AUSTRALIAN JOURNAL OF BASIC AND APPLIED SCIENCES

ISSN:1991-8178 EISSN: 2309-8414
Journal home page: www.ajbasweb.com

The importance of eggplant peels anthocyanins on edible oils as natural antioxidants

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ARTICLE INFO

Article history:
Received 18 September 2015
Accepted 1 October 2015
Available online 16 October 2015

Keywords:
Fish oil, lipid profile, HDL cholesterol, LDL cholesterol, triglycerides

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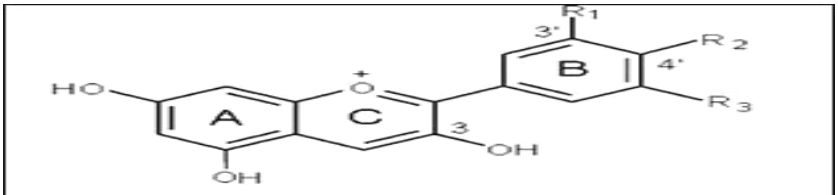
ABSTRACT

The oxidation of edible oils during processing and storage via autoxidation and photosensitized resulting in a large amount of desirable chemical compounds which have harmful effects on human health. So this investigation was carried out to determine the ability of anthocyanins extracts to act as natural antioxidants instead of BHT with edible oils exposed to 180˚±5˚C for continuous 8 hours. The anthocyanins extracted from eggplant peels by using the acidified aqueous technique to give a high yield from anthocyanins. Total extracted anthocyanins and their fractions were determined by using HPLC. Delphinidine-3-(p-coumaroyl-rutinoside)-5-glucoside (nasunin) is the major component of anthocyanin isolated from eggplant peels. The rancimate test and fatty acids composition were determined in all collected samples to discuss the thermal stability in the presence of the extracted anthocyanins. The obtained results highlight the enormous potential of eggplant peels anthocyanins as competitor antioxidants to synthetic antioxidants when used with edible oils.

INTRODUCTION

Anthocyanins are one of the most essential flavonoids which inhibit lipid oxidation by scavenging radicals or by other mechanisms such as singlet oxygen quenching metal chelation and lipoxygenase inhibition (Krinsky,1992, Mohamed *et al.*,1999). Anthocyanins are secondary products of plant metabolism and always exist in nature as glycosides as shown in Fig. (1)



ANTHOCYANIDIN	R_1	R_2	R_3
Pelargonidin (Pg)	H	OH	H
Cyanidin (Cy)	OH	OH	H
Delphinidin (Dp)	OH	OH	OH
Peonidin (Pn)	OMe	OH	H
Petunidin (Pt)	OMe	OH	OH
Malvidin (Mv)	OMe	OH	OMe

Fig.(1): Generalized structure for anthocyanidins.

To Cite This Article: Dalia M. Hikal.2015. **The importance of eggplant peels anthocyanins on edible oils as natural antioxidants** Aust. J. Basic & Appl. Sci., 9(33): 491-493, 2015

Australian Journal of Basic and Applied Sciences, 9(33) October 2015, Pages: 491-496

Edible oils are containing high amounts of polyunsaturated fatty acids which are very sensitive to oxidative deterioration, and form a higher ratio of oxidized products under the effect of frying temperatures (Marquez-Ruiz and Dobarganes, 1996; Lolos *et al.*, 1999).

The term lipid oxidation usually refers to three consecutive reactions or stages, known as initiation, propagation and termination Fig. (2).

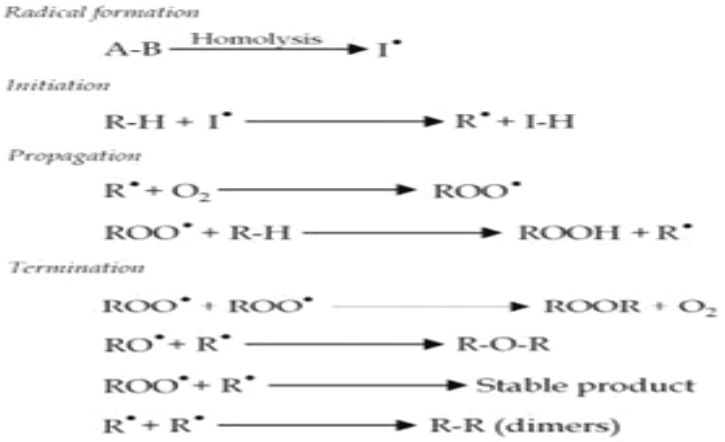


Fig. (2): Lipid Oxidation.

