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Oxidation of synthetic phenolic antioxidants during water chlorination

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ABSTRACT

The degradation of seven phenolic antioxidants and metabolites during chlorination was investigated. Under strong chlorination conditions (10 mg L^{-1} chlorine, 24 h), five of the target compounds were significantly degraded, while only BHT-Q (2,6-di-*tert*-butylcyclohexa-2,5-diene-1,4-dione) and BHT-CHO (3,5-di-*tert*-butyl-4-hydroxybenzaldehyde) were stable. The effect of the presence of bromide to the sample was only significant for BHA (butylated hydroxyanisole) resulting in increased disappearance rate as it is increased. Moreover, the disappearance kinetics were investigated at different concentrations of chlorine and pH of sample using a factorial experimental design. It was observed that the pH of the sample was a significant factor for BHT (butylated hydroxytoluene) and BHA, and chlorine concentration was significant for BHT, resulting in increased disappearance kinetics as they are increased. The degradation of these compounds has revealed two main processes: hydroxylation and oxidation of the aromatic system. The hydroxylated derivatives in some cases (e.g. from BHT-OH (2,6-di-*tert*-butyl-4-(hydroxymethyl)phenol) and BHT-COOH (3,5-di-*tert*-butyl-4-hydroxybenzoic acid)) are formed via the chlorinated and/or brominated intermediate. Moreover, the oxidation of the aromatic system leads to the quinone derivatives. The investigation of these by-products in real samples by solid-phase extraction–gas chromatography–mass spectrometry (SPE–GC–MS) showed that derivatives of BHT, BHT-OH and/or BHT-COOH occurred in wastewater and drinking water samples analysed.

1. Introduction

Antioxidants are substances which prolong the shell-life of foodstuffs by protecting them against deterioration caused by oxidation, such as fat rancidity and colour changes. However, the use of antioxidants is not restricted to foodstuffs. They are permitted in many types of packaging materials, in adhesives that come in contact with food and also in cosmetics, personal care products and pharmaceuticals. The most frequent synthetic antioxidants used are the phenolic antioxidants: butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA) and *tert*-butylhydroquinone (TBHQ).

The results of scientific studies about the effects of consumption of these additives to human health are controversial, since several studies have shown a potential link between BHA, BHT and cancer [1,2], while other studies have shown no link [3,4], and even a protective effect [5].

These compounds have been detected in river, ground and wastewater samples. Levels of these compounds were typically in the 10–2000 ng L^{-1} range, depending on the sample nature [6]. In spite of these findings, there is few data on ecotoxicological risks. Moreover, their degradation products should also be evaluated since they may pose an environmental or human health risk [7].

Studies on the metabolism of BHT have revealed that there are two main metabolic processes [8]; that is, oxidation of the alkyl substituent and oxidation of the aromatic ring system. 3,5-Di-*tert*-butyl-4-hydroxybenzoic acid (BHT-COOH) is a major metabolite formed by oxidation of the alkyl substituent and may be generated via the corresponding alcohol (BHT-OH) and aldehyde (BHT-CHO). Moreover, oxidation of the π-system of BHT leads, among others, to 2,6-di-*tert*-butylcyclohexa-2,5-diene-1,4-dione (BHT-Q). BHT-OH and BHT-CHO have also been identified as BHT photoproducts, among other 9 compounds [9]. The photodegradation mechanisms of BHT proposed were loss of alkylic groups, loss or addition of hydroxyl groups, isomerisation and oxidation processes [9]. Moreover, the oxidation with permanganate of BHT showed the formation of a diversity of both dimeric and monomeric products depending on the oxidation conditions employed [10].

On the other hand, the metabolism of BHA leads to TBHQ formation. As for BHT, the oxidation of BHA afforded both dimeric and monomeric products [11]. The main monomeric product was 2-*tert*-butyl-6-hydroxy-p-benzoquinone (OH-TBQ) which is produced by oxidation of the intermediate 5-*tert*-butylresorcinol.

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The aim of this work was to study the chlorination of phenolic antioxidants and some metabolites, bearing in mind that, according to the European Federation of Chlor-alkali Producers, 98% of the drinking water treatment plants (DWTPs) in Europe use chlorination as one of the main disinfection steps in drinking water production [12] and is sometimes used for tertiary treatment of wastewater. Moreover, residual chlorine in tap water can already react with organic pollutants producing unwanted by-products [13,14]. Thus, the reaction kinetics of phenolic antioxidants were investigated in detail at different chlorine dose and pH by means of a experimental design methodology, and the effect of bromide presence was also considered. Also, several transformation products were tentatively identified by gas chromatography–mass spectrometry (GC–MS) and measured at different environmental samples. To our knowledge, there was not published data on chlorination batch tests of the evaluated analytes.

