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Synthesis, characterization and evaluation of antioxidant activity of tyrosol derivatives from olive mill wastewater

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Abstract

The use of biophenols to synthesize antioxidants has greatly developed due to their capability of solving environmental problems, economical reasons and renewability. In the present work, the tyrosol derived from olive mill wastewater (OMWW) was alkylated to improve its utilization. The synthesized antioxidants were characterized by nuclear magnetic resonance (NMR) and CHN analyses. To study their thermal behavior, thermogravimetry analysis (TGA) and derivative thermogravimetry (DTG) techniques were employed. Antioxidant action of these compounds in gasoline sample was investigated by accelerated oxidation and induction period tests. Induction period results show the best stability time (188 min) at 10 ppm concentration of synthesized antioxidant in a gasoline sample. Reduction of carbonyl and peroxide band areas indicates the good antioxidant activity of these compounds (1.0% concentration) in the gasoline. Considering what was mentioned above, easy synthesis method and using bio-based material provide a highly efficient antioxidant to inhibit the oxidative process of gasoline.

Keywords Antioxidant · Olive mill wastewater · Phenol · Tyrosol · Gasoline

Introduction

Additives in oil industry are the most important chemical compounds to improve specific qualities and solve degradation problem of petrochemical products (Facanha et al. 2007). In recent years, due to the destructive consequences of by-product formation in oxidation reaction in food, pharmaceutical and oil industries, antioxidant additives have been considered remarkably (Bhatnagar and Vergnaud 1983). Antioxidant additives are able to decelerate the oxidation of other compounds and prevent gum formation (Ohkatsu and Nishiyama 2000). Consequently, researchers are interested to use this kind of additives in petrochemical and industrial products (Feng et al. 2017; Gülçin 2012).

From among the wide range of reported antioxidants, bio-based compounds have received a lot of attention. Their most significant advantages are sustainability, low cost, low toxicity and availability (Salimon et al. 2010). In such class of materials, biophenolic compounds exist in nature as intrinsic antioxidants that are capable of directly scavenging peroxy radicals, donating hydrogen atoms or electrons to radical species or removing metal cations through formation of chelate during oxidative degradation (Amarowicz et al. 2004). This potential can be widely considered for inhibiting the oxidation process of petrochemical products like gasoline. There are several types of biophenolic antioxidants such as cardanol (Maia et al. 2015; Voirin et al. 2014), chitosan Schiff base (Guo et al. 2005; Demetgül and Beyazit 2018), rosemary extract (Yang et al. 2016), and green tea (Donlao and Ogawa 2018). In addition, some biophenolic compounds with antioxidant activity have been identified in several agricultural by-products, such as buckwheat hulls (Watanabe et al. 1997), rice hulls (Ramarathnam et al. 1989), almond hulls (Sfahlan et al. 2009) and olive mill wastewater (OMWW) (De Marco et al. 2007; Aissa et al. 2017).

Olive fruit has the most abundant phenolic compounds. In the oiling process, the total phenolic content of the olive fruit is separated into three parts: only 2% remains in the oil phase, approximately 53% is lost in the OMWW and 45%

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remains in the pomace (Rodis et al. 2002). OMWW, as a major by-product of oiling process, is a source of phenolic compounds such as hydroxytyrosol, tyrosol, oleuropein, and a variety of hydroxycinnamic acids (Obied et al. 2005). The phenolic fraction in OMWW causes environmental problems, antimicrobial activities and biological degradation (Bisignano et al. 1999). In this pursuit, extraction of phenolic compounds from olive oil wastewater can solve the environmental problems; meanwhile, these compounds can be used as inexpensive and affordable natural raw materials for antioxidant production.

Among the phenolic content of OMWW, the tyrosol compound has been utilized as a basis for the synthesis of effective antioxidants (Wen et al. 2013; Storozhok et al. 2004). Tyrosol with two hydroxyl groups (phenolic and alcoholic) could be an excellent antioxidant but it is crucial to be modified (Gülçin 2007; Storozhok et al. 2012).

