

## CHEMICAL CONSTITUENTS OF THE DEFENSIVE SECRETION OF THE STRIPED SKUNK (MEPHITIS MEPHITIS)

KENNETH K. ANDERSEN and DAVID T. BERNSTEIN

Department of Chemistry, University of New Hampshire, Durham, NH 03824, U.S.A.

and

ROBERT L. CARET and LEO J. ROMANCZYK JR.

Research and Development Laboratories, McCormick and Co., Inc., 202 Wight Avenue, Hunt Valley, MD 21031,  
U.S.A.

(Received in U.S.A. 29 June 1981)

**Abstract**—The volatile components in the musk of the striped skunk (*Mephitis mephitis*) were analyzed by GC-MS. Several thiols (mercaptans), thioethers (sulfides), and disulfides were identified.

The striped skunk (*Mephitis mephitis*), a member of the weasel or *mustelidae* family is renowned in North America for its unusual method of self-defense.<sup>1,2</sup> Skunks effectively repel most aggressors by spraying them with a vile-smelling musk or scent ejected from two anal glands. This article presents our most recent results on the musk's chemical constitution and reviews earlier work on both this musk and that obtained from other mustelids.

Over seventy species of mustelids are found throughout the world. In the United States and Canada these include such common, or at least well-known, animals as the mink (*Mustela vison*), the otter (*Lutra canadensis*), the badger (*Taxidea taxus*), the wolverine (*Gulo gulo*) and various skunks. Although these animals have anal glands, skunks are the members of the family which use them mainly in self-defense.

Four species of skunks, members of the subfamily *Mephitinae*, are found in the United States.<sup>2,3</sup> These are the striped skunk, the spotted skunk (*Spilogale putorius*), the hog-nosed skunk (*Conepatus leuconotus*) and the hooded skunk (*Mephitis macroura*). The latter two are much less common than the first two and are found in the southern part of the country. The spotted skunk has a more extensive but still southerly range whereas the striped skunk is found throughout the country except in the more arid regions and at the highest elevations.<sup>1</sup> Several subspecies of striped, spotted, and hog-nosed skunks are known.<sup>1-4</sup>

When full grown, the striped skunk is about the size of a large domestic cat and covered by rather luxurious glossy-black fur with two white stripes, variable in length, running along the back from nose to tail. This gives the animal a characteristic and easily-recognized appearance.

Few predators will attack a striped skunk which is reflected in the skunk's confident manner and non-aggressive behavior. An exception is the great horned owl, reputed to prey on skunks. Unless surprised, a skunk will rarely scent (spray its musk) without ample warning. Contrary to popular notion, a skunk is no more odorous than other mammals and keeps its putrid-smelling musk well-contained in its anal glands. In order to scent, a

skunk retracts the folds of skin around the anal opening thereby extending two nipples, one from each gland. Muscular contractions propel the musk for a distance of about 3 m, usually in the form of droplets. Each gland contains several mL of oil so repeated discharges are possible.

The musk as usually applied seems to have no great physiological effect on most recipients other than a definite behavioral response elicited by its repulsive odor. A student, administered skunk musk by the inhalatory route by his classmates, lapsed into unconsciousness but recovered after a night's sleep with no reported lasting ill effects. Even so, the use of skunk musk as an anesthetic was not recommended.<sup>5</sup> Although used by some during the last century as a remedy for asthma, the treatment was considered worse than the disease.<sup>2</sup> In quantity, the musk might be expected to exhibit the toxicity associated with thiols.

Skunks are an important carrier of rabies in the wild and have been studied for this reason. At one time their pelts had considerable commercial value and skunks were extensively trapped, but this is no longer true today.<sup>1</sup>

Chemical investigations of the musk began well over one-hundred years ago. Wohler and Swarts investigated skunk scent in 1862 having received some oil and anal glands from "freunde in Neuyork".<sup>5,6</sup> Low collected samples of musk during a trip through Texas in 1872. Protesting travel companions discouraged his investigation.<sup>7</sup> Later, students and colleagues caused him to give up his project.<sup>8</sup> Even so Wohler, Swarts and Low all concluded—correctly so—that the musk contained thiols (mercaptans) and a nitrogenous base.

