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# ANTIOXIANT ACTIVITY OF SOME SUPPLEMENTARY PHENOLIC COMPOUNDS TO CORN OIL UNDER HIGH TEMPERATURE CONDITIONS

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## ABSTRACT

The effect of some phenolic compounds on the oxidative stability of corn oil during heating at 60, 100 and 180ºC was investigated. This investigation was to search for the most potent antioxidants under high temperature conditions and the relationship between their potency and their chemical structures. Progression of oxidation status was monitored by measurement of peroxide, anisidine, totox values and TBARS content. The Rancimat test was also used to assess the stability of the oil containing phenolic compounds at 100ºC. Results clearly revealed that all of TBHQ, DTBHQ and Gentisic acid (2,5-DHBA) were the most effective antioxidants at elevated temperatures (60, 100, and 180$^{o}$C). The Rancimat test was found to confirm these results at 100$^{o}$C. The efficacy of these compounds was higher than that of the commonly-used food antioxidants e.g. BHT, BHA and α-tocopherol. The superiority of these compounds mainly due to the presence of two hydroxyl groups in para position in their structures. Although other phenolic compounds contain the same structural features e.g. 2,5-DHAc and quinizarin, they exhibited prooxidant activity. This may be attributed to the existence of carbonyl group which was found to accelerate markedly the lipid oxidation process through its electrophilic activity feature. The chemical structure of potent antioxidants at high temperatures must be containing two hydroxyl groups in ortho or para position of its benzene ring and the meta position must be free of them or carbonyl group(s).

**Key words:** Antioxidant - Corn oil - Peroxide value – Anisidine value - Totox value - TBARS - Rancimat - TBHQ - DTBHQ - Gentisic - BHT - BHA - α-Tocopherol - 2,4-DHAc - 2,5-DHAc -3,4-DHBA, 2,5-DHBA - Quinizarin

**Abbreviations:** butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), *tert*-butyl-hydroquinone (TBHQ), di-*tert*-butylhydroquinone (DTBHQ), α-tocopherol (α-Toc), dihydroxyacetophenone (DHAc), dihydroxybenzoic acid (DHBA), 1,4-dihydroxyanthraquinone (quinizarin), propyl gallate (PG).

# INTRODUCTION

The commonly-used food antioxidants e.g. BHA, BHT, PG and TBHQ as well as natural antioxidants e.g. α-tocopherol, ascorbyl palmitate, rosemary and green tea extracts are very effective at room temperature. However, at high temperature conditions they can be evaporated or destroyed and have little carry-through effect (Zhang et. al., 2004). Moreover, the high toxicity of synthetic antioxidants and their suspected action as promotors of carcinogenesis decline their use as food additives (Ito et. al., 1985; Rice-Evans & Burdon, 1993). Although TBHQ was the most effective

Antioxidant in vegetable oils (Zandi & Gordon, 1999; Khan & Shahidi, 2001; Zhang et. al., 2004) and marine oils (Kaitaranta, 1992; Wanasundara & Shahidi, 1998), it has not been approved for food use in Europe, Japan and Canada owing to its high toxicity. Thus, there have been increasing efforts in recent years to develop effective natural antioxidants for edible oils in order to retard lipid oxidation at high temperatures (Jadhav et. al., 1996; Moure et. al., 2001; Oktay et. al., 2003).

The efficacies of various phenolic compounds as antioxidants are greatly varied concomitantly with the difference in their chemical structures. Dealing with monophenolic antioxidants such as BHA and BHT, the presence of bulky branched groups, as in BHT, increases the stability of phenoxy radicals. Hydroxyl group of BHT is chemically sandwiched between two big tert-butyl groups, which keep the BHT radical out of trouble; as compared to the BHA radical, which is a lot more reactive and a lot less stable (King et. al., 1995). This might explain the higher antioxidant activity of BHT compared to BHA in vegetable and marine oils. The introduction of a second hydroxyl group into position 2 or 4 enhances the oxidative stability (Gordon, 1990). Therefore, phenolic compounds which possess multiple

hydroxyl groups in ortho position exhibited good antioxidant activity more effectively than BHT and BHA, which have only one hydroxyl group (Wanasundara & Shahidi, 1998; Zandi & Gordon, 1999; Lalas & Dourtoglou, 2003). Similarly, it has been proposed that the two para hydroxyl groups are responsible for the superior antioxidant activity of TBHQ in various edible oils (Madhavi et. al., 1995). Furthermore, the more polar antioxidants e.g. TBHQ and PG are very active in fats and oils since they are enriched at the surface of fat and come in contact with air.

