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A novel antioxidant: 6,6'-(butane-1,1-diyl) bis(4-methylbenzene-1,2-diol)

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SUMMARY: A novel compound, 6,6'-(butane-1,1-diyl)bis(4-methylbenzene-1,2-diol) (BMB), was synthesized through an acid-catalyzed condensation reaction between 4-methylcatechol (HPC) and butyraldehyde. When evaluated by the Rancimat and deep frying methods, BMB exhibited a stronger antioxidant activity than TBHQ. Its DPPH radical scavenging activity was also fairly higher than TBHQ, but lower compared to its mother phenol, HPC, due to its relative ease of binding DPPH$^{\bullet}$. BMB had the strongest scavenging ability of the 4-methylcatechol analogues reported to date. It could be used effectively to retard lipid peroxidation in both moderate and high temperature food preparations.

KEYWORDS*: 6,6'-(butane-1,1-diyl)bis(4-methylbenzene-1,2-diol); Acid-catalyzed condensation reaction; Antioxidant activity; Deep frying; HPC; TBHQ*

RESUMEN: Un nuevo antioxidante: 6,6'-(butano-1,1-diil)bis(4-metil-benceno-1,2-diol). Un nuevo compuesto, 6,6'-(butano-1,1-diil)bis(4-metilbenceno-1,2-diol) (BMB) fue sintetizado mediante una reacción de condensación catalizada por ácido entre el 4-metilcatecol (HPC) y el butiraldehído. Cuando se evaluó mediante los métodos Rancimat y de fritura, el BMB mostró una actividad antioxidante más fuerte que el TBHQ. Su actividad de eliminación de radicales DPPH también fue bastante mayor que la del TBHQ, pero menor en comparación con el fenol de partida, HPC, debido a su relativa facilidad para unirse a DPPH$^{\bullet}$. BMB tiene una actividad de eliminación más fuerte que los análogos de 4-metilcatecol reportados hasta la fecha. Podría usarse eficazmente para retardar la peroxidación de lípidos en la preparación de alimentos a temperatura moderada y alta.

PALABRAS CLAVE: *6,6'-(butano-1,1-diil)bis(4-metilbenceno-1,2-diol); Actividad antioxidante; Fritura; HPC; Reacción de condensación catalizada por ácido; TBHQ*

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1. INTRODUCTION

Lipid-based foods like dairy products, fast foods and edible oils are susceptible to autoxidation, a spontaneous process that causes foods to deteriorate, resulting in off-flavors and potentially toxic substances. Although refrigeration, nitrogen blanketing, and packaging can be used to protect against food deterioration, they are often not economical or convenient to prevent oxidation in the food industry. Hence, the addition of antioxidants to such foods remains the most operative, resourceful and cost-effective method to prevent lipid oxidation (Wang *et al*., 2000; Weng, 1993).

Antioxidant activity, especially in oil, can be investigated by various *in vitro* means, such as the Rancimat method (Weng and Gordon, 1992), 2,2-diphenyl-1-picrylhydrazyl (DPPH), ferric reducing antioxidant power (FRAP), cupric reducing antioxidant capacity (CUPRAC) and trolox equivalent antioxidant capacity (TEAC) assays (Huang *et al*., 2005). But since natural antioxidants are normally costly and sometimes have undesirable flavors, there has been a growing preference for their synthetic alternatives like *tert*-butylhydroquinone (TBHQ) and other phenolic compounds with strong steric hindrance and synergistic properties at moderate and high temperatures (Shahidi *et al*., 1992). These synthetic phenolic compounds can only be used in lipid foods, either sparingly or in combination at a maximum concentration of 200 mg/kg (Cacho *et al*., 2016; Saad *et al*., 2007).

TBHQ is a widely utilized commercial antioxidant due to its affordable price and strong antioxidant activity, but at high temperatures (*i.e.* deep frying) its potency often becomes weak because it easily vaporizes with steam due to its small molecular weight (Marmesat *et al.*, 2010; Zhang *et al*., 2004). Therefore, high molecular weight antioxidants with improved heat stability under high temperatures are favored.