In 1896, Aldrich distilled the fluid into two fractions.<sup>8</sup> Mercury and lead salts were prepared of the lower boiling fraction and quantitative elemental analyses were performed on these derivatives. Aldrich concluded that this fraction contained one of the butyl mercaptans. The higher boiling fraction was noted to have an odor like isoamyl mercaptan. In fact, the major components are crotyl mercaptan and isoamyl mercaptan.<sup>10</sup>

In an attempt to find large ring ketones suitable for use in perfumery, Stevens in 1945 examined skunk musk after

first precipitating the thiols with mercuric chloride.<sup>9</sup> He found no large ring compounds but did identify dicrotyl sulfide as a constituent of the scent.

In 1975, two of us (KKA and DTB) used gas chromatography to fractionate the volatile components of the musk.<sup>10</sup> Three major fractions were collected. They were identified as 3-methyl-1-butanethiol (isoamyl mercaptan) (1), *trans*-2-butene-1-thiol (crotyl mercaptan) (2), and *trans*-2-butenyl methyl disulfide (3) by NMR and IR spectral comparison with authentic samples. Thiols 1 and 2 were further identified by conversion to 2,4-dinitrophenyl derivatives. After this initial study, we continued

our investigation of the minor volatile components of the scent.

## RESULTS

Two gas chromatograph-mass spectrometer (GC-MS) systems were used for analysis of the volatile scent components. Our results were obtained in two stages. First a packed GC column was used which led to the identification of six more sulfur-containing compounds (4-9).<sup>11</sup> Then, for reasons presented below, we turned to a capillary column GC-MS system and identified several more musk components. Table 1 lists the compounds

Table 1. Some volatile constituents of the musk of the striped skunk (*Mephitis mephitis*)

| Peak No. <sup>a</sup> | Compound                            | Per Cent <sup>b</sup> | Method of Identification |
|-----------------------|-------------------------------------|-----------------------|--------------------------|
| 2-2                   | acetaldehyde                        | <1                    | c                        |
| 2-3                   | propionaldehyde                     | <1                    | c                        |
| 2-4                   | <i>n</i> -propyl mercaptan          | <1                    | c                        |
| 2-5                   | isobutyl mercaptan                  | <1                    | c                        |
| 2-6                   | <i>n</i> -butyl mercaptan (5)       | <1                    | c                        |
| 2-7                   | crotyl and isoamyl mercaptan (1, 2) | 66.2                  | c, a                     |
| 2-12                  | <i>n</i> -hexyl mercaptan           | <1                    | c                        |
| 2-13                  | crotyl ethyl sulfide                | <1                    | f                        |
| 2-16                  | crotyl isoamyl sulfide (6)          | <1                    | d                        |
| 2-17                  | dicrotyl sulfide (7)                | 1.1                   | d, e                     |
| 2-19                  | isomer of 2-17, 23, 24              | <1                    | f                        |
| 2-20                  | isoamyl thioacetate                 | 1.4                   | c                        |
| 2-22                  | crotyl propyl sulfide (4)           | 6.9                   | d                        |
| 2-23                  | isomer of 2-17, 19, 24              | <1                    | f                        |
| 2-24                  | isomer of 2-17, 19, 23              | <1                    | f                        |
| 3-1                   | benzyl mercaptan                    | <1                    | c                        |
| 3-3                   | isoamyl disulfide                   | <1                    | d                        |
| 3-6                   | <i>q</i> -phenethyl mercaptan       | <1                    | c                        |
| 3-5                   | crotyl isoamyl disulfide (8)        | <1                    | e                        |
| 3-7                   | crotyl disulfide (9)                | <1                    | d                        |
| 3-8                   | <i>n</i> -butyl isoamyl disulfide   | 7.1                   | f                        |
| 3-9                   | <i>n</i> -butyl crotyl disulfide    |                       | f                        |
| 3-11                  | isomer of 3-8                       | 3.6                   | f                        |
| 3-13                  | unknown                             | 7.0                   |                          |
| 3-21                  | 2-methylquinoline                   | <1                    | c, d                     |

a. From figures 2 and 3.

b. From GC integration.

c. Mass spectrum match with spectrum from NBS library.

d. Mass spectrum match with spectrum of authentic sample.

e. Previously identified; see refs. 10 and 11.

f. From analysis of mass spectrum fragmentation pattern.

identified. Both sets of results—those obtained with the packed column and those with the capillary column—are given in turn below.

