contribute to the flavor of MBM and pet foods containing this ingredient.

Lipids appear to be the primary source of flavor in MBM. This was also found to be the case in this laboratory's previous study of poultry byproduct meal (PBPM). The majority of compounds isolated in this study and the Greenberg (1981) PBPM study have been identified in literature reports to be products of lipid (specific fatty acid) oxidation reactions. This is further supported by the fact that MBM and PBPM have a high fat content (usually greater than 14%) which, when rendered, can accelerate autoxidation. A literature report has also demonstrated storage instability of fatty acids such as linoleic acid in PBPM.

Future work with MBM will involve attempting to identify more volatile flavor components with the aid of chemical ionization mass spectrometry. Other areas of future study will include the synthesis of authentic standards for compounds tentatively identified, such as 3,5-undecadien-2-one.

ACKNOWLEDGMENT

The author is grateful to Margie Seastone for her assistance in the flavor isolation.

Supplementary Material Available: A listing of the flavor volatiles in Table I and their mass spectra (m/e and relative abundance) values (4 pages). Ordering information is given on any current masthead page.

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Acid-Catalyzed Alteration of 2,3-Dihydro-2,2-dimethyl-7-benzofuranyl (Di-*n*-butylaminosulfenyl)methylcarbamate via Nitrogen–Sulfur Bond Cleavage. 2. Separation and Identification of Polysulfide Derivatives

Noriharu Umetsu, Takaaki Nishioka, and Tetsuo R. Fukuto*

2,3-Dihydro-2,2-dimethyl-7-benzofuranyl (di-*n*-butylaminosulfenyl)methylcarbamate (DBSC) dissolved in dichloromethane–acetic acid (9:1) was converted into a mixture of polysulfide derivatives of DBSC and biscarbofuran *N,N'*-disulfide along with other alteration products. Silica gel KC_{18} reversed-phase thin-layer chromatography provided a simple and convenient method for separating the individual components in the polysulfide mixture. The polysulfide of DBSC was separated into at least eight components, and the structures of the four major components were determined by NMR and MS analyses of purified products. The polysulfide of biscarbofuran *N,N'*-disulfide was separated into at least seven components, and the structures of the four major components were determined. Quantitative determination of the breakdown of DBSC and formation of the individual alteration products, including polysulfide derivatives, was conducted with [*carbonyl*-^{14}C]DBSC. Most of the products showed good insecticidal activity against the housefly, and all of them were significantly less toxic to the white mouse than the parent methylcarbamate carbofuran.

The previous paper in this series (Umetsu et al., 1981) described the different products which were obtained when 2,3-dihydro-2,2-dimethyl-7-benzofuranyl (di-*n*-butylaminosulfenyl)methylcarbamate (DBSC or Marshal) was allowed to stand in the 9:1 dichloromethane–acetic acid solvent at room temperature. The principal alteration products were carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate), di-*n*-butylamine, and a mixture of the polysulfide derivatives of DBSC and biscarbofuran *N,N'*-disulfide. Although spectroscopic evidence was provided that demonstrated the presence of a number of these polysulfide derivatives (n = 2 to about 6), separation of the individual components by silica gel TLC was not accomplished. CFS_nNBu_2 (n = 2–6) and CFS_nCF (n = 3–6) gave single spots on silica gel plates after

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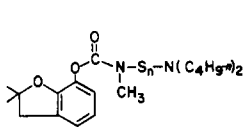
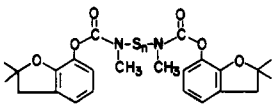


(DBSC polysulfide or CFS_nNBu_2, n = 2, 3, ..., n)



(biscarbofuran N,N'-polysulfide or CFS_nCF, n = 2, 3, ..., n)

development with a wide variety of solvent systems.

In continuing studies, very good separation of each component of the two polysulfide derivatives was achieved by use of KC_{18} reversed-phase TLC. This report describes the separation and identification of the individual components in the polysulfide mixture after allowing DBSC to stand in the 9:1 dichloromethane–acetic acid solvent. Quantitative determination of the breakdown of DBSC and formation of the individual alteration products was carried out by use of [*carbonyl*-^{14}C]DBSC. Most of the products showed favorable toxicological properties.

