Arab Univ. J. Agric. Sci., Ain Shams Univ., Cairo, Egypt
27(2), 1459-1473, 2019
Website: http://ajs.journals.ekb.eg

PHYSICO-CHEMICAL PROPERTIES AND ANTIOXIDANT ACTIVITY OF EXTRACTED ESSENTIAL OILS FROM IRRADIATED ROSEMARY LEAVES AND CLOVE BUDS

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Received 30 March, 2019 Accepted 23 April, 2019

ABSTRACT

Rosemary and clove buds were irradiated with γ-irradiation at different doses (0 to 30kGy) and stored for 12months at room temperature (22±3 ^{0}C). The evaluation of irradiation depended on the chemical studies and antioxidant activity of extracted essential oils. Results showed significant difference for the essential oils yield at different doses during storage time. Compounds were fractionated and identified for extracted essential oils from each of non – irradiated and irradiated rosemary leaves and clove buds samples, the main components of essential oil extracted from either non-irradiated or irradiated rosemary were 1,8 cineole, camphor and γ-pinene 26.36, 12.63 and 16.98%, respectively, while, eugenol was the major component in clove essential oil (which extracted from non-irradiated and irradiated samples (81.69%). No differences were noticed in the % of essential oils constituents. Antioxidant activity as % of DPPH scavenging increased with the increasing of essential oils concentrations (250 up to 2500ppm). Furthermore, the effect of adding these extracted oils from non-irradiated and irradiated samples as well as their mixture (1:1) on the threshold odor scores of sunflower oil was observed. Rancimat test shown the high oxidative stability in sunflower oil supplemented with 0.3% clove essential oil which extracted from 15kGy irradiated sample was 11.99 hrs, its relative stability was 144.11% comparing with the oxidative stability of sunflower oil supplemented with 0.5% rosemary essential oil extracted from non-irradiated sample (9.76hrs) with 117.3% relative stability.

Keywords: Rosemary leaves, Clove buds, Irradiation, Essential oil, GC/MS, Antioxidant activity, Rancimat

INTRODUCTION

Spices, aromatic and medicinal plants, are used in all of the food industry **(Farag et al 1996)**, because of their properties as antimicrobial and antioxidant activities, due to their active compounds which determined by analytical techniques **(Koleva et al 2001).** Clove is a bud of a flowering Southeast Asia native tree (*Syzygium aromaticum*), and rosemary leaves is an evergreen shroud of *Rosmarinus officinalis Lamiaceae,* native to Mediterranean countries **(Nurdjannah and Bermawie, 2012 and Tucker & Maciarello, 1986)**. These plants are good and common example for aromatic plants which widely used in all over the world.

Volatile oils are produced from the primary secretions as secondary metabolites by aromatic plants, which are responsible for their smell, complex compounds obtained by each of distillation methods, localized in Mediterranean and tropical countries. Essential oil had a lot of properties: antimicrobial, antioxidant, antiseptic, anti-inflammatory, analgesic and other medicinal properties, were used in food preservation due to their properties **(Bakkali et al 2008)**. Rosemary and clove buds oils have high activities like: antimicrobial, antioxidant, and anti-inflammatory, these activities were due to presence of eugenol which the main component in the essential oils of those plants **(Amariei et al 2013)**.

Irradiation is known as an effective method for sterilization, pasteurization and food decontamination, considered as safe method **(Alam Khan and Abrahem, 2010)**. Because of these reasons, food irradiation attracted around the world to use "Atoms for Peace" **(Boisseau, 1994)**. Gamma irradiation process with specific doses under control is an effective technique to preserve spices comparing with microwave treatment, where it does not cause flavor compounds losing **(Sadecka et al 2005)**. Each treatment of food causes changes in some of chemical properties of food, meanwhile, irradiation treatment causes a slight difference in these parameters as mentioned by **(Salum et al 2009)**.

So, the aim of this study to evaluate the effect of gamma irradiation on the extracted essential oil, physico-chemical properties of extracted essential oils from rosemary leaves and clove buds and study their antioxidant activities.

MATERIALS AND METHODS

1. Materials

1.1 Plant materials

Dried rosemary leaves (*Rosmarinus officinalis*) were purchased at summer 2016 in June from El-Maghrabi Farm for aromatic plants, El-Nobareya, Egypt. Dried clove buds, (*Syzygium aromaticum*) were purchased at summer 2016 in June from a local market, Cairo, Egypt. Rosemary leaves and clove buds were kept in glass jars in room temperature (22±3 ^{0}C).

1.2 Chemicals

Butylated hydroxytoluene (BHT) as a synthetic antioxidant (of purity 99.9%) was purchased from Sigma Chemical Company, U.S.A. 2, 2-diphenyl-1-1picrylhydrazyl (DPPH) was purchased from Sigma-Aldrich, Germany and solvents were purchased from El- Nasr Pharmaceutical Chemicals Co., Cairo, Egypt.

1.3 Sun flower oil

Sun flower oil (Refined and free from artificial antioxidants) was purchased from ARMA for food industry Co., 10th of Ramadan, Cairo, Egypt.

2. Methods

2.1 Irradiation of plant materials

Irradiation was performed in the National Center for Radiation Research and Technology (NCRRT), Nasr City, Cairo, Egypt. Samples (50 gm.) of rosemary leaves or clove buds were packed in sterilized polyethylene bags and tightly sealed. The packed samples were treated with 0, 5, 10, 15, 20, 25 and 30 kGy of gamma rays using Russian gamma cell, Model Issledovatel utilizing Cobalt- 60 as an irradiation source with a dose rate of 2.5 kGy / h at 20^{0}C. All the samples were stored at laboratory conditions for 12 months at room temperature (22±3^{0}C) under a relative humidity of 50-70 %, till analysis after 0, 3, 6, 9 and 12months.

