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Natural Colorants From Samani Date Processing Wastes

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THIS study was performed to extract, identify and determine the residual natural pigments in samani date processing wastes after manufacturing of date jam. The aim of this study is also extended to investigate the possibility of utilization of the separated natural pigments in coloring some well known candy like products such as Lolita which are very famous among children in Egypt.

The results revealed that carotenoids were the predominant pigments in samani date wastes. The carotenoids content was about 5.84% (on dry weight basis). The fractionation and identification studies revealed about nine components in the separated carotenoids including lycopene, β-carotene, β-Cryptoxanthin, Canxanthin, Antheraxanthin, Zeaxanthin, Echineone, Violaxanthin, and Lutein. It was also ascertained that it may be applicable to utilize the separated natural carotenoids in coloring the Lolita product. The product color was stable during storage of such product up to forty five days.

Keywords: Natural colorants, Samani date wastes, Carotenoids, Extraction and identification, Children candy, Shelf life.

Samani date is considered one of the most popular date varieties grown and consumed in Egypt. Wherein, it is consumed in both fresh and processed forms. Samani date jam is very popular product among consumers, especially children. The remainder wastes of Samani date after processing to jam represent about 30 - 35% of the whole dates. These wastes include peels, fibers and some pulp. Recently, they possessed considerable interests in the recovery and utilization of natural pigments as food colorants and antioxidants rather than dependence on synthetic ones which have been proven to be harmful to human health. Smith, (1981); Richardson and Cowan, (1995); Alan, (1996); and Miller *et al.*, (1996) reported that carotenoids played a very important role as antioxidant due to their conjugated double bonds. On the other hand, Swchartz, (1998) demonstrated that natural carotenoids were very successful when utilized as natural colorants in different food products. Nir and Hartal (1995) stated that carotenoids may have a very significant role in protecting the body against oxidizing agents, mutagens and carcinogens.

This study was designed to investigate the feasibility of separation of natural pigments from large quantities of Samani date processing wastes with an economic procedure. Moreover, studying the possibility of utilization of those separated and identified pigments as natural colorants and natural antioxidants instead of artificial colorants which proved to be not completely safe to human being especially children whom are the predominant consumers of the food products colored with such harmful artificial colorants.

Material and Methods

Materials

Source and preparation of samani date processing wastes

Samani date (*Phoenix dactylifera L.*) processing wastes, including peels, fibers and some pulp, were obtained, during September 2001, from the pilot plant of the Food Technology Res. Institute, Agric. Res. Center in Giza. These wastes were dried at 40°C in a forced air drying oven, then stored at room temperature (25°C +5°C) for further usage.

Analytical methods

Isolation of Natural pigments

The natural colorants of the dehydrated waste materials were extracted (by diethyl ether), concentrated and purified (saponificated and steam distillated) according to the method of Ting and Hendrickson (1969).

Determination of the total carotenoids content

Total carotenoids content of the natural pigments from samani date processed wastes were determined as described by Ranganna (1977). Total carotenoids were extracted by dissolving an aliquot (about 10 g) of dried samani processed wastes in a volume of diethyl ether till complete extraction (no color was in the eluted extractor). The extraction was filtrated, then exactly completed to 50 ml with diethyl ether. The absorbance (A) was measured at 420 nm, which is the optimum wavelength for carotenoids. The moisture content of the aforementioned wastes was determined according to AOAC (1990).

The identification of pigment

1) Spectrophotometric identification method

An Ultraviolet/Visible spectrophotometer, Unican SP 1800 model, was used for the identification of the separated natural pigments. The absorbance (A) was measured at wavelengths range of 400 to 530 nm., which is the optimum wavelength for carotenoids absorption, with an interval of 5 nm.

2) Thin layer chromatographic (TLC) identification method

Fractions of the separated natural pigments were identified using the thin layer chromatography technique as described by Davies (1976). Two TLC adsorbent and solvent systems were applied, *i.e.*, (1) Ca $(OH)_2$: Silica gel G (6:1) adsorbent and petroleum ether: benzene (98:2) solvents, and (2) activated silica gel adsorbent and benzene : ethyl acetate : methanol (75:20:5) solvent

system. The tested sample was identified through R_f values compared to the standard materials as reported by Davies (1976).