In the initiation stage, free radicals are formed through thermolysis, where the break of covalent bonds is induced by heat.

Today, there is a great interest in finding and evaluating natural sources of antioxidants of alternatives and replacements of synthetic antioxidants which provide not to be quite safe and could have some undesirable side effects on human health (Kumar *et al.,* 2013 and Castaneda *et al.,* 2009). Anthocyanins pigment has potent antioxidant in comparing with synthetic antioxidants such as BHT (Narayan *et al.,* 1999).

The eggplant peels (*Solanum melongena*) contain anthocyanin pigments, which have strong antioxidant properties? The extraction of anthocyanins can take place in acidified solution (Monic *et al.,* 2014).

Eggplant is ranked as one of the top ten vegetables in terms of oxygen radical scavenging capacity due to the fruit's phenolic constituents (Cao *et al.,* 1996). This paper aims to discuss the ability of anthocyanins pigments extracting from eggplant peels to act as natural antioxidants in comparing with BHT (Butylated Hydroxytoluene) as synthetic antioxidants to the edible oils such as sunflower oil and cottonseed oil in emulsion system for 8 hours of continuous heating time at 180±5˚C.

MATERIALS AND METHODS

Materials

Sunflower oil, cottonseed oil and eggplant peels were collected from Egyptian markets.

Methods

Extraction of anthocyanins:

The total anthocyanins pigments of eggplant peels (*Solanum melongena*)were extracted by using (ethanol: water: HCL; 70:30:1, v/v/v) as described by (Todaro *et al.*,2009).

Colourimetric determination of extracted anthocyanins:

Anthocyanin pigments contents of the original extracts were determined calorimetrically according to the procedure described by Lees and Francis (2009) using the following equation:-

$$\text{Total (OD/100g)} = \frac{\text{Absorbance at 535 nm} \times \text{Diluted volume} \times \text{Total volume of the extract (ml)}}{\text{The volume of extract used for absorbance measurement} \times \text{Weight of sample (gm)}} \times 100$$

Total anthocyanins (mg/100g) = Total OD/98.2

Fractionation and determination of anthocyanins:

The extracted anthocyanins were fractionated and determined by using HPLC in the Central Laboratory of Food Technol. Res. Inst., Agric. Res. Center, Giza, Egypt.

Samples were analyzed by High-Performance Liquid Chromatography (HPLC) Agilent 1100 series equipped with auto sampler, column compartment set at 45°C, quaternary pump, variable wavelength at 520 nm and

degasser set the flow rate of HPLC system to 1 ml/min across column C18 Hypersil BDS (4.6 × 250 mm, particle size 5 µm).

The oxidative stability of eggplant peels anthocyanins:

Both of BHT and the extracted anthocyanins in the concentration of 200ppm was added to sunflower oil and cottonseed oil for 8 hours of continuous heating time at 180±5˚Cthen the oil samples were collected for further analysis to determine the oxidative stability for the extracted anthocyanins.

Rancimat method:

Rancimat (Metrohm, Herisau, Switzerland) was used to determine the oxidative and thermal stabilities of oil samples as described by Tsakins *et al.*, 1999).

Identification and determination of fatty acids composition:

Fatty acids composition of oil samples was identified and determined using Agilent 6890 GC according to AOAC (2005).

RESULTS AND DISCUSSION

Extraction and quantitative determination of anthocyanins:

The total amount from anthocyanins extracted from eggplant peels was 190.2 mg/100g by using the acidified aqueous technique.

Identification of the individual fractions:

Fig. (3) show the maximum absorption recorded with eggplant peels anthocyanins was at wave length 544 nm.

