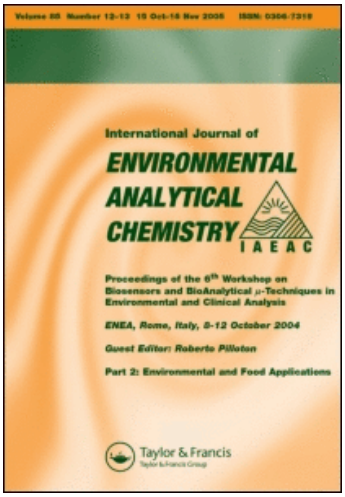

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ISOLATION AND CHARACTERIZATION OF BADGE HYDROLYSIS PRODUCTS

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Heating a suspension of Bisphenol A diglycidyl ether (BADGE) in 20 : 80 tetrahydrofuran/water at 70°C and subsequent passage of the resulting solution through C18 columns allowed isolation and purification to > 97% of each of the two hydrolysis products 2-[4-(2,3-dihydroxypropoxy) phenyl]-2-[4-(2,3-epoxypropoxy)phenyl]propane (1HP) and 2,2-bis[4-(2,3-dihydroxypropoxy)phenyl] propane (2HP), which were characterized by UV, IR, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry.

Keywords: BADGE; BADGE hydrolysis products; Ultraviolet spectroscopy; Infrared spectroscopy; Nuclear magnetic resonance; Mass spectrometry

INTRODUCTION

Bisphenol A diglycidyl ether or 2,2-bis(4-hydroxyphenyl) propane bis(2,3-epoxypropyl) ether (BADGE; CAS No. 1675-54-3; PM/REF. No. 13510) is a monomer used in the formulation of epoxy resins employed to coat materials that would come in contact with foods. Defective formulation or preparation of such materials can allow their components to migrate into the foods with which they come in contact, where they or their reaction products can constitute a risk of toxicity. The stability of BADGE in aqueous food simulants (distilled water, 3% acetic acid and 10% ethanol) under the conditions established by EU legislation[1, 2] has been studied by a number of researchers[3–8]. In these simulants, BADGE is rapidly hydrolysed, successively affording the products 2-[4-(2,3-dihydroxypropoxy)phenyl]-2-[4-(2,3-epoxypropoxy)phenyl] propane (1HP) and 2,2-bis[4-(2,3-dihydroxy propoxy)phenyl] propane (2HP) (Scheme 1). In oily media BADGE is not hydrolysed, its epoxy groups being protected by the oil[9, 10].

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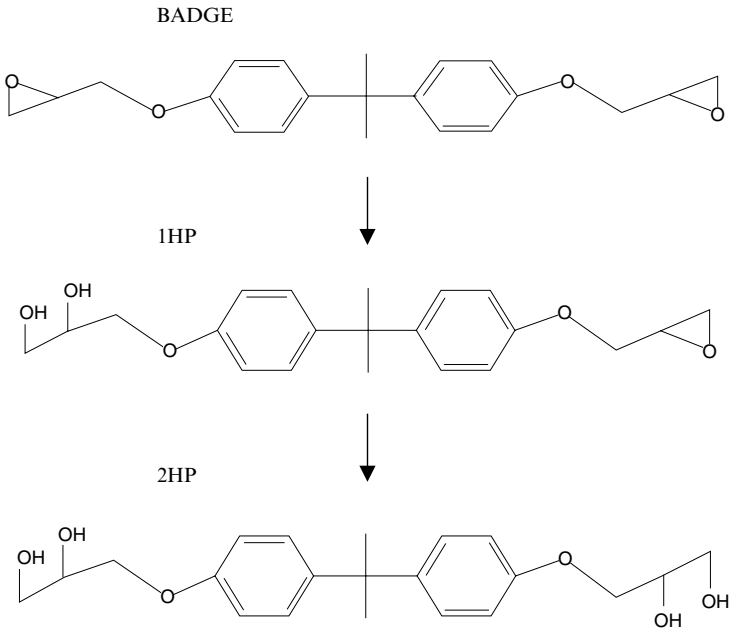
DOI: 0000-0000.00.000000



SCHEME 1

Analytical data and toxicological aspects concerning BADGE and its reaction products were broadly discussed by the Scientific Committee for Food (SCF)[11, 12] that, while waiting for completing the toxicological studies, provisionally recommended a SML (Specific Migration Limit) of 1 mg kg^{-1}. This recommendation was included as a restriction criteria in EU regulations[13, 14] in force up to January 2005.