Several packed GC columns were used to separate the scent. Although some columns worked fairly well, a 10 ft  $\times$  1/8 in stainless steel column packed with 5% Carbowax 1500 on DMCS-treated Chromosorb-W 120/140 and temperature programmed from 50° to 120° at 2.5° min<sup>-1</sup> proved most suitable for use in conjunction with a modified Hitachi RMU-6 computer-assisted mass spectrometer. Imperfect resolution persisted, but a minimum of twenty-two compounds were indicated by resolved peaks or shoulders on the chromatographic trace.

No particular differences were noted in the chromatograms obtained from scent samples from five skunks—two male and three females (one lactating). These samples were run on a 12 ft  $\times$  1/4 in column packed with 20% Carbowax 20 M on Chromosorb-W 60/80, but column bleed prevented this column's use with the mass spectrometer.

About 400 spectra were recorded during the GC-MS run on which our compound identifications are based. An ionization intensity plot was obtained for each  $m/e$  value. The total ionization plot was also recorded. By overlaying the ionization intensity (for given  $m/e$  values) vs spectrum number plots in turn onto the total ionization energy vs spectrum number plot,  $m/e$  values were assigned to the various peaks in this latter plot. These  $m/e$  values result from ionization and fragmentation of the particular compounds giving rise to the various GC peaks or their equivalent recorded in the total ionization energy vs spectrum number plot. Such a procedure was useful in assigning  $m/e$  values in a given spectrum which resulted

from more than one compound; i.e. incomplete resolution in the GC. In particular, isoamyl mercaptan (1) co-eluted with crotyl mercaptan (2) and crotyl methyl disulfide (3) may have co-eluted with crotyl propyl sulfide (4). Besides 1 and 2, six more compounds (4 to 9) were identified. Mass spectral identification of 3 is not secure. This point will be commented on in the Discussion.

Isoamyl mercaptan (1) and n-butyl mercaptan (5) were identified by comparison to authentic mass spectra. The amount of 5 in skunk scent is less than one percent of the total so any earlier reports of its presence must still be considered erroneous. The remaining five compounds, 4 and 6-9, were identified by analysis of their fragmentation patterns.

Our interest in the minor components was renewed when Dr. B. W. Christensen of the Technical University of Denmark analyzed one of our samples of skunk musk using a capillary column GC (WCOT, 82 m, Carbowax 20 M, temperature programmed from 40 to 80° at 1° min<sup>-1</sup>, and 80-200° at 2° min<sup>-1</sup>) equipped with both flame ionization and sulfur photometric detectors. He observed about 160 peaks of which over 150 contained sulfur. Even allowing for artifacts such as disulfides formed by air oxidation of some of the thiols, this large number of S compounds is astonishing. The relatively small number of non-S containing compounds is also remarkable. An investigation employing a capillary GC-MS system was subsequently undertaken.

The total ion chromatogram obtained using a 60 M glass capillary column GC-MS is shown in Fig. 1. Figures 2 and 3 are expanded portions of Fig. 1. A total of 71 mass spectra were obtained. About 24 compounds were identified by matching these spectra with library spectra,

