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Full Paper

Degradation of bisphenol A by ozonation: rate constants, influence of inorganic anions, and by-products

Kheng Soo Tay^{*}, Noorsaadah Abd. Rahman and Mhd. Radzi Bin Abas

Environmental Research Group, Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

* Corresponding author, e-mail: khengsoo@um.edu.my

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Abstract: The second-order rate constants for the reaction between bisphenol A (BPA) and ozone were evaluated over the pH range of 2-12. The rate constants showed minimum values ($\times 10^4$ M⁻¹s⁻¹) under acidic condition (pH < 4) and were of maximum values ($\times 10^9$ M⁻¹s⁻¹) under basic condition (pH >10). From pH 4 to 7, the second-order rate constants were found to increase by a magnitude of almost 10^2 and this was due to the increase in anionic BPA species in the solution. The rate constants increased almost twofold when pH increased from 9.6 to 10.2. The presence of common inorganic anions at levels commonly found in the environment did not affect the rate of degradation of BPA.

The degradation by-products from the ozonation of BPA were identified as 4-(prop-1-en-2yl)phenol, hydroquinone, 4-hydroxyacetophenone, 2-(2-(4-hydroxyphenyl)propan-2-yl)succinaldehyde, 2-(1-(4-hydroxyphenyl)vinyl)pent-2-enal, 3-formyl-4-(4-hydroxyphenyl)-4-methylpent-2enoic acid, monohydroxy-BPA and dihydroxy-BPA. In conclusion, ozonation was found to be an effective method for the removal of BPA even in the presence of common inorganic anions at environmental concentrations. However, incomplete treatment of BPA might produce a variety of degradation by-products.

Keywords: bisphenol A, ozonation, rate constant, anions, competitive kinetics, OH radical

INTRODUCTION

Bisphenol-A (BPA; 2,2-bis(4-hydroxylphenyl)propane) is a commonly used chemical in the synthesis of polymers, especially for food and beverage packages. BPA has been reported to have developmental toxicity, carcinogenicity, possible neurotoxicity [1] and estrogenic effects [2]. This

chemical can leach from plastic products under normal and high temperatures [2-3]. Thus, the leaching of BPA into the environment from disposed plastic materials is expected. So far, legislation on the use of BPA and its discharge into the environment is sorely lacking. Consequently, the occurrences of BPA in the environment have been widely reported [e.g. 4-6]. The presence of BPA in coastal waters and supermarket seafood from Singapore and mussels from South and South-east Asia [7-8] indicates that BPA pollution is severe not only in developed countries but also in the Asian region.

Since BPA has the potential to cause undesirable ecological and human health effects, various treatment technologies have been developed for its removal from water. The oxidative degradation methods for BPA such as ozonation [9-14], photo-Fenton reaction [15], photocatalytic reaction by TiO_2 [16] and ultrasound-UV-iron(II) treatment [17] have been reported. Among the treatment methods, ozonation has been projected to be one of the fastest growing water disinfection technologies in the market [18-19]. It has been shown to be effective in the removal of organic pollutants from water and wastewater [20-24]. During ozonation, organic pollutants undergo a series of oxidation processes by ozone (O₃) and hydroxyl radical (•OH) formed by the decomposition of O₃ in water [25]. In some cases, toxic by-products may be generated [22]. Therefore, evaluation and determination of degradation by-products from the ozonation of organic pollutants is an important consideration.

Although the ozonation of BPA has been widely reported, based on our literature review the influence of inorganic anions on the removal of BPA by ozonation has not been evaluated. The influence of inorganic anions is important since chloride and phosphate ions, for example, can react with O₃ and •OH, thus affecting the rate of removal of the organic pollutants in water [26-27]. The increase in salt concentration has also been reported to affect O₃ solubility in water [28]. The main objective of this study, therefore, is to evaluate the effect of inorganic anions, namely phosphate, nitrate, sulphate and chloride ions. In addition, the second-order rate constants for the reaction between BPA and O₃ at pH 2-12 were determined. The variation in the rate constant at different pH values, especially within the two pK_a values (9.6 and 10.2) of BPA, was studied in detail in order to compare the reactivity of anionic and dianionic species of BPA in aqueous solution towards O₃. The degradation by-products (DBPs) of BPA were also identified. Some DBPs of BPA have already been determined by previous studies [11,13]. However, in this study, we managed to identify a few additional compounds and degradation pathways of BPA during ozonation were proposed.