2.2 Extraction of essential oils

Dried rosemary leaves as well as dried clove buds, which irradiated or non- irradiated were stored for 0,3,6,9 and 12 months at room temperature. The essential oils were extracted from the samples by steam distillation method for 6 hrs. as described by **Guenther, (1961)**. The obtained essential oils were dried over anhydrous sodium sulfate and stored in dark bottles in refrigerator at 5±2^0 C until used.

2.3 Identification of chemical components of extracted essential oils

To identify the components of essential oils of dried rosemary leaves and dried clove buds, GC/MS analyses were done for those irradiated or non- irradiated and stored for 0,3,6,9 and 12 months at room temperature (22±3^{0}C) according to **Damjanovic et al (2005) and Politeo et al (2006)**.

2.4 Percentages of extracted essential oils

The percentages of essential oils contents in either non irradiated or irradiated dried rosemary leaves as well as dried clove buds which stored for 12 months were determined according to **AOAC (1996)**.

2.5 Physicochemical properties of extracted essential oils

Specific gravity, refractive index, acid value and ester value were determined according to **British Pharmacopeia (2004)**. Solubility in diluted alcohol was determined according to **European Pharmacopeia (2001)**.

2.6 Evaluation of adding extracted essential oils on the odor of sunflower oil

Odor evaluation was performed to illustrate the effect of adding rosemary leaves, clove buds essential oils and their mixture (1:1) at concentrations

(0.0%, 0.1%, 0.2%, 0.3%, 0.4% and 0.5% v/v) to sunflower oil according to **Ranganna, (1978)**, and the intensity of the odor was described according to **El-Baroty, (1988)** using the scale of 4 degree as following: 0 = no odor, 1= very weak odor, 2= higher acceptable odor, and 3= non acceptable odor.

2.7 Determination of the antioxidant activity of extracted essential oils

2.7.1 Measurement of scavenging activity

The antioxidant activity of rosemary leaves and clove buds essential oils either non-irradiated or irradiated were measured in terms of hydrogen donating or radical scavenging ability, using the stable radical DPPH (2,2-diphenyl-1-picrylhydrazyl) according to the method of **Brand-William et al (1995)**. Methanolic stock solutions of rosemary leaves and clove buds essential oils in different concentrations were made according to the method of **Politeo et al (2006)**. The decrease in absorbance at 517 nm was determined with Jenway 6300 spectrophotometer after 1h for all samples. Absorbance of the DPPH radical without antioxidant, (the control sample) was measured. Percent inhibition of the DPPH radical by the samples was calculated according to the formula of **Yen and Duh, (1994)** as follows:

$$\% \text{ Inhibition} = ((A_{c\,(0)} - A_{A\,(t)}) / A_{c\,(0)}) \times 100.$$

Where: $A_{c\,(0)}$ is the absorbance of the control at time = 0 min.
$A_{A\,(t)}$ is the absorbance of the antioxidant at time = 1h.

2.7.2 Measurement of different samples of sunflower oil which had different concentrations of extracted essential oils stability as a food system by Rancimat apparatus

The oxidative stability of sunflower oil as affected by the addition of the different concentration of studied essential oils or BHT was determined using A Metrohm Rancimat model 679 (Herisau, Switzerland). The oil samples for all determinations were randomized to determine their position in the heating block. **(Farhoosh and Moosavi, 2007)**.

2.8 Statistical analysis

Comparisons between different treatments were carried out by two ways analysis variance (ANOVA) followed by Tukey-Kramer multiple comparison test according to **SAS, (1996)**.

RESULTS AND DISCUSSION

Effect of γ-irradiation process on the extracted essential oils content (%) from either non-irradiated or irradiated rosemary leaves as well as clove buds samples.

Results are shown in **Table (1)** reporting the γ-irradiation effect at different doses 0 up to 30kGy on essential oils content (%). Also, explain the effect of storage at room temperature up to 12 months on the extracted essential oil from either rosemary leaves or clove buds as percentage. Significant ($p \leq 0.05$) difference could be observed among all the samples, either irradiated or not for their essential oil contents. Non irradiated rosemary yielded 1.41% at zero time, with note that; the percentage of essential oil yield was significant ($p \leq 0.05$) increased as irradiation dose increased up to 30kGy, it was accounted as 2.23%. Weather non- irradiated or irradiated samples showed significant ($p \leq 0.05$) shortage for the essential oil content during storage, where found that, essential oil content (%) of non-irradiated rosemary after 12 months was yielded 0.68%, while, 30kGy irradiated rosemary yielded 1.31% after the same storage period. So, results appeared that, the highest essential oil content was 2.23% yielded from 30kGy irradiated rosemary at zero time, while, the lowest yield was 0.68% extracted from non-irradiated rosemary after 12 months.

The results are in agreement with **Khattak and Simpson, (2010)** who reported that, significant ($p \leq 0.05$) changes were noticed in the extracted essential oil content after any kind of spices irradiated with different doses; they noticed maximum increasing (10.5%) in the essential oil yield especially at 25KGy. **Variyar et al (1997)** reported that, irradiation causing cell wall structure disabling accompanied by the highest extraction rate of oil from tissue.

Irradiation effect of clove buds on the extracted essential oil present was illustrated in the same **Table (1)**, the effect of storage on the oil content showing as can be inferred in the same table, the content of non-irradiated clove buds was 16.33% of essential oil at zero time of storage. While, this yield increased up to 18.03% with an increasing irradiation dose up to 30kGy with direct proportion; moreover, can be observed that, storage time induced decreasing in the extracted essential oil percentage for both samples. There is reverse fit between storage time and essential oil content, where found that, essential oil content of non-irradiated clove buds after 12months storage was

Table 1. Essential oil content (%) of irradiated rosemary as well as clove buds during storage at 0, 3, 6, 9 and 12 months