This study intends to describe the synthesis and characterization of novel and highly efficient agents with excellent antioxidant properties. In this process, tyrosol is alkylated with *tert*-butyl group in the presence of silica gel as catalyst to improve its thermal stability, solubility and volatility. The synthesized compounds were assessed by thermal-oxidative stability and antioxidant activity in gasoline for more accurate identification.

Experimental

Materials

The chemicals and solvents were purchased from commercial suppliers and used without further purification. Gasoline was supplied by Bouali Sina Petrochemical Co. with no further distillation procedure (Mahshahr, Iran).

Thin-layer chromatography (TLC), Merck silica gel 60 F254 plates, was used to follow-up the reaction progress. Purification was done by column chromatography on silica gel 60, Merck (*n*-hexane/ethyl acetate as eluent).

Apparatus and instruments

Fourier transform infrared (FT-IR) spectra were obtained using FT-IR Bruker-Vector 22 spectrophotometer in KBr/Nujol mull in the range of 400–4000 cm^{-1} under ambient conditions. ^1H NMR and ^{13}C NMR spectra were recorded by BRUKER spectrometer, at the frequency of 250 and 62.5 MHz, respectively, in $CDCl_3$.

Elemental CHN analyser (Germany) was used for the CHN analysis of all products.

Thermogravimetry (TG/DTG) measurements were carried out by a PerkinElmer thermogravimetric analyzer using ceramic pan at an increasing rate of 10 °C min^{-1} from ambient temperature to 900 °C. The measurements were carried out in N_2 atmosphere (120 mL min^{-1}) from 25 to 200 °C and O_2 atmosphere (120 mL min^{-1}) from 200 to 900 °C.

Accelerated oxidation tests

Accelerated oxidation test was carried out in a bench-scale oxidation apparatus in laboratory using two samples simultaneously according to modified ASTM D-2440 method (Koh and Butt 1995). The antioxidant capability was investigated for two gasoline samples: one of them without antioxidant and the other one containing 1% antioxidant in the presence of the copper wire spiral. The samples were placed in two 10-mL round-bottom flasks and were kept at constant temperature (60 °C) under a flow of oxygen. Each sample was collected after 72 h and analyzed by FT-IR spectroscopy.

Induction period test for oxidative stability

Specific concentrations of synthesized substances were prepared (5 mL) to accelerate the assays of oxidative stability, induction period test (ASTM D 525) (Petroxy from Petrotest, Germany) until the observation of pressure drop.

Methods

Procedure for the alkylation of tyrosol

Tyrosol (1 mmol, 0.138 g), *tert*-butyl bromide (6 mmol, 0.67 mL), sodium carbonate (12 mmol, 1.272 g) in the presence of silica gel (1 g) in carbon tetrachloride (5 mL) were stirred at 65°C for 24 h. The reaction progress was monitored by TLC. The reaction mixture was washed thoroughly with diethyl ether and filtered off. Following that, the product was concentrated under reduced pressure and purified by column chromatography on silica gel 60, eluting with n-hexane/ethyl acetate (70:30). 2,6-di-*tert*-butyl-4-(2-hydroxyethyl)phenol (di-*tert*-butylated tyrosol) was obtained as a white solid compound (225.3 mg, 90%).

Employing the same procedure, but using a lower amount of *tert*-butyl bromide (2 mmol, 0.22 mL) led to preparing mono-*tert*-butylated tyrosol. 2-*tert*-butyl-4-(2-hydroxyethyl) phenol (mono-*tert*-butylated tyrosol) product was obtained as an oily compound (185.00 mg, 95%). All products were characterized by ^1H NMR, ^{13}C NMR, and CHN analysis.

