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Food Chemistry 84 (2004) 219–222

Food Chemistry

www.elsevier.com/locate/foodchem

Two novel synthetic antioxidants for deep frying oils

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Received 6 November 2002; received in revised form 6 January 2003; accepted 6 January 2003

Abstract

Lauryl *tert*-butylated hydroquinone (LTBHQ) and its oxidized compound, lauryl *tert*-butylated quinone (LTBQ) were synthesized from *tert*-butylated hydroquinone (TBHQ) and lauryl alcohol. Their antioxidant activities were investigated. At temperatures higher than 140 °C, the antioxidant activity of LTBHQ and LTBQ was higher than TBHQ. In emulsions, these two compounds had stronger antioxidant activity than TBHQ, butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA).

Keywords: Antioxidant activity; *tert*-Butylated hydroquinone; Lauryl *tert*-butylated hydroquinone; Lauryl *tert*-butylated quinone; Deep frying

1. Introduction

Butylated hydroxytoluene (BHT), butylated hydroxyanisol (BHA), *tert*-butylated hydroquinone (TBHQ) and propyl gallate are the most widely used antioxidants in the food industry, especially for oils and fatty foods. These synthetic antioxidants are highly active and cheap. They are colourless, odourless and tasteless, but they are generally active only at low temperature. However, at high temperature, such as in deep frying and baking at 150–200 °C, these compounds are ineffective. At high temperatures, BHA, BHT and TBHQ are evaporated with steam and PG decomposes particularly when a large quantity of water is expelled from foods during frying or baking. (Lee & Kim, 1979; Kim & Pratt, 1990; Warner, Daniels, Lin, Joe, & Fazio, 1986).

The frying oils are easily autoxidized at high temperatures and partly polymerized and partly decomposed on oxidizing at high temperature if adequate antioxidants are not present. The oils become viscous and darkened; nutritional components, such as V_E, V_A, V_K, V_D and essential fatty acids in the frying oils, are destroyed quickly (Weng, 1993). Moreover, foods fried in oxidized oil can develop an unpleasant flavour. The shelf lives of fried foods are short and might develop off-flavours if sufficient amounts of antioxidant do not remain in the foods after frying (Yagi, 1988).

Effective antioxidants, for deep frying of oils, are very important in practice. In this paper, two antioxidants, synthesized from TBHQ and *n*-lauryl alcohol for deep frying oils are reported and their antioxidant activity is investigated.

2. Materials and methods

2.1. Materials

Lard was rendered in the laboratory and stored in a deep freezer for use. Soy oil was purchased from Shanghai Oil and Fat Co. (Shanghai, China). TBHQ, BHA, BHT and Tween 20 were purchased from Shanghai Chemical Reagent Co. (Shanghai, China). Other chemicals used in this experiment were all AR grade and from this company. Silica gel was from Qingdao Chemical Factory (Qingdao, China).

2.2. Synthesis and purification of the compounds

A mixture of TBHQ (5 g, 30 mmol) and *n*-lauryl alcohol (5.6 g) was added to 85% phosphoric acid (1.7 g). The reaction mixture was heated on a hot plate with a magnetic stirrer and refluxed in 6 ml toluene for 6.5 h.

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doi:10.1016/S0308-8146(03)00205-X

The products were washed with hot water and isolated by a column (500×40 mm) containing 300 g silica gel. The elution solvent was chloroform in petroleum ether, 0:100 (400 ml), 1:99 (200 ml), 2:98 (150 ml), 5:95 (250 ml), 10:90 (400 ml), 20:80 (400 ml), 30:70 (400 ml).

Thin-layer chromatographic (TLC) plates were prepared by coating 0.5 mm silica gel (F254) onto 200×200 mm glass plates. The plates were activated at 110 °C. Benzene-acetic acid (99:1) was used as TLC developing solvent.

2.3. Spectra recording

Mass spectra were recorded with an HP5989 mass 20 spectroscopic instrument. Ultraviolet (UV) spectra were recorded with a UV-260 spectroscopic instrument. Methanol was used as solvent and a quartz cell was used as vessel. Infrared spectra were recorded using a JASCO IR-8l0 instrument. Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker AM-400. Deuterium methanol (CD_3OD) was used as the solvent for LTBHQ, and deuterium chloroform was used as the solvent for LTBQ. All chemical shifts were compared to the internal standard (TMS). Melting points of LTBHQ and LTBQ were recorded.

