

Shelf-life Determination of Saffron Stigma: Water Activity and Temperature Studies

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Abstract: The quality of dried saffron stigma is highly dependent on the processing and storage conditions. In this study, the effect of different storage conditions (different temperatures, 20, 30 and 40°C along with different water activity, 0.32±0.01, 0.52±0.01 and 0.75±0.01) of saffron stigma during storage time (12 weeks with two-week time intervals), in both light and dark, on coloring strength, aroma and bitterness has been investigated. The results showed that the coloring strength of stigma, decreased considerably as the temperature and water activity increased. Furthermore, after 12 weeks of storage, the color strength had a noticeable decrease and the bitterness also decreased whereas the aroma increased. The results also showed that storage conditions (temperature, water activity and storage time) had a significant effect on the above mentioned parameters ($p<5\%$).

Key words: Saffron . storage . water activity . temperature . coloring strength . aroma . taste . shelf life

INTRODUCTION

Saffron, the dried stigmas of a flower scientifically identified as *Crocus sativus* L., is one of the most expensive agricultural products. It has been named as “red gold” because of its high value [1, 2]. Although the source of saffron is historically unknown, it apparently originated in the area of Iran, Turkey and Greece. While the world’s total annual saffron production is estimated to be 190 tons, Iran produces about 90% of the total, accounting for 150 to 170 tons per year; and 50,000 ha is already under cultivation with this crop. This spice is appreciated for its unique color, bitter taste and aroma, which are the main characteristics showing its quality [1, 2].

The color of saffron comes from the water-soluble glycosidic cis- and trans-carotenoids crocins, glucosyl esters of crocetin (8,8'-diapocarotene-8,8'-dioic acid; $C_{20}H_{24}O_4$) [2]. The carotenoids contents of saffron are also responsible for many biological activities such as anti-cancer property [3].

The bitter-taste of saffron is produced by the picrocrocin ($C_{16}H_{26}O_7$), a monoterpenoid glycoside precursor of safranal ($C_{10}H_{14}O$), that is the main volatile oil responsible for the aroma. β -Glucosidase action on picrocrocin liberates the aglycone, 4-hydroxy-2,6,6-trimethyl-1-cyclohexene-1-carboxaldehyde (HTCC,

$C_{10}H_{16}O_2$), which is then transformed to safranal by dehydration during the drying process of the plant material [1]. The processing and storage conditions are of great importance because they determine the quality and economic value of the final product [2, 4].

The stability of saffron pigments is dependent on the storage conditions employed. Both increasing temperature and water activity exert a strong influence on the degradation kinetics, accelerating the rate of pigment decomposition [4, 5].

The objective of this study was mainly to assess the effect of storage conditions (water activity, temperature and light) on the major characteristics of saffron stigma and, hence, the shelf-life determination.

MATERIALS AND METHODS

The dried stigma of saffron was supplied from a farm in Qaen (Southern Khorasan province, Iran) and kept at 4°C until used.

In order to justify the water activity, the constant relative humidity was maintained by saturated salt solutions in the bottom of glass containers with airtight lids [6]. Three water activity (a_w) levels (0.32±0.01, 0.52±0.01 and 0.75±0.01) obtained using $MgCl_2$, $Mg(NO_3)_2$ and $NaCl$ at 20 and 30°C and $MgCl_2$, $NaBr$ and $NaCl$ at 40°C, respectively. The closed desiccators

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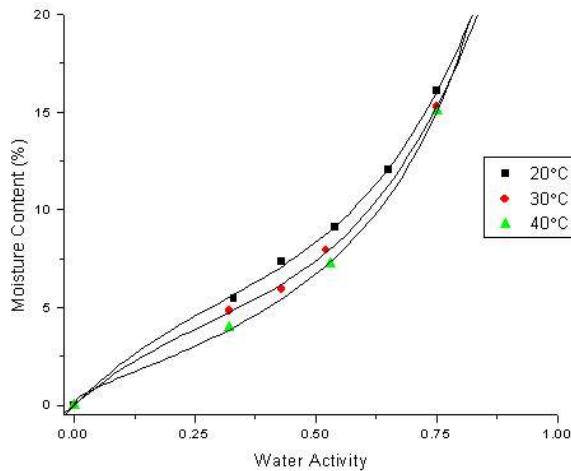


