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BADGE and its Accompanying Compounds in Canned Oily Foods: Further Results

Key words: Bisphenol-A-diglycidyl ether, BADGE, Canned foods, Chlorohydroxy derivatives of BADGE, Oligomers of BADGE

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Introduction

In the early 1996, canned oily foods, such as fish in oil, meat, sauces, or evaporated milk, were found to often contain high concentrations of Bisphenol-A-Diglycidyl Ether (BADGE, with the structure shown in fig. 1). BADGE is a starting point material for producing epoxy polymers, but also an additive (stabilizer, plasticizer) to organosols and polyesters. All three polymers are applied as coatings on the internal and external surface of cans used for food preservation (1). Edible oil efficiently extracts BADGE and other, similar compounds from the coating and protects the epoxide group against hydrolysis even in acidic media (2).

Of 142 samples of canned preserves of oil- or fat-containing foods (> 5% fat) from the Swiss market, 2% contained BADGE at a concentration exceeding 10 mg/kg (referring to the whole content of the can) and 15% between 1 and 10 mg/kg. 55% of all samples analyzed exceeded the Swiss legal limit of «not detectable at a detection limit of 20 µg/kg» (3). Since almost all products were imported, it is asumed that similar results would have been found in other countries. Samples containing BADGE at a concentration exceeding 100 µg/kg related to the whole content of the can were removed from the market.

In addition, the maximum content of BADGE in an object in contact with foods is limited to 1 mg/kg. Most of the beverage cans exceed this limit (*Spinner* et al. (4)).

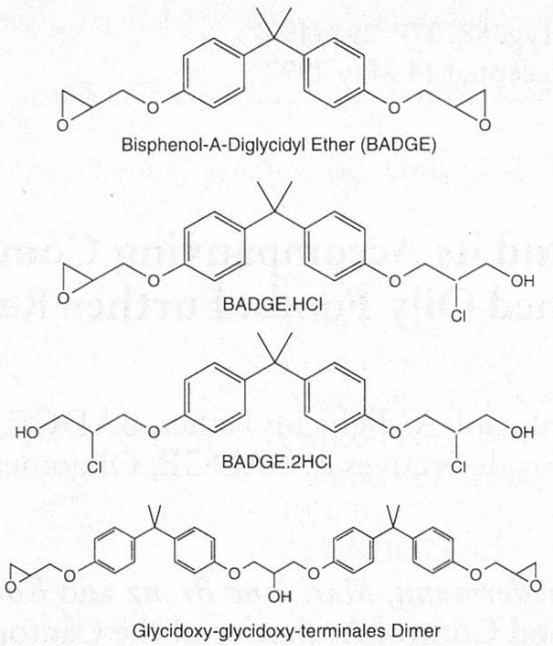

Fig. 1. Structure of BADGE, possible chlorohydroxy derivatives and of its glycidoxy-glycidoxy dimer

In June 1996, the EU Scientific Committee for Food (SCF) came to the conclusion that it was not in a position to set a value for the tolerable daily intake (TDI) for BADGE because of the absence of an adequate oral study on carcinogenicity and mutagenic activity. Two years were given and for the mean time, it recommended to enforce a temporary restriction at a limit of 1 mg/kg of food.

In November 1996, the German authorities released a statement (5) based on the recommendation by the SCF that BADGE contents exceeding 1 mg/kg in foods should be considered as a potential hazard to health.

Since toxicology does not provide a conclusive answer, the principle gains in importance that technically avoidable food contaminants must be eliminated. The question remains to answer, how far BADGE and similar compounds can be avoided. To this end it is informative that before taking any measures (cans analyzed before May 1996), 45% of the cans were acceptable even for the low Swiss limit, i.e. that there have been means of producing cans virtually free of BADGE already for some time.

This paper reports results on three subjects:

1. Canned preserves from the Swiss market sampled from June 1996 to February 1997 confirm that all products sold previously can be made available in cans respecting the low Swiss limit for BADGE.
2. BADGE is added to organosol (PVC) coatings in order to remove hydrochloric acid by reaction with the epoxide group. This results in chlorohydroxy compounds, the toxicity of which is again largely unknown.
3. BADGE is often accompanied by oligomers, particularly when released from epoxy coatings. Concentrations of the dimers and trimers easily exceed those of BADGE many times, i.e. canned foods with BADGE contents below the Swiss limit may contain them at concentrations far above the latter.

These three subjects were of interest in the context of the discussion on the legal limit(s) and may be also on the types of coatings to be applied in future.

Bisphenol-F-Diglycidyl Ether (BFDGE) or Novolac Glycidyl Ethers (NOGE) are possible replacers of BADGE. They will be discussed in more detail in a separate paper (6), but some results will be reported here.