2.4. Antioxidant activity

An oxidative stability instrument (OSI, made by Omnion 30 Inc., USA) was used to determine the OSI values of the oil samples. The air flow rate was controlled at 20 l/h, the temperature was controlled according to the experiment needed.

Five hundred grammes of oil samples containing different antioxidants (0.02%) were each placed in a frying pan. The oils were subjected to heating 9 h at 190±5 °C and then cooling at room temperature for 15 h, seven times. A fresh potato slice was added to the oil every 10 min, then removed from the oil repeatedly. About 20 grammes of fresh potato slices were used every 3 h. The oil samples were taken from the pan for determination of data every 3 h.

Twenty grammes of purified soy oil, 2 g Tween 20 and 180 g water were placed in 500 ml conical flasks, and shaken rigorously for 6 min. The emulsions of oil in water were prepared and different antioxidants (1500 μM) were each added to the samples. The samples were stored in an oven at 60±2 °C. Their peroxide values were determined once every day.

Samples (50 g) were stored in an oven at 60±2 °C and peroxide values determined daily.

Peroxide value (PV), iodine values (IV), acid values (AV) and conjugated dienes were determined according to IUPAC methods (Paquot, 1979a, b).

All the data, in this paper are the average values of duplicates.

3. Results and discussion

Lauryl *tert*-butylate hydroquinone (LTBHQ) and lauryl *tert*-butylated quinone (LTBQ) were synthesized from *n*-lauryl alcohol and TBHQ. Phosphoric acid (0.5 mol/mol TBHQ) was used as catalyst. The mixture of TBHQ and lauryl alcohol (1:1, mol/mol) were refluxed in toluene (200 ml/mol TBHQ) for 6.5 h. The yields were 16.0±0.8% for LTBHQ and 6.1±0.9% for LTBQ.

The lauryl group can attach at the 5- or 6-position of TBHQ, but the 5-isomer may be slightly more than the 6-isomer, because the 5-position is the *p*-position of the *tert*-butyl group. So both LTBHQ and LTBQ are mixtures of isomers.

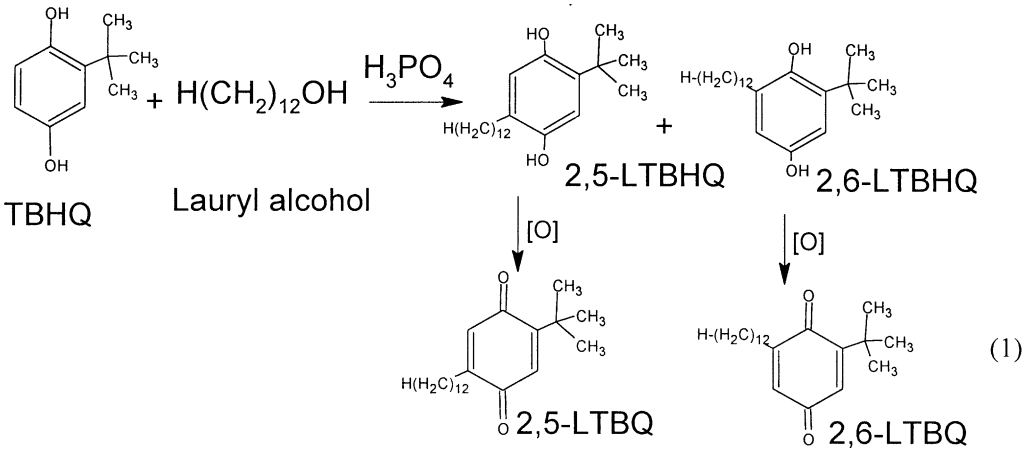
Rf values of LTBHQ, LTBQ and TBHQ were 0.65, 0.82 and 0.26, respectively. The melting point of LTBHQ was 135–138 °C. LTBHQ had a strong absorption at 247 nm and a weak absorption at 309 nm in the UV spectra. When potassium hydroxide was added to the LTBHQ solution, the absorption was strengthened and had a red shift to 292.6 nm and the weak peak disappeared at 309 mm. This confirmed that LTHQ was a phenolic compound. There was a sharp and strong absorption at 3410 cm^{-1} in the IR spectra, which further confirmed that LTBHQ was a phenolic compound (Scheme 1).