Utilization of the separated pigments in coloring specified children candies

Lolita is a very famous candy consumed by a lot of Egyptian children. The ingredients of the experimental candy were: one liter water, 500 g sugar (sucrose), citric acid (in order to adjust the pH value to 4) and a varied amount (0.5, 1.0 or 1.5 g/100 ml) of natural colorant crude extract from samani date processing wastes. The Lolita candy was produced by mixing the sugar with water until the sugar was completely dissolved. Citric acid was added to adjust the pH value of the mixture to about 4, and the tested amount of the colorant, which was suspended on soluble starch as a carrier, was added to the mixture. The prepared solution was pasteurized at 76.5°C for 30 sec., according to the method adopted by Rothschild *et al.*, (1975) and the color index of the resulted product was recorded. The solution was then packaged in cellophane pouches. A control sample of Lolita was prepared by using the artificial coloring material (1.5 g tartarzine/100 ml mixture) ,which is a yellow coloring agent forbidden in some countries but still used in Egypt and other developing countries. The control and the test samples were stored at -18°C, the recommended stored temperature for such products. The color index of the control and the tested sample were recorded every three days up to 45 days, according to the method of Ting and Hendrickson (1969). The samples were labeled as (A) Lolita colored with the artificial color, (B) Lolita colored with 0.5 g extracted color, (C) Lolita colored with 1.0 g extracted color and (D) Lolita colored with 1.5 g extracted color/100 ml mixture.

Statistical Analysis

To estimate the palatability of the artificial vs. natural pigments, the Lolita samples were introduced to fifteen trained panelists of FTRI researcher staff. They were asked to evaluate the different Lolita samples color by using 5 degree for the most preferable color and 1 degree for the least preferred. These records were translated to ranking presentation system as Roscoe (1969) recommendation, where the lowest record value was given 1 and the highest was given 4. The most preferable and palatable color was that obtaining the highest total ranks.

Results and Discussion

Carotenoids and moisture contents of samani date processed wastes

Data presented in Table (1), observed that the moisture content of samani date processing wastes was about 12.86% (on dry weight basis). The total carotenoids content in these wastes were about 5.84 g/100g wastes (on dry weight basis). This means that every ton of such wastes could produce about 58.4 kg natural carotenoids. These results are in agreement with that reported by Francis (1995).

TABLE 1. Carotenoids and moisture content in samani date processed wastes.

Item	Carotenoids %*	Moisture %
Samani date processed wastes	5.84	12.86

* Calculated on dry weight basis.

Identification of natural pigments isolated from samani date processing wastes

1) Spectrophotometric identification

Data presented in Table (2) show that the maximum absorption of the natural colorants were recorded at specified wavelengths in the range of 425 and 485 nm., indicating that the separated pigments from samani date wastes were basically carotenoids. These results are in agreement with Lombardi *et al.*, (2001), Hamed (2000) and El-Seesy and Hamed (1998), who demonstrated that the absorption spectra of carotenoids were in the visible region (400 to 500 nm). Moreover this region was widely and mostly used for such pigments identification.

TABLE 2. The absorbance of natural pigments separated from date processed wastes at wavelengths range of 400 and 530 nm.

Wavelength nm.	Absorbance	Wavelength nm.	Absorbance	Wavelength nm.	Absorbance
400	0.452	445	0.330	490	0.382
405	0.398	450	0.688	495	0.365
410	0.368	455	0.418	500	0.300
415	0.334	460	0.400	505	0.285
420	0.398	465	0.485	510	0.215
425	0.485	470	0.575	515	0.200
430	0.335	475	0.780	520	0.175
435	0.320	480	0.580	525	0.165
440	0.580	485	0.485	530	0.120

2) Thin Layer Chromatographic fractionation and identification

Nine carotenoid compounds were identified by using TLC technique for fractionation and identification of the tested wastes (Table 3). The R_f values of the fraction components of the tested samples given were mostly close to R_f values of the standard pigments reported by Davies (1976).

Utilization of the natural pigments isolated from samani date processing wastes in reverse to synthetic one

Statistical analysis of the organoleptic tests values of the Lolita samples colored with the natural carotenoids and synthetically (by tartarzine) colored samples. It was observed from Table (4) that, the higher concentration of the natural carotenoids usage in Lolita, the higher the sum of color rank. In other words, sensory color evaluation was positively correlated with the concentration

of the natural colorants. Moreover, it could be also revealed that the utilization of the natural pigments in coloring Lolita with 1.5 g/100 ml mixture was more preferable and palatable than the lower concentration and even more than the synthetic colorant (tartarzine) with the same concentration.

TABLE 3. Thin Layer Chromatography (TLC) identification of carotenoids fractions from samani date processed wastes by using two adsorbent and solvent systems.

TLC system (adsorbent & solvent)	Standard fractions			Identified fraction sample		
	Component	R_f value	color	Component	R_f value	color
Ca(OH)2:Silica Gel & petroleum ether:benzene	Lycopene	15	Dark red	Lycopene	15.3	Dark red
	B-carotein	84	Light orange	B-carotein	84.3	Light orange
Activated silica gel & Benzene: ethyl acetate: methanol	B-cryptoxanthin	70	Light orange	B-cryptoxanthin	70.3	Light orange
	Canxanthin	82	Yellow	Canxanthin	81.8	Yellow
	Antheraxanthin	40	Yellow	Antheraxanthin	40.2	Yellow
	Zeaxanthin	53	Light orange	Zeaxanthin	53.2	Light orange
	Echinone	90	Dark red	Echineone	90.2	Dark red
	Violaxanthin	35	Yellow	Violaxanthin	53.1	Yellow
	Lutein	57	Light orange	Lutein	56.8	Light orange

TABLE 4 . Statistical analysis of panelists score of artificially and naturally colored Lolita.