At the present time, the main analytical difficulties are related with the quantification and positive identification of these compounds in the food simulants as well as in canned foods.

Studies of 1HP and 2HP, and their quantification in foods, have hitherto been hampered by the lack of reliable methods for preparing sufficient quantities of the pure compounds. Only very recently it has been possible to get 2HP commercially but not 1HP. For characterization purposes by GC-MS they have previously been prepared by treating BADGE with 3 : 2 (v/v) water : acetone at 105°C, but in that study they were not separated and purified[15]. Here we describe a methodology for preparing, isolating and purifying enough quantities of 1HP and 2HP, and we report their UV, IR, mass and ^{1}H and ^{13}C NMR spectral characteristics.

EXPERIMENTAL

Preparation, isolation and purification

Procedure for 1HP

Hydrolysis A 400 mg L^{-1} suspension of BADGE (Epikote 828, from Shell, purified to > 99%[16]) in 20 : 80 tetrahydrofuran (THF) : water was prepared by placing approximately 200 mg of BADGE in a 500 mL flask, adding 100 mL of THF and making up

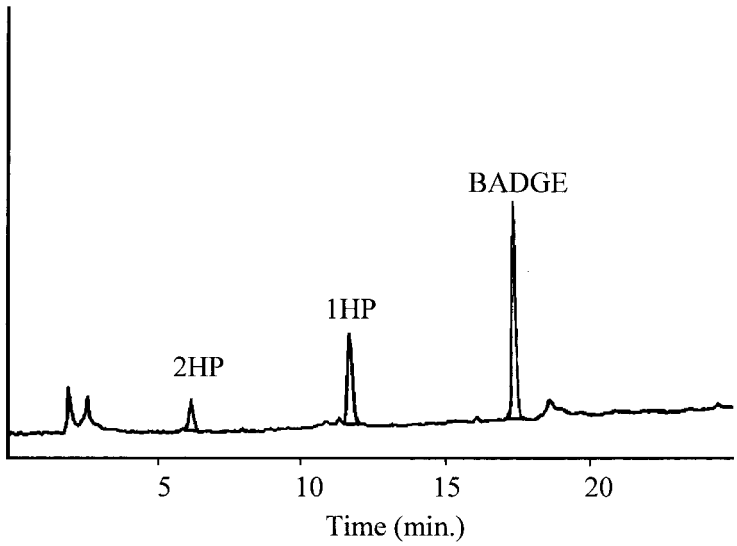


FIGURE 1 HPLC chromatogram of BADGE and its two hydrolysis products (1HP and 2HP) obtained with fluorescence detection. Experimental conditions are specified in the text.

to the mark with water. The solution was heated in an oven at $70 \pm 1^{\circ}C$ until 1HP peak (after approx. 16–18 h heating), exceeded those of BADGE and 2HP.

Analysis was performed by HPLC under the following conditions as described previously[6]: Column: 15 cm × 4.6 mm i.d., packing 5 μm Spherisorb ODS2. Isocratic elution with 30 : 70 acetonitrile/water (2 min), linear gradient to 80% acetonitrile (18 min), linear gradient to 100% acetonitrile (3 min), isocratic elution with 100% acetonitrile (2 min); flow rate, 1 mL min^{-1}. For fluorescence detection, excitation and emission wavelengths of respectively 225 and 305 nm were used, and for UV detection, a wavelength of 225 nm.