MATERIALS AND METHODS

Chemicals

BPA (>99% purity) was obtained from Aldrich and used without further purification. Its stock solution (200 mg/L) was prepared by dissolving in boiling ultrapure deionised water (Elcagan, UK). All chemicals were used without further purification. Sodium phosphate (96%) and sodium dihydrogen phosphate (99%) was obtained from Aldrich. Sodium chloride (\geq 99.5%), sodium nitrate (99%) sodium sulphate decahydrate (>99%), sodium phosphate monobasic (99%) and *tert*-butyl alcohol (*t*-BuOH) (99.5%) were purchased from Sigma. Sodium phosphate dibasic (99%) and disodium hydrogen phosphate (99%) were purchased from Riedel-de-Haën. A mixture of BSTFA

(*N*,*O*-bis(trimethylsilyl)trifluoroacetamide) and TMCS (trimethylchlorosilane) in a ratio of 99:1 was obtained from Supelco. All solvents (HPLC grade) and phosphoric acid (85%) were obtained from Merck. Sodium hydroxide (>98%) was purchased from Fluka. Purified oxygen (99.8%) was obtained from MOX-linde (Malaysia). Phosphate buffer (0.5 mol/L) was prepared using sodium dihydrogen phosphate and/or disodium hydrogen phosphate and the pH was adjusted using either phosphoric acid or sodium hydroxide solutions. O_3 was produced from purified oxygen by an ozone generator (model OZX03K, Enaly Trade Co. Ltd., Canada). All tubing from the ozone generator was of ozone-inert silicone material.

Ozonation of BPA

Determination of second-order rate constant for reaction of BPA with O_3

A detailed description of the rate constant determination was given in our previous study [29]. Briefly, a competitive kinetic method was applied using phenol as a reference compound. Experiments were performed at room temperature (27-30°C) in 20-mL vials with solution containing equal concentration of BPA and phenol (4 μ mol/L) as well as 20 mmol/L of *t*-BuOH. The pH of the solution was adjusted using 20 mmol/L of phosphate buffer. Ozone solutions with concentrations ranging from 1.5 to 7.5 μ mol/L were added. The aqueous O₃ stock solution was prepared by sparging O₃ at a rate of 0.70 g/hr into deionised water placed inside a water-jacketed beaker at 2°C. The concentration of O₃ was measured by the indigo method [30]. The final volume of the mixtures was 20 mL, which also minimised the headspace. Each vial was then shaken vigorously. The time of total ozone consumption was estimated from the half-life of ozone in the BPA solution under different pH conditions. The half-lives for ozone in BPA solution were found to be 28, 9 and <2 min. at pH 2, 7 and 12 respectively. To ensure the reaction was completed, the reaction mixtures were shaken for 12 hr using a shaker. The remaining concentrations of BPA and phenol were determined by high performance liquid chromatography (HPLC).

Effect of selected anions on ozonation of BPA

All experiments were performed under heterogeneous conditions in which O_3 was bubbled at a rate of 0.70 g/hr through a gas dispersion tube into a 1000-mL jacketed beaker containing 1000 mL of magnetically-stirred BPA solution (100 mg/L) and an anion. The reaction temperature was maintained by means of a circulating water bath at 25 ± 0.1 °C. Aliquots were withdrawn at defined time intervals and analysed by HPLC in order to monitor the remaining concentrations of BPA.

Extraction of degradation by-products of BPA ozonation

Ozone was bubbled at a rate of 0.70 g/hr through a gas dispersion tube into a 1000-mL jacketed beaker containing 1000 mL of magnetically-stirred BPA solution (100 mg/L). In this experiment, ozonation was carried out without *t*-BuOH in order to study the contribution of both O_3 and •OH in the degradation of BPA. The reaction temperature was maintained by means of a circulating water bath at 25 ± 0.1 °C. A 10-mL aliquot was withdrawn every 2 min. for a period of 10 min. and, after removing residual ozone with nitrogen gas [31], subjected to a liquid-liquid extraction using ethyl acetate. The organic extract was then silylated with BSTFA + TMCS (99:1) at 70°C for 4

hr. The silvlated extract was dried with nitrogen stream and redissolved in 30 μ L of dichloromethane, 1.2 μ L of which was analysed by gas chromatography-mass spectrometry (GC-MS).

