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Spice paprika oleoresin extraction under different conditions involving acetone and ethanol

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Abstract

This paper describes the oleoresin extraction from the spice paprika under different extraction conditions that involves acetone and ethanol as an extracting solvent in percolatory system. Moreover, the influence of paprika particle size, solvent flow rate and the temperature on the extraction procedure was also studied. It was revealed that better extraction efficiency was achieved with 2 ml/min solvent flow rate. The particle size is more important when acetone for paprika oleoresin extraction is used. The increase of temperature up to 40°C positively influences on the mass transfer processes. The functional dependence of the colour yield (P) in the paprika oleoresin from the extraction time (t) is expressed by the function $P = a\,t^b$. The relation between colour yield and the extraction time is presented with the exponential function type. The suitable extraction conditions established for proposed system, intended for paprika oleoresin extraction, were found to be 2 ml/min acetone flow rate, 40°C extraction temperature and particle size from 0.5 to 1 mm.

Key words: Paprika, oleoresin, colour, extraction, percolation, acetone, ethanol.

Introduction

Paprika, primarily referred as *Capsicum annuum* L., fruit is widely used in nourishment, manufacture of broad spectrum of commercial products known for their colour and even as a source of some valuable components for pharmaceutical interest. Red pepper varieties are famous as natural colorant due to their content of carotenoid pigments, predominantly capsanthin and capsorubin [1-3]. It is well acknowledged that ground spicy red pepper is used for aesthetic or physical purposes, to improve a product's performance such as aroma, taste and colour [4-6]. Moreover, the food technology is interested in carotenoids because of their nutritional value [7-11]. They have also become of interest due to some pharmacological characteristics [12].

An increased demand in oleoresins and other natural products for taste improvement and trade qualities of food products has been observed. Special interest is paid to paprika oleoresins [13-15]. They all contain valuable fat-soluble components such as pigments, flavours and taste agents, vitamins and fatty oil in the seed of paprika fruits [16-18]. When analysing the similarities of spice paprika and paprika oleoresins, besides some features such as intensive aroma, the paprika oleoresins are more advantageous due to their higher colour concentration [19], better high temperature stability [20-22] and limited presence of microorganisms [23]. In addition, high storage stability of oleoresin with proper packing is of great economical benefit. This valuable feature is drawing more attention in various industries.

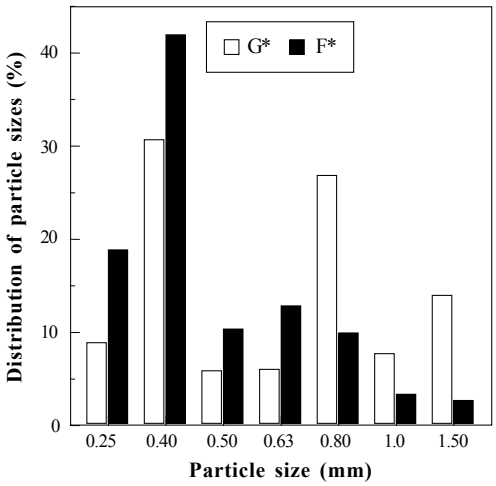
The paprika oleoresins are produced by solvent extraction of dried, ground spice red paprika fruits, using a solvent-system compatible with the lipophilic/hydrophilic characteristics of the extract sought and subsequent solvent-system removal [24]. The most commonly used solvents for paprika oleoresin extraction are trichloroethylene, ethylacetate, acetone, propan-2-ol, methanol, ethanol and hexane [25-28]. Additionally, the supercritical fluids for paprika extraction are also subject of the research interest [29-31].

Paprika is native to Republic of Macedonia, widely distributed throughout many regions and cultivated in many varieties with different quality factors, from the very mild to the very hot in taste. Its fruit appears in different sizes and shapes. In turn, this has stimulated interest and highlighted the need for various procedures for its components extraction.