Methods

Instrumentation and materials

LC and LC-LC were performed on an automated LC-GC system (Dualchrom 3000, C.E. Instruments, Milan, Italy) equipped with an autosampler, two syringe pumps, a fluorescence detector (Merck F1050), and three switching valves in the LC part. GC-MS was performed on an 8000 Series gas chromatograph equipped with an autosampler for large volume on-column injection which was coupled to a mass spectrometer MD-800 (all C.E. Instruments).

LC was performed on 25 cm × 2 mm i.d. columns packed with silicagel Spherisorb Si 5 µm and a cyano phase GromsilCN 2 PR 5 µm (Stagroma, Wallisellen, Switzerland). Pentane of technical grade (Siegfried, Zofingen, Switzerland) and methyl *tert.* butyl ether (MTBE, Merck) were redistilled.

GC involved an 8 m × 0.25 mm i.d. capillary column coated with an 0.2 µm film of SOP-50, a symmetric 50% phenyl polysiloxane obtained from W. Blum (Ciba, Basel, Switzerland). The precolumn system ahead of the early vapor exit consisted of a 1.5 m × 0.53 mm i.d. uncoated precolumn, deactivated by phenyldimethyl silylation or by coating with a 1 nm layer of OV-1701 (7), and a 1.5 m × 0.32 mm i.d. retaining precolumn coated with PS-255 (a methyl polysiloxane, Fluka) of 0.15 µm film thickness.

Standards of BADGE and epoxy resins were obtained from Ciba (Basel, Switzerland) and Vernicolor (Grüningen, Switzerland). The following standards will be available by Fluka (Buchs, Switzerland) in the near future: BADGE (15138), Bisphenol-A-bis-(chlorohydroxypropyl) ether (BADGE.2HCl, 15136) and Bisphenol-A-bis-(2,3-dihydroxypropyl) ether (15137).

Analytical concepts

The methods applied were based on direct analysis of the oil phase or a food extract by LC or LC-LC with fluorescence detection (FD) as described in (2). For samples containing a separate oil phase, some oil was analyzed first, using single step LC-FD on the cyano column. This provided first information about the presence of BADGE, Bisphenol-F-Diglycidyl Ether (BFDGE) and the chlorohydroxy compounds, but also enabled to eliminate the samples free of the compounds of interest from further analysis.

Concentrations of BADGE were confirmed by LC-LC-FD with heart cutting to the silicagel column. Some results were further confirmed by GC-MS after clean-up of the sample by LC-LC or LC-backflush-LC and large volume on-column injection into GC. Chlorohydroxy compounds were analyzed by LC-FD on the cyano column and confirmed in the same way by GC-MS. Oligomers of BADGE were analyzed by normal phase LC-FD on a cyano column after peak identification by RPLC-MS.

LC-FD

Screening procedure. Cans were partially opened and 150 mg of oil transferred into an autosampler vial. Care must be taken not to analyze oil that came into contact with the outer surface of the can, since the latter may contain high concentrations of BADGE. After filling the vial with heptane, 100 µl were injected on to the cyano column and chromatographed with 20% MTBE in pentane. Detection occurred at 225/295 nm. The column was backflushed with MTBE after each analysis. Quantitation occurred by external standards (see results).

Extraction procedure. The whole content of a can was transferred into a 500 ml beaker glass and mixed with an equal quantity of water using a blender. 2 g of the homogenate were extracted with 5 ml of 20% MTBE in heptane and the extract analyzed as described above. For a sample of tuna in oil, recoveries ranged between 85 and 100%.

FD response of BADGE.HCl and BADGE.2HCl. Since no pure standards were available, no calibration of the FD response was possible. The extract of an empty can containing a substantial amount of BADGE and its chlorohydroxy compounds was analyzed by LC-FD as well as by GC-FID. Assuming equal response on FID and using BADGE as a reference, BADGE.HCl had an FD response factor of 0.9 and BADGE.2HCl one of 0.3. However, GC analysis after on-column injection of the BADGE.2HCl fraction from LC showed formation of BADGE and BADGE.HCl during passage through the column. Hence, at the high temperatures required (around 260 °C), GC analysis suffered from re-formation of the epoxy groups by elimination of HCl, suggesting that the GC-FID response observed, particularly for BADGE.2HCl, was too low. It was concluded that, for the moment, the assumption of FD responses for BADGE.HCl and BADGE.2HCl corresponding to BADGE is the best choice.

LC-LC-FD

As described previously (2), LC-LC was performed in such a way that the peak of interest was observed twice by the same detector, i.e. after elution from the first (cyano) and the second (silicagel) column. To avoid the back pressure of the second column on the detector cell, the fraction of interest was transferred by means of a loop with an internal volume adjusted to the volume of the fraction. The first column was backflushed after each run.