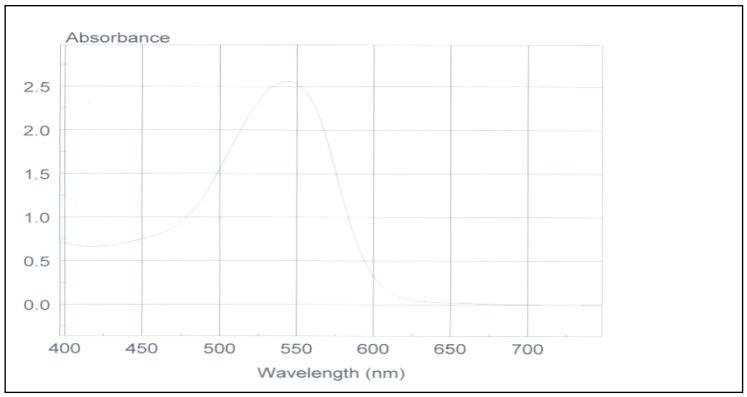


Fig. (3): U.V spectrum of eggplant peels anthocyanins.

Fractionation and determination of anthocyanins using High-Performance Liquid Chromatography (HPLC):

The extracted eggplant peels anthocyanins were fractionated and determined by using HPLC. The fractions detected) were delphinidin (90.7%) at Rt 14.855 and petunidin (9.3%) at Rt 8.592 min (Fig.4). These data were in agreement with Noda *et al.*,1998 and Monic *et al.*, 2014. They confirmed thatDelphinidine-3-(p-coumaroyl-rutinoside)-5-glucoside (nasunin) is the significant component of anthocyanin isolated from eggplant peels.

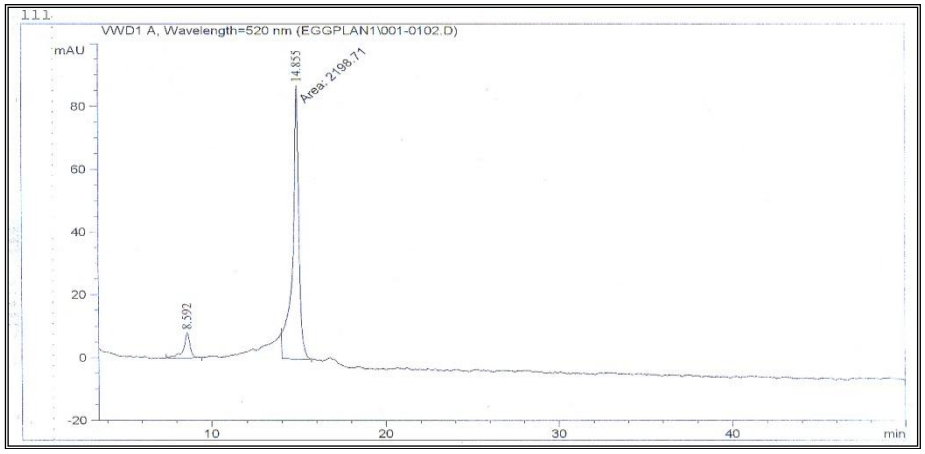


Fig.(4): HPLC chromatogram of anthocyanins extracted from eggplant peels.

Effect of eggplant peels anthocyanins on oxidative stability of edible oils:

The oxidative and thermal stabilities of sunflower and cottonseed oils with and without extracted anthocyanins from eggplant peels were assessed by the Reanimate method at 100ºC. Data presented in Table (1) showed that the induction period of sunflower and cottonseed oils was 0.9.30 and 0.9.97 h, respectively, meanwhile, it was 11.50 and 12.20 h, respectively by the addition of 200ppm BHT. But, it became 14.13 and 12.75, respectively with oil samples with eggplant peels anthocyanins in the same concentration (200ppm).

These results indicated that oil samples with both synthetic and natural tested antioxidants had observed oxidative stability under the effect of heat at 180˚±5˚C especially that with eggplant anthocyanins. The presence of hydroxyl groups in the composition of anthocyanins led to the formation of several hydrogen bonds which consume large amounts of energy during heating. Thus hydrogen bonding was found to diminish the influence of temperature on edible oil oxidations (Morley *et al.*, 2007). On the other hand, sunflower oil samples were more stable than samples of cottonseed oil with extracted anthocyanins. This result was in agreement with (Whittaker 1996 and Steel *et al.*, 2006), who reported that sunflower contained high amounts of natural antioxidants such as tocopherols which responsible for its oxidative stability.

So, it could be concluded that eggplant peels anthocyanins are more efficient as natural antioxidants than the BHT as a synthetic antioxidant, especially when added to edible oil such as sunflower and cottonseed oils. Edible oils are susceptible to oxidation which produces undesirable volatile compounds and cause detrimental flavour effects to food.