The purpose of this study was to establish appropriate conditions for the extraction of paprika oleoresins from variety Bukovka, using acetone and ethanol. The main goals were to study the influence of solvent flow rate, extraction temperature and paprika particle size on the oleoresin extraction efficiency.

Materials and Methods

Paprika: Dried and ground red paprika (*Capsicum annuum* L.) variety Bukovka (6.60% moisture content) with sweet taste was used for oleoresin extraction. The content of moisture and the colour content in the paprika were determined according to the methods given in AOAC [32]. To study the influence of the particle size on the extraction efficiency, paprika samples with the distribution of the particle size from 0.25 to 1.50 mm were prepared (Fig. 1) using sieving method of previously ground paprika in the laboratory cutting mill (Retch, Brinkmann, Germany).



G* - ground paprika with particle size from 1.50 mm to 0.50 mm
F* - ground paprika with particle size from 0.50 mm to 0.25 mm

Figure 1. Distribution of ground paprika particle size.

Reagents: All solvents used, i.e., acetone and ethanol (96% vol) with high purity (p.a.), were purchased from the A.D. Alkaloid, Skopje, Republic of Macedonia.

Extraction procedure: For paprika oleoresin extraction thermostatic percolatory column with 15 cm height and 2 cm inner diameter was used. The column was filled with paprika samples up to height of 10 cm (~17 g paprika). In all experiments performed paprika with particle size from 0.50 to 1.50 mm designated as G* is used. However, in the developmental stage of the extraction when the influence of the paprika particle size on the extraction efficiency was studied, paprika with particle size from 0.25 to 0.50 mm (F *) was also included.

The solvent for extraction was poured to the upper column using one channel peristaltic pump with possibility of the flow rate regulation (Model P-1, Amersham Pharmacia Biotech, Switzerland). The overall extraction time was 250 min. In the first hour of the extraction, the paprika oleoresin was collected in every 15 min, after that in every 30 min. The column temperature (up to 40°C) was kept by circulating water from a thermostatic bath through the water jacket of the column. In the paprika oleoresin the content of colour expressed as capsanthin was determined by spectrophotometric method.

Oleoresin analysis: The efficiency of paprika oleoresin extraction, expressed as yield of colour, was followed as the paprika colour content determined in acetone according to the procedure given in AOAC [32] method 30002-4. Accordingly, for colour quantification, 1 ml of extract was dissolved in 25 ml acetone. The absorbance was measured at 460 nm (UV-VIS spectrophotometer HP UV 8452, Switzerland). Thereafter, the concentration of pigments in the oleoresin was calculated by using the extinction coefficient of the major pigment capsanthin ($^{1\%}E_{460nm}$ = 2300) in acetone. Spectrophotometrical measurements were repeated five times (n = 5, RSD < 2%). The empirical correlations of the colour yield from the solvent flow rate and extraction time were calculated using the experimental data and the program STATISTICA 6.0 (StatSoft Inc., 1984-2001).

Results and Discussion

On the basis of the colour content obtained (i.e., 6.5729 g capsanthin/kg dry matter) paprika sample rich in capsanthin was confirmed [15, 16, 33].

Influence of the solvent flow rate: The influence of the solvent flow rate on the oleoresin extraction from paprika is shown in Fig. 2. The results (Fig. 2, Curves 3 and 4) confirmed that oleoresin extraction with 2 ml/min solvent flow rate gave consistently higher values than those obtained with 1 ml/min solvent flow rate.