Analytical methods

The concentration of BPA in the reaction mixture was determined using HPLC (Thermo Separation Product HPLC System P2000, HiTech Trader, USA) equipped with a UV detector and a degasser. A 250×4.6 mm RP-8 (5µm) Lichrospher-100 analytical column (Merck) was used for separation. Acetonitrile (65%) in deionised water with 0.1% trifluoroacetic acid was used as the mobile phase. The separation was carried out under isocratic condition. The separated components were detected at 230 nm. The flow rate was maintained at 1.0 mL/min for all runs and the sample volume for HPLC analysis was 20 µL.

The analysis of the degradation by-products was carried out using a Hewlett-Packard HP 6890 gas chromatograph coupled with HP5972 mass spectrometer. The column was HP-5 (5% phenylmethylpolysiloxane) column with the dimension of 30 m \times 0.25 mm and 0.25 µm of film thickness. Helium was used as the carrier gas with an average flow rate of 40 cm/sec., and the GC oven temperature was initially 60°C (maintained for 2 min.) and increased to 280°C at the rate of 6°C/min and maintained at this temperature for 2 min. The temperatures of the injection port and the transfer line were set at 290°C and 300°C respectively. The data for quantitative analysis was acquired in the electron impact mode (70 eV) with scanning in the range of 50-600 amu at 1.5 sec./scan.

RESULTS AND DISCUSSION

Kinetics of Degradation of BPA by Ozonation

The reaction of ozone with an organic compound has been reported to be of first order with respect to both ozone and the organic compound. Thus, the kinetics of ozonation can be expressed as a second-order reaction [32]. The determination of its rate constants was performed using a competitive kinetics method with phenol as reference compound [20, 29, 33-34]. Phenol was selected because it was expected to have a similar decomposition pathway and rate constant as BPA in the ozonation [34]. For phenol, the second-order rate constants for the reaction with O₃ at different pH values ($k_{app,Phenol-O_3}$) were calculated using equation 1:

$$k_{\text{app,Phenol-O}_{3}} = k_{\text{O}_{3},\text{Phenol}} \left(\frac{10^{\text{-pH}}}{10^{\text{-pKa}} + 10^{\text{-pH}}} \right) + k_{\text{O}_{3},\text{Phenolate}} \left(\frac{10^{\text{-pKa}}}{10^{\text{-pKa}} + 10^{\text{-pH}}} \right)$$
(1)

where pK_a of phenol was 9.9 and the intrinsic rate constants for phenol and phenolate were 1.3×10^3 M⁻¹ s⁻¹ ($k_{O_3,Phenol}$) and 1.4×10^9 M⁻¹ s⁻¹ ($k_{O_3,Phenolate}$) respectively [9, 34]. The rate constants for the reaction between O₃ and BPA (k_{O_3-BPA}) were estimated using competitive kinetics method derived from equation 2 [35, 36]:

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$$\ln\left(\frac{[\text{BPA}]_n}{[\text{BPA}]_0}\right) = \frac{k_{\text{O}_3-\text{BPA}}}{k_{\text{app},\text{O}_3-\text{Phenol}}} \ln\left(\frac{[\text{Phenol}]_n}{[\text{Phenol}]_0}\right)$$
(2)

where $[BPA]_0$ and $[Phenol]_0$ represent the initial concentration of BPA and phenol and $[BPA]_n$ and $[Phenol]_n$ represent the concentration of BPA and phenol after the ozonation reaction at different ozone dose, *n*.

Ozonation of BPA was carried out at pH 2.0-12.0 in the presence of excess *t*-BuOH ([*t*-BuOH] / [O₃] > 300). *t*-BuOH is a radical scavenger added to scavenge the •OH radical, thus allowing BPA to react only with O₃ during ozonation. Lee et al. [9] and Deborde et al. [34] reported k_{o_3-BPA} at 20°C = 1.68×10^4 and 1.30×10^4 M⁻¹ s⁻¹ at pH 2, and 1.11×10^9 and 1.60×10^9 M⁻¹ s⁻¹ at pH 12 respectively. In this work, somewhat higher values of k_{o_3-BPA} were obtained, viz. $(1.7\pm0.5)\times10^4$ and $(9.0\pm0.5)\times10^9$ M⁻¹s⁻¹ at pH 2 and 12 respectively. This difference might be due to a large error that can occur in the competitive kinetics method [20] and also to a higher reaction temperature that was selected in this study.