Catechol is an organic compound commonly used as starting material in the production of pesticides, perfumes and pharmaceuticals (Helmut *et al*., 2002). 4-methylcatechol (HPC), an analogue of catechol, is a weak antioxidant for bulky oils owing to a lack of steric synergy between its constituent hydroxyl groups (Huang *et al*., 2014; Weng and Huang, 2014). There is no report of an *in vitro* experiment on the structure-antioxidant activity relationship of a tetrahydroxybisphenyl analogue of HPC, even though studies (Duan *et al*., 1998; Li *et al*., 2006) indicated that such a compound can exert a stronger antioxidant activity than its corresponding monomer, as well as TBHQ.

The present study focuses on 6,6'-(butane-1,1-diyl)bis(4-methylbenzene-1,2-diol) (BMB), a novel tetrahydroxybisphenyl compound with improved functionality, synthesized by an acid-catalyzed condensation reaction between butyraldehyde and 4-methylcatechol. The structure-antioxidant activities of this compound were also studied using the results of the Rancimat test, DPPH$^{\bullet}$ spectrophotometric assay and deep frying.

2. MATERIALS AND METHODS

2.1. Materials

HPC was purchased from Shanghai Macklin Biochemical Co., Ltd (Shanghai, China). 2,2-diphenyl-1-picrylhydrazyl (DPPH$^{\bullet}$), butyraldehyde, TBHQ, silica gel and other chemicals were purchased from Shanghai Chemical Reagent Co. Ltd (Shanghai, China). Lard was carefully rendered in the laboratory and stored below −18 °C for subsequent use. Soybean oil was purchased from Shanghai Oil and Fat Co. Ltd (Shanghai, China). Potatoes were purchased from the local market. All chemicals used in this experiment were of analytical grade and used without further purification. Analytical thin-layer chromatography (TLC) was carried out on 0.25 mm pre-coated silica gel glass plates. The protection factors of the antioxidant samples were measured by Rancimat 743 (Metrohm, Herisau, Switzerland). NMR spectra were recorded with a Bruker Avance 600 MHz spectrometer (USA) and UV-2450 spectrophotometer (Shimadzu Corp, Kyoto, Japan) for UV spectroscopy using methanol as solvent. All samples were analyzed in duplicate and expressed as mean ± SD. Statistical significances between various groups were examined by analysis of variance (ANOVA) using OriginPro version 9.1, followed by Duncan's multiple comparison test ($P < 0.05$).

2.2. Synthesis and purification of BMB

A mixture of HPC (1 mol, 12.4 g), 50 mL ethanol and hydrochloric acid (37%, 10 ml) was added to a 250 mL three-neck flask at 70 °C under stirring followed by drop-wise addition of butyraldehyde (1 mol, 7.2 g) for 20 min. After 2 h, the reaction mixture was evaporated under vacuum and the residue was washed with hot water (100 mL×3) followed by ethyl acetate (25 mL). The organic phase was then dried over Na_2SO_4, concentrated again under reduced pressure and the resulting product was purified by column chromatography (dichloromethane/methanol, 10:1) to yield BMB (75%), which was re-crystallized from acetone to afford white flaky crystals. ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.57 (s, 2H, OH), 7.48 (s, 2H, OH), 6.61 (s, 4H, $H^{8, 8', 10, 10'}$), 4.02 (t, J = 7.5 Hz, 1H, H^4), 2.12 (s, 6H, H^{11}), 1.76 (q, J = 7.6 Hz, 2H, H^3), 1.36 (h, J = 7.4 Hz, 2H, H^2), 0.92 (t, J = 7.3 Hz, 3H, H^1). ^{13}C NMR (150 MHz, Acetone-d_6) δ 142.65, 142.49, 134.53, 126.94, 117.20, 114.36 [Aromatic C^{5-10}], 41.05, [C^4]; 38.27, [C^3]; 20.93, [C^2];

17.93, [C^{11}]; 13.51, [C^{1}]. HRMS (ESI): Calcd for $C_{18}H_{22}O_4$: 302.15, found: 301.1438 [M-H]$^-$.