GC-MS confirmation

Since capillary GC involved on-column injection, the sample had to be largely free of fat. For clean up, LC was preferred to other methods because it was readily available and also removed other interferences. On the first LC column, however, the triglycerides tailed into the fraction of BADGE to such an extent that further cleaning was necessary for most components. For the confirmation of a single component, fractions were obtained by the LC-LC procedure also analytically used. For GC-MS of a wider range of compounds (i.e. BADGE and its chlorohydroxy derivatives), the system was modified to perform LC-backflush-LC: Shortly before the elution of the first peak of interest, the cyano column was backflushed onto the second column and the fraction(s) of interest recovered from there.

LC fractions were evaporated to 200 µl, 100 µl of which were injected using concurrent eluent evaporation with the on-column interface (8). The injection rate by the autosampler was 3 µl/s. Helium was provided at 110 kPa. During transfer, the column temperature was 80 °C. It was then programmed at 15 °/min to 200 °C, at 7 °/min to 280 °C and at 20 °/min to 320 °C (10 min, removing triglycerides). The vapor exit was closed 40 s after starting injection.

Dimers of BADGE were analyzed by GC-MS. A 3 m × 0.25 mm i.d. fused silica capillary was coated with a 20 nm film of PS-255. The sample was injected on-column. The GC-MS interface was heated to 300 °C, the ion source to 200 °C. Temperature was programmed at 15 °/min to 330 °C.

LC-FD for oligomers

Oligomers of BADGE were analyzed on the cyano column mentioned above, using 25% 2-propanol in pentane as mobile phase at 400 µl/min and injecting 100 µl of the samples obtained as described.

LC-MS

Oligomers of BADGE were identified using a Finnigan MAT SSQ 710 C mass spectrometer operated in the Atmospheric Pressure Chemical Ionization (APCI) mode and equipped with a ThermoSeparation Products (TSP) Consta Metric 4100 HPLC system. HPLC separation was performed on a RP 125 × 2 mm i.d. column packed with Nucleosil 100-5 C_{18} phase (Macherey Nagel, Oensingen, Switzerland). Isocratic mobile systems consisted of 5 and 15% water in methanol (330 µl/min). For some analyses, a 10 mmol solution of ammonium acetate was added postcolumn at 5 µl/min in order to enhance cation formation in the ion source. UV detection occurred at 235 nm on a Hewlett Packard 1100 series diode array detector. Sample solutions of 10–20 ng/µl were injected using a Rheodyne injector with a 5 µl loop.

Chlorine (Beilstein)

Chlorine in the coatings of cans was determined by the flame method: some material was picked up by a hot copper wire and brought into a flame, detecting the presence of chlorine by the latter turning green.

Results

Improvements on the Swiss market

From June 1996 to February 1997, the Swiss market was checked for the effect of the previous campaign. All canned products containing some 5% fat or oil at least were collected in the shops of the Canton of Zürich. Over half of them consisted of fish or sea foods in oil. Of the products known to be most critical, samples from different lots and different vendors were analyzed.

As shown in table 1, only 1 out of 242 samples contained BADGE at a concentration exceeding 1 mg/kg (1.7 mg/kg referring to whole can content), compared to 24 of 142 samples (17%) and a maximum of 23 mg/kg before taking action. In 98.5% of the samples, the BADGE concentration was below 0.4 mg/kg. Merely 7.5% of the samples exceeded the 100 µg/kg of BADGE above which they were confiscated, compared to previous 40%. Two of the three highest concentrations concerned products in water, which had not been considered to be a problem so far.

The products analyzed comprised all available previously, i.e. fish and sea foods in oil, water, or various sauces, meat products, evaporated milk, salads, sauces, roasted potatoes, ravioli, lentils and puddings. The results also showed that no product had to be totally removed from the market.

Table 1. BADGE in 242 fat- and oil-containing canned foods from the Swiss market sampled from June 1996 to February 1997

Concentration	Number of samples
> 1000 µg/kg	1 (0.4%), value, 1700 µg/kg
400–1000 µg/kg	3 (1%)
100–400 µg/kg	14 (6%)
20–100 µg/kg	29 (12%)
< 20 µg/kg	195 (81%)

Chlorohydroxy Derivatives

BADGE is added to organosol coatings in order to improve the thermostability of the PVC polymer during the curing process which is typically performed between 180 and 220 °C. If cans are also decorated outside, easily five steps of printing and heating are needed and the coatings applied first (often the internal one) must be stabilized to withstand all of them. Reaction with hydrochloric acid opens the epoxy group and results in chlorohydroxy compounds. An LC-FD chromatogram of an extract of an empty can is shown in figure 2.

