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*Full Length Research Paper*

# γ-Irradiation and Maillard reaction products (MRPs) effect on phenolic content, antiradical and volatile compounds of Sewi dates

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**This study was to determine the influence of γ-irradiation at 1.0 kGy and maillard reaction products (MRPs) derived from cysteine/glucose on the selected quality parameters, namely phenolic content, antiradical activity, polyphenoloxidae inhibition, sensory evaluation and volatile compounds of Egyptian Sewi date palm fruits (SDPFs) during storage for three months at various temperatures. The total phenolic content of the treated samples ranged from 0.30 to 0.38 mg/g in γ-irradiation at 25 $^0$C and in MRPs at -18 $^0$C, respectively after three months of storage. MRPs showed higher antioxidant activity during storage at all temperatures applied in this study compared to γ-irradiation. However, sensory properties were not affected by γ-irradiation significantly, MRPs treatment revealed unpleasant taste. The main volatile compounds positively identified in the date palm fruit were ethyl acetate (18.4%), ethyl benzoate(7.31%), benzaldehyde (4.14%), furfural (2.37%), while linalool (5.34%).**

**Keywords:** Sewi date, irradiation, MRPs, antiradical activity, volatile compounds.

## INTRODUCTION

Nowadays, the consumption of fruit and vegetables is widely regarded as important and good for health, epidemiological evidence suggests that a diet rich in fruits and vegetables promotes a lower incidence of chronic diseases such as cancer, cardiovascular disorders and diabetes (Kchaou et al., 2013). Indeed, date palm fruit possess antioxidant and antimutagenic properties *in vitro* and this is due, partly, to its high content of polyphenolic compounds and vitamins as important dietary constituents (Al-Turki et al*.,* 2010).

Date consumption, therefore, can a contribution to management of these degenerative oxidative diseases.

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Postharvest contamination of palm dates by microorganisms is very common under the hot, humid climate such as that prevailing in Egypt. The spoilage of dry fruits by insect, colour deterioration and chemical changes during storage is a serious problem. Irradiation technology has been proved to be effective in reducing postharvest losses, controlling the stored product insects and controlling the microorganisms (Mohammadzai *et al.,* 2010)

Polyphenoloxidases (PPO) are responsible for the enzymatic browning reactions occurring during the handling, storage and processing of fruits and vegetables. The browning pigments lead to organoleptic and nutritional modifications, thus depreciating the food product.Several methods such as the addition of sulfites and the exclusionof oxygen as well as thermal processing have been used to inhibit enzymatic browning (Dincer *et al.,* 2002).

However, for inactivation of polyphenoloxidase, thermal processing has limits like loss of sensory and nutritional quality of food products (Sun *et al.,* 2002). Also consumer awareness of the risks associated with sulfite-containing anti-browning agents and increased regulatory scrutiny have created the need for substitutes. Therefore, the development of alternative safe and efficient antibrowning agents has become crucial in order to preserve or minimize the loss of fresh fruits and vegetables. Many papers have reported the inhibition activity of polyphenoloxidase by Maillard reaction products or antibrowning agents (Billaud *et al.,* 2005, Wu *et al.,* 2008).

In studies about date palm fruit volatiles at the mature stage, approximately 100 compounds have been identified, including alcohols, aldehydes, esters, ketones, lactones and terpenes (Torres *et al.,* 1996). Until now only Reynes et al. (1996) had studied the aroma volatile compositions of three mature Tunisian date fruits but no research was performed about the evolution of volatiles in date fruits during irradiation or treatment with antibrowning agents. Hence, the present study was undertaken to compare the response of Sewi date palm fruits to γ-radiation and MRPs treatment with respect to phenolic content, antiradical activity, polyphenoloxidase inhibition, sensory evaluation and volatile constituents changes during storage at various temperatures.

## MATERIALS AND METHODS

### Plant materials

Sewi date variety was procured from New valley (EL-Wady El-Gadeed) governorate, Egypt, at the beginning of 2012-2013 harvest seasons. Mature fruit at tamr stage of uniform size, free of physical damage and injury from insects and fungal infection, were selected and used for all experiments.

### Irradiation of date fruits

The irradiation process was carried out at National Centre for Radiation Research and Technology. The selected fruits were irradiated with γ- rays at one dose 1.0 kGY which use for disinfestations. The irradiation processes were performed at room temperature using a $Co^{60}$γ-source with dose rate of ~2.77 kGY/h. The irradiation source had been calibrated by the National Physical Laboratory (NPL, Teddington, UK) using the dichromate dosimetry.

### Chemicals and standards

Glucose,L-cysteine,DPPH$^0$(2,2'-diphenyl-1-picryhydrazylradical, Ferrozine and gallic acid (3,4,5-trihydroxybenzoic) were from Sigma, hydrochloric acid; Folin–Ciocalteu's phenol reagent and acetic acid were from Merck; sodium chloride, methanol and sodium sulphate; diethyl ether, $FeCl_2$, sodium bicarbonate was from Fluka.

### Maillard reaction products (MRPs) preparation

Glucose (0.1 M) and L-cysteine (0.25 M) aqueous solutions were used to prepare model MRPs. Aliquots (150 mL) of these solutions were placed without pH control in pyrex vials (200 mL). Samples were heated at 95 $^0$C for 120 min, in an air convection oven. After the vials were cooled in ice, aliquots of the soluble part of MRPs were used to determine their effect on the selected quality parameters in date fruits after dipping for 30 min.