MATERIALS AND METHODS

Chemicals. [*carbonyl*-^{14}C]DBSC (sp act. 25.20 mCi/mmol; Umetsu et al., 1979), biscarbofuran N,N'-sulfide (CFSCF), biscarbofuran N,N'-disulfide (CFS_2CF), and bis(di-*n*-butylamino) N,N'-polysulfide ($Bu_2NS_nNBu_2$) were available from previous studies (Umetsu et al., 1980, 1981). Other chemicals were analytical reagent grade and redistilled solvents were used.

Alteration of DBSC in Dichloromethane–Acetic Acid. In general, the conversion of DBSC into the polysulfide derivatives, CFS_nNBu_2 and CFS_nCF, was carried out as previously described (Umetsu et al., 1981). Briefly, 2.0 g of DBSC was dissolved in 40 mL of dichloromethane–acetic acid (9:1) and stirred for 72 h at 23 °C. After the reaction mixture was washed with water and the dichloromethane phase was dried over anhydrous sodium sulfate, removal of the solvent gave a gummy residue which was subjected to repeated silica gel TLC, using hexane–ether (7:3) as the developing solvent. The yield of CFS_nNBu_2 was 235 mg and that of CFS_nCF ($n \geq 3$) was 157 mg.

Separation of the individual components in CFS_nNBu_2 and CFS_nCF was achieved by use of $KC_{18}F$ reversed-phase TLC plates (0.2-mm thickness; Whatman, Inc.) and acetonitrile or 9:1 acetonitrile–water as the developing solvent. Location of each component on the plate was by ultraviolet detection. The same plates were used for the isolation of larger quantities required for spectroscopic analysis and toxicological evaluation.

[*carbonyl*-^{14}C]DBSC was used to determine the effect of time on the alteration of DBSC. A mixture of 20 mg of purified DBSC and 2.49 μCi (37.7 μg) of [*carbonyl*-^{14}C]DBSC in 200 μL of dichloromethane was added to a 200 μL of dichloromethane–acetic acid (4:1) mixture. Duplicate samples (2 μL) were removed at different time intervals, and the contents were examined by two-dimensional TLC using $KC_{18}F$ reversed-phase plates and acetonitrile (first) and 9:1 acetonitrile–water (second). The plates were allowed to stand in the developing solvent for an additional 20–25 min after the solvent front had reached the top of the plate. This practice resulted in better separation of the spots.

Simultaneous samples of 40 μL were taken at each time interval for preparative TLC using silica gel plates (10 × 20 cm; 0.25-mm thickness) and hexane–ether (7:3) as the developing solvent. The zones containing CFS_nNBu_2 and CFS_nCF were each extracted with ether, the extract was concentrated, and the residue was subjected to $KC_{18}F$ TLC using acetonitrile (for CFS_nNBu_2) and 9:1 acetonitrile–water (for CFS_nCF) as solvents.

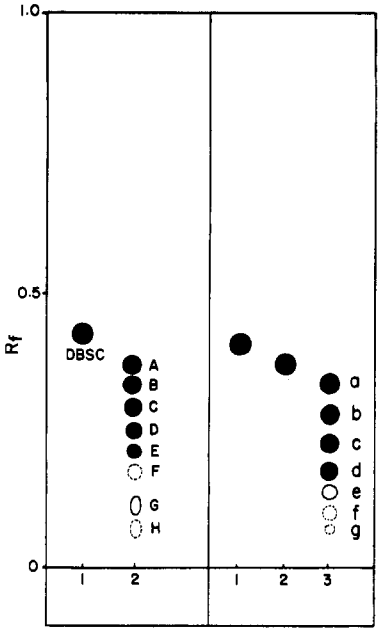


Figure 1. KC_{18} reversed-phase thin-layer chromatograms of CFS_nNBu_2 (left) and CFS_nCF (right). (Left) 1, DBSC ($CFSNBu_2$); 2, CFS_nNBu_2 (n = 2 + 3 + ... + n); solvent = acetonitrile. (Right) 1, CFSCF; 2, CFS_2CF; 3, CFS_nCF (n = 3 + 4 + ... + n); solvent = acetonitrile–water (4:1) (two migrations).

Analyses. NMR and mass spectral analyses were carried out as previously described (Umetsu et al., 1981). Localization of radioactive spots on TLC plates and quantitation of radioactivity were by methods also previously described (Umetsu et al., 1981).