As a first step, a chlorohydroxy-epoxy compound (BADGE.HCl) is obtained, which may further react to a dichlorohydroxy compound BADGE.2HCl when BADGE is approaching depletion. Since each of these compounds is eluted as a

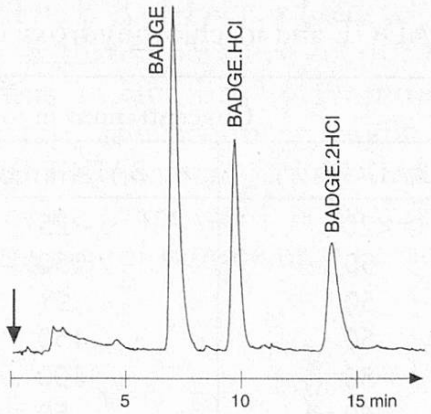

Fig. 2. LC-FD chromatogram of the extract from a can with an internal coating containing BADGE as well as its chlorohydroxy (BADGE.HCl) and dichloro-dihydroxy (BADGE.2HCl) compounds

single, homogeneous peak also in capillary GC, it is assumed that only one positional isomer is formed. Reactivity in the acidic environment suggests attack of the chlorine at the center carbon atom of the glycidyl group, which results in the structures shown in figure 1: Bisphenol-A-glycidyl-(2-chlor-3-hydroxypropyl) ether (BADGE.HCl) and Bisphenol-A-bis-(2-chlor-3-hydroxypropyl) ether (BADGE.2HCl). The mass spectra shown in figure 3 provide no evidence in favor or against this hypothesis.

Table 2 shows concentrations of chlorohydroxy compounds in 30 samples of canned foods. In some of the samples, the chlorohydroxy compounds were hardly detectable, presumably because BADGE was from an epoxy or a polyester coating.

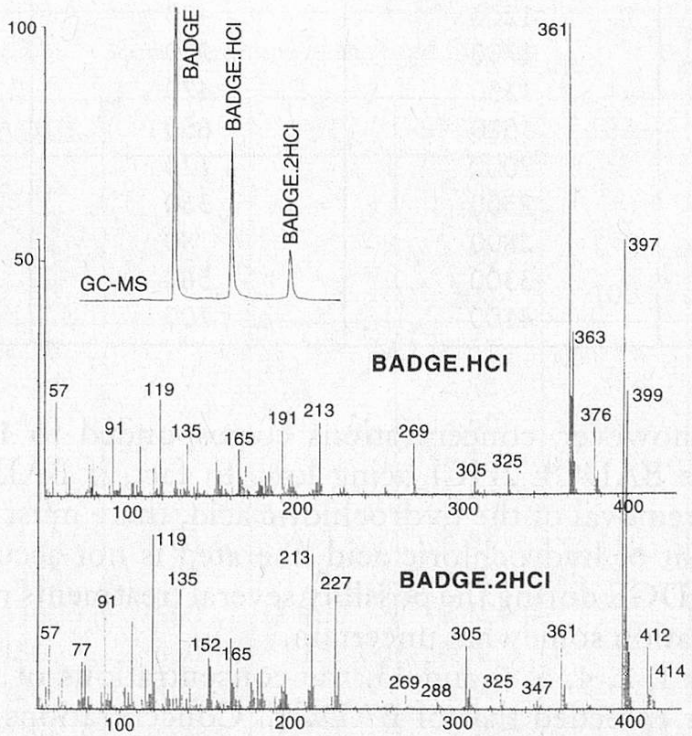

Fig. 3. MS(EI)-spectra of the chlorohydroxy compounds BADGE.HCl and BADGE.2HCl (M^+ 376 and 414), with the relevant section of the GC-MS trace inserted

Table 2. Concentrations of BADGE and its chlorohydroxy compounds in canned foods

Nr.	Concentrations in food (µg/kg)		
	BADGE	BADGE.HCl	BADGE.2HCl
1	<20	25	900
2	50	150	350
3	50	≤5	
4	50	150	1100
5	50	100	2700
6	60	50	670
7	70	≤5	
8	100	65	?
9	160	50	
10	200	100	30
11	220	30	
12	350	45	8
13	360	25	600
14	390	90	
15	450	80	40
16	500	100	
17	690	120	
18	730	175	≤30
19	900	330	?
20	1000	670	550
21	1100	250	110
22	1200	400	
23	1700	370	
24	1350	470	
25	1500	650	150
26	2000	120	?
27	2500	380	50
28	2800	80	
29	3300	560	100
30	4100	700	160

Most frequently, however, concentrations corresponded to 15–50% of that of BADGE, with the BADGE.2HCl being low. In fact, if BADGE is added as a stabilizer for safe removal of the hydrochloric acid, there must be a certain excess because the amount of hydrochloric acid liberated is not accurately known and evaporation of BADGE during the possibly several treatments renders the residual BADGE concentration somewhat uncertain.