2-*tert*-Butyl-4-(2-hydroxyethyl)phenol (mono-*tert*-butylated tyrosol)(2a)

Oily compound; ^1H NMR (250 MHz, $CDCl_3$, δ/ppm): 7.15 (1H, s), 6.97 (1H, d, $J = 8.00$ Hz), 6.65 (1H, d, $J = 8.00$ Hz), 5.11 (1H, s), 3.57 (3H, t, $J = 8.00$ Hz), 3.13 (3H, t,

$J = 8.00$ Hz), 1.47 (9H, s); ^{13}C NMR (62.9 MHz, $CDCl_3$, δ/ppm): 153.16, 136.30, 130.83, 127.54, 126.94, 116.60, 39.10, 33.48, 30.31, 29.55.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19, H, 9.34 and O, 16.47. Found: C, 72.20, H, 9.30 and O, 18.50.

2,6-Di-*tert*-butyl-4-(2-hydroxyethyl)phenol (di-*tert*-butylated tyrosol)(2b)

White solid; m.p.: 75–78 °C; ^{1}H NMR (250 MHz, $CDCl_3$, δ/ppm): 7.04 (2H, s), 5.19 (1H, s), 3.56 (3H, t, $J = 8.00$ Hz), 3.11 (3H, t, $J = 8.00$ Hz), 1.48 (18H, s); ^{13}C NMR (62.9 MHz, $CDCl_3$, δ/ppm): 152.69, 136.04, 129.71, 125.24, 39.75, 33.43, 30.26, 29.69.

Anal. Calcd. for $C_{16}H_{26}O_2$: C, 76.75, H, 10.47 and O, 12.78. Found: C, 74.70, H, 10.40 and O, 14.90.

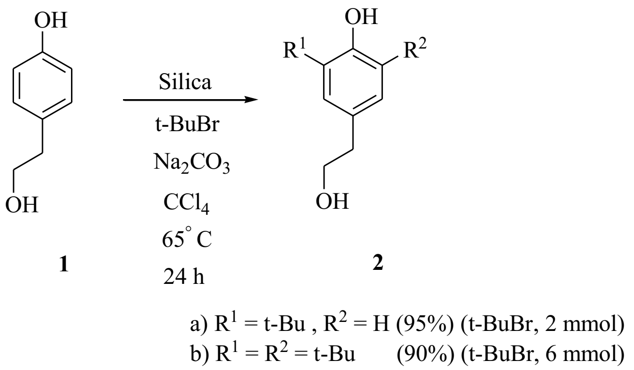
Results and discussion

Synthesis and characterization of *tert*-butylated tyrosol derivatives

According to antioxidant ability of biophenolic compounds and improvement of the solubility and stability properties by alkylation, in this work, two antioxidants were designed and synthesized based on tyrosol. This biophenol is the representative of natural compound with two functional groups.

To synthesize the efficient antioxidants, tyrosol was alkylated in the presence of silica gel as a Lewis acid catalyst (Scheme 1) (Kamitori et al. 1984). The reaction was performed in CCl_4 at 65 °C for 24 h.

2-*tert*-Butyl-4-(2-hydroxyethyl)phenol (mono-*tert*-butylated tyrosol) (**2a**) and 2,6-di-*tert*-butyl-4-(2-hydroxyethyl)phenol (di-*tert*-butylated tyrosol) (**2b**) products were obtained in excellent yield. It is worth mentioning that different t-BuBr amounts lead to different ratios of mono and di-alkylated products. In the presence of the excess amount of t-BuBr (6 mmol) and less amount of t-BuBr (2 mmol), di-*tert*-butylated and mono-*tert*-butylated compounds are the major products, respectively.



a) R^1 = t-Bu , R^2 = H (95%) (t-BuBr, 2 mmol)
b) $R^1 = R^2$ = t-Bu (90%) (t-BuBr, 6 mmol)

Scheme 1 General procedure for alkylation of tyrosol in the presence of silica gel

The NMR spectroscopy and CHN analysis were employed to characterize the obtained products. For mono-*tert*-butylated tyrosol in ^{1}HNMR, three peaks in 6.65, 6.97 and 7.15 ppm were referred to the aromatic hydrogen atoms. For proton of phenolic group, one singlet peak was observed at 5.11 ppm. Aliphatic hydrogen atoms appeared in 3.13 and 3.57 ppm as two triplet peaks. The nine protons of the CH_3 groups of t-Bu were observable at 1.47 ppm as a singlet peak (Fig. 1a).