### Sewi date palm fruits extraction

The edible parts of treated samples were pitted, crushed and cut to small pieces with a sharp knife and dry-blended for 3 min with a blender (Panasonic, Penang, Malaysia). The blends were then extracted with 300 ml methanol–water (4:1, v/v), at room temperature (25 $^0$C for 5 h. The extracts were then filtered and centrifuged (HERMLEZ 323 K, German) at 4000 xg, for 10 min and the supernatant was concentrated under reduced pressure at 40 $^0$C for ~3 h using a rotary evaporator (Heidolph laboratory 4000 efficient) to obtain themethanolic crude extract. The crude extracts were kept in dark glass bottles inside the freezer until use.

### Estimation of total phenolic content by the Folin–Ciocalteu test

Total phenolics were determined using Folin–Ciocalteau reagents (Singleton and Rossi, 1965). Results were expressed as mg gallic acid equivalents (GAE)/ g sample.

### Polyphenoloxidase (PPO) assay

### Crude enzyme extract

Fruit tissue (10g) was homogenized with 200 mMTris–HCl buffer, pH 7.2 using a homogenizer. The homogenate was centrifuged at 21000 xg for 10 min at 4 $^0$C. The supernatant was designated as crude extract and stored at −20 $^0$C for further analysis.

### Spectrophotometeric assay of PPO

Polyphenoloxidase activity was carried out with catechol as a substrate according to the spectrophotometric procedure of Mustapha and Selselet-Attou, (2007). The percentage of relative inhibition for each compound was compared with that of the control (100% activity).

**Antiradical activity measurements**

**DPPH$^0$ radical scavenging activity**

Free radical scavenging activity of methanolic extract was determined using the 2,2'-diphenyl-1-picrylhydrazyl (DPPH$^0$) method (Ao *et al.,* 2008). Scavenging activity (%) was calculated using the following formula:
% Inhibition = [($A_{control} - A_{treatment}/=A_{control}$)] X 100
where: $A_{control}$: is the absorbance of the control; $A_{treatment}$: is the absorbance of the treatments.

**Metal chelating assay**

The metal chelating ability of the samples under investigationwas determined according to the method of Decker and Welch (1990). The ability of the extract to chelate ferrous ion was calculated using the following equation:
% chelating effect = [1– $Abs_{sample}$/ $Abs_{control}$] X 100

**Sensory evaluation**

Sensory evaluations were conducted on γ-irradiated, MRPs treatment and control (unirradiated) samples. The quality attributes, including colour, texture, taste and overall acceptability were evaluated by a 10 judges from the staff of food science and technology division, national research center. The evaluation was based on a nine-point hedonic scale with 9 representing like extremely and 1 representing dislike extremely**.**

**Volatile compounds analysis**

**Volatile isolation**

The volatiles in headspace of well ground fruit tissues for the control and treatments under study were isolated by using a dynamic headspace system. The samples were purged for ~3 h with nitrogen gas (grade of $N_2$> 99.99 %). The headspace volatiles were swept into cold traps containing diethyl ether and pentane (1:1, v/v) and hold at –10 ºC. The solvents containing the volatiles were dried over sodium sulfate anhydrous for 1 h. The volatiles were obtained by evaporation of the solvents under reduced pressure.

**Gas Chromatography/Mass Spectrometry (GC-MS)**

GC-MS analyses were performed with a Varian (Perkin-Elmer Autosystem gas chromatograph equipped with a DB-5 capillary column (60 m X 0.25 mm X 0.25 um; Agilent) and a Varian Saturn 2000 ion trap mass detector. Analytical conditions were as follows: injector and transfer line temperatures were 250 and 240 $^0$C, respectively; oven temperature was programmed from 40 to 250 $^0$C at 3 $^0$C/min; carrier gas was helium at 1 ml/min; splitless injection.

**Compounds Identification**

The linear retention index (RI) values for unknowns were determined based on retention time data obtained by analyzing a series of normal alkanes ($C_6$-$C_{22}$). Volatile components were positively identified by matching their RI values and mass spectra with those of standards, also run under identical chromatographic conditions in the laboratory (Adams, 2007).

**Statistical analysis**

Data are presented as means ± standard deviation. One way analysis of variance (ANOVA) was performed using SPSS.14 software to analyze the statistical significance. The value $P< 0.05$ considered as significant level.

**RESULTS AND DISCUSSION**

**Phenolic content**

The effect of γ-irradiation and MRPs on Sewi date fruit presented a phenolic content in the range 0.13–0.58 mg/g FW (Fig.1). The MRPs treatment showed the highest value after three months of storage at -18 $^0$C, followed by γ-irradiation, while the untreated samples had the lowest value 0.13 mg/g at 25 $^0$ C at the end of storage. During storage at ambient temperature, the phenolic compounds in untreated dates, decreased gradually for the 3 months of storage. The results in the present showed that the Sewi date fruit has equal to or higher phenolic content compared with other fruits, such as strawberries (330±4 mg/100g FW), raspberries (228±6 mg/100g FW), apples (48±1 mg/100g FW) and tomato (30±1 mg/100g FW) (Proteggente *et al.,* 2002). However, the current results contradict with those of Mansouri, Embarek *et al.* (2005) who found lower levels of phenols for some Algerian date cultivars ranged from 2.49 to 8.36 mg/100g FW, using a similar measuring technique. This is possibly due to cultivar variation and/or environmental conditions as well as irradiation and treatment with MRPs which may lead to significantly ($P\leq0.05$) increase in phenolic content.The obtained results are remained weaker than those observed by Wu *et al.* (2004) who showed that the phenol content can vary from 572 to 661 mg GAE/100 g FW in two date varieties consumed in the U.S.A. but higher than Al-Farsi *et al.* (2007) who mentioned that the concentration varied from 172 to 246 mg GAE/100 g FW in three native sun-dried date varieties grown in Oman. The decrease in phenolic content during storage may be due to the conversion of soluble tannin into insoluble tannin (Mutlak and Mann, 1984).