According to Staples et al. [37], the two dissociation constants of BPA are 9.6 (pK_a1) and 10.2 (pK_a2). BPA is therefore a weak organic acid which can dissociate in solution as either an anionic or dianionic species. Generally, when $pH = pK_a$, the undissociated and ionic species exist at equal concentration in solution. When $pH < pK_a$, the undissociated species is predominant and when pH > pKa, the ionic species is predominant [38]. Therefore, for BPA, when $pH < pK_a1$, undissociated BPA exists predominantly in water. When $pK_a1 < pH < pK_a2$, anionic BPA is the predominant species and when $pH > pK_a2$, dianionic BPA are predominant (Figure 1).



Figure 1. Dissociation of BPA

It has been previously shown that in the presence of the •OH radical, the rate of BPA degradation by ozone increases from pH 2 to 7 and then decreases at pH 10 due to •OH scavenging by carbonate and bicarbonate ions [14]. In this study, *t*-BuOH was added to scavenge the •OH radical from the beginning in order to study the rate constants for BPA degradation by O₃ only. The results are shown in Figure 2, indicating that the reactivity increases as the pH increases from 2 to 12. Under acidic condition (pH < 7), the reaction would be mainly between O₃ and undissociated BPA. Between pH 4-7, the rate constant was observed to increase by a magnitude of almost 10^2 and this would be due to the increase of anionic species of BPA in the solution. The rate constant increased almost twofold when the pH increased from 9.6 (= pK_a1) to 10.2 (= pK_a2).



Figure 2. Variation of second-order rate constant of BPA-ozone reaction at different pH values

In order to study the effect of the ratio of $[BPA^{2-}] / [BPA^{-}]$ on the rate constant, the obtained second-order rate constants were plotted against $[BPA^{2-}] / [BPA^{-}]$ values at pH between 9.6-10.3 (Figure 3). The ratio of $[BPA^{2-}] / [BPA^{-}]$ was estimated using Henderson-Hasselbach equation as follows [39]:

$$pH = pK_a 2 + \log\left[\frac{[BPA^{2-}]}{[BPA^{-}]}\right]$$
(3)



Figure 3. Effect of [BPA²⁻] / [BPA⁻] on second-order rate constant of BPA-ozone reaction at the pH 9.6-10.3

From Figure 3, the rate constant increases proportionally with $[BPA^{2-}] / [BPA^{-}]$, which implies that the dianionic species of BPA (BPA²⁻) is more easily oxidised by O₃ compared to its anionic counterpart (BPA⁻). From Figure 2, it can be clearly observed that when the pH value

increases further from 10.2 to 12.0, the reactivity of BPA with O_3 remains almost constant. This is most likely due to the fact that the maximum fraction of BPA²⁻ has been reached at pH 10.2 and further increasing of pH does not influence the amount of BPA²⁻ anymore.

Influence of Inorganic Anions

Most wastewaters normally contain inorganic anions coexisting with organic pollutants. The effects of the anions on the rate of BPA degradation was studied at concentrations found in wastewaters [40-42]. Figure 4 shows plots of BPA degradation in the presence of phosphate, nitrate, chloride and sulphate ions. The results indicate that the presence of common inorganic anions at concentration levels in the wastewaters does not significantly affect the rate of BPA degradation. This might be due to the fast reaction between O_3 and BPA as indicated by the determined second-order rate constants.



Figure 4. Effect of (a) phosphate, (b) nitrate, (c) chloride and (d) sulphate ions on the degradation of BPA (temperature = 25° C; O₃ dose = 0.69 g/h; pH = 6.5; [BPA]₀ = 100 mg/L)

Degradation By-Products (DBPs) of BPA

GCMS analyses were performed by comparing the chromatogram of BPA with those of the aliquots taken at different ozonation times. All samples were subjected to similar derivatisation

procedure as mentioned in the experimental section. A chromatogram showing the distribution of DBPs of BPA is presented in Figure 5 and the proposed DBPs are presented in Table 1. All derivatised compounds occurred as trimethylsilyl derivatives characterised by the peak at m/z 73 in the mass spectrum. Identification of DBPs was carried out based on fragmentation patterns in the mass spectrum and/or by comparing the mass spectrum with the library available in the instrument database.