The above mentioned literatures concluded that number and position of the hydroxyl groups are the most important properties determining the action of phenolic compounds as antioxidants. Therefore, a relatively large number of phenolic compounds differ in number and positions of attached hydroxyl groups, were investigated in this study. Thus, the compounds containing two para hydroxyl groups; TBHQ, DTBHQ, 2,5-DHBA, 2,5-DHAc and quinizarin were given particular attention. The potencies of the tested phenolic compounds were evaluated in corn oil under high temperature conditions.

# MATERIALS AND METHODS

## 1- Materials

**1-1-** Corn oil free of any synthetic antioxidants was obtained from Savola Sime Egypt Co. ($10^{th}$ of Ramadan Industrial Zone, Egypt).

**1-2-** Synthetic antioxidants, butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), *tert*-butylhydroquinone (TBHQ) and α-tocopherol (α-Toc) were purchased from Fluka AG (Buchs, Switzerland).

**1-3-** The chemicals, 3,4-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid (gentisic acid), 2,4-, 2,5-dihydroxyacetophenone and 1,4-dihydroxyanthraquinone (quinizarin) were obtained from Sigma Chemical Co. (St. Louis, MO).

**1-4-** Di-*tert*-butylhydroquinone (DTBHQ) was synthesized according to the procedure described by Zhang *et. al.*, (2004).

## 2- Methods

### 2-1- Preparation of corn oil samples

Phenolic compounds and commercial antioxidants (200 ppm) as well as α-tocopherol (500 ppm), were dissolved in a minimum volume of absolute ethanol and added to corn oil in a 100 ml Pyrex beakers. After addition of the antioxidants, the oil samples were mixed for 15 min by stirring at 60$^{o}$C. α-Tocopherol was used at 500 ppm, rather than other synthetic antioxidants, because its conc. of 200 ppm was exhibited prooxidant effect in heated oils (Gottstein & Grosch, 1990). Oil samples, with and without the various additives, were subjected to heating experiments.

### 2-2- Accelerated oxidation tests in an oven at 60, 100 and 180$^{o}$C

**2-2-1-** Corn oil samples (25 g) containing phenolic compounds or commercial antioxidants were continuously heated at 60$^{o}$C for 20 days as well as at 100$^{o}$C for 20 hours.

**2-2-2-** Corn oil samples with and without different additives, were subjected to intermittent heating at 180 ± 5$^{o}$C for 10 hours in high-temperature oven, since heating at 180$^{o}$C was run for 2.5 hours at 1 hour intervals, twice per day for two consecutive days.

At the end of accelerated oxidation tests, oil samples were removed to measure the different oxidation parameters.

### 2-3- Lipid Oxidation Status

The oxidation status of all oil samples were examined by different oxidation parameters:

**2-3-1-** Peroxide value (PV) was determined according to Takagi *et. al.,* (1978).

**2-3-2-** Thiobarbituric acid reactive substances (TBARS) in heated oil samples were determined as described by Kosugi & Kikugawa, (1985).

**2-3-3-** Anisidine value (AnV) was determined according to the method of IUPAC (1979).

**2-3-4-** Totox value (TV) was calculated using the peroxide value conjunction with the anisidine value according to Rossell, (1983) using the formula (TV = 2 PV + AnV).

All analyses of the accelerated oxidation tests were run in triplicate, and the results presented are the average of the obtained values.

**2-4- Oxidative stability by the Rancimat test**

The Rancimat method is an accelerated oxidation test that is run at elevated temperatures and exposes the sample to air. Stability of corn oil to oxidation with different potent antioxidants: TBHQ, DTBHQ and 2,5-DHBA at concentration of 200 ppm as well as control oil (free of additives) were determined according to the method described by Tsakins et. al., (1999).

The test was performed using five grams of oil on the Rancimat instrument 679 (Metrohm, Herisau, Switzerland) by measuring the induction period at 100oC, and an airflow rate of 20 L/h. Induction period is defined as the length of time before detectable rancidity, or time before rapid acceleration of lipid oxidation. The induction periods were 36, 30, 21 and 13 hours of corn oil samples in the presence and absence of previous additives, respectively.

## RESULTS AND DISCUSSION

Because of the importance of the protection of the oil during frying at high levels of temperature by adding antioxidant to this oil, the important questions are:

**- What is the convenient antioxidant that could protect the oil at frying temperature?**

**- Hence, what is the chemical structural feature of this potent antioxidant?**

In replying to this important questions and give-satisfied answer, we applied different antioxidants; α-Toc, BHT, BHA, TBHQ, DTBHQ, 2,4-DHAc, 2.5-DHAc, 3,4-DHBA, 2,5-DHBA and quinizarin individually to corn oil and each of them was subjected to three different levels of temperature; 60, 100 and 180 oC in comparison with control oil (free of antioxidant).