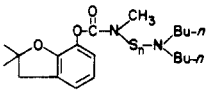
Toxicological Evaluation. The toxicity of the individual compounds to houseflies was determined with the susceptible NAIDM strain according to March and Metcalf (1949). Mammalian toxicity of the products was determined by oral administration to Swiss white mice (Simonsen Laboratories, Gilroy, CA) using corn oil and propylene glycol as the carrier. Compounds which were not soluble were suspended in the carrier.

RESULTS

Reversed-Phase TLC of Alteration Products. CFS_nNBu_2 ($n \geq 2$) and CFS_nCF ($n \geq 3$) which gave distinct single spots by silica gel TLC with a wide variety of developing solvents were separated into a number of components by reversed-phase TLC (see Figure 1). CFS_nNBu_2 was separated into at least eight components (A–H) and CFS_nCF into at least seven components (a–g). Compounds A–E proved to be CFS_nNBu_2 analogues with n = 2–6 and compounds a–d were CFS_nCF analogues with n = 3–6 (Identification of CFS_nNBu_2 Components). The R_f values of G and H corresponded to the bis(di-*n*-butylamino) polysulfides which may have been formed during the workup procedure. Figure 1 reveals that CFSCF and CFS_2CF also were separable from CFS_nCF by reverse-phase TLC.

Identification of CFS_nNBu_2 Components. Preparative KC_{18} reversed-phase TLC of 70 mg of CFS_nNBu_2 using acetonitrile as the developing solvent yielded four pure products, i.e., 36 mg of A (R_f 0.49–0.56), 13 mg of B (R_f 0.42–0.47), 7 mg of C (R_f 0.35–0.40), and 3.5 mg of D (R_f 0.30–0.34). Except for the N-CH_3 protons, the NMR spectra of A–D were identical with the spectrum of the polysulfide mixture CFS_nNBu_2. Earlier work (Umetsu et al., 1981) showed a multiplet for the N-CH_3 protons of CFS_nNBu_2 at δ 3.3–3.42 (Me_4Si; $CDCl_3$). In contrast, the N-CH_3 absorptions for A–D were distinct singlets in the

Table I. Summary on Structure and Chemical Properties of Each Polysulfide Derivative of DBSC



compound	R_f value for TLC system[a] I	II	III	structure	abbreviation	MS, molecular ion peak, m/e	NMR, δ N-CH_3	N-$(CH_2)_2$
DBSC	0.43	0.43	0.61	$n = 1$		380	3.35	3.17
CFS_nNBu_2	0.49			$n = 2 + 3 + \ldots + n$	CFS_nNBu_2		3.33-3.42	2.95
A	0.49	0.37	0.54	$n = 2$	CFS_2NBu_2	412	3.35	2.95
B	0.49	0.33	0.49	$n = 3$	CFS_3NBu_2	444	3.38	2.95
C	0.49	0.30	0.43	$n = 4$	CFS_4NBu_2	476	3.41	2.95
D	0.49	0.26	0.37	$n = 5$	CFS_5NBu_2	508	3.42	2.95
E	0.49	0.21	0.32	$n = 6$[b]	CFS_6NBu_2[b]			
F	0.49	0.11	0.17	$n = 7$[b]	CFS_7NBu_2[b]			

[a] TLC and solvent system: (I) silica gel TLC, hexane–ether (7:3); (II) reversed-phase silica gel TLC, acetonitrile; (III) reversed-phase silica gel TLC, acetonitrile (two migrations). [b] Tentatively assigned.

