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ANTIOXIDANT EFFECT OF POWDER AND EXTRACTS OF THE DATE SEED BY-PRODUCTS THAT CAUSE ENVIRONMENTAL PROBLEMS ON THE OXIDATIVE STABILITY OF SESAME OIL

АНТИОКСИДАНТНОЕ ВЛИЯНИЕ ПОРОШКА И ЭКСТРАКТА ФИНИКОВ КАК ПРИЧИНА ЭКОЛОГИЧЕСКИХ ПРОБЛЕМ В ОКИСЛИТЕЛЬНОЙ СТАБИЛЬНОСТИ КУНЖУТНОГО МАСЛА

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Antioxidant effects of the date powder and extracts on the oxidative stability of sesame oil stored at 70 °C were investigated. For this purpose, the date powder (at the concentration of 2 %, 6 % and 10 %) and extract (at the concentration of 1 %, 3 % and 5 %) were added into sesame oil. Effects of the date powder and extract on the oxidative stability of sesame oil were assessed as connected with colour (Hunter *L, a* and*b*), viscosity, free fatty acid (FFA%) and peroxide value. The consequences were compared with 0.02% BHA and control sample. All concentrations of the date powder and extracts also showed greater activity than BHA on sesame oil. But the addition of 10 % date powder was shown the greatest effect. The addition of 10 % date powder has been determined to show best impact on peroxide value of sesame oil.

Исследованы антиоксидантное влияние порошка и экстрактов фиников на окислительную стабильность кунжутного масла, хранящегося при температуре 70 °С. Для этой цели порошок (в концентрации 2 %, 6 % и 10 %) и экстракт фиников (в концентрации 1 %, 3 % и 5 %) добавляли в кунжутное масло. Влияние порошка и экстракта фиников на окислительную стабильность кунжутного масла оценили как связанные с цветом (Hunter *L*, *a* andb), вязкостью, величиной свободных жирных кислот (СЖК%) и перекисным числом. Результаты сравнивали с 0,02 % БГА и контрольной пробой. Все концентрации порошка и экстрактов фиников также показали большую активность, чем БГА в кунжутном масле. Добавление 10 % порошка фиников показало наибольший эффект. Установлено, что добавление 10 % порошка фиников наилучшим образом влияет на перекисное число кунжутного масла.

Keywords: date powder, date extract, sesame oil, antioxidan, BHA.

Ключевые слова: порошок фиников, экстракт фиников, кунжутное масло, антиоксидант, БГА.

Oxidative degradation of lipids is one of the main factors limiting the shelf-life of food products. Oxidative degradation occurring fats and oils leads to the formation of unwanted taste and odor, the emergence of a large number of compounds harmful to human health, a decrease in nutritional value. The oxidation reactions due to the fatty acids may be inhibited by antioxidants that present naturally in oils and fats or subsequently added to foods such as tocopherols, sulphur compounds, ascorbic acid or phenolic substances. Antioxidant is the name the overall group of compound that free radicals caused by oxidation reactions stopping or slowing down. Because of these properties, antioxidants may protect food quality by preventing oxidative deterioration. Antioxidants, we can divide to two groups as of synthetic (unnatural) and natural antioxidants (Alaca and Arabacı, 2005).

Synthetic antioxidants have been used to retard undesirable changes as a result of oxidation in many foods for over 50 years. There are certain safety concerns and carcinogenic issues related to the used of synthetic antioxidants such as butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA) and tertiary butylhydroquinone (TBHQ) and hence their use in foods is being discouraged. Especially tertiary butylhydroquinoneusage is banned in certain countries. For a long time, due to damages of synthetic antioxidants and consumers prefer natural antioxidants, for improve the properties of foods such as smell and taste, used as contribution oilseeds, spices and natural aromatic plants, in particular their essential oils has gained increasing importance (Ali, 2010; Çoban and Patır, 2010; Mechergui et al., 2010). *Date* species are getting increasing economic importance as their fruits are cherished as both fresh and processed fruits which result in production of substantial quantities of inedible date seed as waste although it has been reported to contain valuable natural antioxidants. Increasing date fruit consumption has resulted in efforts to utilize potential nutritional benefits of date seed. In general plant seeds are considered as valuable sources for producing edible oil for nutritional, industrial, and pharmaceutical applications. There are few reports on the utilization of date seed natural products for their effects in other food products. Antioxidant activity of extract of rosemary was evaluated in natural olive and sesame oils stored at 55 °C (Özcan, 1999).