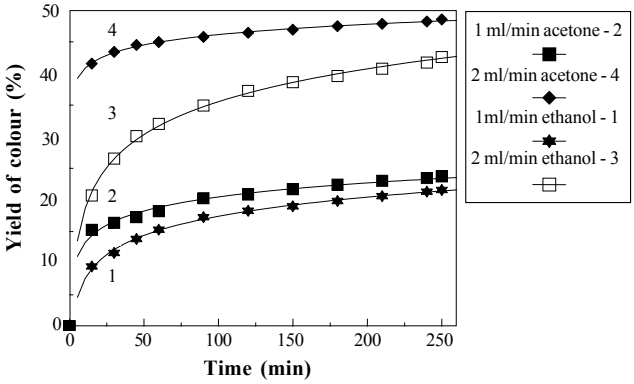


Figure 2. Influence of the solvent flow rate on paprika oleoresin extraction (20°C, G* - grinded paprika).

The differences between the colour yields during the extraction time, obtained with acetone and ethanol, are probably caused by the physicochemical characteristics of the applied solvent, i.e., the molecular weight, dynamical viscosity, polarity degree and the ability to mix with the water present in the raw material. The dynamic change of the colour component contents in the paprika oleoresin is slower when the ethanol is used as an extraction solvent (Fig. 2, Curves 1 and 3). So far, comparison of the data given in Fig. 3 demonstrates that the differences of the colour component contents in paprika oleoresins obtained with 1 ml/min and 2 ml/min ethanol is higher after 60 min extraction time. In the extraction system paprika and acetone the solubility equilibrium condition was reached in the first 15 min of extraction process. The differences in the colour yield in oleoresin obtained with 2 ml/min acetone between 60 min and 250 min extraction time are smaller in comparison to the values for the yield of colour obtained when 1 ml/min acetone flow rate was applied. This indicates that paprika oleoresin extraction with 2 ml/min flow rate of acetone enables extraction time, shorter than 250 min. The functional dependence of the colour yield (P) in the paprika oleoresin from the extraction time (t) is expressed by the function $P = a\ t^b$. The estimated correlation coefficients (Table 1) for the curves given in Fig.1 are above 0.9973.

Table 1. Empirical correlations of the colour yield in paprika oleoresin during the extraction time at different solvent flow rate.

P - yield of colour (%) t - time of extraction (min) $P = a\ t^b$		R - correlation coefficient	Solvent type	Solvent flow rate (ml/min)
a	b			
8.99737	0.1807539	0.9979	Acetone	1
36.29413	0.0518848	0.9999	Acetone	2
4.79962	0.2742376	0.9997	Ethanol	1
12.32179	0.2263439	0.9973	Ethanol	2

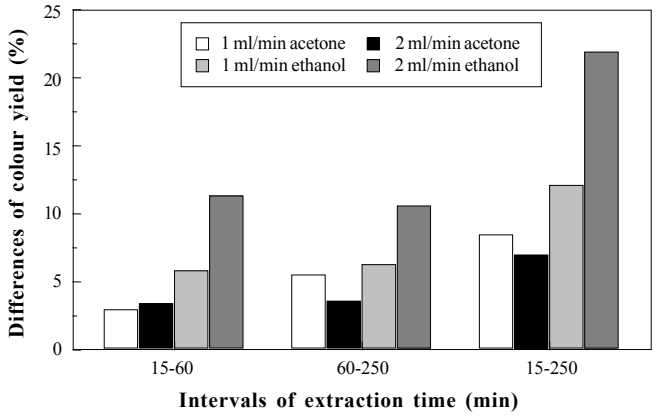


Figure 3. The differences of the colour yield in the paprika oleoresins (estimated by the data given on Fig. 2).

***Influence of the paprika particle size*:** In principle, the most influential factor on the extraction dynamics is the particle size of the ground matrix. Following this observation, experiments were also undertaken to confirm this influence. The results (Fig. 4) show dynamical colour yield curves in the paprika oleoresin, obtained when using various paprika particle size fractions (ranging from 0.25 mm to 1.50 mm). The differences between the two curve sets (1 and 2 for ethanol, 3 and 4 for acetone) shown in Fig. 4 confirm that the influence of the particle size is more important when acetone for paprika oleoresin extraction is used.