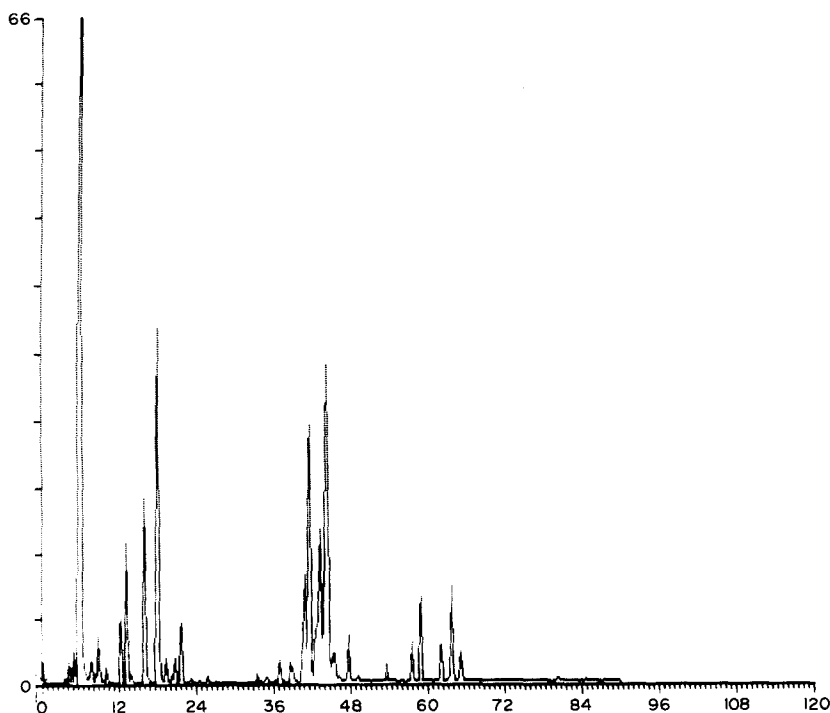


Fig. 1. Ion chromatogram of striped skunk musk.

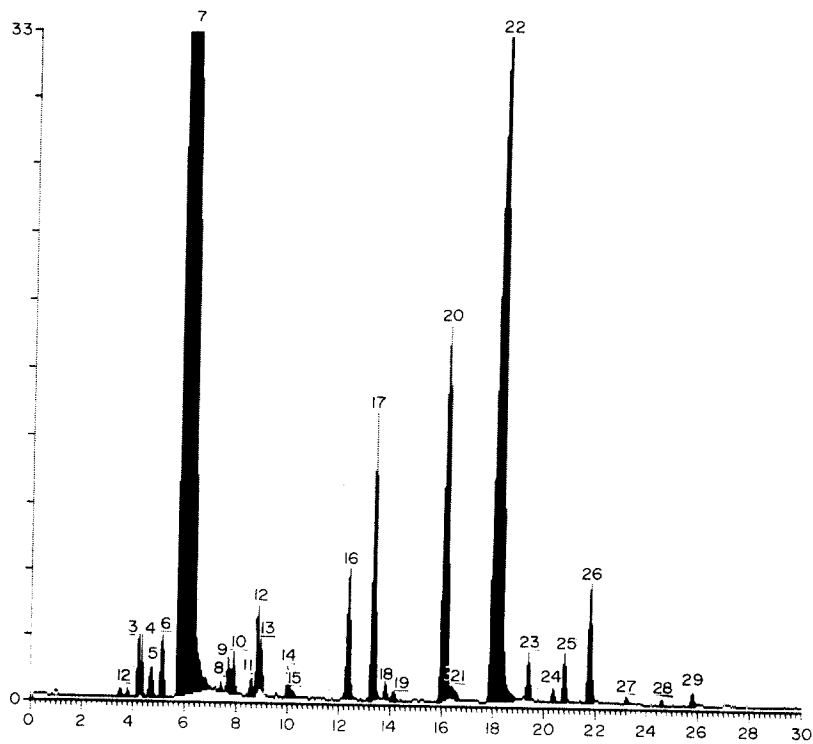


Fig. 2. Ion chromatogram of striped skunk musk (0-30 min).