Storage periods (months)	Irradiated doses (kGy)						
	0	5	10	15	20	25	30
	Rosemary						
Zero time	1.41^{GHIJ}	1.55^{F}	1.71^{DE}	1.85^{BC}	1.95^{B}	2.11^{A}	2.23^{A}
3	1.09^{OPQ}	1.24^{LMN}	1.39^{HIJK}	1.52^{FG}	1.68^{E}	1.82^{CD}	1.96^{B}
6	0.98^{QR}	1.12^{NOP}	1.28^{KLM}	1.34^{FGHI}	1.51^{FGH}	1.69^{E}	1.93^{BC}
9	0.85ST	0.94^{RS}	1.06^{PQR}	1.14^{NOP}	1.29^{JKLM}	1.34^{FGHI}	1.53^{FG}
12	0.68^{U}	0.76^{TU}	0.84ST	0.96^{RS}	1.09^{OPQ}	1.19^{MNO}	1.31^{IJKL}
	Clove buds						
Zero time	16.33^{GHI}	16.64^{EFG}	16.93^{CDE}	17.23^{BC}	17.48^{B}	17.95^{A}	18.03^{A}
3	15.72^{LMNOP}	16.03^{IJKL}	16.32^{GHI}	16.58^{FG}	16.91^{CDE}	17.19^{BCD}	17.47^{B}
6	15.48^{NOPQ}	15.77^{KLMNO}	16.08^{HIJK}	16.37^{GH}	16.62^{EFG}	16.89^{DEF}	17.43^{B}
9	15.21^{QR}	15.42^{PQ}	15.63^{MNOP}	15.79^{KLMN}	16.13^{HIJ}	16.38^{GH}	16.57^{FG}
12	14.89^{R}	15.06^{R}	15.21^{QR}	15.46^{OPQ}	15.72^{LMNOP}	15.91^{JKLM}	16.14^{HIJ}

Comparing information using the Tukey method and 95% confidence, means that dot not share a letter are significantly different.

The statistical analyses were done individually (in the same kind of essential oil).

14.89 %, otherwise, essential oil content of 30kGy irradiated clove buds after 12months was yielded 16.14%. So that, as can be reported in **Table (1)**, the highest essential oil content was 18.03% of 30kGy irradiated clove buds at zero time, meanwhile, the lowest essential oil yield was 14.89% of non-irradiated clove buds after 12months of storage.

These results are in coincidence with **Variyar et al (1998)** results where they mentioned that irradiation processing induced increasing of clove essential oil content (18.88%) comparison to the non-irradiated clove essential oil content (15.25%). **Stattie et al (2004)** recorded that the total essential oil content for spices and medicinal herbs increased with 10kGy of gamma irradiation. Also, **Suhaj and Horvathova, (2007)** mentioned that clove irradiation processing induced increasing in the methanolic extraction yield during storage at 22±3^{o}C for 5months by 2%, and 22% for irradiated ginger.

Identification of extracted essential oil components of either non irradiated or irradiated dried rosemary leaves

The essential oils from dried rosemary leaves which extracted were identified by GC/MS; the results are shown in **Table (2)**. Thirty one compounds were identified for essential oil of the non-irradiated rosemary, represented 96.23%, while unknown constituents was represented 3.77%.

The fractioned components of rosemary essential oil results in **Table (2)** showed that 1,8cineole, α-pinene, camphore and camphen were found to be as the main compounds of the essential oil of non-irradiated rosemary leaves with the rate of percentage 26.36, 16.98, 12.63 and 5.65%, respectively. These results are confirmed with **Giordani et al (2004)** who found that the presence of 1,8 cineole was 24.36% in rosemary leaves essential oil, **Santoyo et al (2005)** who recorded that 1,8 cineole, α-pinene, camphor, Borneol and verbenone were the predominant compounds in rosemary essential oil representing about 80% of the total components of rosemary essential oil. In the same extracted essential oil of non-irradiated rosemary other components were also identified in the rosemary essential oil such as α-thujene, β-pinene, sabinene, myrcene, α-phylandrene, p-cymene, borneol, β-myrcene, verbenone and α-Terpineol those representing 0.34, 3.81, 0.66, 1.67, 0.32, 2.31, 2.14, 0.98 and 1.82 and 2.28%, respectively. These results are in agreement with **Dimitrijevic' et al (2007)**. The essential oils of different irradiated rosemary samples with doses (5, 10, 15, 20, 25 and 30 kGy) were fractionated and identified by GC/MS; results are shown in the same **Table (2)**. Thirty one compounds were identified, represented 96.22, 96.57, 96.59, 96.51, 96.59 and 96.72% for irradiated treatments by 5, 10, 15, 20, 25 and 30kGy, respectively. Also results show that, the γ-irradiated rosemary by 30kGy caused a decreasing in content (%) of

Table 2. Percentages of the identified components for extracted essential oils of irradiated dry rosemary leaves