Typical retention times for BADGE, 1HP and 2HP were 17.4, 11.9 and 6.3 min, respectively (Fig. 1). Relative proportions of the three analytes were calculated from peak areas.

Separation 50 mL of the hydrolysate was passed through a series of three Sep-Pak C18 minicolumns preconditioned by passage of 10 mL of methanol followed by 10 mL of the appropriate solvent. The eluate was discarded, and the retained compounds were eluted from the columns by passing four or five 25 mL doses of 50 : 50 methanol : water, which were collected separately. Eluate samples, containing BADGE, 1HP and 2HP, were analysed by HPLC. Eluates in which 1HP content was less than 85% were discarded, and the others were pooled. After measurement of its volume, this pool was diluted with 25% of water and passed through another set of three C18 minicolumns. HPLC of the eluate showed no 1HP. The retained material was eluted with 15 mL of methanol, giving an eluate in which about 90% of the contents was 1HP, as shown by HPLC. Evaporation of this eluate to dryness under nitrogen afforded approximately 12 mg of a viscous, oily, whitish semisolid residue. This procedure was repeated to obtain 30 mg of 1HP.

Purification A solution of 30 mg of the above product in 10 mL of 50 : 50 methanol : - water was treated as in the Separation step except that, after the first passage through C18 columns, fractions were discarded if less than 3% of the total contents was 1HP.

Procedure for 2HP

A 400 mg L^{-1} suspension of BADGE in 20 : 80 THF : water was heated in an oven at $70 \pm 1°C$ for about 50 h, when at least 97% of the total contents was 2HP. 50 mL of the hydrolysate was passed through a series of three Sep-Pak C18 minicolumns, the eluate was discarded and the retained material was eluted from the columns by passage of 15 mL of methanol. HPLC of this eluate showed about 97% of the total contents to be 2HP. Evaporation to dryness under nitrogen afforded approximately 15 mg of a white solid residue. Finally, several such batches were pooled and recrystallized in approximately 50 mg lots from a mixture of ethyl acetate and hexane.

Characterization

IR spectra (4000–400 cm^{-1}) were recorded from KBr discs in a Bruker IFS 66 v spectrometer controlled by OPUS^{NT} v.2.06 software. UV spectra were obtained by injecting 5 mg L^{-1} aqueous solutions of BADGE, 1HP or 2HP into the HPLC apparatus with the UV detector connected, and scanning from 190 to 340 nm when the peak emerged. FAB and EI mass spectra were obtained using solutions of 1.5–3.0 mg of analyte in 2 mL of carbon disulfide (for the FAB spectra of 1HP and 2HP, a drop of dimethylsulfoxide was included); FAB were run on a Kratos MS-50TC high-resolution apparatus controlled by MACH3 software running under UNIX, and EI spectra on a Hewlett Packard 5988A low-resolution apparatus controlled by MSTOP. Positive and negative mode atmospheric pressure chemical ionization (APCI) mass spectra were obtained using an APCI interface to couple the HPLC system to a Fisons Instruments VG Platform 3280 apparatus controlled by MassLynx for Windows 2.0; 5 mg L^{-1} solutions in acetonitrile were injected into the HPLC system. ^{1}H and ^{13}C NMR spectra of solutions of 1 mg of analyte in 0.5 mL of $CDCl_3$ containing a drop of dimethylsulfoxide were run in a Bruker AMX 300 NMR spectrometer operating at 300.13 MHz for ^{1}H spectra (11 μs 90° pulse) or 75.47 MHz for ^{13}C spectra (4μs 90° pulse) under UXNMR 94.5 software; signals are referred to tetramethylsilane. The melting point of 2HP was determined in a Reichert Kofler Thermopan apparatus and is uncorrected.