2. Materials and methods

2.1. Chemicals and stock solutions

The structures of the studied antioxidants are presented in Fig. 1. BHT (2,6-di-*tert*-butyl-4-methyl-phenol), BHA (2-*tert*-butyl-4-methoxy-phenol), BHT-COOH (3,5-di-*tert*-butyl-4-hydroxybenzoic acid), BHT-Q (2,6-di-*tert*-butylcyclohexa-2,5-diene-1,4-dione), BHT-OH (2,6-di-*tert*-butyl-4-(hydroxymethyl)phenol) and TBHQ (2-*tert*-butylbenzene-1,4-diol) were obtained from Sigma–Aldrich (Steinheim, Germany) and BHT-CHO (3,5-di-*tert*-butyl-4-hydroxybenzaldehyde) from TCI Europe (Zwijndrecht, Belgium). Deuterated BHT (2,6-di-(*tert*-butyl-d_1)-4-methyl-d_3-phenol-3,5-d_2; BHT-d_7) and *n*-propyl paraben (*n*-propyl 4-hydroxybenzoate-2,3,5,6-d_4; PrP-d_4), used as surrogate internal standards (ISs) were obtained from CDN Isotopes (Quebec, Canada).

Acetone, methanol and ethyl acetate (all of chromatographic analysis grade) were purchased from Merck (Darmstadt, Germany). Hydrochloric acid was purchased from Panreac (Castellar del Vallès, Spain). Pure water was obtained from a Milli-Q system (Millipore, Billerica, MA, USA). Potassium bromide was from Merck and ascorbic acid, potassium dihydrogen phosphate, dipotassium hydrogen phosphate and sodium hypochlorite solution (~10%) from Sigma–Aldrich. Sodium hypochlorite stock solutions at the desired level were prepared daily by dilution in Milli-Q water and their concentration was determined using the N,N-diethyl-p-phenylenediamine procedure with photometric detection [15].

Individual stock solutions were prepared in acetone at the 2 mg mL^{-1} level. Mix standard solutions were prepared at the 20 μg mL^{-1} in acetone and subsequently diluted as necessary. Calibration standards were prepared in ethyl acetate.

2.2. Chlorination experiments

Chlorination of antioxidants was performed on 16 mL amber closed vials that were maintained at room temperature (20 ± 2 °C). Parallel control samples (without chlorine) were also measured.

Preliminary experiments to determine the stability of antioxidants were done (two replicates) with 10 mL of Milli-Q water, adjusted to pH 7.1 with a phosphate buffer and spiked with the tested compounds at the 1 μg mL^{-1} level and 10 mg L^{-1} Cl_2. Seven aliquots of 1 mL each were taken at different reaction times and the reaction stopped with ascorbic acid (0.6 mg mL^{-1}). The analytes were extracted by liquid–liquid extraction in 0.5 mL of ethyl acetate. Moreover, the effect of the presence of a high concentration of bromide (100 μg L^{-1}) on the degradation was evaluated. These experiments were also used for identification of chlorination by-products.

Further experiments to study chlorination kinetics were performed in a similar way, but with lower antioxidants concentrations (50 μg L^{-1}) and different concentrations of chlorine (1–10 mg L^{-1}) and pH of sample (5.7–8.3) being considered. In these experiments, five aliquots were taken at different reaction times and the reaction stopped with ascorbic acid.

2.3. GC–MS determination

GC–MS determination was performed on a Varian 450-GC gas chromatograph equipped with an ion trap mass selective detector

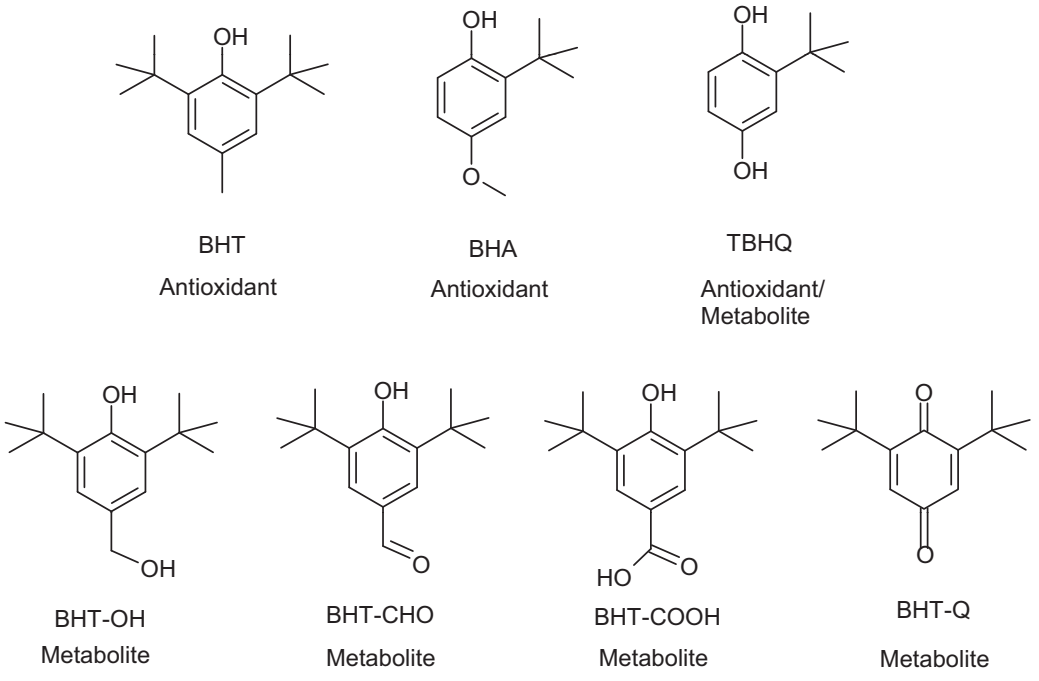

Fig. 1. Structures of the studied antioxidants and metabolites.