**DPPH$^0$ assay**

The antioxidant activity, as measured by DPPH$^0$ radical scavenging %, was at the maximum level at treatment with MRPs and significantly ($P\leq0.05$) decreases in control sample

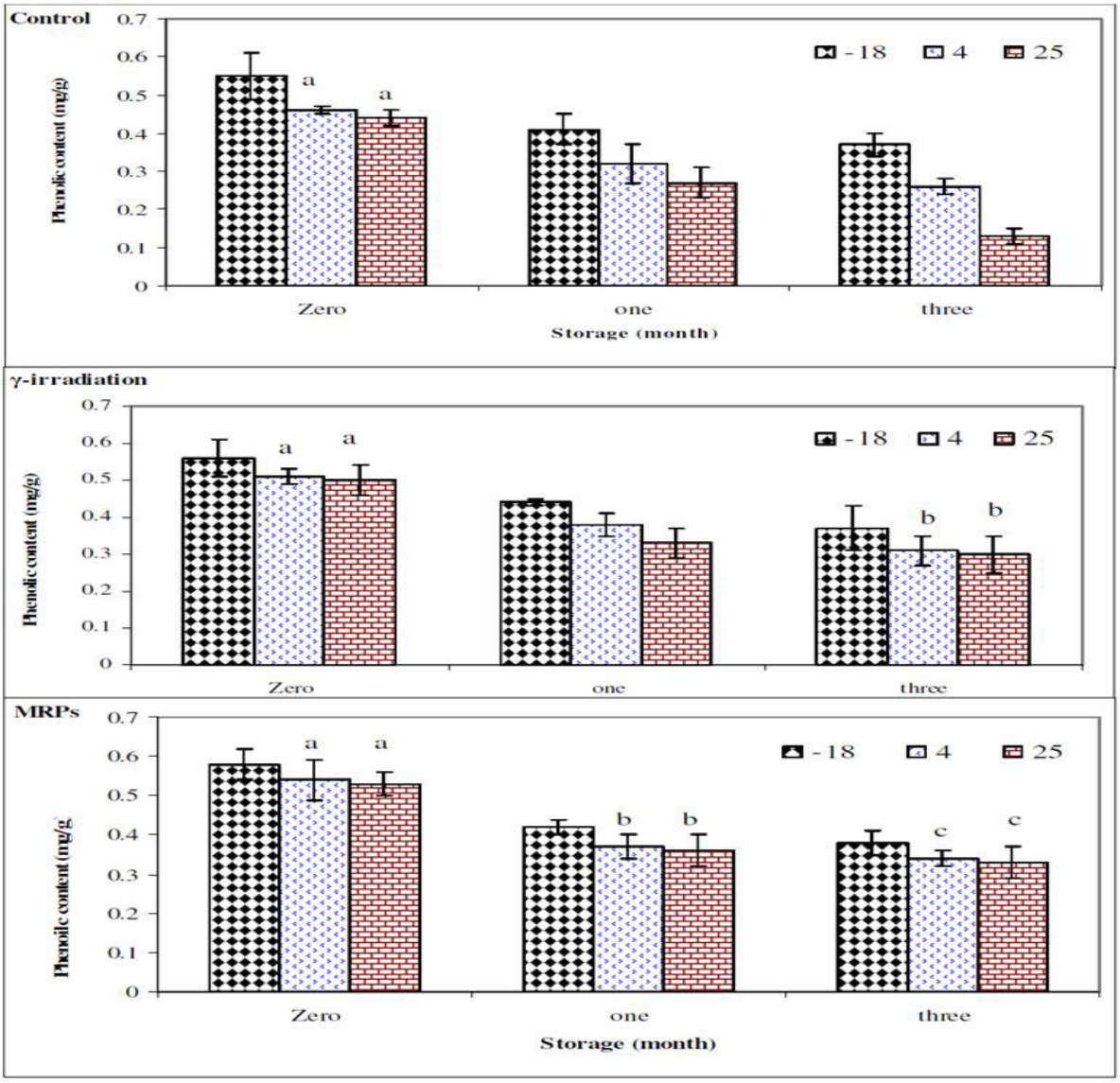


**Figure 1 Effect of γ-irradiation and Maillard reaction products (MRPs) on phenolic content (mg/g) of Sewi date during storage at different temperature ($^0$ C).** Values with the same letter within the same column are not significant ($P \leq 0.05$).

during storage as shown in Table (1). The scavenging property of date fruit extract can be attributed due to presence of hydroxyl groups which can donate the electron and neutralize the existing free radical in the reaction mixture. The obtained data in agreement with Guo *et al.* (2003) who reported that dates had the second highest antioxidant value of 28 fruits commonly consumed in China.

The antioxidant activity of date fruits have also been assessed and reported by other researchers using different methods. Seven of the Algerian ripe date fruit varieties have been evaluated by 2,2'-diphenyl-1-picry-hyrazyl (DPPH) radical method and reported to have antiradical efficiency (AE = 1 / $EC_{50}$) ranging from 0.08 to 0.22 (Mansouri *et al.,* 2005). Three sun-dried Omani date cultivars showed an antioxidant activity ranging from 8.2 to 12.5 mm Trolox $g^{-1}$ using the Oxygen Radical Absorbance Capacity (ORAC) assay (Al-Farsi *et al.,* 2005).