There were finger print peaks at 1626.5, 1427.8, 1222.2, 1117.8, 1020.6, 874.2, 701.7 cm^{-1} in the IR spectra. There were peaks at δ 1.17 (34H, alky hydrogen), δ 16.64, (2H aroma, hydrogen) in the NMR spectra. In the mass spectrum of LTBHQ, there was a molecular ion peak at *m*/*z* 334 (1.7), and there were fragment peaks at *m*/*z* 278 (4.3), *m*/*z* 110 (16.5), *m*/*z* 222 (33.6), *m*/*z* 207 (100), *m*/*z* 192 (3.0), *m*/*z* 82 (3.4). All spectra data confirm that the structure of the LTBHQ is as shown in Scheme 1.

LTBQ had light yellowish colour. Its UV spectrum only showed a strong peak at 254.8 nm. It did not show red shift when potassium hydroxide was added. This meant that there were no phenolic hydroxyl groups on the LTBQ ring.

There was a very strong peak at 1648.3 cm^{-1}, which indicated a carbonyl group, and other peaks at 3063.4, 1596.7, 1457.8, 125.3, 1017.9, 945.6, 632.7 cm^{-1} in the IR spectra. There were peaks at δ 1.22 (alkyl group, 33H), δ 1.56 (1 H, CH linked at the quinone ring), δ 6.46 (2H, on quinone ring) in the NMR spectra. The mass spectra showed the molecular ion peak at *m*/*z* 332 (4.5), and fragment ion peaks at *m*/*z* 248 (0.8), *m*/*z* 220 (74.2), *m*/*z* 163 (75.5), m/z 135 (35.6), *m*/*z* 205 (100), *m*/*z* 165 (6.1), *m*/*z* 107 (18.3), *m*/*z* 78 (6.5). All the spectra data confirmed LTBQ structure in Scheme 1.

TBHQ is one of the most powerful antioxidants among the synthetic food antioxidants at room temperature. The antioxidant activities of LTBHQ and



Scheme 1.

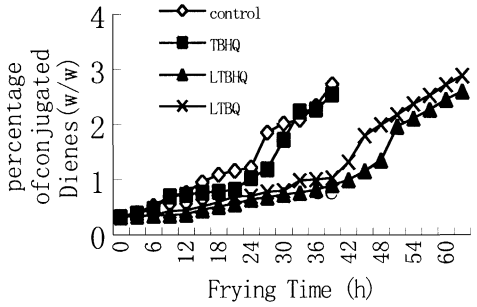


Fig. 1. The changes of the percentage of conjugated linoleic acid in oils at 233 nm of the samples containing 0.02% (w/w) different antioxidants at 190±5 °C during frying over time. Note: Soy oil is refined oil without further purification. The soy oil was further purified for use as the substrate of control and other samples.

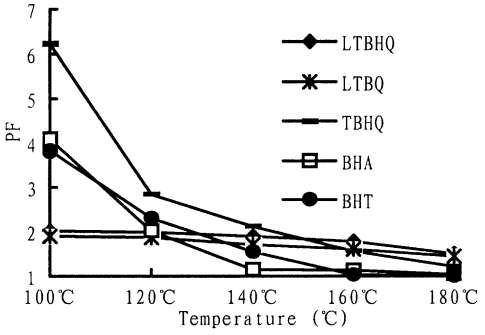


Fig. 2. PF changes of lard samples containing 0.02% (w/w) of antioxidants at different temperatures, on OSI instrument.

LTBQ were higher than TBHQ at 0.02% (w/w) during frying at 190 °C (Fig. 1). LTBHQ and LTBQ were strong antioxidants at 0.02%, the IPs of the samples were extended from 24 h to 48 and 42 h for LTBHQ and LTBQ, respectively, at 190 °C during frying potato chips (Fig. 1).