In samples Nr. 1, 2, 4, 5, 6 and 13, the concentrations of BADGE.HCl and BADGE.2HCl far exceeded that of BADGE. Concentrations of BADGE.2HCl reached as high as 2.7 mg/kg. The strong prevalence of BADGE.2HCl shows that almost all the epoxy groups available were consumed. It suggests that either an

insufficient amount of BADGE had been added to the coating or that curing occurred at an excessively high temperature or during too long a period. The internal coating of the lid was, in fact, brownish, indicating some degradation of the polymer. As an alternative, the producer might have attempted to remove BADGE by hard heat treatment, not being aware that BADGE was converted to BADGE.2HCl instead of being evaporated as he might have expected. Figure 4 shows the LC-FD chromatogram of sample nr. 4 in table 2.

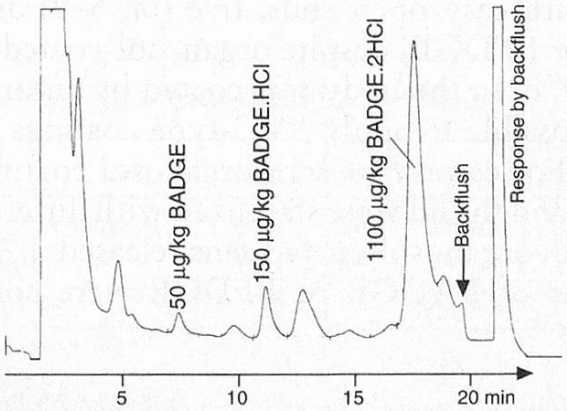

Fig. 4. Analysis of a (diluted) extract from canned mackerels in oil with large concentrations of chlorohydroxy derivatives of BADGE

Table 3. Concentrations of BADGE, BFDGE and their chlorohydroxy compounds in the foods and presence of chlorine in the coating of the can. Type of can: 2p, 3p, two or three piece can; ea, easy open lid

	Type of can	Concentrations in the food (µg/kg)					Chlorine in the coating	
		BADGE	HCl	2HCl	BFDGE	HCl	lid	body
1	3p	< 20			< 50		–	–
2	2p	< 20			< 50		–	–
3	2p	20			< 50		–	–
4	2p	20			300	100	–	+
5	3p ea	< 20			< 50		–	–
6	2p ea	< 20			< 50		+	–
7	2p ea	< 20			< 50		+	–
8	2p ea	< 20			< 50		+	–
9	2p ea	< 20			< 50		+	+
10	2p ea	130	85		< 50		+	+
11	2p ea	450	80	40	< 50		+	–
12	2p ea	3300	560	100	< 50		+	–
13	2p ea	1500	650	150	< 50		+	–
14	2p ea	1200	400		< 50		+	+
15	2p ea	4100	700	160	< 50		+	+
16	2p ea	500	100		1350	450	+	+

Table 3 confirms that organosol (PVC) coatings are the principal source of BADGE, BFDGE, and their chlorohydroxy compounds. Concentrations found in the foods are related to the presence of chlorine in the coating of the can as determined by the flame (Beilstein) method. Samples 1–4 were conventional cans, whereas the others had easy open lids. As shown previously, cans without easy open lids hardly ever released massive amounts of BADGE. Sample 4 was in a deep-drawn 2-piece can, the body of which was coated by an organosol stabilized by BFDGE or novolac.

Among the cans with easy open ends, five (nr. 5–9) did not release relevant amounts of BADGE or BFDGE, despite organosol-coated ends on four of them. Of the can of sample 9, even the body was coated by an organosol. This suggests that it is technically possible to apply PVC-type coatings virtually not releasing BADGE or BFDGE. For can nr. 16 with organosol coatings on both parts, it is assumed that the body and the lid were stabilized with different epoxy compounds.

In conclusion, not all organosol-coated cans released BADGE or BFDGE, but all high concentrations of BADGE or BFDGE were correlated with coatings containing chlorine.