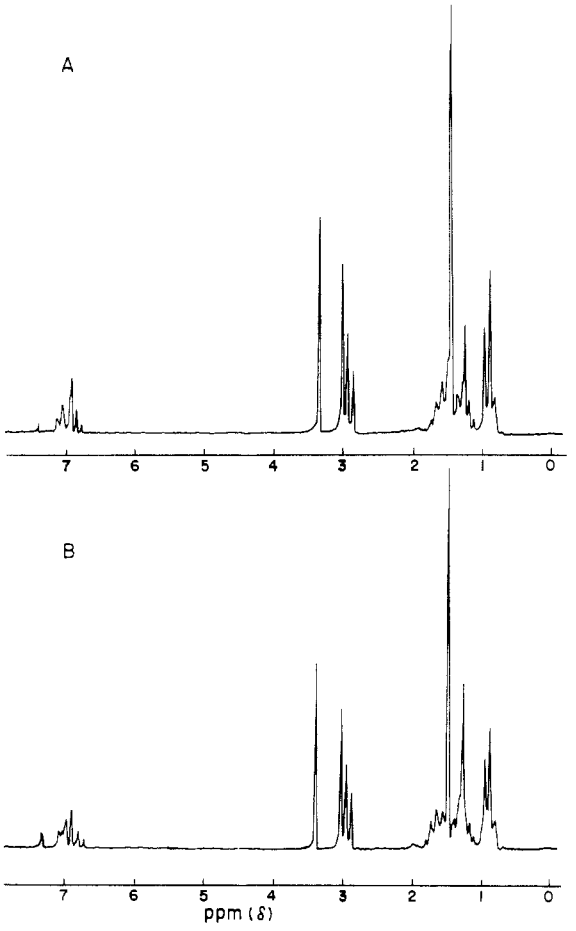


Figure 2. NMR spectra of products A (above) and B (below).

3.3–3.4-ppm region, indicating each to be a single compound (see Figure 2). The mass spectrum of each compound indicated a molecular ion peak of 412 for A, 444 for B, 476 for C, and 508 for D. These molecular ion peaks were all observed in the mass spectrum of the polysulfide mixture CFS_nNBu_2 (Figure 3). From NMR and mass spectral data the following structural assignments were made: A, CFS_2NBu_2; B, CFS_3NBu_2; C, CFS_4NBu_2; D, CFS_5NBu_2.

Components E and F were isolated in trace amounts and appeared to be contaminated with material from the reversed-phase TLC plates. Definitive NMR or mass spectral data for these components could not be obtained. However, based on reversed-phase TLC properties of these compounds, E and F are tentatively considered to be

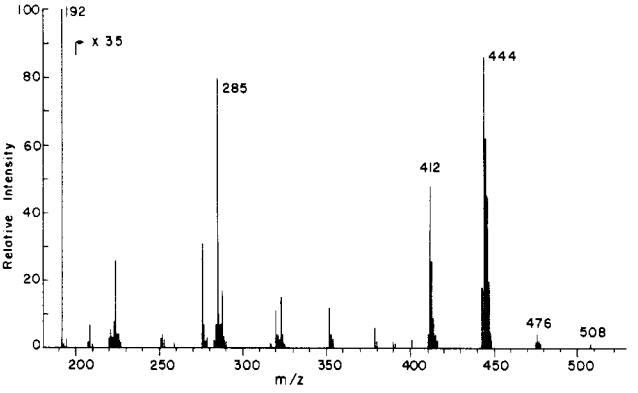


Figure 3. Mass spectrum of CFS_nNBu_2 ($n = 2 + 3 + \ldots + n$).

CFS_6NBu_2 and CFS_7NBu_2, respectively.

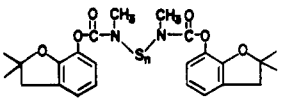
Data summarizing the TLC and spectroscopic properties of the polysulfide derivatives of DBSC are presented in Table I.

Identification of CFS_nCF Components. Preparative reversed-phase TLC of 78 mg of CFS_nCF gave at least five different products: 36 mg of a (R_f 0.46–0.53), 16 mg of b (R_f 0.37–0.43), 2.3 mg of c (R_f 0.31–0.36), 1 mg of d (R_f 0.24–0.28), and 2.0 mg of e (R_f 0.09–0.22). Analytical reversed-phase TLC of each of these products showed that a–d were single-component products. As in the case of the individual components of CFS_nNBu_2, the NMR spectra of a–d were identical with the spectrum of the polysulfide mixture CFS_nCF, except for the signals for the N-CH_3 protons. In contrast to the multiplet observed previously for the N-CH_3 protons (δ 3.37–3.44) for CFS_nCF (Umetsu et al., 1981), distinct singlets in the same region were observed for a–d (Figure 4). Reversed-phase TLC and NMR spectra therefore indicated a–d to be single-component products. The mass spectrum of each compound showed a molecular ion peak of 536 for a, 568 for b, 600 for c, and 632 for d. From TLC and NMR and mass spectral data, a was assigned the structure CFS_3CF, b was assigned CFS_4-CF, c was assigned CFS_5CF, and d was assigned CFS_6-CF. Components e–g were small amounts and were also contaminated with material from the TLC plates, and a definitive NMR spectrum could not be obtained. As in the case of E and F, e, f, and g are believed to be CFS_7CF, CFS_8CF, and CFS_9CF on the basis of their TLC behavior.