2.3. Rancimat test

The antioxidant activities of BMB, HPC and TBHQ were measured according to (Shi *et al.*, 2017). 3 g Lard samples containing varying concentrations (0.01%, 0.02%, and 0.04%) of compounds were subjected to oxidation at temperatures of up to 120 °C and an air flow rate fixed at 20 L/h. The induction period (IP) is the time taken until abrupt acceleration of the oxidative process is reached (Silva *et al.*, 2001). The tests were carried out in duplicate and the protection factors (Pf) through which the structure to antioxidant activities of compounds can be elucidated, were calculated accordingly:

$$Pf = IP_A/IP_O$$

Where, IP_A is the induction period of oil samples with added antioxidants, and IP_O is the induction period of those without antioxidants.

2.4. DPPH$^\bullet$ spectrophotometric method

The free radical scavenging and hydrogen-donating capacity of HPC, BMB and TBHQ were measured according to previous methods with slight modifications (Jiang *et al.*, 2014; Tseng *et al.*, 2008). Exactly 0.5 mL of each antioxidant of varying concentrations in ethanol (1.5 to 48 µM) was mixed with 3 mL (0.1 mM) DPPH solution. The resulting mixture was adequately shaken and its absorbance was read at 517 nm against a blank after being left to react in a dark chamber for 30 min. All the spectrophotometric readings were done with a UV-2450 spectrophotometer (Shimadzu Corp, Kyoto, Japan) and EC_{50}, which is simply the effective concentration needed to obtain a 50% antioxidant activity of a compound (Chen *et al.*, 2013) was extrapolated from the linear regression of plots between antioxidant concentrations and their scavenging activity (%). DPPH radical scavenging activity was calculated accordingly:

$$\text{Scavenging activity (\%)} = [(Abs_{control} - Abs_{sample})/Abs_{control}]\times 100$$

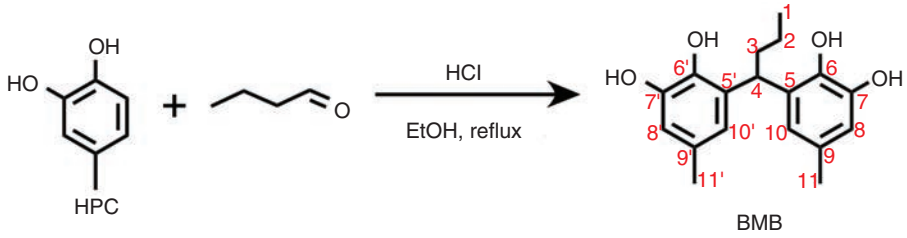
2.5. Deep frying test

The soybean oil used in this experiment was stripped of endogenous pro-oxidants and antioxidants by column chromatography according to the method by Lampi *et al.*, (1999) with minor modifications. Fresh potato slices (30 g) of about 2 mm thickness were fried at 180 °C in 500 g oil samples containing 0.02% (w/w) antioxidants every hour for 8 min. Each sample was tested every 3 h during continuous frying, which lasted for 60 h. The conjugated dienes (CD), acid value (AV) and iodine value (IV) of all the samples were evaluated according to the IUPAC method (Paquot, 1979; Zuta *et al.*, 2007).