Compounds		Gamma irradiation dose(kGy)					
	0	5	10	15	20	25	30
β-Myrcene	0.98	0.98	0.98	0.98	0.98	0.98	0.98
Tricyclene	0.29	0.29	0.29	0.29	0.29	0.29	0.29
α-Thujene	0.34	0.32	0.30	0.29	0.27	0.26	0.24
α-Pinene	16.98	16.97	16.94	16.92	16.90	16.89	16.88
Camphene	5.65	5.65	5.66	5.67	5.67	5.68	5.68
β-Pinene	3.81	3.81	3.81	3.72	3.69	3.67	3.61
Sabinene	0.66	0.66	0.66	0.66	0.66	0.66	0.66
Myrcene	1.67	1.67	1.67	1.67	1.67	1.67	1.67
α-phylandrene	0.32	0.31	0.33	0.32	0.31	0.31	0.31
γ-3-Carene	0.28	0.28	0.28	0.28	0.28	0.28	0.28
α-Terpinene	0.36	0.36	0.36	0.36	0.36	0.36	0.36
ρ-Cymene	2.31	2.31	2.41	2.51	2.53	2.56	2.59
O-Cymene	0.67	0.67	0.73	0.81	0.84	0.84	0.91
Limonene	3.75	3.73	3.69	3.54	3.43	3.36	3.31
1,8Cineole	26.36	26.36	26.36	26.36	26.36	26.36	26.36
γ-Terpinene	0.74	0.72	0.69	0.65	0.65	0.64	0.63
Terpinolene	0.91	0.91	0.91	0.91	0.91	0.91	0.91
α-Terpinolene	0.20	0.2	0.2	0.2	0.2	0.2	0.2
Linalool	2.39	2.39	2.37	2.34	2.3	2.3	2.29
Camphore	12.63	12.63	12.63	12.63	12.63	12.63	12.63
Borneol	2.14	2.14	2.14	2.14	2.14	2.14	2.14
Terpinene-4-ol	0.97	0.95	0.94	0.93	0.89	0.88	0.86
α-Terpineol	2.28	2.28	2.29	2.29	2.28	2.28	2.28
Verbenone	1.82	1.82	1.82	1.83	1.86	1.86	1.86
Citronellol	0.17	0.17	0.17	0.17	0.17	0.17	0.17
Geraniol	1.54	1.54	1.54	1.54	1.54	1.54	1.54
Bornyl acetate	2.01	2.01	2.01	2.01	2.01	2.01	2.01
β-Caryophyllene	1.75	1.73	1.72	1.7	1.68	1.67	1.67
Caryophyllene	0.05	0.05	0.25	0.38	0.42	0.45	0.54
Caryophyllene oxide	0.14	0.25	0.37	0.43	0.53	0.68	0.81
α-Humulene	2.06	2.06	2.06	2.06	2.06	2.06	2.06
Total identified compounds%	96.23	96.22	96.57	96.59	96.51	96.59	96.72
Total unidentified compounds%	3.77	3.78	3.43	3.41	3.49	3.41	3.28

some essential oils components as α-pinene, α-thujene, β-pinene, limonene, γ-Terpinene, linalool, Terpinene-4-ol and β-caryophyllene, those representing 16.88, 0.24, 3.61, 3.31, 0.63, 2.29, 0.86 and 1.67%, respectively. Meanwhile, the same dose of γ-irradiated samples induced increasing of some essential oils compounds as camphen, p-cymene, o-cymene, verbenone, caryophyllene and caryophyllene oxide, represented 5.68, 2.59, 0.91, 1.86, 0.54 and 0.81%, respectively. While, other essential oils compounds such as β-myrcene, sabinene, myrcene, α-terpinene, 1,8cineole, camphor and borneol were not changed at any dose of γ-irradiation.

These results are in agreement with the results of **Sadecka and Polovka, (2008); Machhour et al (2011); Silva et al (2013); Fatemi et al (2014); Elizalde and Espinoza, (2014) and Kirkin et al (2014).** Those studies reported that the cause of induced changes is due to the ionizing radiation sensitively, for example, hydrocarbon can react sensitively with ionizing radiation and resulted reduction of monoterpenes such as α-pinene and β-pinene and an increasing of sesquiterpenes as caryophyllene. Also, **Al-shawi, (2016)** noticed an increasing of the amount of limonene in essential oil of tested irradiated black pepper samples at different irradiation doses.

Identification of extracted essential oil components of either non irradiated or irradiated dried clove buds

The essential oils which extracted from clove buds were identified by GC/MS; the results are shown in **Table (3)**. Fourteen compounds were identified for the extracted oil from non- irradiated clove buds. They represented 99.97%, and 0.03% for unknown components. Eugenol was considered as the major compound in clove essential oil accounted 81.69%. The second major compound was indicated as eugenyl acetate, represented 8.31%. **Alshawi, (2016)** reported that the amount of eugenol and eugenyl acetate in clove essential oil were 73.5% and 10.81%, respectively. Caryophyllene was considered as moderate component that accounted 4.32%. Other components were also fractioned such as α-pinene, linalool, β-caryophyllene α-Humulene, and Δ-cadinene found in law quantities represented 0.47, 0.62, 1.73, 1.45 and 0.51%, respectively, while, fractioned minor components such as γ-cadinene, β-cadinene , cis-isoeugenol and δ-cadinene represented 0.051, 0.043, 0.024 and 0.002%, respectively. **Amelia et al (2017)** reported that the amount of eugenol in clove essential oil was 74.64%, eugenyl acetate represented 8.7%, other components were also identified such as caryophyllene, α-humulene, γ-cadinene, β-cadinene and caryophyllene oxide represented 12.79, 1.53, 0.034, 0.039 and 0.48%, respectively.

The essential oils of different irradiated clove bud samples with doses (5, 10, 15, 20, 25 and 30kGy) were fractioned and identified by GC/MS; results are shown in the same **Table (3)**. Fourteen compounds were identified, represented 99.77, 99.902, 99.942, 99.723, 99.683and 99.741% for γ-irradiation treatments by (5, 10, 15, 20, 25 and 30kGy, respectively. Results show that, the γ-irradiated clove buds under different doses induced reduction of the percentage of some essential oils components as α-pinene, linalool, α-humulene and β-caryophyllene at 30kGy, those representing 0.4, 0.32, 1.19 and 1.19%, respectively. The recorded results also found that the decreasing in some essential oil components due to increasing of γ-irradiation dose from 10up to 30kGy, these results agree with those of **Abozaid & El-Sayed (2013) and Guat et al (2007)**. Generally, no exceptional changes were noticed in the essential oil components at low radiation doses that are confirmed as safe maximal dose (toxicologically and nutritionally) according to **Wilkinson and Gould, (1998)**. The low dose of irradiation treatment is known to be as a cold physical process for food, due to the reason for ignoring a significant heating of product (the product temperature may rise by max 4^{o}C at the dose of 10kGy).

The results are in agreement with the results of **Sadecka, (2010)**, reported that the most important change could be noticed at the dose of 30 kGy, as well as the configurationally change can caused by high irradiation dose, such as changes in the double bonds positions and functional groups. On the other hand, in the results of this study, the increasing of caryophyllene oxide by increasing the dose of irradiation process may be due to the reaction between terpens and free radicals which can generate from the water contained in spices (approx.. 10%) as indirect effect or by which of hydroxylation or oxidation of the aromatic ring of terpene to produce terpene oxides or terpene alcohole according to **Urbian, (1986)**.