Previous studies showed, that in many heated foods, a nonenzymatic brown reaction can occur leading to the formation of complex series of compounds called Maillard reaction products (MRPs: natural hydrophilic and hydrophobic brown pigments) (Whitfield 1992) which explain the high antioxidant activity in the present work. These MRPs may cause wrong correlations between the antioxidant capacity and the phenolic content. A product that has a low amount of phenol but a high amount of MRPs may show a high antioxidant activity.

**Table 1: Antioxidant activity of Sewi date fruit treated with γ- irradiation and MRPs during storage for three months at various temperatures at three levels "uL" as determined by DPPH$^0$**

| Treatment and storage | Zero time | | | One month | | | three months | | |
|---|---|---|---|---|---|---|---|---|---|
| Temperature ($^0$C) | 150 | 300 | 450 | 150 | 300 | 450 | 150 | 300 | 450 |
| | **Control** | | | | | | | | |
| **-18** | 28.3±0.14* | 31.6±0.21 | 34.6±0.21 | 23.7±0.21 | 28.4±0.14 | 31.7±0.23 | 19.4±0.12 | 23.7±0.11 | 29.8±0.14 |
| **4** | 27.4±0.21 | 30.2±0.15 | 32.4±0.16 | 22.4±0.18 | 26.4±0.13 | 29.3±0.18 | 18.2±0.14 | 22.4±0.18 | 28.4±0.19 |
| **25** | 26.9±0.19 | 29.5±0.14 | 31.7±0.12 | 21.3±0.12 | 25.8±0.10 | 28.2±0.13 | 16.8±0.19 | 19.6±0.14 | 25.7±0.16 |
| | **MRPs** | | | | | | | | |
| **-18** | 32.5±0.18$^a$ | 41.98±0.37 | 49.52±0.17$^a$ | 54.15±0.38$^a$ | 56.23±0.31 | 57.65±0.32 | 59.16±0.28 | 61.35±0.25$^a$ | 65.17±0.22 |
| **4** | 31.7±0.41 | 39.5±0.25$^a$ | 46.7±0.13 | 53.20±0.16$^a$ | 54.63±0.19 | 56.41±0.17 | 57.80±0.41$^a$ | 60.11±0.16$^a$ | 63.52±0.28 |
| **25** | 33.4±0.21$^a$ | 38.7±0.15$^a$ | 48.3±0.19$^a$ | 43.59±0.17 | 50.18±0.24 | 54.80±0.31 | 57.09±0.18$^a$ | 59.57±0.11 | 60.46±0.18 |
| | **γ– irradiation** | | | | | | | | |
| **-18** | 32.5±0.18 | 41.98±0.37 | 49.52±0.17$^a$ | 33.09±0.14 | 36.47±0.12 | 43.24±0.18 | 37.83±0.27$^a$ | 48.65±0.17 | 57.65±0.11 |
| **4** | 31.7±0.41$^a$ | 39.5±0.25 | 48.7±0.13$^a$ | 25.51±1.2$^a$ | 32.21±0.15 | 38.43±0.24 | 36.52±0.34$^a$ | 39.12±0.27 | 40.54±0.14$^a$ |
| **25** | 30.4±0.21$^a$ | 38.7±0.15 | 46.3±0.19 | 24.38±0.23$^a$ | 30.78±0.31 | 37.37±0.31 | 34.77±0.18 | 37.54±0.16 | 39.25±0.16$^a$ |
| | **BHA 200 ppm** | | | | | | | | |
| **-18** | 55.7±0.8 | | | 55.3±0.9 | | | 54.2±0.18 | | |
| **4** | 54.9±0.13 | | | 54.6±0.17 | | | 53.7±0.5 | | |
| **25** | 56.8±0.18 | | | 56.4±0.8 | | | 55.6±0.19 | | |
| | **TBHQ at 200 ppm** | | | | | | | | |
| **-18** | 59.7±0.11 | | | 59.3±0.18 | | | 58.4±0.14 | | |
| **4** | 58.3±0.14 | | | 57.4±0.13 | | | 56.8±0.17 | | |
| **25** | 57.4±0.12 | | | 56.7±0.12 | | | 55.4±0.16 | | |

*: Values are expressed as mean ± SD (n=3); Values with the same letter within the same column are not significant ($P \leq 0.05$)

**Metal chelating assay**

Data in **Table (2)** showed that the antioxidant activity decreased with prolonged storage time and increase in storage temperatures -18, 4 and 25 $^0$C, respectively, an opposite trend was noticed for the concentrations of MRPs. In contrast to many fruits that tend to lose stability over storage, γ-irradiated and MRPs treatments of Sewi date fruit are relatively stable over a long period of time if kept ina refrigeration conditions (Table 3). The antioxidant activities of diverse plants or foods were reported to be enhanced by γ-irradiation (Dixit *et al.,* 2010).

**Antiradical activity**

In the current study, the variations in the level of antioxidant activity in MRPs and γ-irradiated treatment with Sewi dates were 1.66 to 2.23 folds, based on DPPH$^0$ and metal chelating assay, respectively. Such large variations were reported by others working with different dietary plants and plant products (Prior *et al.,* 1998). The obtained results revealed that, MRPs showed higher antioxidant activity compared to γ-irradiation, this activity originated from the hydrophobic fraction probably due to the presence of several MRPs. Generally, the hydrophilic antioxidants such as water-soluble fraction of phenolic compounds and MRPs were mainly preferred by consumers. Therefore, MRPs can be used not only for human nutrition but also for technological purposes. Indeed, MRPs confer on food different interesting properties such as colour, flavour, nutritional value and certain stability during its conservation (Mastrocola and Munari, 2000).