Fig. 1: Absorption isotherm of saffron stigma

were stored in incubators at three different temperatures (20, 30 and 40°C). To study the effect of light on the characteristics of stigma, the samples were divided into two groups: one exposed to the light using a fluorescent lamp of $2.5\mu\text{mol m}^{-2}\text{s}^{-1}$ and the other kept in dark. For balancing, the standard salt solutions were left at mentioned temperatures for 2 days. In addition, the moisture content of the stigma after the equilibrium was determined according to the ISO 3632-2 and then the sorption isotherm (Fig. 1) obtained [7].

The chemical properties including the coloring strength, aroma and bitterness, were measured after storing the samples at mentioned temperatures for 12 weeks using the ISO-3632-2. In this standard method, the absorbance of the saffron solution was measured at the wavelengths of 440, 330 and 257nm by a UV-visible spectrophotometer after preparation and dilution process. Then, the coloring strength ($E^{1\%}_{440\text{nm}}$), aroma ($E^{1\%}_{330\text{nm}}$) and bitterness ($E^{1\%}_{257\text{nm}}$) were calculated using the following formula [7, 8]:

$$E^{1\%}_{\lambda \text{ max}} = A/C \text{ (g/cm}^3)$$

where, A stands for absorbance and C for concentration.

And finally, the data were analyzed using split plots design during the 12-week storage and the mean values were compared with Duncan test. The results were analyzed within the level of 5%.

RESULTS AND DISCUSSIONS

Coloring strength changes: For all samples, the coloring strength changed significantly with time ($p<5\%$). Water activity (Fig. 2) and temperature (Fig. 3) had strong effect on the crocin degradation. The coloring strength decreased more than 50% during

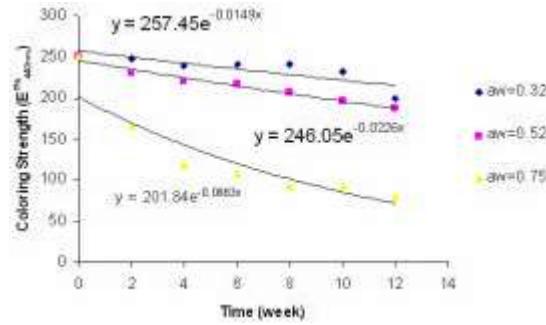


Fig. 2: Mutual effect of water activity and storage time on the coloring strength of saffron stigma kept in dark

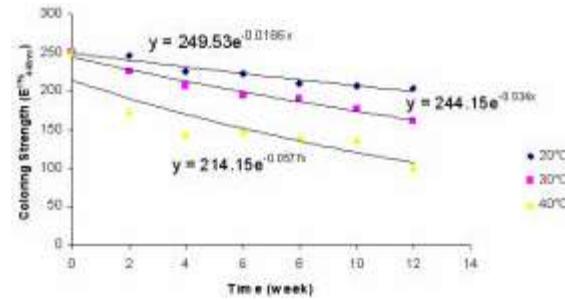


Fig. 3: Mutual effect of temperature and storage time on the coloring strength of saffron stigma kept in dark

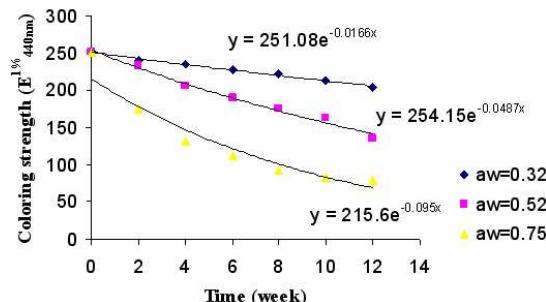


Fig. 4: Mutual effect of water activity and storage time on the coloring strength of saffron stigma exposed to the light

12 weeks in the samples kept at 40°C, whilst the samples kept at 20°C showed less than 20% reduction, which seems to be due to the temperature effect on the reaction rate [8]. The same result concluded for increasing of water activity from 0.32 to 0.75. This may be related to the higher water solubility of saffron carotenoids than the other sources, resulted from a greater access of dissolved oxygen to the pigments [5].