For di-*tert*-butylated tyrosol a singlet peak in 7.04 ppm verified the existence of two aromatic hydrogen atoms. The proton of phenolic group appeared at 5.19. Two triplet peaks at 3.56 and 3.11 ppm were attributed to methylene groups of the aliphatic chain. The peak that appeared at 1.48 ppm with 18 integral corresponded to the presence of two t-Bu groups (Fig. 1b).

The ^{13}CNMR of mono-*tert*-butylated tyrosol showed six peaks at 153.16, 136.30, 130.83, 127.54, 126.94 and 116.60 ppm for six carbons of aromatic ring. The peaks at 39.10 and 33.48 ppm were attributed to the aliphatic chain (ethyl alcohol). In addition, the carbons of t-Bu group appeared at 30.31 and 29.55 ppm which belong to tertiary and primary carbons, respectively. The ^{13}CNMR for di-*tert*-butylated tyrosol exhibited four peaks at 152.69, 136.04, 129.71 and 125.24 ppm which verify the symmetry of aromatic ring. The carbons of aliphatic groups (*tert*-butyl and ethyl alcohol) appeared at 39.75, 33.43, 30.26 and 29.69 ppm (supplemental material).

Thermal studies

Thermogravimetric analysis (TGA) and differential thermoanalysis (DTA) were applied to determine the thermal stability of the di-*tert*-butylated tyrosol. Essentially, two weight losses were observed from 25 to 900 °C. The first weight loss at around 110 °C was attributed to the release of the organic solvents. The major and sharp weight loss between 152 and 195 °C corresponded to carbon skeleton decomposition (Fig. 2.). The result indicated the thermal stability of the prepared antioxidant.

Study of the antioxidative capacity of the products

Due to the novelty of the synthesized compounds for use in oil industry, and to study the antioxidant capacity of these products, accelerated oxidation test and induction period test were performed.

