INFLUENCE OF LIGHT AND TEMPERATURE ON LIPID OXIDATION AND COLOUR CHANGES OF CORN OIL INCLUDING CURCUMIN

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Abstract: In order to introduce a natural antioxidant for food industry, the active substance of turmeric rhizome (curcumin) was extracted and identified with thin layer chromatography (TLC) and nuclear magnetic resonance (NMR). To evaluate the lipid oxidation and colour changes of corn oil samples, including different concentrations of curcumin (0.02%, 0.04% and 0.08%) stored at 25˚C and 45˚C in lightness and darkness, the Iodine value (IV), acid value (AV) and L* a* b* values for colour changes during 90 days monitored. The result of TLC analysis and NMR spectra corroborated the chemical structure of curcumin. Results from IV and AV showed that increasing curcumin concentration leads to decreasing the oxidation rate significantly. The results from the colour changes of the samples showed the total colour change (ΔE) in darkness and lightness was thoroughly different. But temperature had not any significant effect.

Keywords: Acid value, Colour changes, Corn oil, Curcumin, Iodine value, Natural antioxidant

I. INTRODUCTION

The rhizome of Curcuma longa L.(turmeric) is widely used as a spice, coloring, flavoring, and traditional medicinal preparations. Curcuminoids are the phenolic yellowish pigments of turmeric, which have anti-inflammatory, antioxidative, anticarcinogenic and hypocholesterolemic activities. Moreover, curcumin inhibits the Helicobactor pylori growth, which causes gastric ulcers. Curcumin also has protective role in human body such as lowering cholesterol and triglyceride levels, inhibiting platelet aggregation and decreasing susceptibility of low density lipoprotein (LDL) to lipid peroxidation [1].
Oxidation is one of the serious threats to the quality of edible oils during storage or heating process. During reaction with oxygen, edible oils undergo changes which lead to the formation of volatile and nonvolatile products such as free fatty acids, hydroxy acids, ketones and hydrocarbons which reduce their quality, beneficial effects and nutritional value. Exposure to light also causes oxidative deterioration of lipids, vitamins and colorants in edible oil through both photolytic autoxidation and photosensitized oxidation [2].
Nowadays, recent awareness and consumer concerns about the long term effects of synthetic antioxidants on health, lead to the utilization of natural antioxidants like curcumin. The edible oil industry often analyses the oil colour as an indicator of oxidation during storage, especially the oils which have high amount of carotenoids and/or chlorophyll pigments. Measuring of oil colour by image analysis developed by Fengxia and co-workers [3]. The aim of the present study was to evaluate of extent of oxidative deterioration of corn oil including different concentrations of curcumin (0.02%, 0.04% and 0.08%) under lightness and darkness at two temperatures (25˚C and 45˚C) for 90 days by monitoring acid value (AV), Iodine value (IV) and color changes of corn oil samples.

II. DETAILS EXPERIMENTAL

2.1. Materials

Corn oil with no added components was purchased from Damoon (Fariman, Iran). Rhizome of turmeric was provided by local store. All chemicals and solvents were obtained from Merck and Sigma Chemical Companies. Standard curcumin purchased from sigma company.

2.2. Methods

2.2.1. Extraction of curcumin

The rhizomes of turmeric (Curcuma longa L.) were powdered and sieved. 500 g dried powder was soaked in hexane for 48 hours in a shaker with 750 rpm. The combined hexane solution was filtered and evaporated to produce turmeric oil in the form of a yellow oil. This operation was done twice due to increasing the extraction yield. The residuum of hexane extraction was further steeped for 24 hours in 95% ethanol by agitation (750 rpm) and this process was repeated. The combined alcoholic extract was concentrated using a rotary evaporator. Then, concentrated mixture was poured in dish to eliminate remained solvent in the room temperature and darkness. Then sedimentation was done by adding 1:5 mixture of water: ethanol. After filtration and drying at room temperature, curcumin in the form of yellow-orange powder was obtained.

2.2.2. Identification of the curcumin

A dichloromethane solution (5%) of the extracted curcumin and standard curcumin (50 mg/plate) was streaked by a thin-layer chromatography (TLC) applicator on a precoated silica gel plate 2×10 cm which had been already activated at 100°C for 15

min. Then, the plate was developed in the rising direction for 10 cm with the solvent system dichloromethane: methane (9.9: 0.1, by volume). The NMR spectra were recorded by a NMR instrument (Bruker AC-80) at 300 MHz at room temperature, using methanol as a solvent. A solution was prepared by dissolving 10 mg of curcumin in 0.5 mL of methanol to NMR tube.