Another explanation for the ability of the studied treatments to exhibit the antioxidant activity can be attributed to the presence of two major types of antioxidant compounds. The first can be the wide range of phenolic compounds including *p*-coumaric, ferulic, gallic, cafeic and sinapic acids, flavonoids, and procyanidins (Hong *et al.,* 2006); the second, the presence of other water soluble antioxidants, such as vitamin C and oligo-elements (Al-Farsi *et al.,* 2007).

**Table 2: Antioxidant activity of Sewi date fruit treated with γ-irradiation and MRPs during storage for three months at various temperatures at three levels "uL" as determined by metal chelating assay**

| Treatment and storage | Zero time | One month | | | | | three months | | |
|---|---|---|---|---|---|---|---|---|---|
| Temperature ( $^0$C) | 150 | 300 | 450 | 150 | 300 | 450 | 150 | 300 | 450 |
| | **Control** | | | | | | | | |
| **-18** | 28.3±0.14* | 31.6±0.21 | 34.6±0.21 | 24.6±0.22 | 26.9±0.24 | 32.5±0.17 | 22.7±0.12 | 26.8±0.14 | 30.4±0.13 |
| **4** | 27.4±0.21 | 30.2±0.15 | 32.4±0.16 | 23.5±0.18 | 25.2±0.13 | 30.6±0.12 | 21.6±0.19 | 24.2±0.21 | 29.5±0.17 |
| **25** | 26.9±0.19 | 29.5±0.14 | 31.7±0.12 | 21.6±0.15 | 24.9±0.17 | 29.7±0.24 | 19.3±0.11 | 23.7±0.16 | 25.5±0.12 |
| | **MRPs** | | | | | | | | |
| **-18** | 43.8±0.14[a] | 52.6±0.13 | 61.3±0.24[a] | 57.2±0.26 | 63.4±0.12 | 67.5±0.19 | 56.8±0.28 | 59.7±0.15 | 64.5±0.16 |
| **4** | 42.4±0.19[a] | 52.3±0.27 | 60.8±0.14[a] | 53.4±0.14 | 56.1±0.19 | 58.4±0.32 | 52.6±0.14[a] | 57.3±0.24 | 62.7±0.17 |
| **25** | 39.7±0.21 | 49.7±0.15 | 58.4±0.17 | 50.7±0.13 | 52.7±0.18 | 56.8±0.29 | 51.3±0.18[a] | 54.2±0.17 | 58.7±0.26 |
| | **γ irradiation** | | | | | | | | |
| **-18** | 43.8±0.14[a] | 52.6±0.13[a] | 61.3±0.24 | 52.4±0.15 | 58.2±0.34 | 63.2±0.29 | 46.5±0.21 | 48.5±0.19 | 51.6±0.16 |
| **4** | 42.4±0.19[a] | 52.3±0.27[a] | 60.8±0.14 | 50.6±0.24 | 51.7±0.18 | 55.8±0.26 | 42.7±0.25 | 45.4±0.11 | 47.3±0.12 |
| **25** | 39.7±0.21 | 49.7±0.15 | 58.4±0.17 | 48.3±0.19 | 47.9±0.32 | 53.6±0.24 | 39.2±0.18 | 40.8±0.15 | 42.8±0.14 |
| | **BHA 200 ppm** | | | | | | | | |
| **-18** | 53.4±0.22 | | | 52.7±0.19 | | | 51.8±0.14 | | |
| **4** | 52.8±0.18 | | | 51.4±0.16 | | | 50.4±0.19 | | |
| **25** | 52.9±0.15 | | | 51.2±0.12 | | | 49.7±0.11 | | |
| | **TBHQ at 200 ppm** | | | | | | | | |
| **-18** | 55.2±0.17 | | | 54.8±0.11 | | | 53.7±0.22 | | |
| **4** | 54.6±0.13 | | | 53.6±0.16 | | | 51.6±0.12 | | |
| **25** | 54.3±0.14 | | | 52.4±0.19 | | | 50.8±0.23 | | |

**Inhibitory effect of MRPs and γ-irradiation on Sewi date PPO**

The inhibitory effect of Maillard reaction products (MRPs) and γ-irradiation on Sewi palm date polyphenoloxidase during storage at various temperatures are exhibited in Fig. 2.Our results in good agreement with Nicoli *et al.,* (1991) who reported that MRPs showed two different effects on polyphenoloxidase: an inhibition of the enzyme activity and the appearance of aninitial lag phase, due to the chelating properties of polyphenol oxidase on $Cu^{2+}$ and the reducing properties of the MRPs.

In literature, it was mentioned that MRPs and⁄orcaramelisation products formed from sucrose or glucose and glycine mixtures caused a strong decrease in the browning catalysed by PPO from apple or mushroom tyrosinase as well as decrease in peroxidase activity extracted from apple and⁄or carrot. It was hypothesized that thiol-derived MRPs could partly repress PPO activity by interacting with copper at the active site of the protein (Brun-Merimee *et al.,* 2004). As shown in the obtained data MRPs produced from cysteine/glucose were more active polyphenoloxidase inhibitors than γ-irradiation treatment.

The main properties of the MRPs structure that make it a potential inhibitor the amadori rearrangement product, which is a type of amino reductone that possess chelating, reducing and oxygen-scavenging properties. The deterioration in antibrowning activities of MRPs could be caused by their degradation (Wu *et al.,* 2008).

**Sensory evaluation**

Table 3 shows the sensory evaluation of MRPs, γ-irradiated and non-irradiated dates during storage for up to 3 months. Irradiation at 1.0 KGY followed by 1 or 3 months post-irradiation storage at room temperature did not affect the sensory properties of Sewi dates.

