Table I. Recoveries of Emodin and Standard Deviations

matrix	ppm added	% recovery	SD
corn	0.5	81.8	9.1
	1.0	86.1	5.2
	2.0	86.2	2.3
oats	0.5	85.6	12.4
	1.0	80.7	16.8
	2.0	80.1	27.6
mixed feed	0.5	102.6	7.2
	1.0	94.0	10.0

0.2–0.3 ppm of emodin. The chief limitation is not detector sensitivity but the amount of background interference present, since the cleanup procedure is minimal. If necessary, some background interference may be reduced by partitioning the sample extract in about 2 mL of chloroform or methylene chloride with an equal volume of 1 M NaOH. The aqueous alkaline fraction is then acidified with dilute HCl, and the emodin may then be back-extracted into chloroform or methylene chloride and concentrated.

RESULTS AND DISCUSSION

Recoveries of emodin were calculated by adding known amounts of emodin to nonmolded corn, oats, and a ground swine feed. After extraction, quantification was performed by using HPLC. Three to four replicates of each concentration were determined in each sample matrix. The recoveries and standard deviations are given in Table I. Recoveries were usually fairly consistent, with the exception of oats, which gave erratic results at the higher concentrations for unknown reasons.

While HPLC determination was somewhat more sensitive than thin-layer chromatography under these conditions, the latter is probably more selective. The characteristic color reactions of emodin are important for confirmation, particularly in complex samples.

Since a number of mycotoxin analytical methods based on acetonitrile extraction have been developed (Pons et al., 1973; Stoloff et al., 1971), it would seem possible to include emodin in a multi-mycotoxin screening procedure. Other hydroxyanthraquinones might be expected to behave similarly, though emodin appears to be the most widespread and is also commerically available as a standard.

Registry No. Emodin, 518-82-1.

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Photodecomposition of a Commercial Polybrominated Biphenyl Fire Retardant: High-Resolution Gas Chromatographic Analysis

The photolytic degradation of fireMaster BP-6, a commerical polybrominated biphenyl (PBB) fire retardant, was investigated by using high-resolution, isomer-specific, fused silica capillary gas chromatography. During photolysis the more highly brominated PBB congeners diminished in concentration, while those possessing three, four, or five bromines per biphenyl increased, consistent with a reductive dehalogenation pathway. Unlike the photolysis of single cogeners, a preferential loss of ortho bromines was not found. Those PBBs which have been identified as the most toxic (i.e., those containing no ortho bromines) did, nevertheless, increase approximately 4-fold, and this increase may explain the enhanced toxicity of photolyzed fireMaster BP-6.

Studies on the photolytic degradation of isomeric polyhalogenated biphenyls have revealed the following: (1) at environmentally significant wavelengths (>290 nm) polyhalogenated biphenyls undergo a stepwise reductive dehalogenation (Safe and Hutzinger, 1971; Ruzo et al., 1972), (2) polybrominated biphenyls (PBBs) are in general more reactive than the polychlorinated biphenyls (Ruzo and Zabik, 1975), and (3) ortho halogens cleave first and at a faster rate when para halogens are present on the same ring (Ruzo et al., 1975; 1976; Bunce et al., 1975).

Recent work in several laboratories indicates that PCBs and PBBs possessing one or no ortho halogens, and two para halogens, are quite potent in causing numerous biologic effects and are the most toxic polyhalogenated biphenyl congeners (producing a wasting syndrome, lymphoid involution and immunosuppression, tetratogenicity and embryotoxicity, and porphyria; Parkinson and Safe, 1981; Robertson et al., 1982; Render et al., 1982; Kawanishi et al., 1981; Marks et al., 1981; Silkworth and Grabstein, 1982). It is reasonable then to speculate that the preferential loss of ortho halogens during photolysis should lead to polyhalogenated biphenyls which are more toxic. For example, PBB congener **153** [numbering system adopted from Ballschmiter and Zell (1980)], 2,2′,4,4′,5,5′-hexabromobiphenyl, the major component of fireMaster BP-6, would be expected during photolysis to yield 2,3′,4,4′,5-