RESULTS AND DISCUSSION

Preparation of 1HP and 2HP

BADGE is poorly soluble in water, but highly soluble in THF (CLOGP calculations of log *P* predict an octanol–water partition coefficient of 3.98[17]). We found in preliminary experiments that an appropriate balance between increasing the concentration of solute (by increasing the proportion of THF) and increasing the rate of hydrolysis (by increasing the proportion of water) was achieved using 20 : 80 THF : water, which maximized the overall rate of production of 2HP. For 1HP, slower hydrolysis

(more THF) might allow more accurate determination of the point of maximum 1HP concentration.

The working temperature, 70°C, was lower than the temperature used by Rauter *et al.*[15] when they hydrolysed a solution of BADGE in acetone–water, 105°C. This lengthened the reaction time somewhat (from 2 days[15] to about 2.5 days), but avoided esterification of the hydrolysis products.

Before recrystallization, both 1HP and 2HP preparations were at least 97% pure. Recrystallization of 2HP from a mixture of ethyl acetate and hexane afforded a solid with a melting point of 86–87.5°C (cf. 103°C reported for 2HP recrystallized from *tert*-butyl methyl ether[15], or 91–97°C reported for 97% pure 2HP[18]). Repeated attempts to crystallize 1HP from a variety of solvent mixtures all failed, therefore we could not afford a precise determination of its melting point.

Differential characteristics

The UV spectra of BADGE, 1HP and 2HP do not differentiate the three (absorbance values maximized at 200, 225 and 275 nm), but their IR spectra allow them to distinguish by the presence or absence of epoxy and hydroxyl bands. Besides the expected bands for substituted aromatics (at 1607, 1510 and 831 cm^{-1}), ethers (at 1249 cm^{-1}) and methylene groups (at 1459 and 1363 cm^{-1}[19,20], bands attributable to epoxy groups appear only in the spectra of BADGE and 1HP (at 916, 881 and 863 cm^{-1}) and significant hydroxyl bands only in those of 1HP and 2HP (around 3400 and 1108 cm^{-1}).

Mass-spectrometric characterization of epoxy resins formulated with BADGE has previously been performed by HPLC-MS with a TSP interface[21] by GC-MS[22], by LC-GC-MS[23], or by APCI-MS-MS[24]. The FAB and EI mass spectra of BADGE, 1HP and 2HP obtained in this work are summarized in Table I. With fast atom bombardment, the most abundant fragment of both BADGE and 1HP is an ion with m/z 191 containing an epoxy ring, while in 2HP the same fragmentation affords as the major signal, at m/z 209, a fragment with two hydroxyls (see Table III). In EI mode the most abundant fragments are in all three cases produced by the loss of a methyl group, which affords fragments at m/z 325 for BADGE, 343 for 1HP and 361 for 2HP (see Table III). It was not possible to obtain a negative-mode APCI mass spectrum of BADGE; in those of 1HP and 2HP, the major fragments corresponded to the loss of a 2,3-dihydroxypropyl or 2,3-epoxypropyl group and a proton at 30 V, and to the loss of both ether partners at 60 V. In the positive-mode APCI spectra of BADGE and 1HP, the salient feature is the appearance, at m/z 400 and 382, of signals indicating the formation of quasimolecular clusters comprising the analyte and a molecule of acetonitrile, the HPLC mobile phase.

The APCI spectra of 2HP show weak signals at m/z 191 and 269 (Table II) corresponding to structures with an epoxy ring (Table III). Since the purity of the 2HP used (97%) makes it unlikely that they represent residual BADGE or 1HP, these fragments are probably formed by the loss of a water molecule from the two hydroxyl groups of the structure shown in Table III with m/z 209 and an analogous structure with m/z 287. It seems less likely that they have structures similar to those assigned to m/z 191 and 269 in Table III but with one methyl group less and two hydroxyls instead of an epoxy group.