The obtained data in good manner with El-Sayed and Baeshin (1983) who found no change in sensory quality of four irradiated varieties of dates at 0.2 kGY. In another work by Grecz *et al.* (1986), panelists could not discriminate between unirradiated dates and those irradiated at levels of 1.0 to 6.0 KGY0.

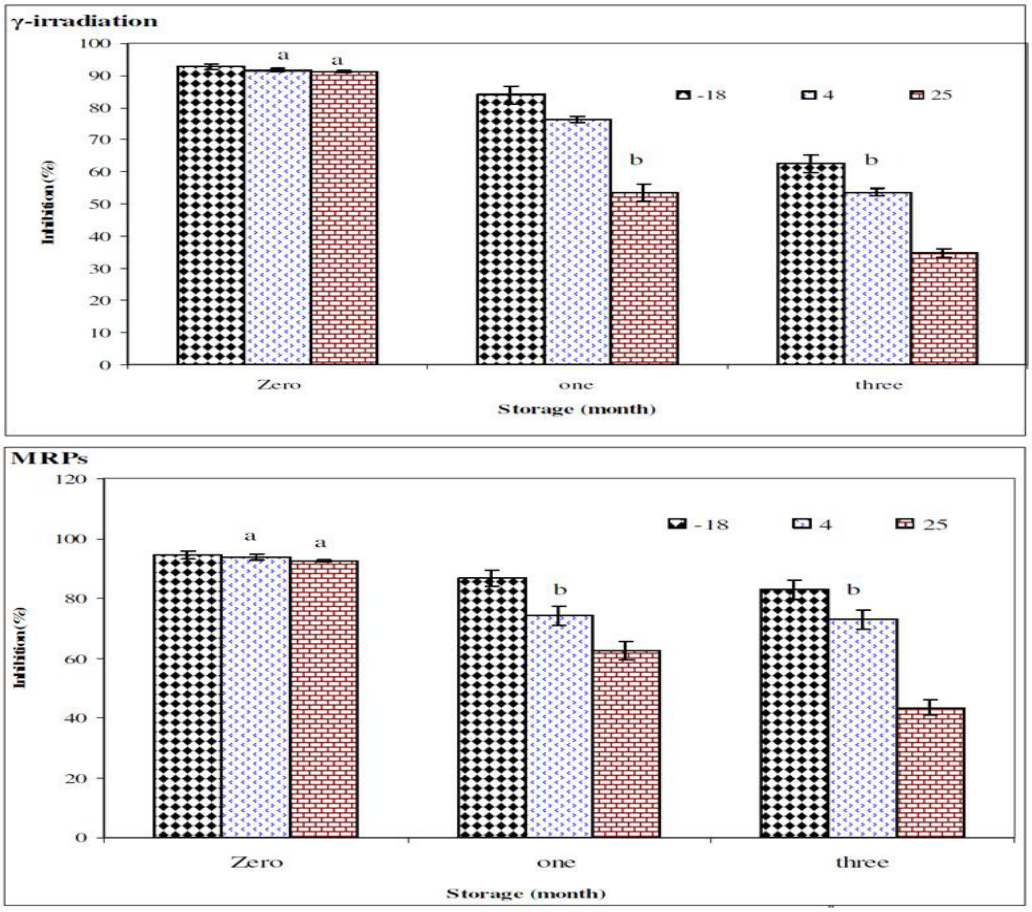


**Figure 2: Inhibition of Sewi date PPO by γ-irradiation and MRPs during storage at various temperature($^0$ C).** Values with the same letter within the same column are not significant ($P \leq 0.05$)

Sewi is a semi-dry date fruit and its insensitivity towards irradiation is probably due to the low water activity and low protein content as compared with many other fruits and vegetable where threshold for undesirable organoleptic changes was found in the range of a few hundred krad (Hasegawa *et al.,* 1969).

The obtained results showed that the sensory quality of the MRPs decreased with the storage time, and it appeared to be the worst at storage of month 3 especially in taste. Panelists evaluated that the MRPs treatment showed (Table 3) unpleasant taste at the end of storage at 25 $^0$C. However, immediately after irradiation the overall sensory scores of the irradiated and non-irradiated samples were not significantly ($P \leq 0.05$) different.

Our results are in agreement with general results reported in the literature on the effect of radiation on sensory characteristics of other similar Lescano and Narvaiz (1992).

**Effect of γ-irradiation and MRPs on aroma volatiles of Sewi date palm fruits**

A total of 28 volatile compounds were detected, namely 12 esters, 3 alcohols, 6 aldehydes, 6 terpenoids and 1 ketones (Table 4). The data lists the retention indices and peak area percent values for various volatile components which had identified.

The main volatile compounds positively identified in the Sewi date palm fruit were ethyl acetate (18.4%), ethyl benzoate(7.31%), benzaldehyde (4.14%), furfural (2.37%), while linalool (5.34%). Although 3 alcohols were identified, their total concentration was low (1.69%) compared to that of the esters (61.83%) present in Sewi date palm fruits. A little higher percentage (12.42%) of aldehydes compounds may be characteristic to the flavour of date palm fruits.