3. RESULTS AND DISCUSSION

3.1. Analytical characterization of the compound

BMB was obtained as white flaky crystals from a condensation reaction between 4-methycatechol (HPC) and butyraldehyde catalyzed hydrochloric acid (37%) (Scheme 1). The mole ratio of the three reactants (*i.e.*, HPC: butyraldehyde: hydrochloric acid (37%)) was 1:1:0.96. The Rf values for HPC and BMB were 0.74 and 0.40, respectively (dichloromethane/ methanol, 10:1). BMB had a strong UV absorption at 242 nm and a weak one at 305 nm. After adding the KOH solution to the BMB solution, the two absorptions were strengthened and had red shifts to 250 and 320 nm, respectively. This indicated the presence of phenolic hydroxyl groups on BMB. The ^{1}H NMR spectrum of BMB exhibited two phenolic hydroxyl proton signals at 7.57 and 7.48 ppm, and one aromatic proton signal at 6.61 ppm. A tertiary benzyl proton signal was assigned at 4.02 ppm, three aliphatic proton peaks at 1.76, 1.36 and 0.92 ppm, and two methyl protons attached to two aromatic rings at 2.12 ppm. In the ^{13}C NMR, six aromatic carbon peaks above 100 ppm were observed and 5 aliphatic carbon peaks were observed in the spectrum. In the HRMS (ESI) spectrum a single specie at *m/z* 301.1438 was observed, which was assigned to $[C_{18}H_{21}O_4]^-$, which was obtained by the loss of one H^+ from the catechol hydroxyl functional group. All spectral data confirmed BMB as a tetrahydroxybisphenyl compound bearing two 4-methyl-catechol moieties linked by aliphatic butane as shown in Scheme 1.



SCHEME 1. Synthesis of BMB from condensation reaction between HPC and Butyraldehyde.

3.2. Evaluation of antioxidant activity by the Rancimat test

Pf was used to evaluate the structure-antioxidant activities of the compounds *i.e.*, the oxidative stability capacity of antioxidants in lard samples under different temperatures and concentrations. The Pf values of antioxidants are shown in Figures 1 and 2. According to Wang *et al.*, (2000), a higher Pf value corresponds to a stronger antioxidant activity. That is, Pf < 1 means the compound has pro-oxidant activity; Pf = 1, means no antioxidant activity; 2 > Pf > 1, there is weak antioxidant activity; 3 > Pf > 2, there is a significant antioxidant activity and Pf > 3, means the compound has a strong antioxidant activity. The Pf of the antioxidants between temperatures of 80 to 120 °C at 0.02% (w/w) (Figure 1),

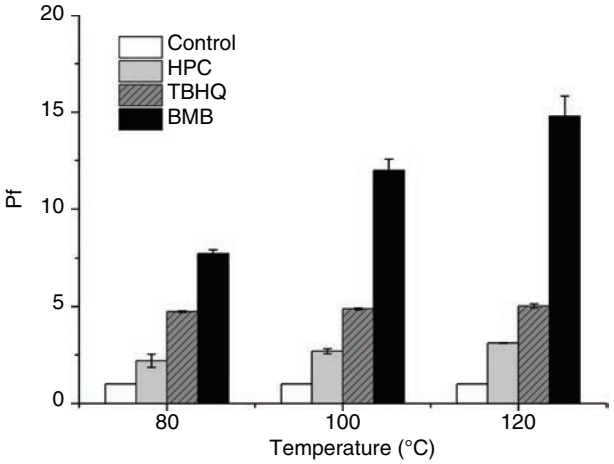


FIGURE 1. Pf changes in lard samples containing 0.02% (w/w) antioxidants at different temperatures. Each value is expressed as Mean ± SD (n=2). Statistical significance at $p \leq 0.05$.