To follow up the antioxidant activity of all applied antioxidants, four parameters have been determined; peroxide value (PV), TBARS content, anisidine value (AnV) and totox value (TV) at the three levels of applied temperatures.

Based on the obtained data, this study may reveal that the top three antioxidants could be used for the protection of frying oil under investigation are TBHQ, DTBHQ and 2,5-DHBA.

Discussions of the obtained results in comparison with those in the previous literature could achieve the summarized following aspects:

**1- Antioxidant activity of Supplementary Phenolic Compounds at 60$^{o}$C**

Data presented in Tables (1-4) illustrate the superiority of three phenolic compounds as potent antioxidants among other investigated compounds. The highest antioxidant activity was shown by TBHQ followed by 2,5-DHBA and then DTBHQ. These results were confirmed by those obtaining of Wanasundara & Shahidi, (1998), which they ranked the commonly-used food antioxidants as TBHQ >> BHT > BHA > α-tocopherol. Some phenolic compounds showed moderate potency such as 3,4-DHBA and BHA, while some others gave no or little potency such as quinizarin, 2,4-DHAc and α-tocopherol. These antioxidant efficacies were evidenced by peroxide, anisidine, totox and TBARS values.

The superiority of TBHQ, 2,5-DHBA and DTBHQ mainly due to the presence of two hydroxyl groups in para position (Madhavi et. al., 1995). While, the weak antioxidant activity of α-tocopherol may be attributed to its high reactivity owing to the existence of numerous methyl substituents as electron repelling groups in the chromanol moiety of α-tocopherol which cause high sensitivity and in turn low stability toward oxidation (Yoshida et. al., 1993). In the same area of relatively weak antioxidant, it was found 2,5-DHAc and 2,4-DHAc. Comparatively, the 2, 5-DHAc exhibited low potency while the 2,4-DHAc has pro-oxidant effect. The low potency of 2,5-DHAc may be attributed to the presence of the carbonyl group while the pro-oxidant activity of 2,4-DHAc may due to its hydroxyl groups attached to meta position. The same reason of activity could be found in benzoic acid derivatives (2,5-DHBA & 3,4-DHBA), since, the former showed strong antioxidative effect while the latter showed moderate potency. This owing mainly to the presence of their hydroxyl groups in para and ortho positions, respectively (Wanasundara & Shahidi, 1998).

**Table (1): Effect of The Studied Phenolic Compounds in Retarding of Corn Oil Oxidationat 60, 100 and 180°C, Assessed By The Change in Peroxide Value (PV) (meq/kg).**

| Phenolic Compounds | PV, 60°C after 20 days | PV, 100°C after 20 hours | PV, 180°C after 10 hours |
|---|---|---|---|
| α-Toc | 230.2 | 124.0 | 16.6 |
| BHT | 97.4 | 101.0 | 14.3 |
| BHA | 194.2 | 116.8 | 18.5 |
| TBHQ | 30.1 | 21.6 | 9.6 |
| DTBHQ | 54.6 | 57.6 | 9.9 |
| 2,4-DHAc | 261.4 | 132.0 | 16.4 |
| 2,5-DHAc | 205.9 | 120.6 | 15.2 |
| 3,4-DHBA | 142.7 | 126.1 | 12.3 |
| 2,5-DHBA | 42.5 | 27.5 | 9.4 |
| Quinizarin | 250.3 | 112.7 | 17.3 |
| Control | 250.6 | 105.1 | 10.9 |

**Table (2) Effect of the Studied Phenolic Compounds in Retarding of Corn Oil Oxidation at 60, 100 and 180°C, Assessed By the Change in TBARS Content (mmol/kg).**

| Phenolic Compounds | TBARS, 60°C after 20 days | TBARS, 100°C after 20 hours | TBARS, 180°C after 10 hours |
|---|---|---|---|
| α-Toc | 1.816 | 0.981 | 0.955 |
| BHT | 1.046 | 0.891 | 0.882 |
| BHA | 1.731 | 0.970 | 0.916 |
| TBHQ | 0.410 | 0.275 | 0.673 |
| DTBHQ | 0.763 | 0.643 | 0.702 |
| 2,4-DHAc | 2.184 | 0.940 | 0.858 |
| 2,5-DHAc | 1.717 | 1.064 | 0.898 |
| 3,4-DHBA | 1.572 | 0.936 | 0.800 |
| 2,5-DHBA | 0.520 | 0.322 | 0.662 |
| Quinizarin | 1.974 | 1.084 | 0.988 |
| Control | 2.113 | 0.914 | 0.782 |