**Table 3: Sensory evaluation scores for the quality attributes of untreated, irradiated and treated with MRPs dates (Sewi) stored at various temperatures**

| Storage time (months) / Temperature | Treatment | Colour | Texture | Taste | Overall acceptability |
|---|---|---|---|---|---|
| **18-$^0$C** | | | | | |
| Zero time | | 8.3±1.2*[a] | 8.4±0.8[a] | 8.6±0.7[a] | 8.4±0.5[a] |
| 1 | | 7.5±1.5[b] | 6.7±1.1[b] | 7.2±0.9 | 7.1±0.8 |
| 3 | | 6.8±1.4[c] | 5.6±1.3 | 6.7±1.2[b] | 6.4±1.7[b] |
| **4 $^0$C** | | | | | |
| Zero time | | 8.4±0.8[a] | 8.3±0.9[a] | 7.7±1.4 | 8.1±1.3[a] |
| 1 | **Control** | 7.8±1.7[b] | 7.2±1.3 | 6.4±0.7[c] | 6.8±0.5 |
| 3 | | 6.9±0.8 | 6.7±0.8[b] | 6.1±1.3 | 6.3±0.8[b] |
| **25 $^0$C** | | | | | |
| Zero time | | 7.6±0.8[b] | 7.8±1.2 | 8.4±0.7[a] | 7.9±0.8 |
| 1 | | 6.5±1.2 | 6.8±0.9[b] | 6.7±1.4[b] | 6.4±1.7[b] |
| 3 | | 6.3±0.9 | 6.1±0.7[c] | 6.2±0.9 | 6.3±0.8[c] |
| **18-$^0$C** | | | | | |
| Zero time | | 8.5±0.7 | 8.2±0.22 | 7.5±1.4 | 7.8±1.3 |
| 1 | | 7.4±0.9[b] | 7.4±1.1 | 6.5±0.8 | 6.7±0.7 |
| 3 | | 7.1±1.3 | 6.5±1.6 | 6.4±0.9[c] | 6.4±1.2[b] |
| **4 $^0$C** | | | | | |
| Zero time | | 8.3±1.6 | 8.2±1.4 | 7.4±1.2 | 7.8±1.8 |
| 1 | **γ-irradiation** | 7.2±1.2 | 7.1±0.9 | 6.6±1.4[b] | 7.6±1.5 |
| 3 | | 6.8±1.3[c] | 6.5±1.7 | 6.5±1.8 | 6.7±1.3 |
| **25 $^0$C** | | | | | |
| Zero time | | 7.4±1.4 | 7.7±1.3 | 7.6±1.3 | 7.5±1.1 |
| 1 | | 7.2±0.9 | 6.9±1.7 | 7.4±1.4 | 7.3±0.8 |
| 3 | | 6.8±1.6[c] | 6.6±1.3[b] | 6.7±1.9[b] | 6.5±0.19[b] |
| **18-$^0$C** | | | | | |
| Zero time | | 7.9±0.16 | 7.1±0.18 | 7.2±0.7 | 7.5±1.3 |
| 1 | | 7.5±1.5[b] | 6.7±1.4[b] | 6.9±1.2 | 7.3±1.4 |
| 3 | | 7.2±0.9 | 6.4±1.1 | 6.3±1.5[c] | 6.8±1.2 |
| **4 $^0$C** | | | | | |
| Zero time | **MRPs** | 7.5±0.15[b] | 6.7±1.3[b] | 6.5±1.8[b] | 6.8±1.5 |
| 1 | | 6.8±1.7[c] | 6.4±1.8 | 6.3±1.3 | 6.4±1.6[b] |
| 3 | | 6.5±1.5 | 6.1±1.1[c] | 6.2±0.9 | 6.3±1.7[c] |
| **25 $^0$C** | | | | | |
| Zero time | | 6.9±1.2[c] | 6.5±1.7[b] | 6.4±1.6[c] | 6.3±1.4[c] |
| 1 | | 6.4±1.3 | 6.3±1.1[c] | 6.2±1.4 | 6.1±1.3 |
| 3 | | 6.2±1.8 | 6.4±1.5 | 6. 1±1.2 | 6.2±1.5[c] |

- *Means in the same column for each individual storage time with the same superscript are not significantly ($P \leq 0.05$).
- Scoring scale: 1=dislike extremely, 9 =like extremely, Score (mean ± SD; n=10)

In general, each volatile compound is characterized by an odour threshold, so even if the qualitative composition of different fruits is almost the same, the aroma may vary when the relative proportions are different (Visai and Vanoli 1997).

Alcohols, aldehydes, ketones, and terpenes are responsible for the citrus, floral and fruity characteristics of date aroma (Richard, 1992).

The esters represent a higher number as well as percent area representation of compounds present in Sewi date palm fruits (Table 4). It may hence be concluded that the generation of these

**Table 4: Effect of γ-irradiation and MRPs on volatile compounds of Sewi palm date fruits stored for three months at -18 $^0$ C**