Meanwhile, oleic acid was the predominant unsaturated fatty acid that has a physiological effect in reducing serum blood cholesterol and prevent cardiac disease (Lumor and Akoh, 2005).

Table (1). Effect of eggplant peels anthocyanins on oxidative stability of edible oils.

Oil samples	Induction Time (hours)
Sunflower oil	09.30
Cottonseed oil	09.97
Sunflower oil with BHT 200 PPM	11.50
Cottonseed oil with BHT 200 PPM	12.20
Sunflower oil with extracted anthocyanins 200 PPM	14.13
Cottonseed oil with extracted anthocyanins 200 PPM	12.75

Fatty acids composition of edible oils with eggplant peels anthocyanins:

From Data presented in Table (2), it could be noticed that lauric, myristic, stearic acids and the palmitic acid were the predominant saturated fatty acids. While oleic and linoleic acids were the unsaturated fatty acids which detected in all oil samples. The percentages of palmitic acid (C16:0) of sunflower and cottonseed oils were 10.2 and 11.5 %, in the oil samples with 200 ppm BHT were was the predominant saturated fatty acid which detected in sunflower oil control, sunflower oil treated with 200 ppm BHT were 11.6 and 13.53%, respectively and they were 12.77 and 11.29 %, respectively in oil samples with eggplant peels anthocyanins 200 ppm. On the other hand, the Linoleic acid (C18:2) were 60.94,57.06;57.17,55.13; 51.45 and 53.18, respectively. Also, from the collected data it could be noticed that eggplant peels anthocyanins played as natural antioxidants more better than BHT in compared with oil samples, especially with sunflower oil samples.

These data were in agreement with (Schuler, 1990) and El-Sheikh(1993) who reported that cottonseed oil has a high level of gamma and delta tocopherol than alpha-tocopherol nearly 40% of its natural tocopherol. Meanwhile, Sunflower oil has a high level of alpha tocopherols nearly 95% from its natural tocopherol. Alpha-tocopherol is fully substituted benzoquinone derivative and is the most effective antioxidants than beta, delta and gamma tocopherol being highly reactive with peroxy radicals and prevent them from participating in propagation reactions. By forming α tocopheroxy radical which is stable because of a resonance, structure forms the benzoquinone ring (Kamal-Eldin and Appelqvist,1996).

When two alpha tocopherol radicals interact with each other, they form alpha tocopheryl quinone which regenerated back alpha-tocopherol in the presence of reducing agent(Nawar,1996 and Hikal,2003). Also, primary antioxidants are mono or poly hydroxyl phenols with various ring substitution like anthocyanins. The substitution with electron donating groups (e.g. CH) in ortho and para position to the hydroxyl group of phenol, increase the antioxidantactivity of the compound by an inductive effect (Rajalakshmi and Narasimhan,1996 and Hikal,2011). The same authors concluded that alpha-tocopherol is the most reactive tocopherol, so the sunflower oil has more stable than cottonseed oil.

Table (2): Fatty acids composition of edible oils with eggplant peels anthocyanins.

Fatty acids	Sunflower oil	Cottonseed oil	Sunflower oil + 200 ppm BHT	cottonseed oil +200 ppm BHT	Sunflower oil + 200 ppm eggplant peels anthocyanins	cottonseed oil + 200 ppm eggplant peels anthocyanins
Myristic C14:0	1.10	1.76	3.23	4.33	4.74	5.47
Palmatic C16:0	10.2	11.5	11.6	13.53	12.77	11.29
Stearic C18:0	1.4	2.3	1.58	2.76	2.82	2.6
TSFA	12.7	15.56	14.41	20,62	20.33	17.36
Oleic C18:1	21.51	23.37	23.78	22.07	25.22	25.12
Linoleic C18:2	60.94	57.06	57.17	55.13	51.45	53.18
Linolenic C18:3	4.85	4.01	2.64	2.18	3.0	3.34
TUSFA	87.3	84.44	85.59	79.38	79.67	81.64

CONCLUSION

Finally, it could be concluded that anthocyanins extracted from eggplant peels had highly antioxidative activity when added to the edible oils such as sunflower and cottonseed oils under the effect of 180˚±5 ˚C.

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