Figure 5. Gas chromatogram of BPA after 4 min. of ozonation time ([BPA]₀ = 100 mg/L, pH = 6.5, temperature = 25 °C, O₃ dose = 0.70 g/hr)

The mass spectrum of BPA shows the molecular ion peak at m/z 372 (Figure 6a). Besides the peak at m/z 357 representing the loss of methyl group from trimethylsilyl group ((M-CH₃)⁺), the other significant peak is at m/z 207 representing the loss of trimethyl(phenoxy)silane from silylated BPA. *DBP*₁, *DBP*₂ and *DBP*₃ represent the breakdown products of BPA and their mass spectra (as silylated derivatives) are presented in Figures 6 (b-d). The formation of *DBP*₁, *DBP*₂ and *DBP*₃ has also been detected in previous studies [13,15,16].

The mass spectra of DBP_4 and DBP_5 , formed by aromatic-ring opening during the ozonation process, are presented in Figures 7a and 7b respectively. Silylated DBP_5 with a molecular weight of 292 amu shows a peak representing $(M-1)^+$ at m/z 291 (Figure 7b). DBP_6 is a BPA degradation by-product proposed by Deborde et al. [11]. The structure of this compound was derived based on its fragmentation pattern in the mass spectrum (Figure 7c). The peak at m/z 378 corresponds to the molecular ion peak of silylated DBP_6 . Other major peaks are at m/z 212 and 217. The peak at m/z 212 represents the radical cation of silylated 3-formyl-4-methylpenta-2,4-dienoic acid. The peak at m/z 217 represents the loss of silylated carboxylic acid and aldehyde functional groups from the parent compound.

Monohydroxylated (DBP_7) and dihydroxylated (DBP_8) BPA were also detected during the ozonation process. The molecular ion peaks of DBP_7 and DBP_8 are at m/z 460 (Figure 7d) and m/z 548 (Figure 7e) respectively. Additional 88 amu and 176 amu over the molecular ion peak of

silylated BPA (m/z 372) indicated the addition of one and two [(CH₃)₃SiO]⁺ groups to silylated BPA respectively.

Compound identified	Retention time (min.) (Label)	Proposed structure of compound (Molecular weight)	Name
тмзо (<i>m/z</i> 372)	25.01 BPA	но (228.3)	Bisphenol A
TMS0 (<i>m/z</i> 206)	15.71 (<i>DBP</i> ₁)	но (134.1)	4-(Prop-1-en-2-yl)phenol
тмso (<i>m/z</i> 254)	16.23 (<i>DBP</i> ₂)	но (110.0)	Hydroquinone
TMSO (<i>m/z</i> 208)	17.15 (<i>DBP</i> ₃)	но (136.1)	4-Hydroxyacetophenone
тмзо (<i>m/z</i> 292)	19.23 (<i>DBP</i> ₄)	но (220.1)	2-(2-(4- Hydroxyphenyl)propan- 2-yl)succinaldehyde
тмзо (<i>m/z</i> 274)	20.24 (<i>DBP</i> ₅)	но (202.1)	2-(1-(4- Hydroxyphenyl)vinyl)- pent-2-enal
тмзо (<i>m/z</i> 378)	25.09 (<i>DBP</i> ₆)	но (234.1)	3-Formyl-4-(4- hydroxyphenyl)-4- methylpent-2-enoic acid
тмзо (<i>m/z</i> 460) отмз	26.20 (<i>DBP</i> ₇)	но (244.1)	Monohydroxy-BPA
TMSO TMSO (<i>m/z</i> 548)	27.01 (<i>DBP</i> ₈)	но он (260.1)	Dihydroxy-BPA

Table 1. Degradation by-products of BPA



Figure 6. Mass spectra of DBP_1 , DBP_2 , DBP_3 and BPA

Figure 8 shows the time profiles of the major DBPs, most of which were successfully removed after 10 min. of ozonation, with the exception of DBP_3 , DBP_6 and DBP_8 . These three by-products thus seemed to be more resistant to ozonation compared to others. In the degradation experiment, ozonation was performed without a radical scavenger, so BPA could react with both O₃ and •OH. As compared to the reaction between O₃ and BPA [11], the results in this study show that the presence of •OH seemed to produce more species of the breakdown products such as DBP_1 , DBP_3 and DBP_4 , which was most likely due to the non-selective behaviour of •OH, which can also react at the aliphatic chain and aromatic ring of BPA [33, 43].