| Compounds | RI[a] | Control | | | γ-irradiation | | MRPs | | Characteristic odour | Identification method [c] |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Fresh | Stored | | | | | | | |
| | | | 1 | 3 | 1 | 3 | 1 | 3 | | |
| | | | | | | | | | | **Esters** |
| Ethyl acetate | 612 | 18.4[b] | 11.29 | 9.63 | 16.42 | 15.83 | 17.31 | 16.51 | Pineapple, ethereal | St, KI |
| Isoamyl acetate | 875 | 3.18 | 2.45 | 1.97 | 4.31 | 3.85 | 3.12 | 2.56 | | St, KI, MS |
| Ethyl hexanoate | 998 | 5.48 | 3.48 | 2.76 | 4.97 | 3.56 | 4.67 | 4.57 | | St, KI, MS |
| Hexyl acetate | 1008 | 6.18 | 5.27 | 4.68 | 5.36 | 4.37 | 5.61 | 4.82 | Apple, floral | St, KI |
| Pentylpropanoate | 1018 | 2.41 | 1.28 | 1.18 | n.d | 1.42 | 2.35 | 1.86 | | St, KI, MS |
| Methyl benzoate | 1093 | 2.82 | 1.61 | 2.31 | 1.34 | 1.84 | 2.71 | 2.64 | | St, KI |
| Ethyl heptanoate | 1096 | 3.25 | 1.28 | 1.42 | 2.91 | 2.92 | 2.95 | 2.74 | | St, KI, MS |
| Ethyl benzoate | 1176 | 7.31 | 1.94 | 1.64 | 5.67 | 4.83 | 5.62 | 4.29 | | St, KI |
| Ethyl octanoate | 1197 | 3.27 | 2.43 | 2.46 | 2.58 | 1.97 | 2.94 | 2.53 | | St, KI, MS |
| Hexyl isovalerate | 1247 | 2.58 | 1.49 | 1.37 | 1.29 | 1.21 | 2.83 | 2.79 | | St, KI, MS |
| Ethyl decanoate | 1396 | 3.46 | 2.42 | 3.53 | 2.97 | 3.27 | 3.26 | 2.76 | | St, KI, MS |
| Ethyl dodecanoate | 1596 | 3.49 | 1.49 | 1.62 | 2.98 | 2.59 | 3.26 | 3.17 | | St, KI, MS |
| **Alcohols** | | | | | | | | | | |
| 1-Pentanol | 762 | n.d | 1.53 | 4.25 | 1.28 | 1.37 | 3.18 | 2.51 | | St, KI |
| 1-octanol | 1070 | Tr | 4.25 | 4.31 | 2.42 | 2.31 | 1.97 | 1.83 | | St, KI, MS |
| 3-nonanol | 1110 | 1.68 | 2.51 | 3.61 | 1.34 | 2.46 | 1.72 | 1.68 | | St, KI, MS |
| **Aldehydes** | | | | | | | | | | |
| Hexanal | 807 | Tr | 2.34 | 3.41 | 1.65 | 2.34 | 2.34 | 1.94 | Fatty, fruity, green. | St, KI, MS |
| Furfural | 842 | 2.37 | 1.18 | 1.13 | 2.37 | 1.94 | 2.46 | 2.37 | Sweet, woody | St, KI |
| Benzaldehyde | 957 | 4.14 | 2.94 | 2.83 | 1.37 | 2.41 | 3.74 | 2.98 | | St, KI |
| Nonanal | 1103 | 1.37 | 3.46 | 5.61 | tr | n.d | tr | 1.19 | Apple, cocconut, grape, grapefruit. | St, KI, MS |
| Decanal | 1208 | 2.59 | 3.12 | 3.25 | 1.67 | 2.65 | 3.17 | 2.84 | | St, KI |
| Undecanal | 1310 | 1.95 | 1.73 | 2.42 | tr | 1.16 | 1.87 | 1.54 | | St, KI, MS |
| **Terpenoids** | | | | | | | | | | |
| Limonene | 1031 | 2.53 | 1.64 | 1.54 | 3.46 | 2.71 | 1.92 | 1.67 | Lemon, citrus, sweet. | St, KI, MS |
| 1,8-cineole | 1036 | Tr | 3.46 | 4.26 | 1.37 | 1.18 | 1.35 | 1.26 | | St, KI |
| Linalool | 1100 | 5.34 | 3.26 | 2.56 | 4.92 | 3.15 | 4.56 | 3.91 | Lemon, orange, floral. | St, K |
| Camphor | 1145 | 2.34 | 1.34 | 1.17 | 1.94 | 2.31 | 2.28 | 2.16 | | St, KI, MS |
| 4-terpineol | 1180 | 2.84 | 4.25 | 5.37 | 3.19 | 2.34 | 2.63 | 2.58 | | St, KI, MS |
| γ-citronellol | 1230 | 4.12 | 2.58 | 1.94 | 3.28 | 3.24 | 3.65 | 2.39 | | St, KI, MS |
| **Ketons** | | | | | | | | | | |
| γ-ionone | 1488 | 1.24 | 1.26 | 2.37 | 1.16 | 2.35 | 1.31 | 1.28 | Almond, berry, grape. | St, KI |

[a]: Linear retention indices (DB-5 column). [b]: Values are expressed as relative area percentage tr: ≤0.1% trace; n.d: not detected [C]: components identified by GC-MS and/or Kovat indices on DB-5 and Standard compounds (ST) run under similar conditions

compounds is characteristic to date palm aroma. The pronounced increase in the concentration of ethyl acetate and ethyl benzoatein date palm fruit shows that these compounds could contribute significantly for thefruity aroma.

Acetate esters such as 2-phenylethyl acetate, ethyl acetate and hexyl acetate are characterised by fruity, apple and pineapple odours (Richard, 1992). Two straight chain aldehydes, nonanal and decanal are expected to be responsible for the fresh and slightly green notes of dates (Crouzet, 1992).

The obtained results showed that γ-irradiation did not have significant effect on volatile compounds (Table 4) especially in esters and alcohols concentrations. The effects of irradiation on the flavour and aroma of other fruits were also quite variable. Strawberries irradiated at 0 to 2 kGy resulted in no significant differences in flavour and off-flavour (Yu *et al.,* 1995).

## CONCLUSION

On the basis of our finding, we conclude that Sewi date palm fruit constitutes a natural source of potent antioxidants that may prevent many diseases and could potentially be used in food and neutraceutical formulations. However, it is very interesting to accomplish this study by other interventions to know more about the different phenolic compounds using HPLC responsible for the antioxidant activity. To the best of our knowledge this the first study on the comparative efficiency of MRPs and γ-irradiation on sensory and volatile compounds of Sewi date fruits, therefore the study will be extend to identify and fractionation the main compounds of MRPs using GC-MS which cause the anti browning effect.

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