Physico-chemical properties of extracted essential oils from either non-irradiated or irradiated dried rosemary leaves and dried clove buds

The results of Physico-chemical properties of the non-irradiated and irradiated rosemary leaves and clove buds essential oils are shown in **Table (4)**.

Specific gravity at 20^{o}C of the essential oils from rosemary or clove buds at 0kGy was 0.896 and 1.047, respectively. The specific gravity values of each sample showed some changes that can be observed throughout the irradiation process. The value of extracted essential oil from irradiated rosemary at 10kGy was 0.900, while, increased up to 0.916 at 30kGy. The results of γ-irradiated clove buds showed the same changes for its essential oils, the specific gravity values changed from 1.048 at 5kGy to 1.063 at 20kGy, changed also to 1.068 at 30kGy.

Refractive index of the rosemary essential oils or clove buds showed slightly increments, it could be noticed for extracted essential oils from γ-irradiated rosemary and clove buds as a results of irradiation process, refractive index of rosemary essential oil was 1.4700, 1.4900 at 0kGy and 30kGy, respectively, while, was 1.5360, 1.5560 for the clove buds essential oil at the same doses.

From the same **Table (4)**, solubility in ethyl alcohol of rosemary essential oil changed from 1.6 for non-irradiated to 2.6 for irradiated at 30kGy; meanwhile it changed from 1.4 to 2.5 for clove buds essential oil at the same conditions.

Table 3. Percentages of the identified components for extracted essential oils of irradiated dry clove buds

Compounds	Gamma irradiation dose(kGy)						
	0	5	10	15	20	25	30
α-pinene	0.47	0.47	0.46	0.45	0.43	0.41	0.4
Linalool	0.62	0.62	0.6	0.57	0.51	0.4	0.32
Copaene	0.13	0.13	0.34	0.36	0.39	0.41	0.43
Eugenol	81.69	81.69	81.69	81.76	81.8	81.9	82.1
β-caryophyllene	1.73	1.73	1.7	1.62	1.51	1.32	1.19
caryophyllene	4.32	4.32	4.41	4.48	4.51	4.53	4.58
caryophyllene oxide	0.62	0.62	0.62	0.62	0.62	0.76	0.76
α-Humulene	1.45	1.45	1.21	1.21	1.19	1.19	1.19
γ-cadinene	0.051	0.051	0.053	0.053	0.054	0.054	0.062
β-cadinene	0.043	0.043	0.043	0.043	0.043	0.043	0.043
δ-cadinene	0.002	0.002	0.002	0.002	0.002	0.002	0.002
cis-isoeugenol	0.024	0.024	0.024	0.024	0.024	0.024	0.024
Δ-cadinene	0.51	0.51	0.51	0.51	0.51	0.51	0.51
Eugenyl acetate	8.31	8.11	8.24	8.24	8.13	8.13	8.13
Total identified compounds%	99.97	99.77	99.902	99.942	99.723	99.683	99.741
Total unidentified compounds%	0.03	0.23	0.098	0.058	0.277	0.317	0.259

Table 4. Physico-chemical properties of extracted essential oils from dry rosemary leaves as well as dry clove buds either non-irradiated or irradiated

Property	Dose of γ-irradiation(kGy)						
	0	5	10	15	20	25	30
	Rosemary						
Specific gravity at 20^{0}C	0.896	0.897	0.900	0.904	0.912	0.917	0.916
%change	100	100.1	100.4	100.8	101.7	102.3	102.2
Refractive index at 20^{0}C	1.4700	1.4700	1.4750	1.4770	1.4890	1.4930	1.4900
%change	100	100	100.43	100.47	101.29	101.56	101.36
Solubility in alcohol 90%	1.6	1.6	1.6	1.6	2.1	2.3	2.6
%change	100	100	100	100	131.25	143.75	162.5
Acid value mg KOH/g oil	0.41	0.42	0.49	0.5	0.51	0.516	0.52
%change	100	102.43	119.51	121.95	124.39	125.85	126.82
Ester number mg KOH/ g oil	2.91	2.9	2.88	2.83	2.81	2.61	2.37
%change	100	99.65	98.96	97.25	96.56	89.69	81.44
	Clove buds						
Specific gravity at 20^{0}C	1.047	1.048	1.0518	1.0558	1.063	1.067	1.068
%change	100	100.09	100.45	100.84	101.52	101.91	102.0
Refractive index at 20^{0}C	1.5360	1.5360	1.5410	1.5430	1.5550	1.5590	1.5560
%change	100	100	100.32	100.45	101.23	101.49	101.3
Solubility in alcohol 90%	1.4	1.4	1.4	1.4	1.9	2.1	2.5
%change	100	100	100	100	135.71	150	178.57
Acid value mg KOH/g oil	3.68	3.67	3.74	3.75	3.77	3.77	3.8
%change	100	99.72	101.63	101.9	102.44	102.44	103.26
Ester number mg KOH/ g oil	1.84	1.83	1.8	1.75	1.73	1.54	1.29
%change	100	99.45	97.82	95.1	94.02	83.69	70.1

Results recorded that, the acid values of the tested oils, were 0.41 and 3.68 mg KOH/1g oil for rosemary and clove buds essential oils, respectively, which extracted from non- irradiated sample. While, observed data showed an incremental pattern in this parameter among different doses of irradiation, it reached 0.52 and 3.8mgKOH/g oil for rosemary and clove buds essential oils at 30kGy, respectively.

Results in **Table (4)** show the values of ester number of rosemary and clove buds essential oils from non – irradiated and irradiated samples, the values were 2.91, 2.88, 2.61 and 2.37mg KOH/ 1g oil for rosemary essential oils at 0, 10, 25 and 30kGy, respectively; while, were 1.84, 1.8, 1.54 and 1.29 mg KOH/1g oil for clove buds essential oil at the same dose.