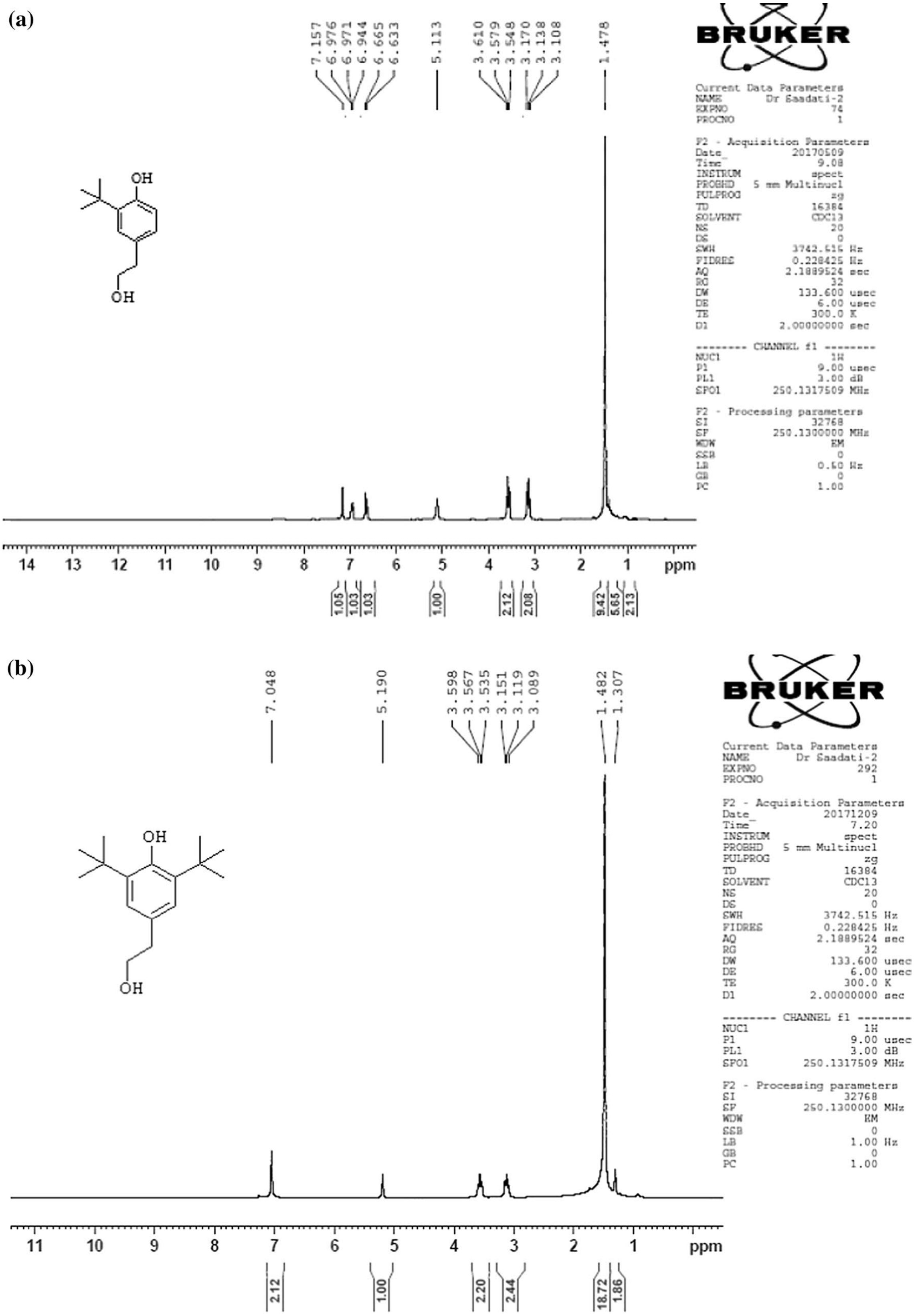


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Fig. 1 ^{1}H NMR of mono-*tert*-butylated tyrosol (**a**) and di-*tert*-butylated tyrosol (**b**)

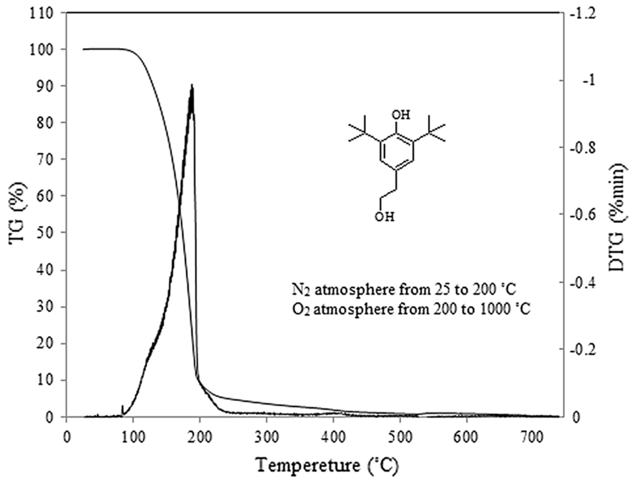


Fig. 2 Thermogravimetric diagram of di-*tert*-butylated tyrosol

Accelerated oxidation test of di-*tert*-butylated tyrosol (2b)

For accelerated oxidation test two samples were employed: gasoline with 1.00% w/v antioxidant (**2b**) and gasoline without antioxidant (blank). Different compounds such as ketones, acids, aldehydes and peroxides were formed due to the oxidation reaction and degradation in the sample. The formation of these compounds with C=O and OH functional group leads to the appearance of vibrational peaks for carbonyl (C=O) and peroxides (ROOH) at 1706 and 3429 cm^{-1}, respectively (Bowman and Stachowiak 1996).