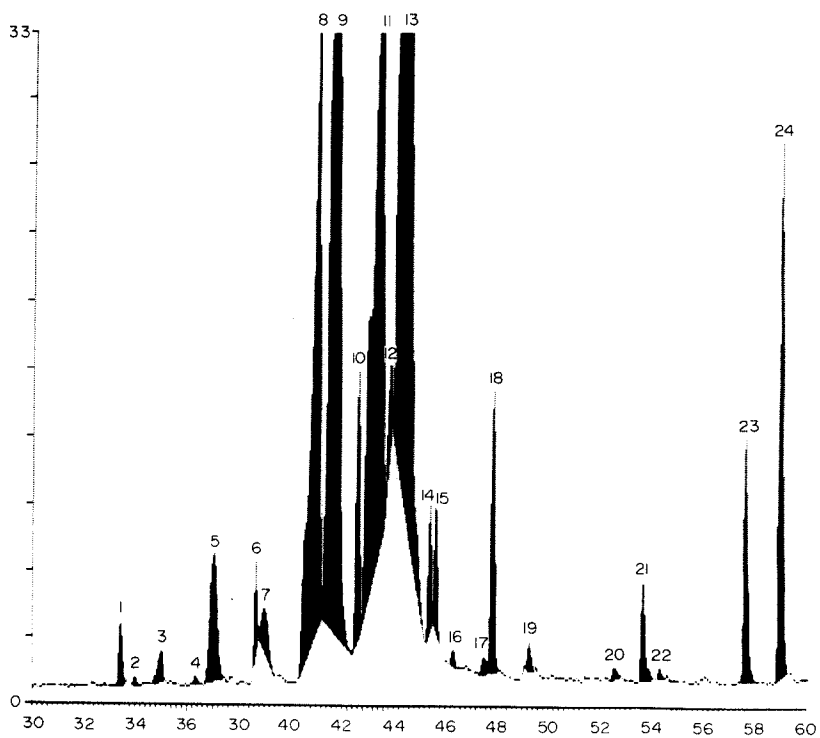


Fig. 3. Ion chromatogram of striped skunk musk (30-60 min).

by matching with spectra obtained from authentic material, and/or by analysis of the fragmentation patterns. Assignment of molecular ions was often a problem. Doubtless incomplete chromatographic resolution confounded interpretations as did the presence of isomers. The spectra obtained from the peaks shown in Figs. 2 and 3 will be commented on in turn.

Peak one in Fig. 2 (0–30 min) is carbon dioxide. Peaks 2 through 6 were identified by comparison with literature spectra and require no special comment. Peak 7 represents over sixty percent of the total ion current; it arises from a mixture of 1 and 2, the principal scent components.

Peaks 8–11 were not identified. Peaks 8 and 10 had molecular ions at  $m/e$  102. But neither spectrum matched those reported by Crump<sup>12,13</sup> for 1,1-dimethyl-, *cis* or *trans*-1,2-dimethyl-, or 1-ethyl-thietane. Peaks 9 and 12 were also due to isomers with molecular ions at  $m/e$  118. These spectra were very similar with  $m/e$  values of 118, 84 ( $-H_2S$ ), 69 and 56. Most likely they are isomeric hexanethiols. Peak 11 had a molecular ion at 118 and appears to be a sulfide,  $C_7H_{16}S$ . Peak 13 is likely due to ethyl crotyl sulfide. The spectrum does not fit that of 1-ethylthietane. Peaks 14, 15, 18 and 21 gave spectra too weak for interpretation, Peaks 16 and 17 gave spectra which match those of crotyl isoamyl sulfide and dicrotyl sulfide obtained earlier.<sup>11</sup> The spectra resulting from peaks 17, 19 and 23 were almost identical. This suggests that they might be three stereoisomers of dicrotyl sulfide—the *trans*, *trans*, the *cis*, *cis* and the *trans*, *cis*. The spectrum from peak 20 matched fairly well the library spectrum of isoamyl thioacetate. Peak 22 gave a spectrum which matched that due to crotyl propyl sulfide identified earlier.<sup>11</sup> The spectrum of peak 24 was almost identical to that of peak 23 but lacking in the  $m/e$  113 value found in the spectra of 17, 19 and 23. Ionization at the crotyl double bond followed by a shift of the  $\alpha$ -H to the  $\gamma$ -C and subsequent loss of  $C_2H_5$ , gives  $C_4H_7SC_2H_5^+$  with  $m/e$  113. Peak 24 seems due to a sulfide with one crotyl group and one group isomeric with crotyl. The spectra from peaks 25 and 26 were virtually identical except for the intensities. Both lost  $H_2S$  in going from the molecular ion at  $m/e$  122 to  $m/e$  88. This suggests they are thiols of formula  $C_4H_{10}S_2$  with two thiol groups attached to a  $C_4$ -chain. However, neither spectrum matched the library spectrum of 1,4-butanedithiol nor did their GC retention times coincide. Peak 27 with molecular ion  $m/e$  156 appears to be a butenyl pentenyl sulfide. Peak 28 gave a spectrum of low intensity. Peak 29 may be the disulfide of the compound responsible for peaks 25 or 26.