Data summarizing the TLC and spectroscopic properties of CFS_nCF and its components are given in Table II.

Kinetic and Product Analysis of the Acid-Catalyzed Alteration of [*carbonyl*-^{14}C]DBSC. [*carbonyl*-^{14}C]DBSC was allowed to stand in 9:1 dichloromethane–

Table II. Summary on Structure and Chemical Properties of Polysulfide Derivatives of Biscarbofuran Disulfide



compound	R_f value for TLC system[a] I	II	structure	abbreviation	MS, molecular ion peak, m/e	NMR, δ N-CH_3
DBSC	0.43	0.23			380	3.35
CFS_2CF	0.26	0.39	$n = 2$	CFS_2CF	504	3.42
CFS_nCF	0.23		$n = 3 + 4 + \ldots + n$			3.38 ~ 3.45
a	0.23	0.37	$n = 3$	CFS_3CF	536	3.42
b	0.23	0.30	$n = 4$	CFS_4CF	568	3.39
c	0.23	0.25	$n = 5$	CFS_5CF	600	3.42
d	0.23	0.21	$n = 6$	CFS_6CF	632	3.44
e	0.23	0.16	$n = 7$[b]	CFS_7CF[b]		
f	0.23	0.14	$n = 8$[b]	CFS_8CF[b]		
g	0.23	0.11	$n = 9$[b]	CFS_9CF[b]		
carbofuran	0.10	0.71		CF	221	2.82

[a] TLC and solvent system: (I) silica gel TLC, hexane–ether (7:3); (II) reversed-phase silica gel TLC, acetonitrile–water (9:1). [b] Tentatively assigned.

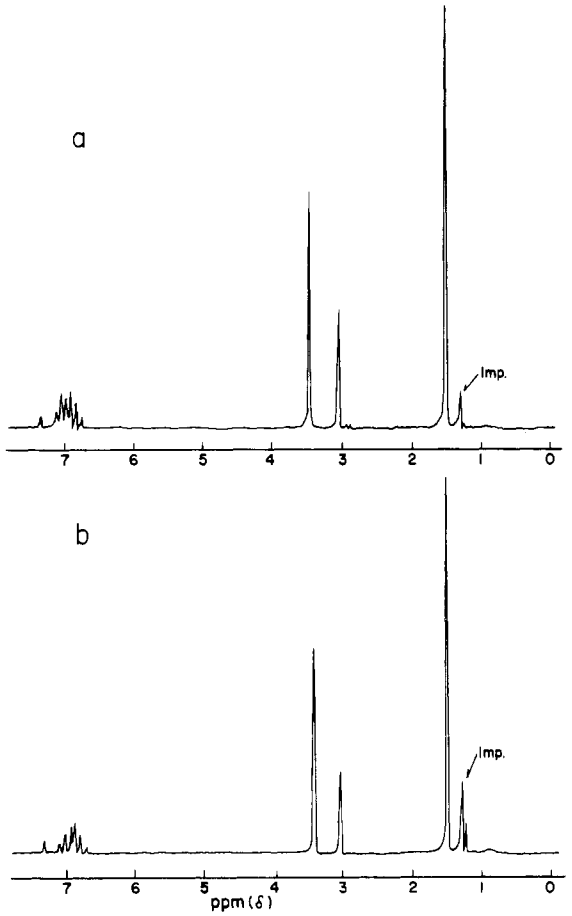


Figure 4. NMR spectra of products a (above) and b (below). The impurity is from the KC_{18} reversed-phase TLC plate.

acetic acid for 120 h, and the breakdown of DBSC and formation of alteration products were monitored at 24-h intervals. A two-dimensional reversed-phase chromatogram of a sample of products observed after 48 h is shown in Figure 5. The presence of carbofuran (40%), CFS_2NBu_2 (12%), and CFS_2CF (7%) as major products is indicated. Minor products observed were CFS_nNBu_2 where n = 3, 4, 5, and 6, CFS_nCF where n = 3, 4, and 5, and several unknown compounds. CFS_6CF and CFS_7CF, if present, were hidden by the large DBSC spot.