According to accelerated test measurements with the OSI, the antioxidant powers of 0.02% (w/w) TBHQ, BHT and BHA decrease quickly with increase of temperature, but those of LTBHQ and LHBQ almost do not. Here, oxidation protection factors (PF) are the values of the induction periods (IP) of the samples with antioxidants divided by the induction period of lard (Control):

$$PF = IP_{(Control+Antioxidants)/IP\ Control}$$

According to accelerated test measurements with the OSI, LTBHQ and LTBQ are good antioxidants at high temperature but not at temperatures below 140 °C. At 180 °C, TBHQ, BHA and BHT only show very weak antioxidant activities. The decreasing speed of antioxidant power rises with increasing temperature as follows:

TBHQ > BHA > BHT > LTBHQ ~ LTBQ (Fig. 2)

When autoxidized, some polyunsaturated fatty acids became conjugated, and some double bonds were destroyed; iodine values decreased.

IV changes at 190 °C increased as follows:

TBHQ > BHA > BHT > LTBQ ~ LTBHQ (Fig. 3)

TBHQ had a stronger antioxidant activity than either LTBHQ or LTBQ when 1500 μM (different) antioxidants were added to oil samples separately and put in an oven at 60 °C. The oxidation stability decreases as follows:

TBHQ >> LTBQ ~ LTBHQ >> BHA > BHT > Control (Fig. 4)

When 1500 μM (different) compounds were added the emulsion samples (based on oil), all the compounds showed more obvious antioxidant effects at 60 °C. The antioxidant activity of the compounds decreased as follows:

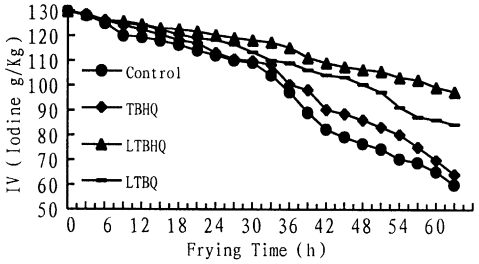


Fig. 3. Iodine value changes of the samples containing 0.02% (w/w) of different antioxidants at 190±5 °C.

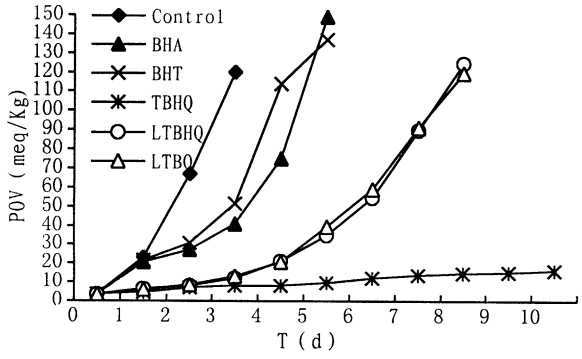


Fig. 4. POV changes of the samples containing 1500 μM (different) antioxidants at 60±2 °C over time.

LTBQ ~ LTBHQ > BHA ~ BHT > TBHQ > Control (Fig. 5)

This shows that the orders of activity of the antioxidants between oils and emulsions are different. These differences in antioxidant action can be explained by the same interfacial phenomenon as observed with α-tocopherol and Trolox (Frankel, Huang, Kanner, & German, 1994). LTBHQ and LTBQ have long fatty alkyl groups and their polarity is very weak; they partition into the oil phase in the emulsion, so they can effectively act as antioxidants. TBHQ partitions into the water phase in the emulsion, so TBHQ shows weak antioxidant activity in the emulsions.

In conclusion, LTBHQ and LTBQ are good antioxidants for deep frying of oils and emulsions, but are not good for bulk oils at temperatures below 140 °C.

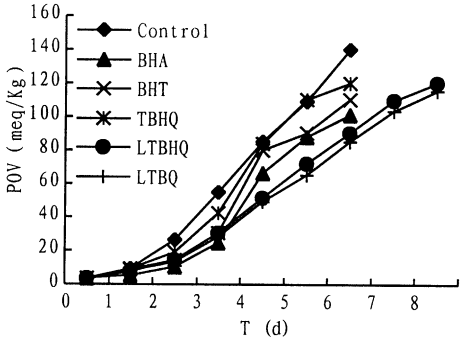


Fig. 5. POV changes of the emulsion samples containing 1500 μM (different) antioxidants at 60±2 °C over time.

Acknowledgements

The authors thank the Natural Science Foundation Commission of China for the research grant (approval number: 20242007).

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