**Table (3) Effect of the Studied Phenolic Compounds in Retarding of Corn Oil Oxidation at 60, 100 and 180°C, Assessed By the Change in Anisidine Value (AnV) (meq/kg).**

| Phenolic Compounds | AnV, 60°C after 20 days | AnV, 100°C after 20 hours | AnV, 180°C after 10 hours |
|---|---|---|---|
| α-Toc | 25.1 | 25.8 | 339.1 |
| BHT | 12.7 | 18.5 | 283.5 |
| BHA | 21.6 | 22.6 | 333.7 |
| TBHQ | 5.8 | 4.7 | 228.3 |
| DTBHQ | 11.7 | 9.6 | 235.9 |
| 2,4-DHAc | 30.4 | 30.1 | 290.5 |
| 2,5-DHAc | 22.9 | 24.1 | 323.4 |
| 3,4-DHBA | 16.6 | 26.3 | 274.3 |
| 2,5-DHBA | 7.1 | 5.6 | 223.9 |
| Quinizarin | 26.3 | 21.6 | 301.3 |
| Control | 27.8 | 19.5 | 253.8 |

**Table (4) Effect of the Studied Phenolic Compounds in Retarding of Corn Oil Oxidation at 60, 100 and 180°C, Assessed By the Change in Totox Value (TV) (meq/kg).**

| Phenolic Compounds | TV, 60°C after 20 days | TV, 100°C after 20 hours | TV, 180°C after 10 hours |
|---|---|---|---|
| α-Toc | 485.5 | 273.8 | 372.3 |
| BHT | 207.5 | 220.5 | 312.1 |
| BHA | 410.0 | 256.2 | 370.7 |
| TBHQ | 66.0 | 47.9 | 247.5 |
| DTBHQ | 120.9 | 124.8 | 255.7 |
| 2,4-DHAc | 553.2 | 294.1 | 323.3 |
| 2,5-DHAc | 434.7 | 265.3 | 353.8 |
| 3,4-DHBA | 302.0 | 278.5 | 298.9 |
| 2,5-DHBA | 92.1 | 60.6 | 242.7 |
| Quinizarin | 526.9 | 247.0 | 335.9 |
| Control | 529.0 | 229.7 | 275.6 |

The results of King et. al., (1995) showed marked differences among the antioxidant activity of TBHQ, BHT, BHA and α-tocopherol which supported our results concerning the pre-mentioned antioxidants.

Based on the above mentioned results, we could conclude that the attached hydroxyl groups especially in para and ortho positions to benzene ring enhance the antioxidant activity and the presence of methyl and/or carbonyl group will reduce its effect as antioxidant enhancer.

**2- Antioxidant activity of Supplementary Phenolic Compounds at 100°C**

Except BHT, the data from the accelerated oxidation tests at 100oC as shown in Tables 1-4 assured the same obtaining at 60oC, concerning the most effective antioxidants in general which are in concomitant with those of Zandi & Gordon, (1999). Still TBHQ, 2,5-DHBA and DTBHQ in this order are occupying the first places as active antioxidants.

On the contrary, other phenolic compounds showed pro-oxidant activity since they gave higher oxidation parameters than those of control counterparts.

Noticeable differences in the behavior of the studied antioxidants and their effect on the oxidative stability of corn oil at 100oC compared to 60oC could be observed. These differences may be attributed to the instability of their phenoxy radicals or oxidized products at high temperatures (100oC), since; the efficiency of antioxidant depends on the stability of its oxidized products (Gordon, 1990). The stability of the oxidized products (phenoxy radicals) of common antioxidants was recognized in the order: BHT radical > BHA radical > α-toc radical. The highest stability was remarked in the oxidized form of the phenolic compounds having two hydroxyl groups in ortho or para position which transform by oxidation to stable adducts (o- or p-quinones) e.g. tert-butylbenzoquinone (TBBQ) (oxidized form of TBHQ) (Madhavi et. al., 1995). It is evident that phenolic compounds having these structural features exhibited the most antioxidative effects in heated oils under high temperature conditions.