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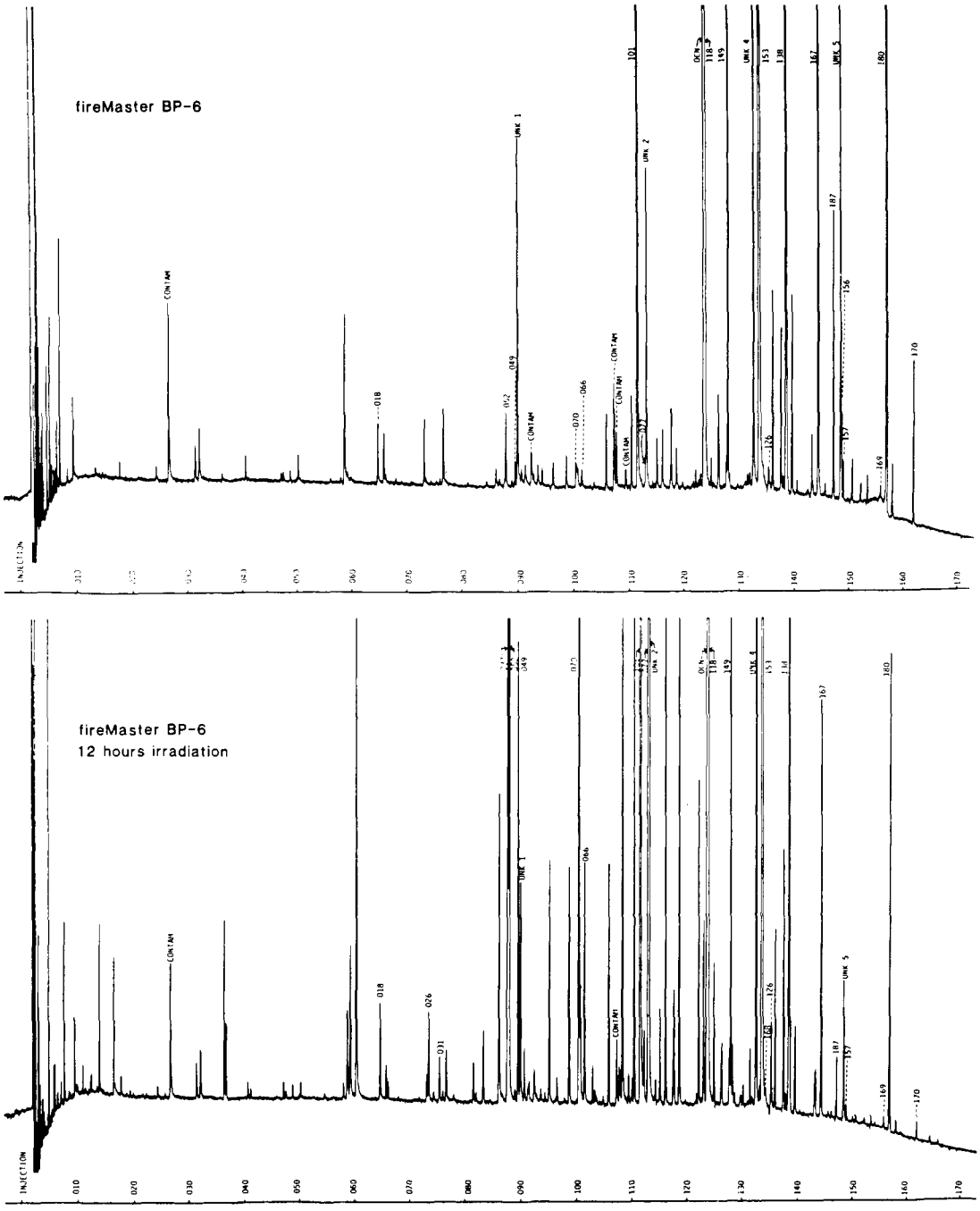