For the samples exposed to the light, the pattern was similar to the samples kept in dark (Fig. 4 and 5),

Table 1: Mutual effect of temperature and storage time on the aroma of saffron stigma kept in dark

Time (week)	Temp.		
	20°C	30°C	40°C
0	34.40	34.40	34.40
2	35.45	36.85	40.93
4	34.84	36.70	36.88
6	36.06	36.60	37.46
8	35.34	33.80	34.12
10	35.63	36.19	35.63
12	35.84	37.42	35.45
Average	35.37 ^a	36.00 ^b	36.41 ^a

*Different letters denote significant difference ($p < 5\%$)

Table 2: Mutual effect of temperature and storage time on the aroma of saffron stigma exposed to light

Time (week)	Temp.		
	20°C	30°C	40°C
0	34.40	34.40	34.40
2	35.72	36.32	39.83
4	34.98	37.12	38.75
6	36.38	36.57	36.87
8	35.62	33.37	32.93
10	35.75	35.65	34.05
12	35.93	37.17	33.72
Average	35.54 ^a	35.80 ^a	35.79 ^a

*Different letters denote significant difference ($p < 5\%$)

Table 3: Mutual effect of water activity and storage time on the aroma of saffron stigma kept in dark

Time (week)	a_w		
	0.32	0.52	0.75
0	34.40	34.40	34.40
2	35.38	37.67	40.18
4	34.91	36.45	37.06
6	36.06	36.96	37.10
8	34.41	34.62	34.23
10	35.52	37.43	34.51
12	37.42	38.06	33.22
Average	35.44 ^{b*}	36.51 ^a	35.81 ^b

*Different letters denote significant difference ($p < 5\%$)

but the pigment decomposition was greater than dark samples because the light acts as a catalyst for the crocin degradation.

Aroma change: The safranal, which is the main aromatic compound in saffron, is produced via the

Table 4: Mutual effect of water activity and storage time on the aroma of saffron stigma exposed to light

Time (week)	a_w		
	0.32	0.52	0.75
0	34.40	34.40	34.40
2	35.42	37.35	39.10
4	35.18	37.72	37.95
6	35.72	38.12	35.98
8	34.08	35.70	32.13
10	35.75	37.97	31.73
12	36.82	39.13	30.87
Average	35.34 ^{b*}	37.20 ^a	34.60 ^c

*Different letters denote significant difference ($p < 5\%$)

Table 5: Mutual effect of water activity and storage time on the bitterness of saffron stigma kept in dark

Time (week)	a_w		
	0.32	0.52	0.75
0	83.15	83.15	83.15
2	75.69	75.93	83.66
4	75.12	74.27	77.85
6	76.92	73.89	76.56
8	78.64	70.68	72.47
10	78.28	73.90	74.19
12	80.00	73.76	73.11
Average	78.26 ^a	75.08 ^c	77.28 ^b

*Different letters denote significant difference ($p < 5\%$).