The purpose of this study was to evaluate compare antioxidant activities of date powder and extract compareto antioxidant activity of BHA in sesame oil.

Sesame oil was provided from the local oil factory of Konya, Turkey. All solvents used were of analytical grade. The seeds of date (*Phoenix dactylifera* L.) (sukary cv.) fruitwere obtained by manually removal them from flesh of date fruit obtained from local market in Riyadh, Saudi Arabia. Manual washing of seed was carried out remove any adhering flesh contents following by drying in air. A further drying process was carried out at 50 °C for 5 h followed by grinding of seeds to form powder passable from 1–2 mm screens. The powder was stored at 4 °C up to analysis.

Isolation of powder and extract of date. At 10 g powdered date seed sample was mixed by shaking with 50 ml of methanol (Merck, Darmstadt, Germany) in a flask at 35 °C for 1 h followed byfiltration and centrifugation. The solvent was removed under reduced pressure using rotary evaporator. Different concentrations of residue were used as natural antioxidant in sesame oil (Özcan and Akgül, 1995).

The addition of antioxidant into sesame oil and storage process. Date powder (2 %, 6 % ve 10 %), date extract (1 %, 3 % ve 5 %) and BHA (0.02 %) as antioxidant were added at particular concentrations into separately 60 mL sesame oil. Sesame oil that was not added date extract was stored as for control group together with other samples at 70 °C. Beginning FFA% value, peroxide value, colour and viscosity value of sesame oil were designated. For each samples, FFA%, peroxide, colour and viscosity were analysed on 2nd, 5th, 8th and 12th days and results were noted.

Determination of peroxide number. About calculated amount of oil sample was weighed in the erlenmayer. 10 mL chloroform, 15 mL acetic acid and 1 mL potassium iodide solution were added upon its and were shaken. Then, closing the mouth of it was kept in a dark environment for ~ 5 min. At the end of this period, 75 ml distilled water and a few drops of starch solution were added upon its and sample was titrated with 0.01 N sodium thiosulfate (AOAC, 1990). Peroxide value were calculated according to the following formula.

$$\text{Peroxide value: } (V / m) \times 10,$$

V – used in titration sodium thiosulfate, ml; m – sample weight, g

Assessment of Instrumental Color. A colorimeter (Minolta Chroma meter CR 400 (Minolta Co., Osaka, Japan) was used for colour analysis. Oil sample (20 mL) was put into a clean petri and the colour value of three different regions was read in the instrument and averages were taken for triplicate reading. A CIELAB colorimetric system was used. The liquid probe of colorimeter was immersed into the sample kept in the petri dish kept on white tile followed by recording of CIE lab coordinates which were the average of ten reading for L*, a* and b*. The L*was attributed to the measurementof whiteness which ranged from 0 (black) to 100 (white). The red color was explained by coordinate a*which showed either positive (red) or negative (green) values. The b*values reflected yellow when positive and blue when negative (Pagliarini and Rastelli, 1994; Criado et al. 2004).

Determination of % free fatty acid. The oil samples were weighed to 5 g fat ± 0.01 for determination of % free fatty acid of frying oil, thawed in 100 mL ether. A few drops of phenolplthalein were added and were shaked. Finally, it titrated with 0,1 N KOH (potassium hydroxide) solution, consumption was recorded. % FFA were calculated according to the following formula:

$$\text{FFA\% : } (V / m) \times 2{,}8,$$

V – consumed KOH solution, ml; m – sample weight, g

Determination of viscosity. 35–45 mL sample of oil was put into the viscometer device. Value was recorded as mPas.