Figure 1. High-resolution fused silica gas chromatogram of fireMaster BP-6, lot 7062, before and after 12 h of irradiation (300 nm) in cyclohexane solution. Note the appearance of earlier eluting photoproducts. The resolution and quantitation of congeneric polybrominated biphenyls and photoproducts are simplified by this analytical method.

pentabromobiphenyl (118) and subsequently 3,3′,4,4′-tetrabromobiphenyl (**077**), both of which possess greatly enhanced biologic and toxic properties (Robertson et al., 1980, 1982). Recent work has in fact confirmed the increased toxicity of photolyzed 2,2′,4,4′,5,5′-hexabromobiphenyl (Patterson et al., 1981) and photolyzed fireMaster BP-6 (Robertson et al., 1981b). In the latter study attempts to identify brominated dibenzofurans, dibenzodioxins, or biphenylenes among the reaction products were unsuccessful.

In the present study the photolytic degradation of fireMaster BP-6 is examined by using high-resolution isomer-specific fused silica capillary gas chromatography.

EXPERIMENTAL SECTION

Chemicals. The congeneric PBBs used as analytical standards in this study were obtained or synthesized as follows: **15**, purchased from Eastman Kodak; **18, 26, 31, 49, 52, 53,** and **70**, synthesized as described (Sundström et al., 1976); **37, 77, 126,** and **169** (Robertson et al., 1982) **66, 101, 138, 153, 157, 167, 168,** and **187** (Robertson et al., 1983); **118** (Robertson et al., 1980); **156** (Robertson et al., 1981a); **149, 170,** and **180** were generously provided by S. D. Aust and co-workers, Michigan State University. FireMaster BP-6, lot 7062, was the gift of Michigan Chemical Corp.

Photolysis. Irradiation of fireMaster BP-6 in cyclohexane (Fisher, spectranalyzed) solution was carried out in a Rayonet photochemical reactor with peak energy output at 300 nm as previously described (Robertson et al., 1981b), and after 2, 5, 8, and 12 h of irradiation, samples were removed for analysis.

Chromatography. High-resolution capillary gas chromatography was performed by using a Varian 3700 gas