Figure 7. Mass spectra and fragmentation patterns of *DBP*₄, *DBP*₅, *DBP*₆, *DBP*₇ and *DBP*₈



Figure 7. (continued)



Figure 8. Time profiles of major BPA degradation by-products ($[BPA]_0 = 100 \text{ mg/L}, \text{pH} = 6.5$, temperature = 25°C, and O₃ dose = 0.69 g/h). Relative abundance of the degradation by-products was calculated by normalising the peak areas at the defined ozonation time to the highest peak areas.

Formation of Degradation By-Products

Formation of DBP₁, DBP₂, DBP₃, DBP₇ and DBP₈

Formation of DBP_7 and DBP_8 can occur through hydroxylation of BPA or via a direct reaction between BPA and O₃ (Figure 9). Hydroxylated BPA is proposed to be an important intermediate of by-products resulting from ring opening, especially DBP_4 , DBP_5 and DBP_6 . Formation of polyhydroxylated BPA through the reaction between BPA and •OH has also been reported during the degradation of BPA by ultrasound-UV-iron (II) treatment [17].

The formation of DBP_1 , DBP_2 and DBP_3 are presented in Figure 9b. Since O₃ with its eletrophilic nature reacts selectively with an electron-rich reaction site, it is proposed that the reaction begins at the side chain of BPA with an initial attack of •OH via hydrogen abstraction and leads to the formation of radical A. Intramolecular rearrangement of radical A then leads to the cleavage of C-C bond to form DBP_1 (4-isopropenylphenol) and a phenol radical, B. B will then react with •OH to form DBP_2 (hydroquinone). DBP_1 can further react with either O₃ or •OH, leading to the formation of dihydroxylated DBP_1 (C). C would then react with •OH via hydrogen abstraction to form radical D, which undergoes a fragmentation to form DBP_3 (4-hydroxyacetophenone).



Figure 9. Proposed pathways for the formation of: (a) DBP_1 , DBP_2 and DBP_3 ; (b) DBP_7 and DBP_8 from BPA during ozonation

Formation of DBP₄, DBP₅ and DBP₆

The formation pathway of DBP_4 is presented in Figure 10. The formation of DBP_6 is proposed to begin with the initial attack of •OH on the monohydroxylated BPA giving a radical intermediate (*F*) (Figure 11a). Intra-molecular rearrangement of *F* and cleavage of C-C bond lead to the opening of an aromatic ring, resulting in the formation of radical *G*, which then rearranges to form radical *H*, which reacts with water to form *I*. Attack of •OH at the enol site of *I* affords radical *J*, which gives radical *K* on cleavage of a C-C bond. Radical *K* further reacts with •OH to form *L*, which upon hydrogen abstraction gives radical *M*. *M* then further reacts with •OH leading to the formation of DBP_6 . The formation pathway of DBP_5 is presented in Figure 11b.



Figure 10. Proposed pathway for the formation of DBP_4



Figure 11. Proposed pathways for the formation of: (a) DBP_5 and (b) DBP_6

CONCLUSIONS

The rate constant for the reaction between BPA and ozone in aqueous solution in the presence of *t*-BuOH increased with increase in pH between pH 2-10, beyond which it was fairly constant between pH 10-12. The reactivity of BPA increased in the order: undissociated form < anionic form < dianionic form. The presence of common inorganic anions (chloride, sulphate, nitrate

and phosphate ions) at environmental levels did not significantly affect the rate of degradation of BPA by ozone.

The degradation products of BPA during ozonation were identified to be 4-(prop-1-en-2-yl)phenol, hydroquinone, 4-hydroxyacetophenone, 2-(2-(4-hydroxyphenyl)propan-2-yl)succinaldehyde, 2-(1-(4-hydroxyphenyl)vinyl)pent-2-enal, 3-formyl-4-(4-hydroxyphenyl)-4-methylpent-2enoic acid, monohydroxy-BPA and dihydroxy-BPA.

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