Therefore, in the study of accelerated oxidation test-specific spectral bands, areas from 1644 to 1763 cm^{-1} and 3144 to 3598 cm^{-1} were calculated (Fig. 3). The comparison was made between fresh gasoline (supplemental material), degraded blank gasoline after 72 h (Fig. 3a) and gasoline with 1% antioxidant after 72 h (Fig. 3b). Following the degradation, due to oxidation reaction in blank gasoline, sharp vibrational peaks regarding C=O and OH at 1701 and 3370 cm^{-1} appeared which show the formation of a great variety of oxidation products. As shown in Fig. 3b, the intensity of functional group peaks, arising from oxidation reaction, is negligible for gasoline with 1% antioxidant sample. For comparison, these results are represented as the ratio between the areas which were obtained for the carbonyl and peroxide bands for the gasoline sample with antioxidants (A_{with}) and without antioxidant ($A_{without}$). Accelerated oxidation test proved excellent efficiency of antioxidant (**2b**) in preventing oxidation reaction and forming gum product (Table 1).

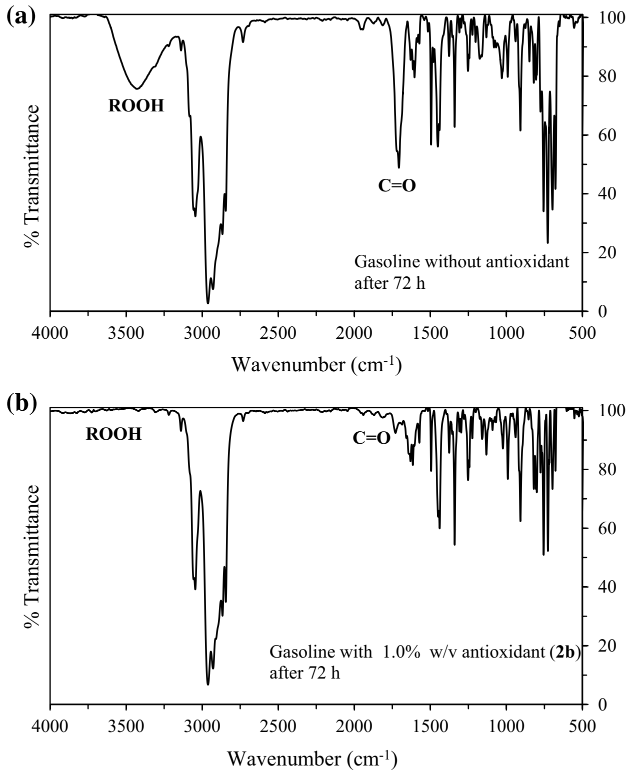


Fig. 3 Infrared spectra of gasoline samples: **a** gasoline without antioxidant (72 h) and **b** gasoline with 1.0% antioxidant (72 h)

Induction period test

Induction period test (ASTM D 525) was performed to study the oxygen stability of gasoline. Auto-oxidation in gasoline during the storage because of the presence of atmospheric oxygen leads to the formation of mono- and di-olefins which causes problems on the stability of the gasoline. In this test, to optimize the concentration of antioxidant, six samples of antioxidant (**2b**) at different concentrations (0, 5, 10, 20, 30 and 200 ppm) were used (Table 2). According to the obtained results, increasing the concentration of antioxidant in gasoline leads to increasing the stability time in induction period test significantly.