Typically, when maceration is applied as extraction technique, better phase contact is enabled with reduced particle size of the matrix. Boyadziev *et al.* [27] have reported on paprika maceration with ethanol in stirred batch reactor using particle size from 0.3 to 1.8 mm. They concluded that carotenoid yield increases by decreasing the paprika particle size. However, placed in the percolatory column, material with smaller particle size is compressed at longer phase contact. Thus performing extraction with constant solvent flow rate through the percolatory column is very often difficult to achieve.

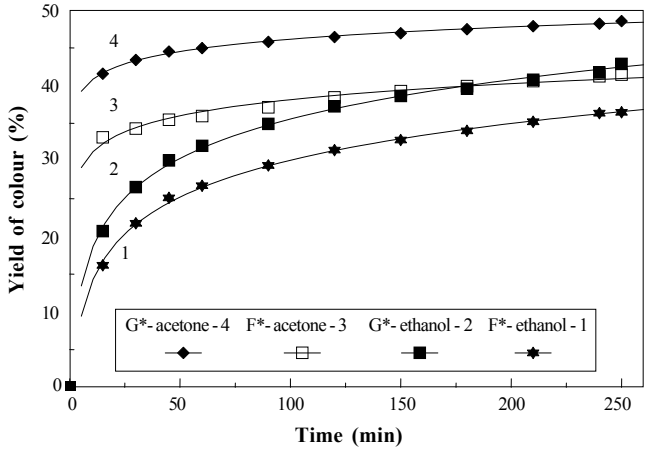


Figure 4. Influence of the particle size on paprika oleoresin extraction (2 ml/min solvent flow rate, 20°C).

Our previous experiments also showed that it is very difficult to maintain permanent flow rate when the paprika particle size lower than 0.25 mm was subjected to percolatory extraction procedure.

Using smaller particle size of the ground matrix the extraction efficiency can be improved by using the smaller quantity of raw material in the percolatory column. In this case, it increases the quantity of used extraction solvent, i.e., the ratio between solid and liquid phase is changed. The influence on the particle size is affected by the quantity content and the different localization of the component of interest at extraction processes.

Other factors associated with oleoresin extraction efficiency were also investigated. The empirical correlations for prediction of the colour yield in paprika oleoresin in accordance to the extraction time at different particle sizes are given in Table 2. The correlation coefficient values higher than 0.99 showed good fitting of the yield of colour (P) with the extraction time (t).

Table 2. Empirical correlations of the colour yield in paprika oleoresin during extraction time at different particle sizes of paprika.

P - yield of colour (%) t - time of extraction (min) $P = a\ t^b$		R - correlation coefficient	Solvent type	Size of particles (mm)
a	b			
36.28333	0.0519630	0.9999	Acetone	G*
25.85270	0.0837945	0.9995	Acetone	F*
12.31732	0.2263649	0.9973	Ethanol	G*
8.72333	0.2616771	0.9967	Ethanol	F*

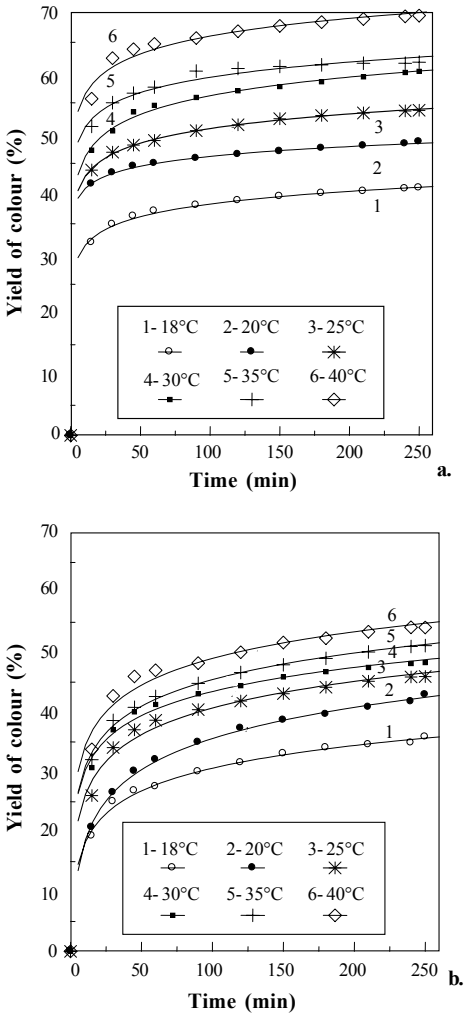
Influence of the extraction temperature: As expected, an increase in temperature raises the extraction rate. The study of the temperature influence on paprika oleoresin extraction with acetone and/or ethanol is given in Fig. 5a-b. From the experimental data shown in Fig. 5 the empirical correlations of the colour yield at different temperatures and the time of extraction are estimated. The relation between colour yield and the extraction time is presented with the exponential function type (Table 3).