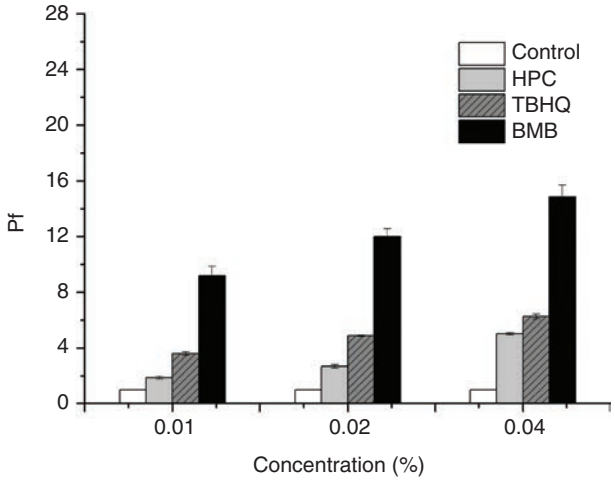
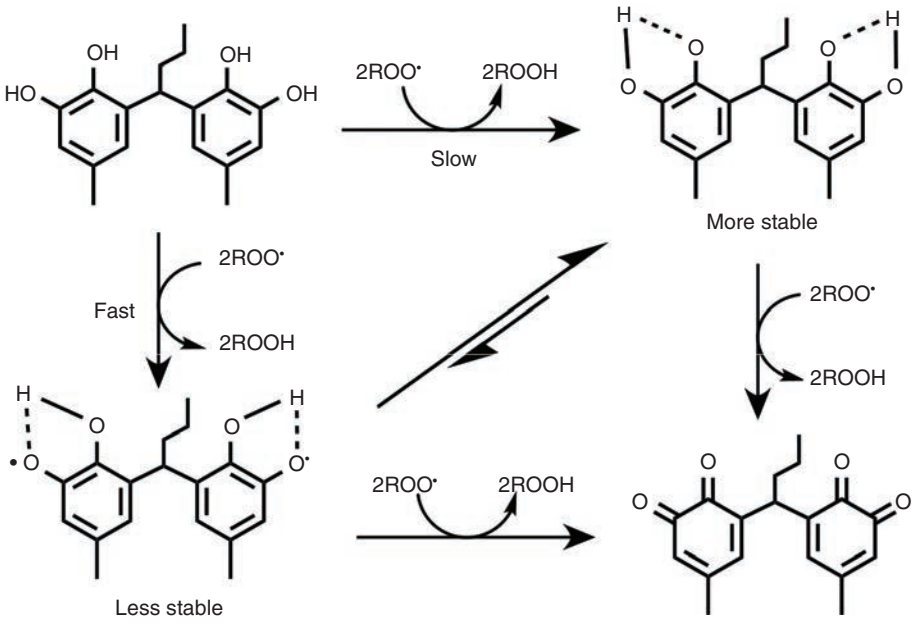


FIGURE 2. Pf changes in lard samples containing different concentrations at 100 °C. Each value is expressed as Mean ± SD (n=2). Statistical significance at $p \leq 0.05$.

decreased as follows: BMB >> TBHQ > HPC> Control. This superior antioxidant activity of BMB compared to TBHQ and HPC with increasing temperature was due its higher molecular weight, which contributed to a less partial volatilization. Similar results based on this phenomenon have been presented by Huang *et al.*, (2014); Jiang *et al.*, (2014) and Shi *et al.*, (2017). In addition, the presence of electron donating substituents, such as methyl and bulky butyl substituents on the 2, 4 and 6-positions can increase the antioxidant activity of phenolic compounds (Kajiyama and Ohkatsu, 2001; Weng and Huang, 2014; Zhang *et al.*, 2004). As a result, the aliphatic butyl substituent linked to the *ortho*-positions of the two hydroxyphenyl moieties (Scheme 2) provided a strong steric hindrance and increased electron density to the neighboring hydroxyl groups thereby allowing them to supply more hydrogen atoms, though slowly, to active radicals. These combined effects promoted the stabilization of the BMB phenoxyl radicals, thereby increasing the oxidative stability of the oil sample at a higher temperature. Also, all three compounds showed an excellent positive correlation between Pf and concentration at 100 °C (Figure 2) *i.e.*, their Pfs increased with increasing concentrations. The obvious stronger antioxidant activity of BMB (0.01%, Pf = 9.19; 0.04%, Pf = 14.85) than TBHQ (0.01%, Pf = 3.60; 0.04%, Pf = 6.26) $P \leq 0.05$, can be attributed to the greater steric synergy exhibited in the form of hydrogen bonding between the two hydroxyl groups on its double catechol moieties (Gordon, 1990), which caused the less stable free radical of BMB to easily convert to a more stable form intramolecularly (Huang *et al.*, 2014). However, the relatively low antioxidant activity of HPC compared to BMB or TBHQ was due to the absence of steric synergy within its molecule.