For comparison, induction period test for mono-*tert*-butylated tyrosol (**2a**) antioxidants was carried out. The

Table 1 Results of the accelerated oxidation test for gasoline samples after 72 h of degradation

	C=O	ROOH
Sample	(A_{sample}/$A_{without}$)	(A_{sample}/$A_{without}$)
Gasoline without antioxidant (72 h)	1	1
Gasoline with 1.0% antioxidant (72 h)	0.1	0.1

Table 2 Results of the induction period test of di-*tert*-butylated tyrosol antioxidant (**2b**) at different concentrations

Entry	Concentration (ppm)	Induction period (min)
1	0	40
2	5	166
3	10	188
4	20	195
5	30	205
6	200	246

obtained result was good because it shows the efficiency of mono-*tert*-butylated tyrosol too (Table 3, entry 2). Furthermore, all the results were compared with the famous commercial antioxidant (BHT) at 10 ppm concentration (Table 3, entry 4). The marked point is that adding very low concentrations of antioxidant leads to very good results and increases the stability time.

Comparison with other reported phenolic antioxidants

The antioxidant action of 2,6-di-*tert*-butyl-4-(2-hydroxyethyl)phenol (**2b**) was compared with that of a number of previously reported phenolic antioxidants in different sources of gasoline samples (Table 4).

In comparison with other antioxidants, the synthesized bio-antioxidant could highly improve induction period time at very low concentration.

Conclusion

An efficient antioxidant based on a biophenol was prepared under a simple protocol and completely characterized. The developed material appears to be an excellent antioxidant for gasoline. Most importantly, the synthesized antioxidant could highly improve induction period time at very low

Table 3 Comparison of the induction period result of all synthesized antioxidants and BHT at 10 ppm concentration

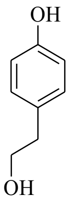
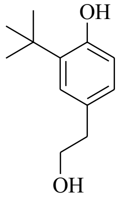
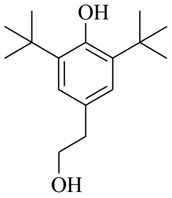
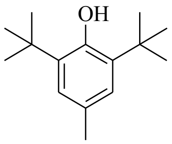
Entry	Additive		Induction period (min)
1		(1)	Insoluble in gasoline
2		(2a)	178
3		(2b)	188
4		BHT	152

Table 4 A comparison of the developed antioxidant with those reported in the literature

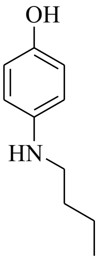
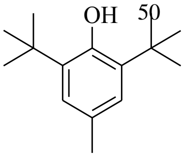
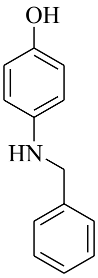
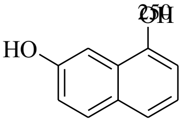
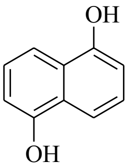
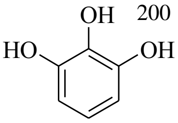
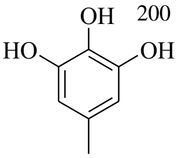
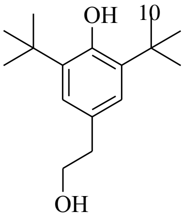
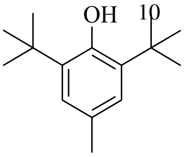
Entry	Antioxidant	Concentration (ppm)	Induction period of blank (min)	Induction period of sample (min)	References
1		50	135	680	Jones et al. (1952)
2		50	135	275	Jones et al. (1952)
3		10	–	310	Pedersen (1949)
4		250	–	1110	Thompson and Chenicek (1955)
5		250	–	1315	Thompson and Chenicek (1955)
6		200	160	890	Scheumann and Haslam (1942)
7		200	160	575	Scheumann and Haslam (1942)
8		10	40	188	This work

Table 4 (continued)

Entry	Antioxidant	Concentration (ppm)	Induction period of blank (min)	Induction period of sample (min)	References
9		10	40	152	This work

concentration. The availability of starting material, easy synthesis, renewability, excellent performance and good thermal behavior led to the formation of efficient antioxidants which were used to break oxidation chain and prevent degradation. Such significant antioxidant efficiency could be attributed to the two steric *tert*-butyl groups in phenolic ring and an alcoholic hydroxyl group in aliphatic chain.

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