2.2.3. Iodine value (IV)

For measuring the IV, the Iodine chloride was used for double- bond saturation analysis and titrated with 0.1 M standard sodium thiosulfate solution to determine the consumed Iodine [4].

2.2.4. Acid value (AV)

The AV was determined according to the AOCS (1993) Official Method Cd 3d-63 [5].

2.2.5. Colour measurement

The colour of corn oil samples containing curcumin was measured during the storage period using, as CIE L*, a* and b* values. In this coordinate system, the L* value is a measure of lightness ranging from 0 (black) to 100 (white), the a* value ranges from -60 (greenness) to +60 (redness), and the b* value ranges from -60 (blueness)to +60 (yellowness). ΔE is the total colour change calculated from:

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (1)$$

2.3. Statistical analysis

All determinations were carried out in triplicate. Statistical analyses were calculated according to SAS software. Significant differences between means were determined by Duncan's multiple range tests. P values less than 0.05 were considered statistically significant.

III. RESULTS AND DISCUSSION

3.1. Curcumin identification analysis

The purity determination of the curcumin was accomplished by two tests including TLC on silica gel and the NMR spectra which by Brucker (Ac-80).

The TLC results indicated 3 separate plots, including curcumin, demethoxycurcumin and bisdemethoxycurcumin which in agreement with the results from standard curcumin. The structure of the curcumin also was confirmed by 1H NMR and the results of NMR spectra was the same as the standard reported spectrum. A siglet corresponding to the two methoxy groups in curcumin was observed at δ 3.92 in 1H NMR spectrum. For demethoxycurcumin, the corresponding siglet was observed at δ 3.82 which in agreement with standard one.

3.2. Colour changes of corn oil including Curcumin during storage time

The colour changes during 90 days of storage for the corn oil samples including different concentrations of curcumin (0.02%, 0.04% and 0.08%) exposed to darkness and lightness at 25˚C and 45˚C, expressed as ΔE with corn oil without any additives as a reference. The total colour change, ΔE of all samples including different concentrations of curcumin stored in darkness did not remarkably change during storage time. For example, the ΔE of samples containing 0.08% curcumin which stored at 45˚C in darkness changed from 11.5 to 13.5, whereas the samples containing 0.04% and 0.02% of curcumin which stores at 45˚C in darkness changed from 13.23 to 15.94 and from 14.72 to 16.5, respectively Fig.1A. However, ΔE of samples including curcumin (0.02%, 0.04% and 0.08%) stored in lightness changed significantly during storage time Fig.2B.

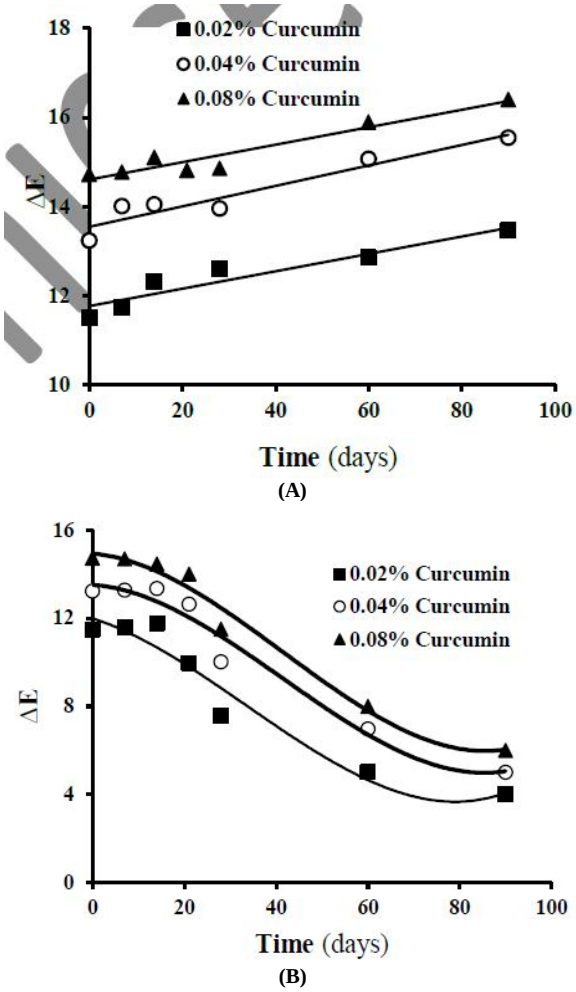


Fig.1. Total color changes (ΔE) for the corn oil samples including different concentrations of curcumin stored A) at 45˚C in darkness, B) at 45˚C in lightness.