3.3. Evaluation of antioxidant activity by DPPH$^{\bullet}$ assay

This method is commonly used to evaluate the antioxidant activity of antioxidants because it is sensitive, rapid and easily reproducible. Its main parameter is the $EC_{50,}$ which is measured in terms of the free radical scavenging and hydrogen-donating capacity of an antioxidant and can simply be defined as the effective concentration required to give 50% antioxidant activity of a compound (Chen *et al.*, 2013). The DPPH scavenging activities of HPC, BMB and TBHQ radicals (Figure 3) increased rapidly between 1.5 and 24 µM. At 24 µM, their scavenging abilities were 80.7, 58.3, and 57.2%, respectively. The EC_{50} values of HPC, BMB, TBHQ were 18.38, 24.39 and 25.16 µM, respectively *i.e.*, their radical scavenging abilities decreased as follows: HPC > BMB ≥ TBHQ. This finding is fairly consistent with the study reported



SCHEME 2. Illustration of steric hindrance effect on the synergism among hydroxyl groups of BMB.

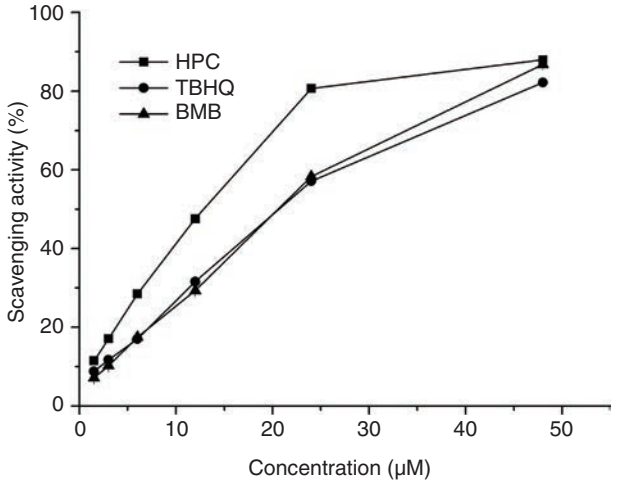


FIGURE 3. DPPH radical scavenging activity of different antioxidants. Each value is expressed as Mean ± SD (n=2). Statistical significance at $p \leq 0.05$.

by Li *et al*., (2006) in which the novel diphenolic antioxidant studied had twice the scavenging capacity (EC_{50} value) of its monomer, TBHQ. And the reason for this was because the aliphatic butyl group stabilized the resonance configuration of the BMB phenoxyl radicals to capture more DPPH$^{\bullet}$ by donating electrons (Danilewicz, 2003), despite its steric hindrance effects concurrently inhibiting the ease of DPPH binding. Also, the combined hydrogen donating capacities of the two catechol moieties doubled the DPPH scavenging ability of BMB, making it stronger than TBHQ. On the other hand, BMB had a weaker scavenging ability compared to its monomer, HPC. This finding is, however, different from those of the Rancimat and deep frying experiments largely due to the bulkiness of the DPPH radical as it can easily bind with phenoxyl radicals with less steric hindrance like HPC (Huang *et al*., 2014). But it is in agreement with similar studies involving the rational design of antioxidants with strong steric hindrance, steric synergy and higher molecular weight (Jiang *et al*., 2014; Weng and Huang, 2014 and Shi *et al*., 2017). Lastly, with the same mass percentage concentration, HPC had a higher phenolic hydroxyl group ratio than BMB (Li *et al*., 2006).