The results of physic-chemical properties are in agreement with **Atti-Santose et al (2005); Clarke, (2008); Bousbia et al (2009); Burdock, (2010) and Egyptian Standards, (2007).**

Antioxidant activity of extracted essential oils from both non-irradiated and irradiated rosemary leaves and clove buds

Rosemary essential oils extracted from irradiated samples at doses (0 up to 30kGy) were tested at different concentrations to evaluate their antioxidant activities measured as % stable radical DPPH scavenging compared with BHT at 200 ppm , results are shown in **Table (5)**. Results recorded that, increasing the essential oil concentrations from 250 to 2500ppm, were accompanied by significant ($p \leq 0.05$) increasing of %DPPH scavenging. Antioxidant activity of essential oils refer to the present of active compounds such as 1,8 cineole, because of the high percentage of main constituents or the presence of minor components, also, can be due to synergy among essential oil components **(Politeo et al 2006)**. Furthermore, **Yanishlieva and Marinova, (1998);** as well as **Tsai et al (2007)** they recorded that, phenolic compounds can stop the reaction of propagation chain by donating hydrogen atom to free radicals during lipid oxidation.

Results are shown that the % of DPPH scavenging of BHT at 200ppm was the lowest activity (7.662%), moreover the percentage of DPPH scavenging for rosemary essential oil extracted from non-irradiated sample at 250ppm was 22.23% higher than the DPPH inhibition % of BHT (as a reference), concentration 250ppm of the essential oil extracted from irradiated rosemary at 30kGy is the lowest scavenging activity (21.42%) of all irradiated samples, while, scavenging ability of 2500ppm of the same essential oil at 0kGy was the highest. Regarding to fractionating and identifying compound by GC/MS, camphor is an oxygenated compound has an antioxidant properties according to **Wang et al (2008)** who reported that camphor and borneol are the cause of antioxidant activity, meanwhile, **Yosr et al (2013)** recorded that Tunisian rosemary essential oil had high percentage of camphor, α-pinene and 1,8 cineol caused high antioxidant activity of rosemary essential oil. These results are in agreement with **Bobilev et al (2011) and Zegura et al (2011)** who reported that, rosemary had strong antioxidant properties, also, **Yesilbag et al (2011)** reported that rosemary has high ability displaying good antioxidant effects. Significant differences could be noticed for each concentration at different irradiation dose. The increase of irradiation dose induced slightly decreasing in %DPPH scavenging for most of the different concentrations of essential oil. These results are in agreement with **Suhaj et al (2006) and Kim et al (2009)**.

Clove essential oils extracted from irradiated samples at diversity doses from 0 to 30kGy were studied at different concentration (250 up to 2500ppm) to determine their antioxidant activities evaluating as % DPPH scavenging in comparison with BHT (200ppm) as a reference, results are shown in **Table (5)**. Increasing % of DPPH scavenging combined with the increasing in clove essential oil concentration, clove essential oil in concentration 250ppm at 30kGy was the lowest scavenging activity (45.218) of all irradiated samples, although the scavenging activity of BHT was lower than it; while, scavenging ability of 2500ppm of the same essential oil at different doses of 5, 10, 15, 20 and 25 had the highest values of scavenging. Decreasing in DPPH concentration significantly due to the antioxidant ability of clove oil, clove oil scavenging activity is the highest in comparison with BHT, α-tocopherol, BHA and trolox, as mentioned by **Gulcin et al (2012) and Rojas-Cortes, et al (2014)** reported that clove essential oil has high percentage of antioxidant compounds as food preservative, **Ibrahium et al (2013)** noticed the effect of clove essential oil on cake preservation due to its antioxidant activity in order to avoid synthetic antioxidant which has harmful effects. Regarding to identification of compounds by GC/MS, the antioxidant activity of clove oil caused by its main compound eugenol.

Table 5. Antioxidant activity of extracted essential oils from either non-irradiated or irradiated rosemary leaves and clove buds

γ-irradiation dose (kGy)	Concentration of essential oil(ppm)					
	250	500	1000	1500	2000	2500
			Rosemary			
0	22.23S	31.36O	45.91K	60.72I	69.47C	71.31A
5	22.11S	31.26O	45.74KL	60.64I	69.28CD	71.22AB
10	22.01ST	30.71P	45.63KLM	60.53IJ	69.17DE	71.13AB
15	21.74TU	30.64P	45.54LM	60.31J	69.09DEF	71.11AB
20	21.69UV	30.51PQ	45.46LMN	62.13H	69.03DEF	71.07AB
25	21.53UV	30.34QR	45.37MN	62.37H	68.91EF	70.93B
30	21.42V	30.17R	45.19N	60.62I	68.82FG	68.54G
BHT(200ppm)	7.662					
	Clove buds					
0	46.666S	55.291O	68.799LM	83.009G	92.989B	93.912A
5	46.08T	55.161OP	68.571LMN	82.818GH	92.723BC	93.98A
10	45.79TU	54.97OPQ	68.43LMN	82.704GHI	92.586BCD	93.864A
15	45.71TUV	54.79OPQR	68.34MN	81.028K	92.456CDE	93.775A
20	45.523UV	54.704PQR	68.212N	82.361HI	92.266CDE	93.639A
25	45.333UV	54.567QR	68.113N	82.209I	92.113DE	93.536A
30	45.218V	54.399R	68.885L	81.607J	91.961E	86.536F
BHT(200ppm)	7.662					

Comparing information using the Tukey method and 95% confidence, means that dot not share a letter are significantly different.

The statistical analyses were done individually (in the same kind of essential oil).