The amounts of the different products formed from DBSC in the dichloromethane–acetic acid mixture at 24-h

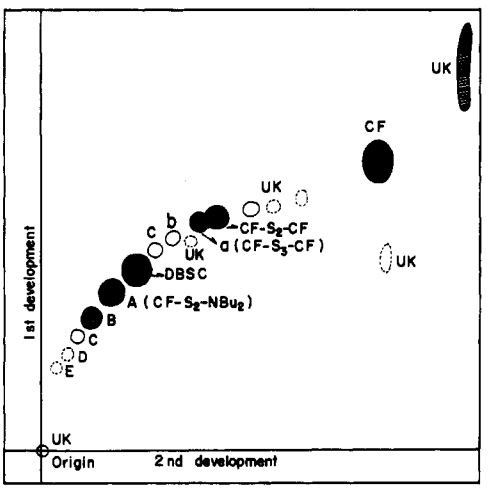


Figure 5. KC_{18} reversed-phase two-dimensional thin-layer chromatogram of [*carbonyl*-^{14}C]DBSC kept in dichloromethane–acetic acid (9:1) for 48 h. Solvent: first development, acetonitrile; second development, acetonitrile–water (9:1). UK = unknown.

Table III. Alteration of [*carbonyl*-^{14}C]DBSC in the Dichloromethane–Acetic Acid (9:1) Mixture after Different Incubation Periods

compound	code	% of total DBSC at 24 h	48 h	72 h	96 h	120 h
DBSC		49.6	30.6	18.9	11.9	6.8
carbofuran		27.4	39.9	47.1	52.4	56.5
CFS_nNBu_2 ($n \geq 2$)						
CFS_2NBu_2	A	7.8	11.7	13.4	13.6	13.0
CFS_3NBu_2	B	1.1	2.3	2.7	3.3	3.7
CFS_4NBu_2	C	0.2	0.3	0.5	0.6	0.7
CFS_5NBu_2	D	0.1	0.1	0.2	0.2	0.2
CFS_6NBu_2	E	<0.1	<0.1	0.1	0.1	0.1
subtotal		9.2	14.4	16.9	17.8	17.7
CFS_nCF ($n \geq 2$)						
CFS_2CF		6.1	7.0	8.3	8.2	8.6
CFS_3CF	a	2.2	2.9	3.0	4.3	4.0
CFS_4CF	b	0.2	0.5	1.1	1.6	2.0
CFS_5CF	c	0.4	0.4	0.7	0.7	0.7
subtotal		8.9	10.8	13.1	14.8	15.3
unknowns		5.0	4.4	4.2	3.4	3.6
total		100.1	100.1	100.2	100.1	99.9

intervals are given in Table III. After 24 h only 50% of the recovered radioactivity was present as the parent

Table IV. Toxicity of the Alteration Products and Related Compounds against Houseflies and Mice

compound	toxicity: housefly LD_{50}, μg/g	toxicity: mouse LD_{50}, mg/kg
CFS_nNBu_2 ($n \geq 2$)	7.5-15.0	127[a] (74-155)[c]
CFS_2NBu_2	9.8	
DBSC ($CFSNBu_2$)	7.8	129[a] (107-148)[c] 74[b] (59-124)[c]
CFS_nCF ($n \geq 3$)	15.0	>100[b]
CFS_3CF	12.2	
CFS_2CF	>250	>100[b]
CFSCF	24.0	50-100[d]
carbofuran	11.0	19.4[a] (16.2-24.3)[c] 11.1[b] (9.8-12.4)[c]

[a] Compound was dissolved or suspended in corn oil. [b] Compound was dissolved or suspended in propylene glycol. [c] 95% confidence limit. [d] Value from Fahmy et al. (1974).

material which gradually decreased during the 120-h test period. The amounts of carbofuran and CFS_nCF (n = 2–5) gradually increased while CFS_nNBu_2 (n = 2–6) reached a maximum at 96 h after which it decreased. These observations are in agreement with results obtained in the previous study in which silica gel TLC was used as a means of separating products (Umetsu et al., 1981). Of the polysulfide derivatives of DBSC, i.e., CFS_nNBu_2, CFS_2NBu_2 was the major product (7.8–13%) throughout the entire test period, followed by CFS_3NBu_2 (1.1–3.7%) and CFS_4NBu_2 (0.2–0.7%). CFS_2NBu_2 reached a maximum after 72 h and remained at a constant level for another 48 h while CFS_3NBu_2 and CFS_4NBu_2 gradually increased throughout the test period.