TABLE I Signals in the FAB and EI mass spectra of BADGE, 1HP and 2HP, with relative abundances

BADGE		*1HP*		*2HP*	
m/z	*Abundance*	*m/z*	*Abundance*	*m/z*	*Abundance*
FAB mode					
92	37.8	75	81.1	92	66.8
107	28.2	92	71.6	110	32.9
119	28.4	135	46.8	135[c]	50.7
135	58.8	**191**[b]	**100.0**	155	57.4
161[b]	42.8	209[c]	68.7	**209**[c]	**100.0**
191[b]	**100.0**	358[a]	40.6	376[a]	71.0
325[b]	54.5				
340[a]	64.4				
EI mode					
57	5.5	71	16.9	119	10.5
119	5.7	119	17.9	135[c]	11.7
152	3.6	213	24.1	213[c]	37.2
165	4.8	269[b]	62.0	287	18.9
213	6.5	325[b]	69.6	**361**[c]	**100.0**
269[b]	8.7	**343**[b,c]	**100.0**	376[a]	18.1
325[b]	**100.0**	358	19.0		
326	23.3				
340[a]	16.6				

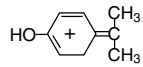
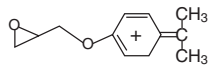
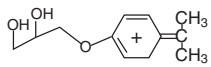
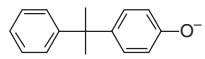
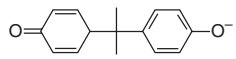
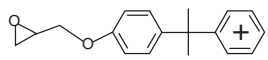
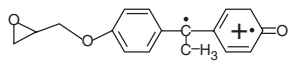
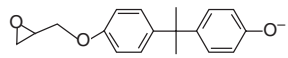
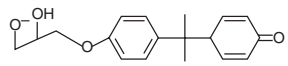
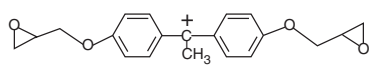
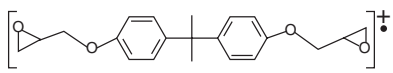
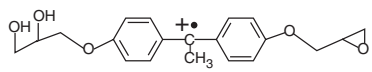
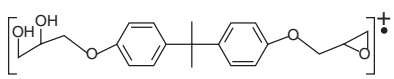
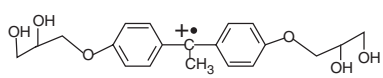
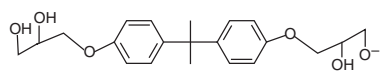
[a]Molecular ions.
[b]Fragments with epoxy groups.
[c]Fragments with hydroxyl groups.

TABLE II Major signals in the positive- and negative-mode APCI mass spectra of BADGE, 1HP and 2HP, with relative abundances (signals of relative abundance < 5% not shown)

	BADGE		*1HP*		*2HP*	
	m/z	*Abundance*	*m/z*	*Abundance*	*m/z*	*Abundance*
$APCI^+$						
30 V	135[c]	14.0	135[c]	79.0	135[c]	30.5
	191[b]	67.0	173	31.0	191[b]	6.0
	382[a]	**100.0**	191[b]	85.0	**209**[c]	**100.0**
			209[c]	81.0	281	8.5
			400[a]	**100.0**		
60 V	107	34.0	107	13.0	107	26
	135[c]	**100.0**	**135**[c]	**100.0**	**135**[c]	**100.0**
	191[b]	76	173	19.5	209[c]	29.5
			191[b]	5.5		
			209[c]	36.0		
$APCI^-$						
30 V	not detected		211	6.5	227	74.5
			227	40.5	269[b]	11.5
			283[b]	93.5	**301**[c]	**100.0**
			301[c]	**100.0**	373[c]	44.0
			357[c]	0.00		
60 V	not detected		211	11.0	211	27.00
			227	**100.0**	**227**	**100.00**
			283[b]	35.00	301[c]	20.50
			301[c]	19.50		
			357[c]	6.50		

[a]Quasimolecular ions $[M + CH_3CN]$.
[b]Fragments with epoxy groups.
[c]Fragments with hydroxyl groups.