No. of panelists	Lolita samples colored with							
	Artificial color (1.5 g Tartarzine/ 100 ml mixture)		Extracted natural colorant					
			0.5 g extraction/100 ml mixture		1.0 g extraction/100 ml mixture		1.5 g extraction/100 ml mixture	
	Value	Ranks	Value	Ranks	Value	Ranks	Value	Ranks
1	3	2.5	1	1	3	2.5	5	4
2	2	2.5	2	2.5	1	1	3	4
3	2.5	1.5	4	3	4.5	4	2.5	1.5
4	4	3	1	1	2	2	5	4
5	3	3	0	1	1	2	4	4
6	5	4	3	1.5	4.5	3	3	1.5
7	3.5	1.5	3.5	1.5	4.5	4	4	3
8	5	4	1	1.5	1	1.5	3	3
9	5	4	1	1	4	3	3	2
10	3	3	0	1	2	2	4.5	4
11	4.5	3	1	1	2	2	5	4
12	3	3	1	1	1.5	2	4	4
13	2	2	1	1	2.5	3	4	4
14	5	3.5	2	1	4	2	5	3.5
15	4.5	3.5	1	1	2	2	4.5	3.5
Total		44		20		36		50

Stability of the separated natural pigments in Lolita product

Color index of Lolita was used as an indicator of the stability of the natural carotenoids separated from date wastes. Data presented in Table (5) show the comparison between the color index of the Lolita colored with natural colorant and that colored with synthetic one. The color index of Lolita with the natural pigments was more stable during storage for 45 days at -18°C than that artificially colored with tartarzine at the same condition and storage period. Miller *et al.*, (1996) and Lombardi *et al.*, (2001) reported that carotenoids are stable and characterized as a higher stable coloring material in some products.

TABLE 5. Color index (Absorbance at 420 nm) of artificially and naturally colored Lolita affected by storage at -18°C.

Storage period (in days)	Lolita samples colored with	
	Natural extraction (1.5 g /100 ml mixture)	Artificial color (1.5g Tartarzine /100 ml mixture)
0	0.835	0.915
3	0.832	0.900
6	0.821	0.815
9	0.810	0.785
12	0.795	0.755
15	0.785	0.730
18	0.775	0.685
21	0.743	0.635
24	0.712	0.555
27	0.698	0.535
30	0.688	0.525
33	0.675	0.475
36	0.661	0.435
39	0.600	0.400
42	0.585	0.375
45	0.575	0.325

Therefore, it could be recommended to produce natural colorants from samani date processing wastes by using the organic solvent (diethyl ether) which possess a high recovery percentage of about 85-90% of the whole colorants. On the other hand, the organic solvent could be easily and nearly complete recovered of the extraction. Moreover, it is advisable, from the economic and healthy views, to utilize such natural colorants in the food product instead of the synthetic one. It could also be considered as good and practical means to partially overcome the pollution and contamination problem caused by such wastes.

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فصل وإستخدام المواد الملونه الطبيعيه من مخلفات تصنيع البلح السمانى

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أجريت هذه الدراسه بغرض الإستخلاص و التعرف على و تقدير الصبغات الطبيعيه الموجوده فى مخلفات تصنيع البلح السمانى والمتبقيه بعد تصنيعه فى صوره مربى البلح . كما تهدف الدراسه أيضا إلى دراسة إمكانية إستخدام أو الإستفاده من هذه المواد الملونه الطبيعيه المفصوله من تلك المخلفات فى أغراض تلوين بعض منتجات حلوى الأطفال مثل منتج اللوليتا الشائع إستعماله فى الأسواق.

وقد دلت النتائج المتحصل عليها أن الكاروتينويدات هى الصبغات شائعة الوجود فى تلك المخلفات ويصل محتواها إلى حوالى ٥,٨٤ % (على أساس وزن جاف) . وقد تم خلال تلك الدراسه التعرف على تسع مكونات من الكاروتينويدات المفصوله من تلك المخلفات وهى : ليكوبين ، بيتاكارونين ، بيتاكربتوزانثين ، كانزانثين ، انثرازانثين ، زيازانثين ، إبينيون ، فيولاكزانثين ، وليوتين. كذلك، تم التأكد خلال تلك الدراسه إنه يمكن بنجاح إستخدام الكاروتينويدات المفصوله فى تلوين حلوى الأطفال مثل اللوليتا والتى ظل لونها ثابتا دون تغير طوال فترة تخزين تصل إلى خمسه وأربعون يوما.