Oligomers of BADGE

Since no standards of BADGE oligomers were available for identifying peaks, a Bisphenol-A-epoxy resin with an epoxy equivalent of 500–525 (Araldit GT 7071) was analyzed by RPLC-MS. LC-UV (235 nm) chromatograms are shown in figure 5. Ionization was possible up to the tetramer. Of the dimers, the glycidoxy-glycidoxy-terminal and a small amount of the phenol-glycidoxy-terminal compound were found. The trimer was far more abundant than the dimer and the tetramer, presumably because it primarily consisted of the non-linear compound formed by addition of BADGE to the alcohol group resulting from dimerization

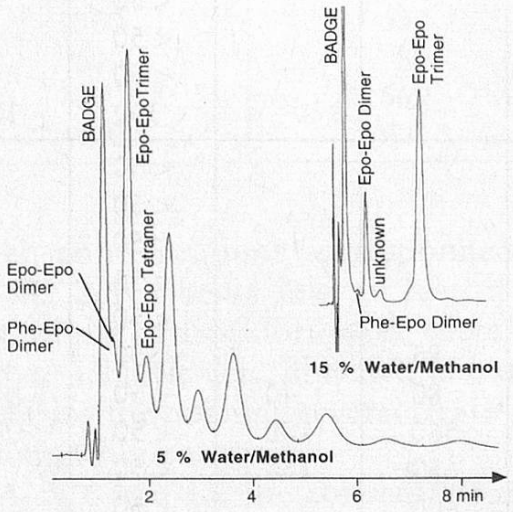

Fig. 5. LC-UV (235 nm) chromatograms of an epoxy resin consisting of low molecular weight oligomers of BADGE. The early part of the chromatogram is better resolved in the upper right corner

(fig. 1). The large peak eluted after the tetramer is likely to represent the pentamer, which could again have consisted of a trimer with two BADGE molecules reacted with the OH-groups. The subsequent peaks probably belong to the oligomers composed of 6–11 BADGE units.

The mass spectra from the LC-MS analysis of BADGE oligomers are summarized in table 4. The most abundant signals represent ions formed either by protonation (M+1) or cationization (ammonium adducts M+18). Loss of water from the pseudomolecular ions (M+1, M+18) also results in signals with relatively high intensities.

Table 4. Key ions of the oligomers identified by LC-MS

Compound	MW	Key ions
Phenol-glycidoxy-terminal dimer	568	569 (100%), 391 (50), 586 (45)
Glycidoxy-glycidoxy dimer	624	642 (100%), 475 (40), 625 (35), 607 (20)
Glycidoxy-glycidoxy trimer	908	926 (100%), 909 (70), 891 (20)

Figure 6 shows the GC-MS(EI) spectra of the two dimers. They were obtained from the Araldit GT 7071 used for the LC-MS identifications. The GC-MS chromatogram is shown at the upper right. The small size of the peaks compared to BADGE indicates that only a minor proportion of the material reached the MS. The phenol-glycidoxy-terminal dimer formed a peak almost as large as the glyci-

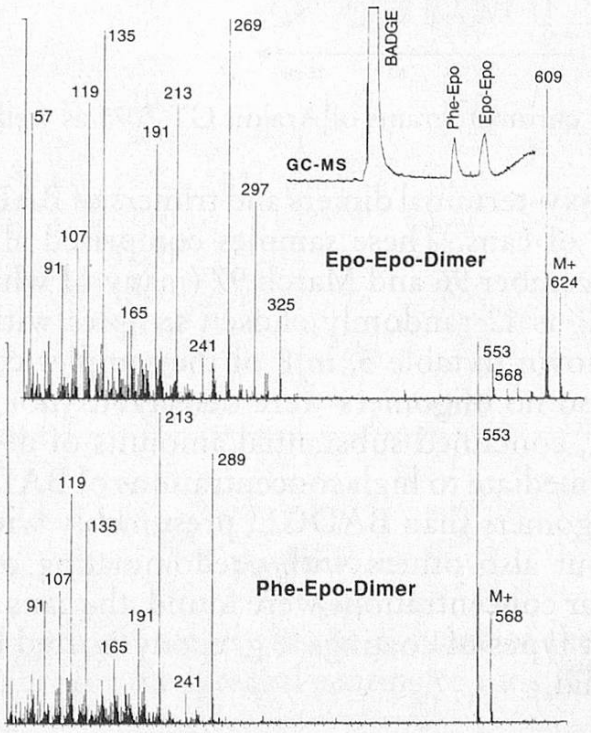

Fig. 6. MS(EI) spectra of the phenol-glycidoxy-terminal dimer (Phe-Epo-Dimer) and the glycidoxy-glycidoxy dimer (Epo-Epo-Dimer), with the gas chromatogram at the top right

doxy-glycidoxy dimer, although it was present in the sample at a far lower concentration. This indicates that reactivity of the epoxy group caused the loss in the GC column (despite of the extremely thin film of the stationary phase).