Table 3. Empirical correlations of the colour yield in paprika oleoresin during extraction time at different temperatures.

Acetone				
T - temperature (°C)	P-yield of colour (%) , t - time of extraction (min); $P = a \exp(b\ t^c)$			R - correlation coefficient
	a	b	c	
18	0.012151	7.6872	0.010663	0.9995
20	0.018148	7.6036	0.006640	0.9999
25	0.005742	8.7651	0.007774	0.9998
30	0.004083	9.1584	0.008552	0.9995
35	0.002826	9.6658	0.006261	0.9989
40	0.003035	9.6901	0.006522	0.9985
$P = -155386.7 + 1535.674\ T - 5.0588\ T^2 + 0.0055\ T^3$				0.9935
Ethanol				
T - temperature (°C)	P-yield of colour (%), t - time of extraction (min); $P = a \exp(b\ t^c)$			R - correlation coefficient
	a	b	c	
18	$1.9025\ 10^{-4}$	11.1120	0.016183	0.9967
20	$1.8075\ 10^{-5}$	13.9728	0.015132	0.9971
25	$3.1976\ 10^{-5}$	13.3267	0.011305	0.9917
30	$1.2297\ 10^{-4}$	12.1438	0.010865	0.9918
35	$1.8191\ 10^{-4}$	11.7564	0.011911	0.9984
40	$9.6156\ 10^{-5}$	12.5231	0.010334	0.9948
$P = -119437.4 + 1179.544\ T - 3.8822\ T^2 + 0.0042\ T^3$				0.9849

According to data presented in Table 3 and Fig. 5, the increase of temperature influences positively on the mass transfer processes, probably due to the lowering of the solvent viscosity,

and thus increases in the colour yield in paprika oleoresin are normally expected. The increased colour yields are also resulting of the changes in cellular structure of biological matrix, such as paprika. On the one hand, the increasing of overall extraction temperature may cause and provoke the browning of raw material [27], on the other hand, due to this circumstances, it is acquired to establish the optimal extraction temperature.



a. 2 ml/min acetone flow rate, G* - ground paprika
b. 2 ml/min ethanol flow rate, G* - ground paprika

Figure 5. Influence of the temperature on paprika oleoresin extraction.

Conclusions

This study for paprika oleoresin extraction shows that acetone is a more effective extraction solvent than ethanol. According to the mass transfer laws that are of importance at extraction processes, including lower boiling point and smaller dynamical viscosity of acetone, it is obvious that acetone is offering a possibility of more effective paprika oleoresin extraction than ethanol. Applying a solvent flow rate of 2 ml/min offers better extraction efficiency. The particle size of the paprika has essential role in the oleoresin extraction. The temperature, increased up to 40°C, positively influences on the mass transfer processes. Optimized extraction conditions are established using percolation as the extraction method. This extraction system could find application in the assessment of paprika varieties and to determine the oleoresin status of paprika matrix.

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