3.4. Evaluation of antioxidant activity in deep frying oil

Deep frying is a common process where food is completely immersed in hot oil to produce crispy food with better palatability. In this study, the continuous over-heating of soybean oil induced the oxidation, degradation and polymerization of compounds like polyunsaturated fatty acids (PUFA) to become conjugated. Among these resulting compounds are conjugated dienes, which can be measured at a UV wavelength of 233 nm and expressed as a percentage. The CD values of the oil samples during frying are presented in Figure 4a. The increase in CD was proportional to the frying time and reached final values of 88.8, 84.7, 72.5 and 35.0% for the control, HPC, TBHQ, and BMB groups, respectively ($p < 0.05$). This means that conjugated dienes were continuously formed during the frying process, which is line with the observation

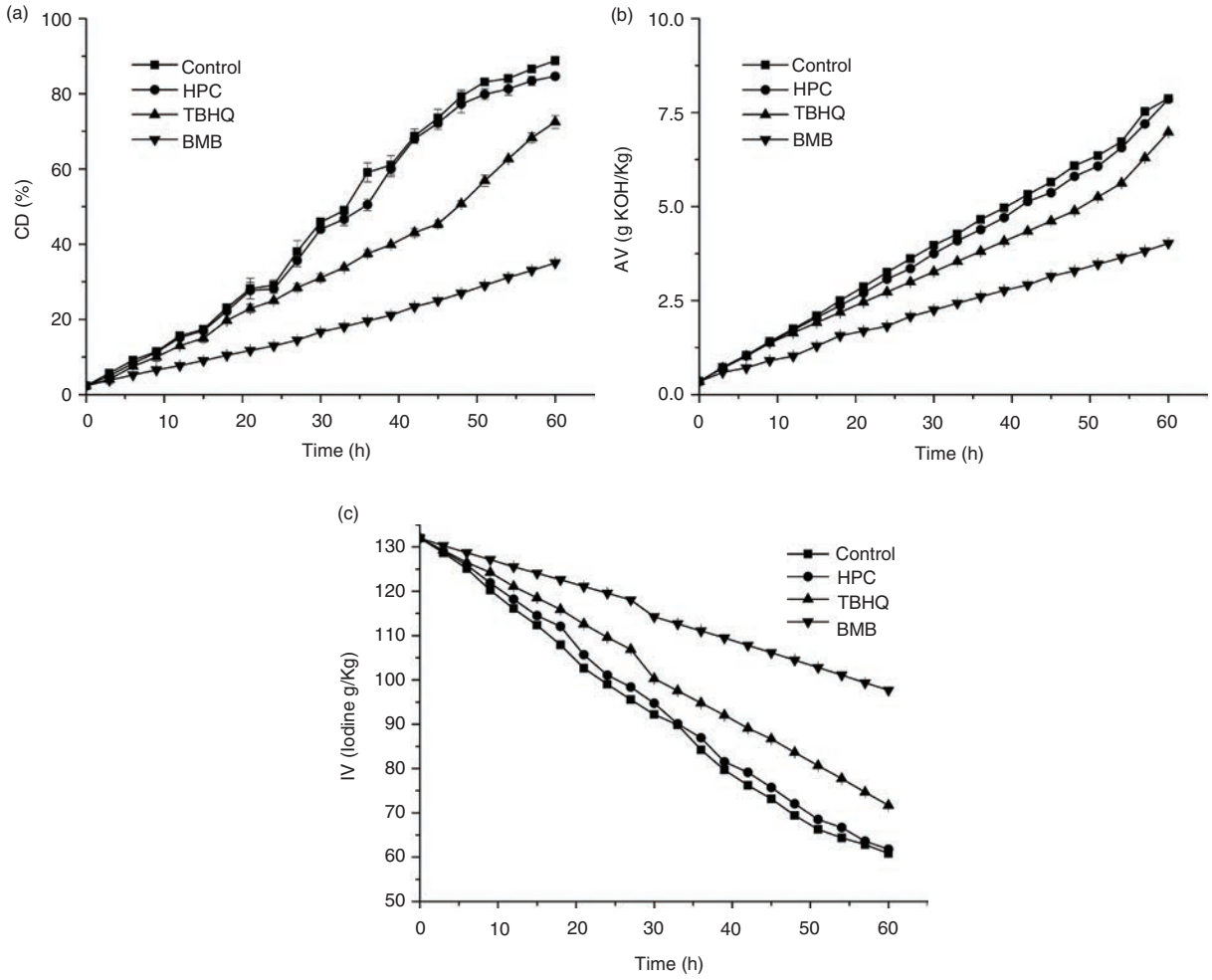


FIGURE 4. Changes in percentage conjugated diene (CD), acid (AV) and iodine (IV) values in oil samples during deep frying at 180 °C. Values are expressed as Mean±SD (n=2). Statistical significance at $p \leq 0.05$.

made by Marinova *et al.*, (2012). Thus, the percentage changes in conjugated dienes (Figure 4a) indicates that the antioxidant stability and activities in oil samples during frying decreased as follows: BMB > TBHQ > HPC ≥ Control.

Acid value (AV) and Iodine value (IV) are another useful quality control parameter used to determine the effectiveness of antioxidants by measuring the amount of free fatty acids (FFA) and double bonds destroyed in the oil samples. During the frying process, the AV of BMB-added oil sample increased slowly to about 4.0 g KOH/kg at the end of the experiment compared to TBHQ, HPC and the control groups, which increased to 7.0, 7.8 and 7.9 g KOH/kg of oil, respectively (Figure 4b). This indicated that BMB was able to suppress lipid oxidation leading to lower production of free fatty acids (FFA). That is, lower acid value is an attribute of good quality oil. The steady increase in the formation of FFA was partly due to the hydrolysis of triglycerides and other carboxylic groups, which then accelerated the decomposition of hydroperoxides during frying (Frega *et al.*, 1999).