Figure 7 shows NPLC-FD chromatograms of Araldit GT 7071, as well as of two food extracts. In sample 1, tuna in olive oil, nr. 34 in table 4, 730 µg of BADGE were accompanied by 1000 µg/kg of the glycidoxy-glycidoxy dimer and 70 µg/kg of the trimer. In sample 2, sardines in olive oil, nr. 28 in table 4, 170 µg/kg of BADGE came along with 215 and 230 µg/kg of the dimer and trimer, respectively.

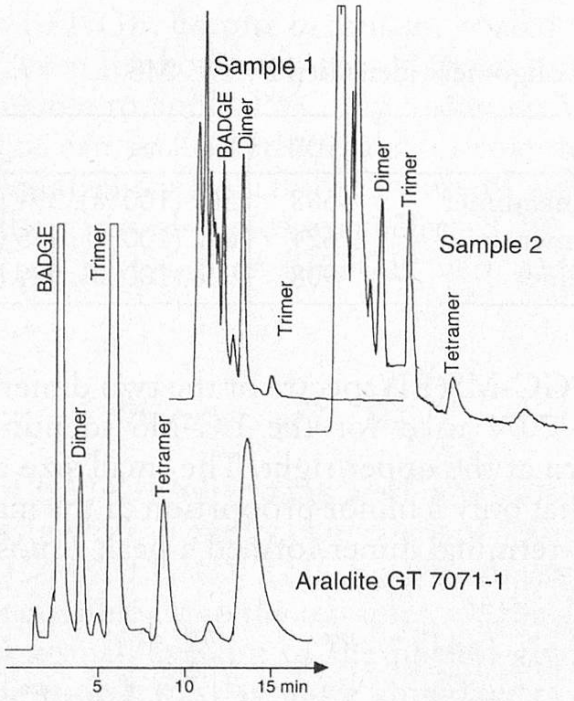

Fig. 7. NPLC-FD chromatograms of Araldit GT 7071 as well sa of food extracts

Glycidoxy-glycidoxy-terminal dimers and trimers of BADGE were determined in 39 whole contents of cans. These samples comprised all containing BADGE analyzed between December 96 and March 97 (many of which were not from the Swiss market), as well as 12 randomly chosen samples with BADGE below the detection limit. As shown in table 5, in 8 of the samples containing less than 20 µg/kg of BADGE, also no oligomers were detectable (nor BFDGE or NOGE). Four others, however, contained substantial amounts of di- and trimers. Among the samples with intermediate to high concentrations of BADGE, there were those containing far less oligomers than BADGE, presumably with BADGE applied as organosol additive, but also others with predominating oligomers from epoxy coatings. Where similar concentrations were found, the cans could have been made of parts with different types of coatings, e.g. epoxy-coated body with an organosol-coated easy open lid.

Table 5. Concentrations (µg/kg) of BADGE as well as its glycidoxy-glycidoxy-terminal dimer and trimer in whole content of cans

Sample	BADGE	Dimer	Trimer
1–8	< 20	< 5	< 5
9	< 20	35	20
10	< 20	40	350
11	< 20	100	< 20
12	< 20	200	30
13	20	20	25
14	20	30	10
15	20	30	< 5
16	20	310	100
17	20	380	< 20
18	30	50	100
19	≤ 40	100	70
20	40	10	10
21	50	55	< 20
22	70	100	90
23	80	320	400
24	80	20	55
25	80	800	500
26	80	1600	1800
27	160	< 5	< 5
28	170	215	230
29	200	250	280
30	220	540	500
31	390	150	< 20
32	400	70	40
33	450	315	40
34	730	1000	70
35	1200	600	20
36	1500	680	80
37	1700	500	≤ 100
38	3300	700	120
39	4500	4200	1300

Conclusions

The above results were of interest in the context of the discussion about the acceptability of polymers for the internal coating of cans. The following conclusions seemed important.

Contamination with BADGE is technically avoidable

After June 1996, 81% of the cans on the Swiss market conformed with the legal limit, i.e. released less than 20 µg/kg BADGE to the food. 93% released less than the 100 µg/kg, above which products were taken from the market. This result can be further improved because a substantial proportion of the rejected products was from the same shop, which did not proceed with sufficient caution. Some other samples had not been recognized as critical previously.

This shows that the full range of products can be offered in cans virtually free of BADGE. Production of canned foods containing less than 20 µg/kg of BADGE is technically feasible. If a restrictive law enables to offer to the consumer products virtually free of BADGE, such measures should be welcomed.

Chlorohydroxy compounds

BADGE used for stabilizing organosols (which is the major source of BADGE in foods) is accompanied by chlorohydroxy compounds (BADGE.HCl and BADGE.2HCl). Their concentrations usually correspond to 15–50% of that of BADGE, but in some samples they far exceed it, reaching up to 2.7 mg/kg. Little is known about their toxicology, nor are they listed under the substances tolerated in foods. They have some similarity to chloropropanediols found in protein hydrolysates used for sauces and soups, which have been shown to be mutagenic in bacterial assays (9). Until further evidence is available, in Switzerland the same limits are applied as for BADGE.