Table 1. Changes in Composition of FireMaster BP-6 During Photolysis

No.*	Structure	Relative[a] Retention Time	Relative[b] Response Factor	BP-6 Conc. (ng/ml)	BP-6 %	BP-6:2hrs Conc. (ng/ml)	BP-6:2hrs %	BP-6:5hrs Conc. (ng/ml)	BP-6:5hrs %	BP-6:8hrs Conc. (ng/ml)	BP-6:8hrs %	BP-6:12hrs Conc. (ng/ml)	BP-6:12hrs %
DIBROMOBIPHENYLS													
015	4,4'-	0.4866	0.7711	<0.056[f]	<0.020[f]	<0.046[f]	<0.016[f]	<0.049[f]	<0.018[f]	<0.055[f]	<0.020[f]	<0.054[f]	<0.019[f]
TRIBROMOBIPHENYLS													
018	2,2',5-	0.5226	1.0973	0.141	0.050	0.095	0.034	0.154	0.055	0.191	0.068	0.212	0.076
026	2,3',5-	0.5934	1.1214	0.067	0.024[e]	<0.032[f]	<0.011[f]	0.064	0.023	0.132	0.047	0.278	0.100
031	2,4',5-	0.6095	1.3660	0.042	0.015[e]	<0.027[f]	<0.010[f]	<0.028[f]	<0.010[f]	0.066	0.024	0.110	0.039
037	3,4,4'-	0.7081	0.9378	0.059	0.021[e]	0.267	0.095	1.09	0.389	2.11	0.755	2.64	0.047
TETRABROMOBIPHENYLS													
049	2,2',4,5'-	0.7228	1.0903	0.069	0.025	0.096	0.034	0.297	0.106	0.631	0.226	1.19	0.428
052	2,2',5,5'-	0.7102	1.1850	0.146	0.052	0.251	0.089	0.758	0.270	1.58	0.565	2.78	0.996
053	2,2',5,6'-	0.6622	1.2005	<0.036[f]	<0.013[f]	<0.030[f]	<0.011[f]	<0.032[f]	<0.011[f]	<0.035[f]	<0.013[f]	<0.035[f]	<0.013[f]
066	2,3',4,4'-	0.8202	0.9773	0.080	0.028	0.113	0.040	0.349	0.124	0.578	0.207	0.813	0.292
070	2,3',4',5-	0.8116	1.1527	0.048	0.017	0.447	0.159	1.33	0.474	2.42	0.866	3.54	1.27
077	3,3',4,4'-	0.9134	0.8805	0.447	0.159	1.527	0.544	3.19	1.14	4.01	1.43	3.70	1.33
PENTABROMOBIPHENYLS													
101	2,2',4,5,5'-	0.9018	1.0680	7.55	2.69	11.8	4.19	21.2	7.57	30.2	10.8	34.1	12.3
118	2,3',4,4',5-	1.0019	0.9230	8.25	2.94	9.73	3.47	13.2	4.72	15.0	5.37	13.3	4.79
126	3,3',4,4',5-	1.0939	0.4493	0.222	0.079	0.990	0.353	1.09	0.388	0.812	0.291	0.481	0.172
HEXABROMOBIPHENYLS													
138	2,2',3,4,4',5'-	1.1197	0.4156	34.6	12.3	27.2	9.70	26.3	9.36	24.4	8.73	18.6	6.69
149	2,2',3,4',5',6-	1.0347	0.3960[c]	6.28	2.24	5.22	1.86	5.86	2.09	5.89	2.11	4.72	1.69
153	2,2',4,4',5,5'-	1.0808	1.1373	151.	53.9	109.	39.0	106.	37.8	88.4	31.6	56.9	20.4
156	2,3,3',4,4',5-	1.1727	0.1037	2.75	0.980	1.85	0.660	0.365[f]	<0.130[f]	<0.406[f]	<0.145[f]	<0.403[f]	<0.145[f]
157	2,3,3',4,4',5'-	1.2049	0.0971	1.48	0.526	1.24	0.441	1.01	0.360	0.900	0.322	0.476	0.171
167	2,3',4,4',5,5'-	1.1671	0.3039	22.3	7.95	14.9	5.32	10.8	3.86	7.57	2.71	4.28	1.54
168	2,3',4,4',5',6-	1.0863	0.6120	<0.071[f]	<0.025[f]	<0.058[f]	<0.021[f]	<0.062[f]	<0.022[f]	0.191	0.068	0.230	0.083
169	3,3',4,4',5,5'-	1.2598	0.1021	0.825	0.294	0.858	0.306	0.305	0.109	0.174	0.062	0.132	0.047
HEPTABROMOBIPHENYLS													
170	2,2',3,3',4,4',5-	1.3089	0.7335[d]	0.720	0.256	0.518	0.185	0.283	0.101	0.157	0.056	0.066	0.024
180	2,2',3,4,4',5,5'-	1.2684	0.7335[d]	19.6	6.97	12.7	4.52	8.12	2.89	4.71	1.69	2.15	0.770
187	2,2',3,4',5,5',6-	1.1897	0.7335	1.10	0.392	0.805	0.287	0.681	0.243	0.491	0.176	0.289	0.103
TOTALS				280.8	91.9	280.67	71.3	280.76	72.1	279.48	68.2	278.59	54.2

*Adopted from Ballschmiter and Zell (1980).

[a] OCN = 1.0000

[b] 1 picogram OCN = 1.0000

[c] Calculated from average RRF for all hexabromobiphenyls analyzed.