Statistical analyses. Analysis of variance (Püskülcü and İkiz, 1989) was applied to the results of properly replicated data for obtaining statistical significance which was defined at $P < 0.05$).

Peroxide value. The peroxide value (PV) is the measure of active oxygen in oils and it is the amount of peroxide oxygen as milieqivalangram in 1 kg oil. As shown while initial peroxide value of sesame oilwas determined as 6.31 meq O_2/kg, from 27.09 meq O_2/kg (2^{nd} day) to 256.95 meq O_2/kg (12^{th} day) of peroxide values of the control sample; from 25.77 meq O_2/kg (2^{nd} day) to 194.52 meq O_2/kg (12^{th} day) of peroxide values of sample that 0.02 % BHA added; from 5.82 meq O_2/kg (2^{nd} day) to 199.51 meq O_2/kg (12^{th} day) of peroxide values of sample that 1 % date extract added; from 6.22 meq O_2/kg (2^{nd} day) to 112.38 meq O_2/kg (12^{th} day) of peroxide values of sample that 3 % date extract added; from 7.46 meq O_2/kg (2^{nd} day) to 152.40 meq O_2/kg (12^{th} day) of peroxide values of sample that 5 % date extract added; from 20.49 meq O_2/kg (2^{nd} day) to 216.27 meq O_2/kg (12^{th} day) of peroxide values of sample that 2 % date powder added; from 15.0 meq O_2/kg (2^{nd} day) to 156.65 meq O_2/kg (12^{th} day) of peroxide values of sample that 6 % date powder added; from 6.76 meq O_2/kg (2^{nd} day) to 70.10 meq O_2/kg (12^{th} day) of peroxide values of sample that 10 % date powder added were seen to increase. Increase for preservation period were seen in peroxide values of all samples. Addition of 1 % and 3% date extract were seen to reduce more than addition of 0.02 % BHA, 3 % date extract and 2 % and % 6 date powder. While addition of 10 % date powder caused by an increase of less than the other samples on peroxide value of sesame oil; 0.02 % BHA addition was not decline too much the peroxide value. Increase in the number of peroxide is thought tobe explainedwith oil and fat to be oxidized exposing to heat, light and air. Inoxidized of oilformed peroxides and hydroperoxide and the peroxide value of oil rises. Increase in peroxide value of all samples was determined in this study. However, thought that addition of 10% date powder showed the greatest effect on oxydative stability of sesame oil.

Color analysis. The highest *L* value was determined in sesame oil that BHA added at the end of 12^{th} day. *L* value of sesame oil that 10% date powder added was changed at least and it is close to '*L'* value of sesame oil that nothing added (0^{th} day). The hydroperoxides fission in double bond fatty acidsas a result of the improve of oxidation with the effect of heat and so alcohols, aldehydes, short-chain acids and hydrocarbons are formed. These formations cause darkening in oil color. At this stage we say that addition of 10 % palm powder has increase minimum thus it has prevent darkening of the oil color. Excluding the 8^{th} day; 'a' values which is designated of sesame oil that BHA added on the 2^{nd}, 5^{th} and 12^{th} days and a volues of sesame oil that 3 %, 5 % date extract added are closest initial value of sesame oil. As to a value is the lowest, in sesame oil that 10 % date powder added was determined. For control, sesame oil that 2% date powder added at the end of 8^{th} day and sesame oil that 6 % date powder added at the end of 2^{nd} and 5^{th} days, 'a' values were determined to be quite high. The initial value (0^{th} day) to the nearest b value was seen in sesame oil that 5% date extract and 10 % date powder added excluding the 12^{th} day of their. While b value of control sample decreased on the 2^{nd}, 5^{th} and 8^{th} days, it increased on the 12^{th} day. Particularly the lowest 'b' value was determined in control sample at the end of 8^{th} day. As to the highest 'b' value was determined in sesame oil that 5% date extract added at the end of 12^{th} day. The sesame oils stored at 70 °C were evaluated according to the Hunter color system. The colour values were expressed as '*L'* (brightness/darkness), *a* (redness/greenness) and *b* (yellowness/blueness).