Acceptable odor levels of both non-irradiated and irradiated rosemary as well as clove buds added to sunflower oil

Rosemary as well as clove buds essential oils extracted from either non-irradiated or irradiated samples and their mixture (1:1), added to sunflower oil in different concentrations 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5% conducting to notice the convenient concentrations of these essential oils to have acceptable odor of sunflower oil and the results are shown in **Table (6)**. The statistical analysis of results showed that, the odor of all sunflower oils supplemented with different concentrations of essential oils extracted from irradiated rosemary, clove buds and their mixture(1:1) were significantly difference($p \leq 0.05$) compared with control sunflower oil without any essential oil.

On the other hand, sunflower oil supplemented with 0.0% rosemary, clove buds essential oils extracted from either non-irradiated or irradiated samples and their mixture (1:1) recorded values whith no odor, while, 0.1, 0.2, 0.3 and 0.4% rosemary oil extracted from all samples added to sunflower oil appeared very weak odor. The results show also that, 0.1 and 0.2% clove buds oils extracted from non-irradiated and irradiated which added to sunflower oil recorded mean values that very weak odor except at 30kGy which recorded the highest acceptable odor. From the same table, sunflower oil supplemented with 0.1, 0.2 and 0.3% of rosemary and clove buds and mixture (1:1) oils extracted from non-irradiated and irradiated samples had very weak odor values. From the results, it can be concluded that, the best concentrations of essential oils added to sunflower oil were 0.5, 0.3 and 0.4% for rosemary, clove buds essential oils extracted from either non-irradiated or irradiated samples and their mixture (1:1) these results coincided with those of to **El-Baroty, (1988), Lucchesi, et al (2004)**, those reported that, the compounds of rosemary essential oil tend to have herbal aroma such as 1,8cineol and camphor.

Effect of different concentrations of irradiated rosemary leaves, clove buds and their mixture (1:1) essential oils on the oxidative stability of sunflower oil assessed by Rancimat

Experiments conducting to evaluate the oxidative stability of sunflower oil supplemented with 0.5% rosemary essential oils extracted from non-irradiated irradiated samples as well as 0.3% of clove buds essential oils extracted from non-irradiated and irradiated samples and 0.4% their

Table 6. Effect of irradiation on the threshold score of rosemary, clove buds and their mixture (1:1) essentials oil added to sun flower oil (Mean of acceptable odor levels)

Concentration	Dose of γ-irradiation						
	0kGy	5kGy	10kGy	15kGy	20kGy	25kGy	30kGy
	Rosemary						
0.0	0.53^{P}	0.54^{P}	0.57^{P}	0.59^{P}	0.59^{P}	0.61^{P}	0.63^{P}
0.1	0.93^{O}	1.05^{NO}	1.11^{MN}	1.17^{LMN}	1.18^{LMN}	1.21^{LM}	1.23^{KLM}
0.2	1.26^{JKL}	1.236^{KLM}	1.31^{JKL}	1.38^{HIJ}	1.39^{GHIJ}	1.36^{IJK}	1.38^{HIJ}
0.3	1.47^{FGHI}	1.51^{EFGH}	1.61^{BCDEF}	1.64^{BCDE}	1.66^{BCD}	1.68^{BC}	1.7^{B}
0.4	1.53^{DEFG}	1.54^{CDEF}	1.63^{BCDE}	1.65^{BCDE}	1.67^{BCD}	1.68^{BC}	1.71^{B}
0.5	2.11^{A}	2.09^{A}	2.13^{A}	2.17^{A}	2.18^{A}	2.2^{A}	2.23^{A}
	Clove buds						
0.0	0.78^{J}	0.82^{J}	0.87^{J}	0.87^{J}	0.88^{J}	0.91^{J}	0.94^{J}
0.1	1.69^{I}	1.86^{HI}	1.89^{H}	1.91^{H}	1.92^{H}	1.94^{H}	1.96^{H}
0.2	1.87^{HI}	1.93^{H}	1.92^{H}	1.953^{H}	1.95^{H}	1.98^{H}	2.00^{GH}
0.3	2.19^{FG}	2.25^{F}	2.26^{EF}	2.27^{EF}	2.27^{EF}	2.28^{EF}	2.32^{CDEF}
0.4	2.21^{F}	2.27^{EF}	2.28^{EF}	2.31^{DEF}	2.32^{CDEF}	2.34^{CDEF}	2.35^{BCDEF}
0.5	2.45^{ABCDE}	2.49^{ABCD}	2.51^{ABC}	2.54^{AB}	2.54^{AB}	2.56^{A}	2.58^{A}
	Their mixture (1:1)						
0.0	0.46^{J}	0.46^{J}	0.46^{J}	0.48^{J}	0.51^{J}	0.53^{J}	0.54^{J}
0.1	1.44^{I}	1.47^{I}	1.48^{I}	1.51^{HI}	1.52^{GHI}	1.56^{FGHI}	1.58^{EFGHI}
0.2	1.46^{I}	1.48^{I}	1.49^{I}	1.496^{I}	1.56^{FGHI}	1.58^{EFGHI}	1.59^{EFGHI}
0.3	1.69^{DEFGH}	1.71^{DE}	1.7^{DEFG}	1.72^{DEF}	1.74^{DEF}	1.76^{CDE}	1.78^{CD}
0.4	1.93^{C}	2.13^{B}	2.17^{B}	2.19^{B}	2.2^{B}	2.25^{B}	2.26^{B}
0.5	2.53^{A}	2.58^{A}	2.62^{A}	2.64^{A}	2.65^{A}	2.546^{A}	2.71^{A}

Comparing information using the Tukey method and 95% confidence, means that dot not share a letter are significantly different.

The statistical analyses were done individually (in the same kind of essential oil).

mixture (1:1) essential oils which extracted from non-irradiated as well as irradiated samples, by irradiation doses 5, 10 and 15kGy, comparing to sunflower oil without any antioxidants as control and sunflower oil supplemented with 0.02% BHT as synthetic antioxidant.