Oligomers

Di- and trimers of BADGE are well extracted from the coating of the can into oily food, whereas higher molecular weight oligomers have hardly been detected. Their concentrations reached several mg/kg also in foods containing less than 100 µg/kg of BADGE. Toxicology of these compounds for oral uptake has not been studied to a sufficient extent. Di- and trimers have molecular weights of 624 and 908 Dalton, respectively, which does not rule out transfer through membranes. Hence, they cannot *a priori* be classified among the physiologically inactive compounds. As the terminal epoxy groups are the same as in BADGE, the di- and trimers may need to be classified as BADGE.

Addendum

For BADGE.2HCl, synthesized form BADGE and hydrochloric acid by Fluka, Buchs, Switzerland, NMR indicated that the structure was Bisphenol-A-bis-(3-chloro-2-hydroxypropyl) ether, i. e. that the chloro and hydroxy groups were exchanged compared to the structure shown in our figure 1. (Courtesy of Dr. B. Schönenberger)

Summary

In canned oil- or fat-containing foods, BADGE, the reaction products with hydrochloric acid (chlorohydroxy derivatives of BADGE) and oligomers were determined by liquid chromatographic techniques with fluorescence detection as well as RPLC-MS and GC-MS.

After having taken measures to reduce BADGE contents, BADGE concentrations in 81% of 242 samples from the Swiss market were below 20 µg/kg. This shows that it is technically feasible to produce cans releasing virtually no BADGE. Chlorohydroxy compounds in the preserved foods mostly corresponded to 15–40% of the BADGE concentration, but in some samples, small concentrations of BADGE came along with up to 2700 µg/kg of BADGE.2HCl. Concentrations of glycidoxy-glycidoxy-terminal dimers and trimers of BADGE ranged from below the detection limit of 5 µg/kg up to 5500 µg/kg food. Hence additional compounds must be considered when evaluating polymers suitable for the internal coating of cans.

Zusammenfassung

In öl- oder fetthaltigen Lebensmitteln aus Konservendosen wurden BADGE, seine Reaktionsprodukte mit Chlorwasserstoff (Chlorhydroxyverbindungen von BADGE) und Oligomere mit flüssigchromatographischen Techniken und Fluoreszenzdetektion, sowie RPLC-MS und GC-MS analysiert.

Nach dem Ergreifen von Massnahmen zur Verringerung der BADGE-Gehalte wurden in 81% von 242 Proben des Schweizer Markts BADGE-Konzentrationen von unter 20 µg/kg gefunden. Das zeigt, dass es technisch möglich ist, Konservendosen praktisch ohne BADGE-Abgabe herzustellen. Die im Lebensmittel gemessenen Konzentrationen der Chlorhydroxyverbindungen entsprachen normalerweise 15–50% derjenigen von BADGE. In einigen Proben, meistens mit geringen BADGE-Gehalten, befand sich allerdings bis zu 2700 µg/kg BADGE.2HCl. Die Konzentrationen der glycidoxy-glycidoxy-terminalen Dimere und Trimere von BADGE reichten von der Nachweisgrenze (5 µg/kg) bis zu 5500 µg/kg. Für die Beurteilung von Kunststoffen zur Innenlackierung von Konservendosen müssen also weitere Substanzen in Betracht gezogen werden.

Résumé

Dans des conserves en boîtes contenant d'huile ou du gras comestible ont été mesurés BADGE, ses produits de réaction avec l'acide chlorhydrique (composés chlorohydroxy) et des oligomères, utilisant des techniques de chromatographie en phase liquide avec détection fluorimétrique, RPLC-MS et GC-MS.

Après avoir pris des mesures pour diminuer les teneurs de BADGE, les concentrations de BADGE était en dessous de 20 µg/kg dans 81% de 242 échantillons du marché suisse. Cela démontre qu'il est techniquement possible de produire des conserves en boîtes practiquement sans BADGE. Les concentrations des composés chlorhydrique mesurées dans les aliments normalement correspondaient à 15–50% de ceux de BADGE. Mais dans quelques échantillons, surtout avec peu de BADGE, on a trouvé jusqu'à 2700 µg/kg de BADGE.2HCl. Les concentrations des dimères et trimères glycidoxy-glycidoxy-terminales étaient dans un

domaine entre non-détectable (5 µg/kg) et 5500 µg/kg. Pour l'évaluation des polymères comme revêtement intérieur des boîtes it faut donc considérer d'autres composés.

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