Indeed, ΔE of the corn oil samples including curcumin exposed to different conditions was almost totally dependent on the decrease in yellowness b*. This decrease was probably as a result of the curcumin oxidation. The other two CIE L* a* b* coordinates, L* (lightness) and a*(redness-greenness), changed less than b*. So that, ΔE changes at 45˚C in lightness changed from 11.9 to 4.5 for corn oil samples containing 0.02% curcumin. This

decrease was more severe in oil samples containing 0.08% curcumin from 14.92 to 5.5. The yellowness of the samples exposed to lightness decreased rapidly and the difference between the samples, including different concentrations of curcumin and the reference was obvious. The total colour changes during the first month was non significance, but after the first month, the decrease of ΔE especially yellowness was more rapid. However, the temperature (25˚C and 45˚C) has not any significant effect on colour changes of corn oil samples (Data not shown). The mere effect of lightness compared with temperature was probably due to a greater effect of light on the photobleaching of curcumin. The other factor of colour measurement (L*) which showed the lightness of the samples was thoroughly different between the samples, including curcumin and control. At 45˚C, L* of 0.02%, 0.04% and 0.08% curcumin changed from 70.72–71.42, 70.72–72.54 and 72.64–72.5 during 90 days of storage time, respectively. Whereas, the control sample changed 70.72 to 70.85. So, the changes of L* in all samples stored at 25˚C and 45˚C whether in darkness or lightness during storage period were not significant (Data not shown). Moreover, the a* of the samples, including curcumin was lower than control. For example, the a* of the control samples at 45˚C in lightness changed from 3.85 to 3.7, whereas the a* of 0.02%, 0.04% and 0.08% of curcumin changed from -5.28–2.95, -5.85–1.84 and -6.95–1.63, respectively. As the concentration of curcumin was higher, the greenness of the samples was more intense. Moreover, the changes of a* and b* in the samples stored at both 25˚C and 45˚C during the storage time were almost the same (Data not shown). Whereas, L* had a significant effect on the samples. The a* of the samples stored at light condition had an upward trend with the time of storage sample (Data not shown). So, the value of greenness became lower due to the curcumin oxidation. Besides, b* (yellowness) during the storage time reduced. So that, the b* changed 47.5-15.44 for corn oil samples including 0.02% curcumin stored at 45˚C in darkness, whereas, b* changed from 49.5 to 24.85 and 50.5 to 30.17 for 0.04% and 0.08%, respectively. Singlet oxygen which generated from triplet oxygen by excitation is responsible for initiating lipid oxidation of vegetable oils, due to its ability to directly react with the electron-rich double bonds of unsaturated fatty acids and other singlet-state compounds. For instance, singlet oxygen reacts with linoleic acid, a common unsaturated fatty acid in vegetable oils, at least 1450 times faster than triplet oxygen. Once singlet oxygen is formed it directlyreacts with compounds that contain high densities of electrons, forming a mixture of conjugated and nonconjugated hydroperoxides that readily break down to produce undesirable compounds. The effects of light on food stability can be explained by both photolytic autoxidation or photosensitized oxidation. Indeed, lipid oxidation due to visible light exposure can be attributed to more photosensitized oxidation rather than photolytic oxidation. Photolytic oxidation, mostly occurred in exposure of unsaturated fatty acids to ultraviolet radiation. Whereas, the unsaturated fatty acids do not absorb visible light, and the photosensitized oxidation requires the presence of photosensitizers. Not only corn oil is susceptible to oxidation due to the high concentration of linoleic acid, but it contains photosensitizers which generate singlet oxygen. Photosensitizers are components that easily absorb visible light and convert to excited state. This molecular interacts rapidly with the lipids to form free radicals, or oxygen to create high reactive singlet oxygen. Curcumin is the natural antioxidant which can be photosensitizer due to its conjugated double bonds. As we expected during the photosensitizer oxidation, the curcumin decayed and the colour perished easily in lightness.

3.2. Evaluation of corn oil oxidation including Curcumin during storage time

AV is one of the most important factors to determine the oil quality. During the oxidation, most of the sensory and chemical properties of corn oil changed. Free fatty acids (FFAs) are low molecular weight products of oil hydrolysis due to moisture, light, temperature and lypolyticezyeme reaction which create off favour in edible oils. Indeed, the oil oxidation propability increased when the fatty acid content of oil raised. Because FFAs are more unstable in the free state than when they have been esterified to glycerol.