Depending upon the fore-mentioned observations, antioxidants such as BHA and BHT were found to exhibit no or little antioxidative

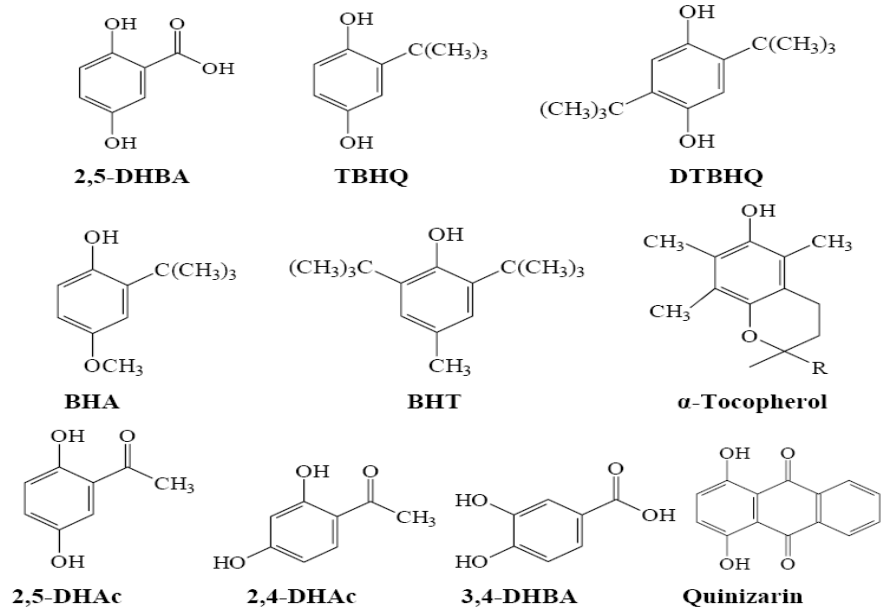
effect at 100oC (Gordon & Kourimska, 1995). Moreover, most phenolic compounds showed pro-oxidant activity at this temperature. This decline in the antioxidant activity of the most additives may be ascribed to their instability of their phenoxy radicals at 100oC. Hence, the pro-oxidant activity at high temperatures was distinctly recorded by the phenolic compounds have only one hydroxyl group on their aromatic ring (Khan & Shahidi, 2001).

Accordingly, TBHQ, DTBHQ and 2,5-DHBA were the most effective antioxidants in corn oil at 100oC. It is clear that all of them produce high stable para quinone analogues via oxidation (Cuvelier et al., 2000). Conversely, the phenolic compounds; 2,5-DHAc and quinizarin exhibited pro-oxidant activity although they have two hydroxyl groups in para position. This may be attributed to the presence of carbonyl group which acts as electrophilic agent. This electrophilic activity was found to promote greatly the decomposition of hydroperoxides to form secondary oxidation products such as aldehydes and ketones. The latter compounds which also have carbonyl groups, play the same role, hence the formation of these compounds cause a dramatic increase in the oxidation rate (Lalas & Dourtoglou, 2003), and then hasten the lipid oxidation and rancidity.

The results concerning 2,5-DHBA and 2,5-DHAc clearly confirmed the concept of antioxidant effect since, the former showed strong antioxidant activity while the latter gave pro-oxidant activity, especially at high temp. Although both compounds have two hydroxyl groups in para position that is ideal structural feature for antioxidant effect, the presence of the carbonyl group instead of the carboxyl group in the latter one reduce its activity.

**Oxidative stability by the Rancimat test at 100oC**

Assessment of the effect of the most potent antioxidants under investigation on the stability of corn oil by the Rancimat test at 100$^{o}$C, confirmed the previous obtained data from the oven test at 100$^{o}$C. TBHQ gave the best results followed by 2,5-DHBA and DTBHQ. Regarding the other common synthetic antioxidants, BHA and BHT had virtually no antioxidant activity by the Rancimat test at 100$^{o}$C, as described by Gordon & Kourimska, (1995) in rapeseed oil.




## 3- Antioxidant activity of Supplementary Phenolic Compounds at 180°C

The usual frying temperature 180oC is the crucial point in this study since it is the normal temperature for frying which it was aimed to protect the oil at this level of heating. Of course, rapid increasing in oxidation parameters of the oil could be observed at such high level of heating (Tables 1-4). The increase in peroxide value (not exceed 20 meq/kg) is due to the spontaneous decomposition of hydroperoxides over 150oC which formed in low levels during the cooling of the oil after heating (Gordon & Kourimska, 1995). The p-anisidine value, that measures mainly unsaturated aldehydes formed from hydroperoxide decomposition, rapidly increased during intermittent heating at 180oC for 10 hours. TBARS contents showed no and/or little increase compared with those obtained at 60 and 100oC. These results of TBARS could means that there was a high rate in either TBARS formation or their loss by evaporation and/or oxidation into acids.

Still the same three antioxidant compounds; TBHQ, 2,5-DHBA and DTBHQ are the best especially at 60oC and 100oC. However, the accelerated oxidation test of corn oil at 180oC, reduced markedly the protective effect of these potent compounds compared with their

strong efficacy at 100oC. These were expected results, because of the extremely elevation of temperature and frequent heating for a long time (Kazernaviciute & Gruzdiene, 2003).