Free fatty acid. Free fatty acids are the weight of milligrams of potassium hydroxide necessary to neutralization of 1 gram oil. The addition of date powder and extract were as effective as BHA on FFA%. The free fatty acids were lowest in sesame oils that 2 % and 6 % date powder added. Free acid values of sesame oil that BHA, date powder and date extract added were lowest than free acid value of sesame oil that nothing added (0^{th} day). According to 0^{th} day, the free acidity increased during experiment. Generally, date powder inhibited oxidation in sesame oil.

Viscosity. Addition of BHA, date powder and extract into sesame oil increased the viscosity. While the addition of BHA increased at the furthest the viscosity, the addition of date powder and extract increased less than addition of BHA. While the peroxide value of all the samples increased their viscosity values also increased. Increasing in viscosity of sample that BHA added was highest (2^{th} day: 44.8 mPa.s; 12^{th} day: 52.1 mPa.s). We can explain this change in viscosity occured with oxidation of oil is exposed to heat, light and air. Hydroperoxides are exposed to dehydration or are transformed into free radicals which become dimers, trimers, epoxides, alcohols and hydrocarbons during the formation of ketones with the advancement of oxidation. The viscosity of oil increases as a result of formed these free radicals. While the peroxide value of sample that 6 % date powder added rised, viscosity of its partially reduced on 5^{th} and 8^{th} days and slightly increased on 12^{th} day (2^{nd} day: 46.3 m Pa.s; 5^{th} day: 44.9 mPa.s; 8^{th} day: 44.8 mPa.s; 12^{th} day: 46.3 mPa.s). Biglari et al. (2008), a study examined the antioxidant activity and phenolic content of various date palm (*Phoenix dactylifera*) fruits from Iran, they have demonstrated the potential of Iranian dates as antioxidant functional food ingredients.

As a result of this study; effects of addition of diverse concentrations of date powder and extract have been examined on sesame oil stored for 12 days at 70 °C. The date powder have been examined to show the antioxidant effect more than the addition of 0.02 % BHA and date extract. As to the best effect, the addition of 10 % date powder has been examined to show. Effects of the date powder and extract on the oxidative stability of sesame oil were assessed as connected with colour (Hunter *L, a* and *b*), viscosity, free fatty acid (FFA%) and peroxide value.

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КВАНТОВО-ХИМИЧЕСКИЙ РАСЧЕТ И СИНТЕЗ НОВЫХ АЗОМЕТИНОВЫХ СОЕДИНЕНИЙ, ОБЛАДАЮЩИХ АНТИОКСИДАНТНОЙ АКТИВНОСТЬЮ

QUANTUM-CHEMICAL CALCULATION AND SYNTHESIS OF NEW AZOMETHINE COMPOUNDS WITH ANTIOXIDANT ACTIVITY

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В работе приведены результаты квантово-химического моделирования новых азометинов перспективных в биологии, биохимии и медицине.

This publication represents some of the data obtained when applying the methods of quantum chemical modeling to azomethine structures, which are promising compounds for use in biological and medical sciences.

Ключевые слова: оптимизация, метод теории функционала плотности, антиоксидантная активность.

Keywords: optimization, density functional theory method, antioxidant activity.

Поиск перспективных препаратов, имеющих определенную биологическую активность, является одним из основных направлений научной деятельности в жизни человека в силу увеличения биоразнообразия микроорганизмов и растущего числа заболеваний, по мере открытия новых биохимических механизмов патологических процессов и модификация уже известных.

Молекулы, имеющие в своем составе –CH=N– связь применяются в неорганической, органической, аналитической, биологической химии и могут проявлять антиоксидантную, противомикробную, противораковую, противовоспалительную, противогельминтную, противогрибковую, противовирусную активность.

Выявление различных химико-биологических свойств соединений эмпирическим путем полезно для обнаружения биологической активности соединений, но такой подход часто дорог в применении и требует много вре-