TABLE III Probable structures of fragments appearing in the mass spectra of BADGE, 1HP and 2HP (Tables I and II)

Molecular weight	*Structure*	*Ionization type*
135		FAB, APCI$^+$
191		FAB, APCI$^+$
209		FAB, APCI$^+$
211		APCI$^-$
227		APCI$^-$
267		FAB
269		EI, APCI$^-$
283		APCI$^-$
301		APCI$^-$
325		FAB, EI
340		EI
343		EI
358		EI
361		EI
375		APCI$^-$

(Table Continued)

TABLE III (Continued)

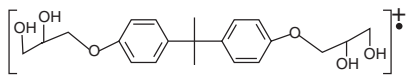
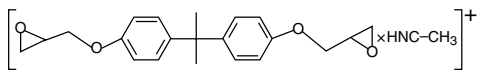
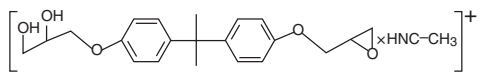
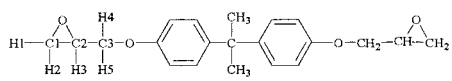
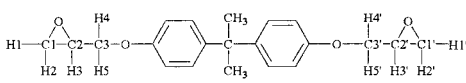
Molecular weight	*Structure*	*Ionization type*
376		EI
382		$APCI^+$
400		$APCI^+$

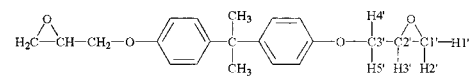
TABLE IV ^1H and ^{13}C NMR differential characteristics and signal assignments spectra of BADGE, 1HP and 2HP



BADGE



1 HP



2 HP

	^1H and ^{13}C NMR for BADGE, 1HP in a mixture of $CDCl_3$ and DMSO-d_6															
	^1H NMR										*^{13}C NMR*					
	H1	*H2*	*H3*	*H4*	*H5*	*H1′*	*H2′*	*H3′*	*H4′*	*H5′*	*C1*	*C2*	*C3*	*C1′*	*C2′*	*C3′*
BADGE	2.74	2.89	3.31–3.36	3.95	4.18						45.17	50.60	69.16			
1HP	2.74	2.89	3.31–3.36	3.94–4.18		3.72	3.82		3.94–4.18		45.18	50.60	68.37	69.13	69.56	70.75
2HP						3.61	3.71		3.92–4.00					64.02	69.29	70.71

Structural characterization of BADGE, 1HP and 2HP has also been performed by ^1H and ^{13}C NMR spectroscopy, the main differences being observed in the chemical shifts for the protons and carbons of the 2,3-epoxypropyl and 2,3-dihydroxypropyl groups of these compounds (Table IV). Thus, ^1H and ^{13}C NMR chemical shifts of the 2,3-epoxypropyl group of BADGE are coincident with those reported in the literature[25–27], and similar to the values showed for the 2,3-epoxypropyl group of 1HP, but quite different from those observed for the 2,3-dihydroxy group at the other end of the molecule. This group showed ^1H and ^{13}C NMR chemical shifts which resulted to be quite close to those found for the 2,3-dihydroxy group of 2HP and, although the ^{13}C NMR data obtained in solution for 2HP were quite different from those reported for the same compound in high resolution solid-state[28], comparable with the data values found in the literature for related structures[29–31]. Table IV summarizes the ^1H and ^{13}C NMR differential characteristics spectra of BADGE, 1HP and 2HP and shows the signal assignments made.

CONCLUSIONS

A simple, reliable method for preparation of the two hydrolysis products of BADGE, 1HP and 2HP has been developed, by heating a suspension of BADGE in 20 : 80 THF : water at 70°C for about 16–18 h (to obtain 1HP) or 2.5 days (for 2HP). Separation and purification on series of three C-18 minicolumns with HPLC-UVD or HPLC-FLD monitoring affords 1HP and 2HP with purities of at least 97%. BADGE, 1HP and 2HP can be easily distinguished on the basis of their IR spectra, their ^{1}H and ^{13}C NMR spectra, or their FAB, EI or positive- or negative-mode APCI mass spectra, but their UV spectra provide no useful differential information.

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