Oil treatment	25˚C	45˚C
0.02% , 0 d	0.034 (±0.003)	0.034 (±0.004)
0.02%, 28 d	0.045 (±0.004)	0.071 (±0.02)
0.02%, 90 d	0.071 (±0.00)	0.11 (±0.03)
0.04%, 0 d	0.034(±0.002)	0.034 (±0.001)
0.04%, 28 d	0.049 (±0.03)	0.064 (±0.00)
0.04%, 90 d	0.064 (±0.002)	0.098 (±0.005)
0.08%, 0 d	0.034 (±0.015)	0.034 (±0.001)
0.08%, 28 d	0.048 (±0.003)	0.064 (±0.00)
0.08%, 90 d	0.058 (±0.005)	0.094 (±0.005)
Control, 0 d	0.034 (±0.00)	0.034 (±0.003)
Control, 28 d	0.056 (±0.006)	0.068 (±0.004)
Control, 90 d	0.083 (±0.00)	0.14 (±0.01)

Table1: Evolution of acid value, AV (mg KOH/ gr oil) of corn oil samples without antioxidants added (Control) and with different concentrations of curcumin (0.02%, 0.04% & 0.08%) in specific intervals (0-28-90 days) in darkness

As can be seen in Table 1 and Table 2, the fatty acid content of samples including different concentrations of curcumin (0.02%, 0.04% and 0.08%) during the storage period whether in lightness and darkness were lower than control without any additives. The trend of

fatty acid formation after 21 days remarkably increased at 45˚C, but at 25˚C the production of FFAs required more time. However, the light had slight effect on the free fatty acids' production. Moreover, their trend in a specific temperature at both lightness and darkness storage condition were the same (Data not shown). Although fatty acids are secondary products of oil oxidation, only volatile fatty acids can make the flavor and aroma deterioration. Accumulation of nonvolatile decomposition products such as FFA during oxidation can lead to colour changes which indicate the extend of oil deterioration.

Oil treatment	25˚C	45˚C
0.02% , 0 d	0.033(±0.001)	0.034 (±0.002)
0.02%, 28 d	0.05 (±0.00)	0.075 (±0.003)
0.02%, 90 d	0.071 (±0.002)	0.146 (±0.01)
0.04%, 0 d	0.033(±0.01)	0.034 (±0.004)
0.04%, 28 d	0.045 (±0.007)	0.068 (±0.002)
0.04%, 90 d	0.064 (±0.002)	0.1 (±0.00)
0.08%, 0 d	0.034 (±0.003)	0.034 (±0.002)
0.08%, 28 d	0.049(±0.004)	0.064 (±0.003)
0.08%, 90 d	0.06 (±0.01)	0.094 (±0.005)
Control, 0 d	0.034(±0.001)	0.03 (±0.001)
Control, 28 d	0.06 (±0.006)	0.07 (±0.001)
Control, 90 d	0.083 (±0.003)	0.15 (±0.045)

Table2: Evolution of acid value, AV (mg KOH/ gr oil) of corn oil samples without antioxidants added (Control) and with different concentrations of curcumin (0.02%, 0.04% & 0.08%) in specific intervals (0-28-90 days) in lightness

IV is a measurement that estimates the degree of unsaturation of fats and oils. A decrease in the IV is consistent with the increase of lipid oxidation. Reduction of IV in lightness is in the following order: 0.08% curcumin < 0.04% curcumin < 0.02% curcumin < control (Data not shown). In fact, lipid oxidation is a phenomenon which includes of a complex series of chemical reactions, is characterized by a decrease in the total unsaturated content of the oil due to abstraction of hydrogen adjacent to a double bond and the formation of free radicals. Hence the higher temperature (45˚C), which could accelerate the oil oxidation, would also maximum reduction of the IVs. The level of unsaturation in the corn oil reduced gently toward the end of 28th day then the reduction of unsaturation increased rapidly due to the high level of oxidation. Nevertheless, lightness has not any significant effect on IV. According to the results obtained, curcumin as a natural antioxidant can be an effective substitute of synthetic antioxidants.

CONCLUSIONS

Exposure to both high temperature and lightness causes oxidative deterioration of lipids, vitamins, proteins and colorants in foods, leading to the formation of off flavours, nutrient losses and discoloration. Curcumin as a natural antioxidant can act on the lipid system to inhibit the lipid oxidation and undesirable changes. The 0.02% of curcumin can dramatically extend the oil shelf life. In this study, we clearly assert, the chemical lipid oxidation of corn oil samples was more effected by temperature, whereas the color deterioration of curcumin boosted at lightness more than high temperature.

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