Furthermore, the antioxidant activity of the BMB was obvious from the markedly higher IV of the soybean oil fortified with it, compared to the control sample (Figure 4c). When frying ended, the IV for the control (60.9 g Iodine/Kg oil) was *ca.* 2 times lower than the BMB-added oil sample (97.7 g Iodine/Kg oil) from the starting Iodine value of 132.0 g Iodine/Kg oil. Consequently, when oil samples undergo heating at 180 °C, some PUFAs became isomerized and conjugated causing an increase in the amount of conjugated dienes and a subsequent decrease in the iodine number due to the destruction of double bonds and conjugated dienes (Shi *et al.*, 2017). Thus, the AV and IV changes during frying decreased as follows: BMB > TBHQ > HPC ≥ Control (Figures 4a and 4b). This finding is in agreement with the study reported by Li *et al.*, (2006), and the main reasons for the excellent antioxidant effectiveness

of BMB was due to the steric hindrance influence of its aliphatic butyl group which stabilized the radical resonance of the BMB phenoxyl structure to capture more peroxyl radicals (Scheme 2), and also contributed to an increase in the relative molecular mass of the compound, enhancing less volatilization than TBHQ.

In conclusion, BMB demonstrated a much stronger antioxidant activity in deep frying and Rancimat analyses than TBHQ due to its higher molecular weight. The steric hindrance of its aliphatic butyl and steric synergy exhibited by the hydroxyls on its double catechol moieties also played an active role. Under DPPH conditions, its radical scavenging ability was good –a great improvement over previously studied methylcatechol derivatives-. Therefore, BMB may be used as a commercial synthetic antioxidant alternative in oil and fatty foods after the proper characterization of its safe consumption, which will be further studied.

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