The results of oxidative stability and relative stability are shown in **Table (7)**, the results revealed that, the oxidative stability of sunflower oil without any antioxidants as control recorded 8.32 hrs with relative stability 100%, while, the oxidative stability of sunflower oil supplemented with 0.02%BHT represented 13.6hrs with relative stability 163.46%. Otherwise, adding different concentrations of rosemary, clove buds essential oils which extracted from different irradiation doses samples and their mixture (1:1) caused slightly increasing in oxidative stability of sunflower oil. Results illustrated that sunflower oil supplemented with 0.5% rosemary essential oil which extracted from non-irradiated sample had the lowest oxidative stability (9.76hrs) with relative stability 117.3% comparing to other treatments but still higher than the oxidative stability of control sample; while oxidative stability of sunflower oil supplemented with 0.3% clove buds essential oil extracted from 15kGy irradiated sample was the highest value reported 11.99hrs with relative stability 144.11%.

Regarding to the results in **Table (7)**, it could be observed that, the increasing of irradiation doses caused an enhancement in the oxidative stability, comparing to control one. Moreover, addition both of 0.5, 0.3 and 0.4% of rosemary, clove buds and their mixture (1:1), respectively. Essential oils extracted from different doses irradiated (0, 5, 10 and 15kGy) samples to sunflower oil caused increasing of oxidative stability of sunflower oil which recorded 9.76, 9.81, 9.83 and 9.84hrs, respectively, for 0.5% rosemary oils; 11.86, 11.93, 11.96 and 11.99hrs, respectively for 0.3% clove buds oils as well as 10.33, 10.41, 10.42 and 10.44hrs, respectively for 0.4% mixture oils (1:1). This is due to antioxidant activities of essential oils which inhibiting the oxidation and have radical scavenging as mentioned by **Bensmira et al (2007)**. Also, Rossel, 1989 reported that, the oxidative stability is a direct index for oxidation changes.

Table 7. Effect of different concentrations of irradiated rosemary leaves, clove buds essential oils and their mixture on the oxidative stability of sunflower oil assessed by Rancimat test

Concentrations	Irradiated treatments							
	0kGy		5kGy		10kGy		15kGy	
	Stability (hrs)	Relative stability (%)	Stability (hrs)	Relative stability (%)	Stability (hrs)	Relative stability (%)	Stability (hrs)	Relative stability (%)
SFO+0.5IR	9.76	117.3	9.81	117.9	9.83	118.14	9.84	118.26
SFO+0.3ICL	11.86	142.54	11.93	143.38	11.96	143.75	11.99	144.11
SFO+0.4IM	10.33	124.15	10.41	125.12	10.42	125.24	10.44	125.48
Control sunflower oil	8.32	100						
Sunflower oil with 0.02% BHT	13.6	163.46						

SFO+0.5IR: Sunflower oil supplemented with 0.5% rosemary oil extracted from either non-irradiated or irradiated samples.

SFO+0.3ICL: Sunflower oil supplemented with 0.3% clove buds oil extracted from either non-irradiated or irradiated samples.

SFO+0.4IM: Sunflower oil supplemented with 0.4% mixture (1:1) of rosemary and clove buds oil extracted from either non-irradiated or irradiated samples.

hrs: Hours.

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مجلة اتحاد الجامعات العربية للعلوم الزراعية ، جامعة عين شمس ، القاهرة ، مصر
مجلد(27)، عدد(2)، 1459-1473، 2019
Website: http://ajs.journals.ekb.eg

الخصائص الفيزيوكيميائية والنشاط المضاد للاكسدة للزيوت العطرية المستخلصة من أوراق الروز ماري وبراعم القرنفل المشععين

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Received 30 March, 2019 Accepted 23 April, 2019

الموجـــــــز

تم معالجة كل من الروز ماري (اكليل الجبل) وبراعم القرنفل باستخدام جرعات مختلفة من أشعة جاما من (0 الي 30 كيلوجراي) وخزنت لمدة 12 شهر علي درجة حرارة الغرفة. تم تقييم كفاءة عملية التشعيع بالتحليلات الكيميائية وقياس النشاط المضاد للأكسدة للزيوت المستخلصة. أظهرت النتائج اختلافات معنوية لنسبة المتحصل عليه من الزيت العطري المستخلص بالجرعات الاشعاعية المختلفة خلال فترة التخزين. تم التعرف علي المركبات الموجودة بالزيت المستخلص من العينات غير المشععة والمشععة لكل من أوراق الروز ماري وبراعم القرنفل، وكانت نسبة المركبات الرئيسية بالزيت المستخلص من عينات الروز ماري المشععة وغير المشععة 1,8 سينيول، كامفور وجاما بينين 26,36، 12,63 و 16,98%، علي الترتيب، بينما كانت نسبة الأيجينول المركب الرئيسي للزيت المستخلص من عينات براعم القرنفل المشععة وغير المشععة 81,69%. لم يلاحظ اختلافات في النسبة المئوية لمكونات الزيوت العطرية. زاد النشاط المضاد للأكسدة (النسبة المئوية لتثبيط الشقوق الحرة) بزيادة تركيزات الزيوت العطرية من 250 حتي 2500 جزء في المليون، علاوة علي ذلك، أمكن ملاحظة تأثير اضافة هذه الزيوت المستخلصة من عينات أوراق الروزماري وبراعم القرنفل ومخلوطهما (1:1) سواء المشععة أو غير المشععة علي قيم متوسط قبول الرائحة. وضح اختبار الرانسمات الثبات الاكسيدي المرتفع (11,99 ساعة) لزيت عباد الشمس المضاف اليه 0,3 % زيت قرنفل مستخلص من العينة المشععة بجرعة 15 كيلوجراي بثبات نسبي قدره 144,11% مقارنة بالثبات الاكسيدي لزيت عباد الشمس المضاف اليه 0,5% زيت روز ماري مستخلص من عينة غير مشععة (9,76 ساعة) بثبات نسبي قدره 117,3%.

الكلمات الدالة: أوراق الروزمارى، براعم القرنفل، التشعيع، الزيت العطرى، GC/MS، النشاط المضاد للأكسدة، الرانسمات

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