In such a level of high temperature 2,5-DHBA became more effective antioxidant among the top three active antioxidants; 2,5-DHBA, TBHQ and DTBHQ although the opposite order was recorded at 60 and 100oC. This may attributed to the high melting point (over 200oC) of 2,5-DHBA compared with that of TBHQ (127oC). Definitely, this reflected the high stability of 2,5-DHBA toward high temperatures, and in turn low volatility during heating compared to TBHQ (Zhang et. al., 2004).

It is important to note that although DTBHQ has the highest melting point (219oC), its potency was found to take the third place in the potent antioxidants at 180oC as well as 60 and 100oC. This mainly due to the presence of more than tert-butyl substituent as electron releasing group which was found to increase the hydrogen-donating ability, and consequently increase the instability of this compound (Peyrat-Maillard et. al., 2003).

**In conclusion**, there were structural features of the phenolic compounds which are characterized by high stability and consequently high efficacy as antioxidants at high temp. This was illustrated from that all of TBHQ, DTBHQ and 2,5-DHBA remain the most effective antioxidants even at high temperatures (180oC). The superiority of these compounds is mainly due to the presence of two hydroxyl groups attached to benzene ring in para position.

As mentioned before that the antioxidant compound is the compound that could be oxidized easily and faster than others which give it the efficacy to protect the other from oxidation. Oxidation is accepting of oxygen or loosing of hydrogen to or from the reduced form of the compound. From our point of view and based on the chemical structures of the three effective antioxidants (2,5-DHBA, TBHQ & DTBHQ), the proposed mechanism as illustrated in Figure (1) could interprets the high efficacy of the three mentioned antioxidants. The para position of the two hydroxyl groups allows easily their hydrogen transfer through the benzene ring which resulted in loosing their two hydrogen atoms and forms the stable para quinone analogue. That means the easy oxidation of such kind of compounds compared to others made them more effective antioxidants. The presence of tertiary butyl group with its effect as an electron repelling

group could cause some obstruction to the hydrogen transfer across the benzene ring which ranked the TBHQ and DTBHQ in the second and third places after 2,5-DHBA.

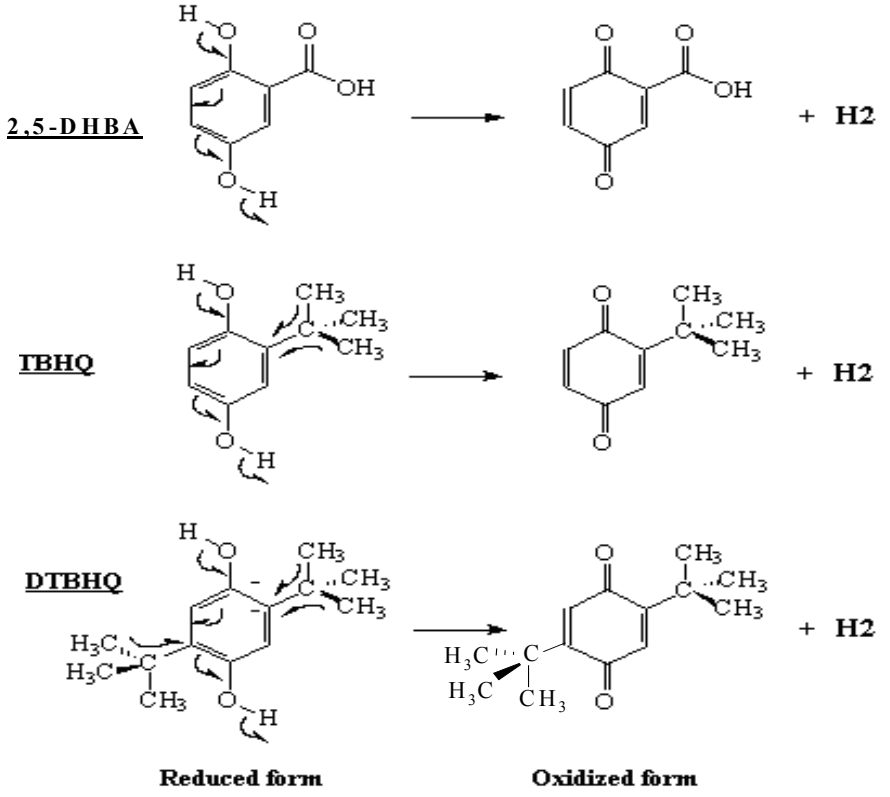



**Fig. 1: The proposed mechanism of the hydrogen transfer along the structures of the most active antioxidants to eliminate hydrogen and forming their oxidized forms**

Based on the same concept of antioxidant activity, the BHT could play a role as antioxidant as illustrated in Figure 2. Although it contains one hydroxyl group in its structure, the presence of the tertiary butyl groups with its effect as an electron repelling group next to the hydroxyl group could cause redistribution of the negative charges along the compound. The redistribution of the negative charges leads to easily loosing of the hydrogen atom of the hydroxyl group and forming the radical. Two radicals could attach together and form the stable complex releasing hydrogen molecule (Oxidation).

