availability. It was, therefore, considered advisable to study the carotenoid content of different indigenous citrus varieties, with a view to utilizing the citrus peels for the production of carotenoid concentrate for its use as colouring, flavouring and vitamin A fortification of foods. No attempt was made to separate and identify the carotenoids here.

Experimental

Material and Apparatus

Commercial solvents such as deactivated alumina (Merck)[1] were used. Beckman DK2A and Unicam spectrophotometers were employed.

Procedure

Fruits purchased locally were hand-peeled, and peels and flesh (pulp) were worked up separately. Peels were chopped and thoroughly mixed to make a composite sample. Similarly, a composite sample was prepared from flesh. Juice was extracted with juice extractor from the flesh of different fruits and filtered through a two-fold muslin cloth separately. A definite weight (10 g) of each of peels, flesh and juice was extracted with 1:1 mixture of petroleum ether and acetone. Carotenoids and carotenes were estimated in terms of β-carotene as described earlier.[3] Carotenoid concentrate can be prepared by removing the solvent under reduced pressure. The results have been recorded in Table 1. The spectra of the total carotenoid solutions of peels and flesh of kinow, lemon, grape-fruit and β-carotene have been recorded in Fig. 1.

Flourescence Studies.—The fluorescence was observed under UV light by chromatographing the total carotenoid solution on alumina column using light petroleum as the eluent.

Partition Test.—Measured volume (25 ml) of total carotenoid solution was shaken with an equal volume of 90% methanol in a separating funnel. Epiphasic layer was washed with 90% methanol until no further pigments were extracted.

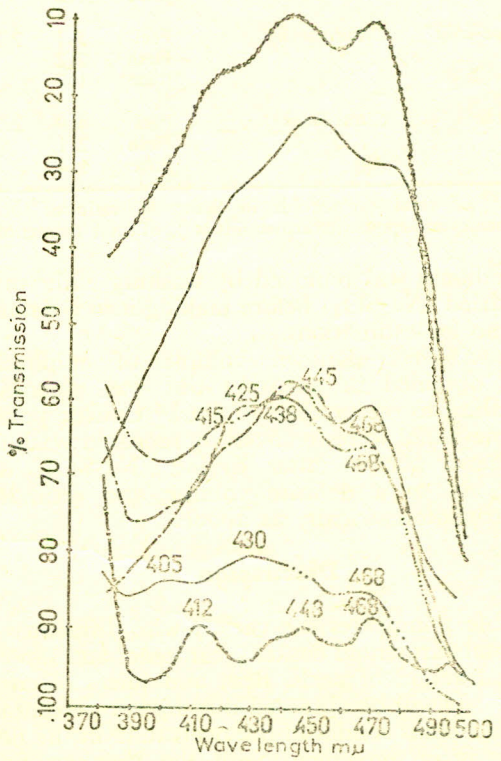

Fig. 1.—β Carotene; – – – –Kinow pulp—●—●—●—Kinow peels:— . — . — Grape-fruit peels; — . . — Lemon pulp; —. . . — . . . — Lemon peels.

TABLE 1.—CAROTENOID CONTENT OF SOME CITRUS FRUITS ESTIMATED IN TERMS OF β-CAROTENE.

Common name	Botanical name	Protein	Total carotenoids before chromatography			Carotenes after chromatography mg/kg			Carotene in epiphase after partition test mg/kg		Carotenoids after saponification mg/kg	Saponifiable carotenoids mg/kg	
			mg/kg	*R*	*P*	*M*	*R*	*S*	X	S	Y	(X-Y)	*R*
Mandarins	*Citrus reticulata*												
Feutrell's Early	var. Feutrell's Early	Peel	180.0	2.8		102.0		57.0	144.0	80	98	46	5.8
		Flesh	64.0			40.0	3.9	62.5	52.0	81	44	8	
		Juice	43.0		67.0	28.0		65.0	35.0	81	26	9	
Kinow	,, Kinow	Peel	137.0	2.8		70.0	2.5	51.0	115.0	84	95	20	6.6
		Flesh	48.0			28.0		58.0	33.0	69	30	3	
		Juice	30.0		62.5	17.0		57.0	23.0	77	19	4	
Sangtara	,, Sangtara	Peel	118.0			57.0		48.0	95.0	80	79	16	8.0
		Flesh	42.0	2.8		29.0	2.0	69.0	32.0	76	20	12	
		Juice	28.0		66.6	16.0		57.0	23.0	82	20	3	
Sweet oranges	*Citrus sinesis*												
Blood-red	var. blood-red	Peel	73.0	7.0		38.0	7.2	52.0	70.0	95	62	8	4.7
		Flesh	10.0			5.3		50.0	6.7	65	5	1.7	
		Juice	7.2		68.0	3.8		53.0	5.4	75	4	1.4	
Mosambi	,, Mosambi	Peel	162.0	8.4		92.0	6.1	57.0	125.0	77	102	23	11.5
		Flesh	16.2		87.0	15.0		78.0	17.1	90	15.1	2.0	
		Juice	16.8			14.2		84.0	15.6	92	15.0	0.6	
Valencia late	,, Valencia late	Peel	160.0	8.0		85.0	7.6	56.0	109	68	89	20	11.0
		Flesh	20.0			11.2		53.0	15.0	72	13.2	1.8	
		Juice	17.0		81.0	8.8		52.0	11.0	65	10.0	1.0	
Grape-fruit	*Citrus paradisi*	Peel	5.1	2.3		2.4		41.0	4.1	80	3.3	.8	—
		Flesh	2.2			0.9		47.0	1.6	73	—	—	—
		Juice	1.7		77.0	0.8		47.0	1.1	65	—	—	
Lemon	*Citrus limon*	Peel	4.9	2.3		2.0	2.2	41.0	3.2	65	2.4	.8	2.0
		Flesh	2.1			0.9		43.0	1.8	85	1.4	.4	2.0
		Juice	1.4		61.6	0.6		43.0	1.2	76	0.9	.3	