[d] RRF for isomer 187 used

[e] Numbers obtained from previous work on another column. [f] Not detected. Maximum concentration and percentage in mixture if present is given.

Table II. Compositional Changes of PBBs Possessing Zero and One Ortho Bromines after 2, 5, 8, and 12 Hours of Irradiation

PBBs	fire Master BP-6	after irradiation 2 h	5 h	8 h	12 h
no ortho bromines (37, 77, 126, 169)	0.553	1.30	2.03	2.54	2.50
one ortho bromine (66, 118, 156, 157, 167)	12.4	9.93	9.06	8.61	6.79

chromatograph equipped with a ^{63}Ni electron capture detector. A 50-m fused silica capillary column (0.2-mm i.d.) coated with SE-54 (Hewlett-Packard) was used to separate the congeneric PBBs. The oven temperature was programmed at a rate of 1.0 °C/min from 100 to 280 °C and held at 280 °C until all peaks eluted. The injector and detector temperatures were 270 and 330 °C, respectively. Sample volume, 4.5 μL, was injected by using an automatic sampler with splitting in the injector (10:1 split ratio, vented from 0.75 to 1.75 min). The hydrogen carrier gas was held at a constant pressure of 2.25 kg/cm^2 to give the optimized linear velocity ($\bar{u}$) at 100 °C of 45 cm/s. The advantages of capillary over packed column gas chromatography are discussed elsewhere (Ballschmitter and Zell, 1980; Mullin and Filkins, 1981; Safe et al., 1983).

RESULTS AND DISCUSSION

The synthesis of congeneric PBBs has permitted the identification, and confirmation (Moore and Aust, 1978), of numerous fireMaster BP-6 components (Table I). During photolysis it is apparent that the hexa- and heptabromobiphenyls decrease in concentration while tetra- and pentabromo congeners increase, a process consistent with a reductive dehalogenation pathway (Figure 1).

Previous studies (Ruzo et al., 1976) with individual PBB congeners have shown that congener **153** was the most photoreactive of the individual PBBs tested. The reactivity of **153** was confirmed in this study (Table I). However the prediction that **153** (which composes 54% of fireMaster BP-6) decomposes with a stepwise preferential loss of ortho bromines (i.e., **153** → **118** → **077**) is not supported. There is not a quantitative relationship between the disappearance of **153** and the increase in **118**. Note also that congener **101**, which may form from **153** by the loss of a para bromine, increases more rapidly than **118**. Furthermore, there is not a general increase in those PBBs possessing one ortho bromine substituent (Table II).

The results suggest that the reductive debromination of ortho substituents is not the predominant photolytic degradation pathway for fireMaster BP-6. However, the photoproducts do contain increased concentrations of the most toxic PBBs (i.e., those congeners possessing no ortho bromines). These coplanar congeners, **37**, **77**, **126**, and **169**, increase from a total 0.553% of fireMaster BP-6 to a maximum of 2.54% after 8 h of irradiation. The increase in the concentration of these toxic PBBs may be sufficient to account for the enhanced toxicity of photolyzed fireMaster BP-6.

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Registry No. **18**, 59080-34-1; **26**, 59080-35-2; **31**, 59080-36-3; **37**, 6683-35-8; **49**, 60044-24-8; **52**, 59080-37-4; **53**, 60044-25-9; **66**, 84303-45-7; **70**, 59080-38-5; **77**, 77102-82-0; **101**, 67888-96-4; **118**, 67888-97-5; **126**, 84303-46-8; **138**, 67888-98-6; **149**, 69278-59-7; **153**, 59080-40-9; **156**, 77607-09-1; **157**, 84303-47-9; **167**, 67888-99-7; **168**, 84303-48-0; **169**, 60044-26-0; **170**, 69278-60-0; **180**, 67733-52-2; **187**, 84303-49-1; fireMaster BP-6, 59536-65-1.

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