Hence, this type of compounds such as BHT, BHA and α-Toc could play a role as antioxidant but not active as the same as the above mentioned 2,5-DHBA, TBHQ and DTBHQ, so they ranked after them because of the fast and easy loosing of hydrogen from one molecule than two.

Conversely, the presence of the carbonyl group next to the hydroxyl group on the benzene ring in spite of the presence of the two para hydroxyl groups (2,5-DHAc), cause of reducing the antioxidant activity, and moreover the pro-oxidant effect. As illustrated in Figure 3, it is known that the carbonyl group acts as electrophilic agent owing to the existence of a partial positive charge on the carbon atom. So, the hydrogen transfer that takes place between the two para hydroxyl groups in the absence of the carbonyl group was found to run as a resonance between the carbonyl group and the next hydroxyl group leading to no loosing of hydrogen (no antioxidant activity). These observations indicated that the carbonyl group represents undesired or refused substituent in the potent antioxidants either in ketone or aldehyde form.

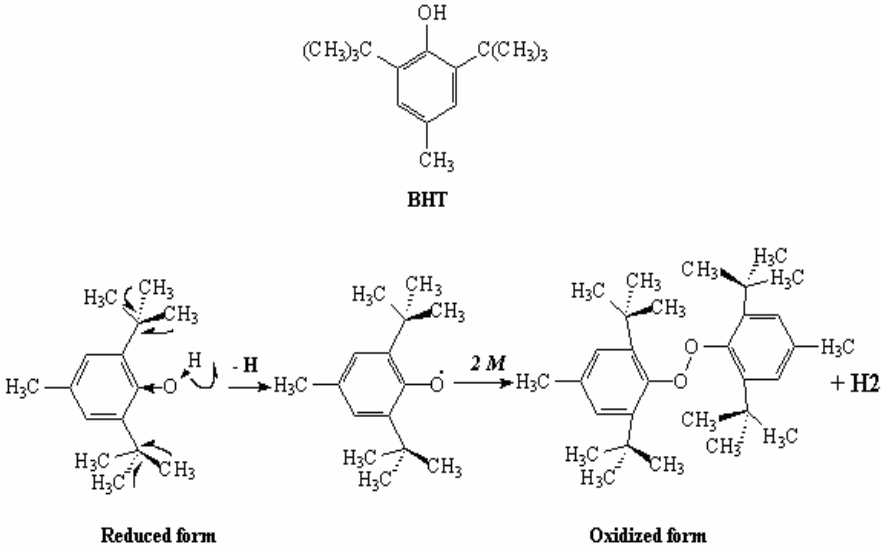



**Fig. 2: The proposed mechanism of the hydrogen transfer along the structure BHT as active antioxidant to eliminate hydrogen and forming its oxidized form**

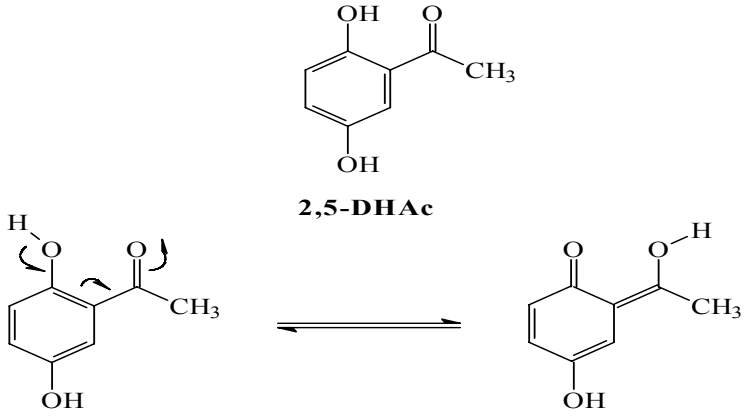



**Fig. 3: The proposed mechanism of the hydrogen transfer along the structure of 2,5-DHAc showing the tautomerism between the carbonyl group and the hydroxyl group**