Of the biscarbofuran polysulfide derivatives, CFS_2CF was the major product (6.1–8.6%) at each time interval, followed by CFS_3CF (2.2–4.0%), CFS_4CF (0.2–0.3%), and CFS_5CF (0.4–0.7%). Most of these derivatives showed a gradual increase over the test period. Of interest is the constant 3:2 ratio between the amount of carbofuran and total amounts of polysulfide derivatives (CFS_nNBu_2 + CFS_nCF) which was observed during the 120-h study.

Toxicological Properties of the Alteration Products. Data for the toxicity of several of the acid-catalyzed alteration products of DBSC to the housefly and white mouse are given in Table IV. With the exception of CFS_2CF, all of the compounds showed good insecticidal activity against the housefly, comparable in activity to that of carbofuran. For reasons which are not clear, CFS_2CF was nontoxic to houseflies at 250 μg/g. In contrast to housefly toxicity, all of the alteration products were significantly less toxic to the white mouse than the parent methylcarbamate, carbofuran. Because of solubility difficulties, it was necessary to use either or both corn oil and propylene glycol as the carrier for the mouse toxicity study. In those cases where both carriers were used to examine a single compound, toxicity to mice was greater with propylene glycol.

DISCUSSION

Silica gel KC_{18} reversed-phase TLC provided a simple and convenient method for separating the individual components in the polysulfide mixtures of DBSC and biscarbofuran disulfide which previously could not be separated by conventional silica gel TLC. CFS_nNBu_2, the polysulfide of DBSC, was separated into at least eight components, and CFS_nCF, the biscarbofuran derivatives, was separated into seven components. In the reversed-phase separation of these components, general correspondence between R_f values and the number of sulfur atoms was observed; i.e., R_f values decreased as the number of sulfur atoms increased. Successful separation by reversed-phase TLC depends on hydrophobic interaction between lipophilic groups in a compound and the hydrocarbyl moiety, in this case octadecyl, of the TLC plate. Good separation of the various polysulfide derivatives by KC_{18} reversed-phase TLC is undoubtedly attributable to the change in lipophilicity of the polysulfides as the number of sulfur atoms is increased. In contrast, separation by silica gel TLC depends largely on polar binding interactions, and evidently, the principal polar binding groups in the polysulfides are not affected by the increase in sulfur atoms.

The effect of the number of sulfur atoms on the NMR signal for the N-CH_3 protons of CFS_nNBu_2 was of interest. The N-CH_3 signal for each of the purified components was a singlet, the chemical shift depending on the number of sulfur atoms. In the polysulfide mixture (CFS_nNBu_2) the N-CH_3 protons appeared as a multiplet comprised of the singlets from the individual components. In contrast, a slightly different effect was exerted by sulfur on the NMR signal of the methylene protons in the dibutylamino moiety, even though the sulfur atoms were about the same distance away from the methylene protons as they were from the N-CH_3 protons. In this case, the same chemical shift was observed for the methylene protons in all polysulfides of CFS_nNBu_2 ($n \geq 2$) and a distinct triplet was obtained for this mixture. Different chemical shifts were observed for methylene protons in DBSC and CFS_nNBu_2. The sulfur atoms of the polysulfide linkage also affected the N-CH_3 proton signals in the biscarbofuran derivatives.

Although the overall structure of each component in CFS_nNBu_2 and CFS_nCF was established by NMR and mass spectral analysis, it was not possible to determine the exact nature of the polysulfide moiety. Mass spectra of these components provided information relating to the number of sulfur atoms but did not indicate whether the sulfur atoms existed in a straight chain or were branched or were part of a ring system. Polysulfides of elemental sulfur have been shown to exist in all three forms (Meyer, 1976).

The poor insecticidal activity of CFS_2CF was unexpected in light of the good activity observed for the other derivatives. A good explanation for the poor activity of this compound is presently not available. It is possible that the disulfide linkage in this compound is uniquely different from that of the other polysulfide derivatives so as to prevent or reduce formation of carbofuran in the housefly.

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