Table 6: Mutual effect of water activity and storage time on the bitterness of saffron stigma exposed to light

Time (week)	a_w		
	0.32	0.52	0.75
0	83.15	83.15	83.15
2	75.90	75.55	83.00
4	75.62	77.13	81.07
6	75.98	75.40	75.90
8	76.55	71.68	69.70
10	78.93	76.48	71.48
12	79.42	76.18	69.53
Average	77.94 ^a	76.51 ^b	76.26 ^b

*Different letters denote significant difference ($p < 5\%$).

picrocrocin degradation during storage [9, 10]. Our results confirmed this fact and proved that increasing in temperature will result the safranal production. This is thought to be due to the effect of temperature on the rate of picrocrocin degradation. Besides, the effect of temperature on the aroma development is significant in

Table 7: Shelf life of saffron stigma in different storage conditions

Shelf-life (week)		a_w	Temp. (°C)				
		0.32	0.52	0.75	20	30	40
	Dark storage	40.88	24.95	4.24	31.07	16.36	7.37
	Light storage	35.19	12.24	4.55	23.51	11.31	6.30

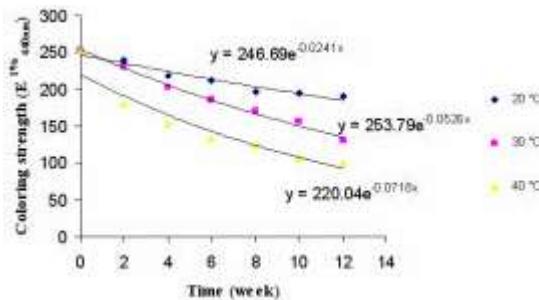


Fig. 5: Mutual effect of temperature and storage time on the coloring strength of saffron stigma exposed to light

the stigma kept in dark (Table 1), but not in light-exposed samples (Table 2). It may conclude that the safranal degrade or denature under the light, so the produced safranal is destroyed, resulting in no significant increase in aroma.

The results from water activity showed that the samples containing 0.52 water activity had more aroma than the others, both in dark and light samples resulted in a more picrocrocin degradation (Table 3 and 4).

Bitterness changes: The bitterness decreased during the storage significantly (from 83.1 to 75.6) But, the effect of temperature on bitterness was not significant. According to the analysed data for bitterness, a noticeable difference was found between the stigma with different water activity both in dark and light conditions (Table 5 and 6). The samples with $a_w=0.52$, presented the least bitterness, which is probably related to the safranal production (Table 3). It may conclude that this water activity is optimum for the picrocrocin degradation, because the safranal is maximum at the mentioned water activity level and, moreover, the effect of dilution will occur at higher a_w .

As it can be seen, the bitterness (and also aroma) fluctuated over time. A probable explanation is that the picrocrocin is an intermediate compound, which is produced by zeaxanthin degradation and at the same time hydrolyzed to safranal [9]. Also, the picrocrocin may have an inhibitory effect on zeaxanthin degradation, which is still being investigated.

Shelf life determination: Since, the color strength changes more noticeably than the aroma and bitterness,

it is believed that the shelf life of saffron is related mainly to the fate of its pigment and consequently the decrease of color strength [4]. Being highly unsaturated, the crocin isomers are prone to isomerization and oxidation reactions, giving rise to fade the color strength of the spice [4].

According to the new revision of Iran national standard for saffron (No. 259-1), the least color strength for the poorest saffron stigma (grade 4), is 140 [11]. The shelf life of stigma, therefore, was calculated by fitting suitable equations to the experimental data, considering 140 as a cut-off value (Fig. 2 and 5).

The data analysis shows that the shelf life of stigma kept at $a_w=0.75$ gives the shortest value, whilst those at $a_w=0.32$ has the longest (Table 7). Interestingly, if the saffron stigma is kept at $a_w=0.32$ and in dark, then the shelf life will be more than 3 years.

CONCLUSIONS

The effect of temperature, water activity and light on the main chemical characteristics of saffron stigma has been studied during the storage. The behaviors of coloring strength, aroma and bitterness against time were modeled using the least-square fitting to the experimental data. The shelf life of saffron was estimated according to the poorest acceptable coloring strength value defined by the Institute of Standards and Industrial Research of Iran (ISIRI).

The study showed that for high production of saffron with the best quality, the fresh stigma should be dried as soon as possible, then stored in a dark, cool and dry place.

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