It is worth noting that, 2,5-DHBA in corn oil at 60 and 100$^{o}$C and more over at 180$^{o}$C is the most protective antioxidant among the others high protective TBHQ & DTBHQ. It also owns a natural origin in addition to its high safety compared to other potent antioxidants which are prepared synthetically and have high toxicity. 2,5-DHBA is water soluble compound, which means that it is hydrophilic antioxidant. Water solubility of 2,5-DHBA frequently facilitates the removing it from the human body, as recognized by many investigators who found that 2,5-DHBA represents an aspirin or salicylate metabolite. However, 2,5-DHBA as a natural compound existed with other phenolic acids and widely distributed in several plants such as grape and strawberry. Moreover, many studies *in vivo* proved that 2,5-DHBA inhibits LDL oxidation initiated by superoxide/nitric oxide radicals (Hermann *et. al.,* 1999), and inhibits glucose autoxidation-mediated atherogenic modification of LDL (Exner *et. al.,* 2000). Furthermore, Ashidate *et. al.,* (2005) found that 2,5-DHBA inhibits oxidation of LDL induced by 2,2'-azobis or $Cu^{+2}$, inhibits the formation of cholesterol ester hydroperoxides in human plasma and had a potent free radical scavenging activity.

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# النشاط المضاد للأكسدة لبعض المركبات الفينولية المضافة لزيت الذرة تحت ظروف الحرارة المرتفعة

**مجدى فؤاد توفيق - سمير الهادى- على رزق نصار - فاروق جندى معوض**
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- تم تقييم تأثير بعض المركبات الفينولية على درجة مقاومة زيت الذرة للأكسدة أثناء تسخينه على درجات حرارة مرتفعة 60 و 100°م وحتى درجة حرارة القلى المعتادة 180°م.

**- الهدف من هذا التقييم هو:**
1- البحث عن المركبات الفينولية الأكثر فعالية كمضادات أكسدة تحت ظروف الحرارة المرتفعة
2- توضيح العلاقة بين نشاط هذه المركبات خاصة الفعالة منها وتركيبها الكيميائي.

- تم تتبع التقدم في درجة الأكسدة بقياس كلاً من أرقام البيروكسيد والأنزيدين والتوتوكس والمواد المتفاعلة مع حمض الثيوباربتيوريك وذلك أثناء المعاملات الحرارية وفى وجود المركبات الفينولية المختلفة والمستخدمة فى هذة الدراسة كما تم إستخدام جهاز Rancimat لتقييم درجة ثبات الزيت في وجود المركبات الفينولية الأكثر فعالية على 100 °م.

**أوضحت النتائج المتحصل عليها من هذة الدراسة الأتى:**

1- أن كلاً من مركبات 2و5- داى هيدروكسي بنزويك أسيد و TBHQ و DTBHQ كانت هي المركبات الفينولية الأكثر فعالية كمضادات أكسدة تحت ظروف الحرارة المرتفعة.
2- أكد اختبار Rancimat تفوق هذه المركبات كمضادات أكسدة في زيت الذرة عند 100 °م.
3- أكدت النتائج أن فعالية هذه المركبات أعلى بكثير من مضادات الأكسدة الأكثر شيوعاً وهى BHT و BHA
4- مضاد الأكسدة الطبيعي (α-tocopherol) يظهر نشاطاً محفزاً للأكسدة تحت ظروف الحرارة المرتفعة وليس مانع للأكسدة.
5- تفوق هذه المركبات يرجع إلي احتوائها على مجموعتي هيدروكسيل في الوضع بارا.
6- على الرغم من أن هناك مركبات أخرى تحتوي أيضاً على هذا التركيب وهي 2و5- داى هيدروكسي أسيتوفينون & 1و4- داى هيدروكسي أنثراكينون إلا إنها أظهرت نشاطاً محفزاً للأكسدة وليس مانع للأكسدة.
7- وجود مجموعة الكربونيل ذات النشاط الإلكتروفيلي ضمن التركيب الكيميائى هو الذي أدى الى أن 2 و5- داى هيدروكسي أسيتوفينون و 1و4- داى هيدروكسي أنثراكينون تظهر نشاطاً محفزاً للأكسدة وليس مانع للأكسدة.
8- المركبات الفينولية الأكثر فعالية كمضادات أكسدة تحت ظروف الحرارة المرتفعة لابد أن تحتوي على مجموعتي هيدروكسيل ضمن تركيبها الكيميائى بدلاً من واحدة وذلك في الوضع أرثو أو بارا بالنسبة لبعضهما وليس في الوضع ميتا بالإضافة إلي خلوها تماماً من مجموعات الكربونيل أو غيرها من المجموعات ذات النشاط الإلكتروفيلي .