P, % of total carotenoids in flesh; *R*, ratio of total carotenoids / carotenes and saponifiable carotenoids in peels and flesh; *S*, carotenes and epiphasic carotenoids as % of total carotenoids.

Methanol was removed by washing with water and dried (Na_2SO_4) before making into a definite volume for estimations.

Saponification.—Known volume of epiphasic layer obtained in partition test was saponified according to the method of Curl.[6] Caustic potash and methanol were removed by repeated washing. Epiphasic portion after drying (Na_2SO_4) was made up to a definite volume and estimated spectrophotometrically as above.

Discussion

Table 1 indicates the variety-wise difference in the total carotenoid content, carotenes and saponifiable fraction of peels, flesh and juices of citrus fruits. It will be observed that higher percentage of carotenoids resides in the peels than in the flesh which is in agreement with the previous findings.[5,6] It is interesting to note that the ratio of total carotenoids in peels and flesh of kinow, Feutrell's Early, sangtara, grape-fruit and lemon is 2.3–2.8 while in others it varies from 7.0–8.4. In case of carotenes this ratio varies from 6 to 7.6 in red blood, mosambi and valencia while in others it varies from 2 to 3.9. Extraction of carotenoids in the juices of different citrus fruits varies from 62 to 88% of the total carotenoids in the flesh and the rest is retained in the rag.*

Feutrell's Early has been found to be the richest in total carotenoids, carotenes and saponifiable carotenoids. Although the peels of all the fruits are richer in carotenoids than their respective flesh and juice but flesh and juice contain higher percentage of carotenes than the former with the exception of red blood malta and grape-fruit. Both flesh and juice of mosambi are the richest in carotenes containing 78 and 84% respectively of the total carotenoids.

The flesh of red blood variety is distinctly redder in appearance but the carotenoid content of its peels and flesh is less than that of others with the

exception of grape-fruit and lemon. It signifies that its deeper colour is due to pigments other than carotenoids. Table 1 shows that higher percentage of total carotenoids consists of xanthophylls soluble in 90% methanol in all the portions of the fruits varying from 65 to 95% of the total carotenoids in case of peels. The difference between the values of columns X and M indicates the amount of oxygenated derivatives of carotenes which are retained in the epiphase.

The difference between columns X and Y (Table 1) represents the amount of saponifiable carotenoids (xanthophyll esters). These are hydrolysed to yield the corresponding xanthophylls and fatty acids which are extracted into the methanolic hypophase during repeated washing with water. It is stated here that alkali-liable carotenoids like astaxanthin and fucoxanthin are destroyed by saponification. It would be observed that peels contain greater amounts of these compounds than the flesh, and Feutrell's Early is the richest source. The ratio of saponifiable carotenoids in the peels and flesh of first four fruits varies from 4.7 to 8. This ratio is quite high (11–11.5) in mosambi and valencia while in lemon it is 2.

The spectra of total carotenoids of peels and flesh of all the varieties except lemon and grape-fruit, are similar and differ from that of pure β-carotene as shown in Fig. 1. Spectra of kinow are recorded as a specimen. It may be, therefore, inferred that similar type of carotenoids are present both in peels and flesh of these varieties. The position of maxima shows the presence of more saturated or less polar carotenes than β-carotene as the major constituents.

The spectra of peels and flesh of lemon and grape-fruit are different and, unlike other varieties, show decrease in % transmission after about 390 nm showing thereby, the presence of some compounds which absorb in the UV region. Fluorescence studies on the column has revealed the presence of two compounds of similar fluorescence (bluish-green) in all the fruits. One is mobile and moves ahead of β-carotene while the other is retained on the top. Lemon and grape-fruit also contain another fluorescent compound (blue) which is mobile and occupies the central position. The decrease in % transmission may be due to this compound.

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