Figure 3 (30–60 min) shows 24 peaks for which spectra were obtained. Peaks 1, 6 and 21 were identified by matching with library spectra. Peak 2 gave a spectrum for which a molecular ion could not be assigned with any confidence. Values of  $m/e$  at 55 and 87 indicated the presence of a crotyl-S group. Similarly, peaks 3, 4 and 5 gave spectra for which we could not assign a molecular ion with any confidence although the presence of alkyl-S groups were indicated. Peak 7 was identified as dicrotyl disulfide by comparison with a spectrum previously assigned to dicrotyl disulfide.<sup>11</sup> Peaks 8 and 11 gave rise to spectra with molecular ions at  $m/e$  192 corresponding to  $C_9H_{20}S_2$ . Disulfides with  $C_4$  and  $C_5$  alkyl groups are structures which might give these spectra. Peaks 9, 10 and 12 have common molecular ions at  $m/e$  176. Spectra from 10 and 12 are almost identical with respect to both

$m/e$  and intensity values. Disulfides with crotyl and butyl groups are possible candidates for these compounds as are 1,3-dithianes. Peak 13 gave no clearcut molecular ion. There was a very weak peak at  $m/e$  177 and then an intense peak at  $m/e$  121. Values of  $m/e$  at 87 and 55 suggest a crotyl-S group. In spite of the relatively large amount of this compound in the skunk musk, no structural assignment was made. Although spectra were obtained for peaks 14–24, only one was assigned to a structure—peak 21—identified as originating from 2-methylquinoline. With the exception of peak 21, the spectra obtained had  $m/e$  values of 87 and 55 indicating the presence of  $C_4H_7S^+$  fragments.

In spite of obtaining 18 more spectra after 60 min, we were unable to make any conclusive structural assignments. High resolution spectra would certainly aid in further structural elucidation, but such instrumentation was not available for this project. The spectra exhibit many similarities which suggest isomers and homologues similar in many respects to those mentioned above. In a few cases, odd  $m/e$  values, if they were molecular ions, would indicate the presence of nitrogen. However, only two minor nitrogen containing substances which eluted very early, were detected, except for 2-methylquinoline, when the musk was analyzed using a capillary column GC equipped with a N-P detector.

#### DISCUSSION

The volatile portion of striped skunk musk is obviously rich in low molecular weight S-containing compounds mainly thiols (mercaptans), thioethers (sulfides), and disulfides. Musks from a few other mustelids have also been examined. Some notable differences in composition are observed, which raise interesting questions about the biosynthetic origins of the scents.

The large number of low molecular weight sulfur compounds in skunk scent is particularly striking. Isoamyl and crotyl groups are heavily represented among these compounds. Three functional groups—thiols, sulfides and disulfides—are present. Disulfides may arise from air oxidation of the thiols during sample handling and storage, but we believe the evidence suggests some occur naturally, at least in part. This evidence is presented below. It is also conceivable some compounds arise from thermally-induced processes such as [2,3]sigmatropic rearrangements of crotyl disulfides.<sup>14,15</sup> Noteworthy is the absence of any thietanes which occur in some other mustelid musks.<sup>12,13</sup> As determined earlier, 1 and 2 are the principal scent components. Lack of mass spectral evidence for 3 is puzzling. Perhaps it does not survive the high injector temperature (235°).

The anal gland secretions of two mustelids which use their scent for defense have been examined but without the benefit of modern techniques. Beckmann reported in 1896 that musk of the Phillipine teledu (*Mydaus marchei* Huet or *Suillotaxas marchei*) contained n-butyl mercaptan based on his conversion of it to di-n-butyl sulfone.<sup>16</sup> Fester and Bertuzzi steam distilled a sample of musk from the South American zorrino (*Conepatus suffocans*), carried out a quantitative elemental analysis on the distillate, and concluded it contained a mixture of 1 and its disulfide (9).<sup>17</sup>

In recent times the musks of the American mink (*Mustela vison*),<sup>11,18–20</sup> the ermine or stoat (*Mustela erminea*),<sup>12</sup> and the ferret or polecat (*Mustela putorius*)<sup>13</sup> have been examined using GC-MS. Thietanes (4-mem-

bered cyclic sulfides), dithiolanes (5-membered cyclic disulfides), sulfides, and disulfides were identified, but no thiols were present except for a trace of n-butyl mercaptan in mink.<sup>20</sup> Since disulfides were found in mink but not thiols, this suggests that disulfides are not formed solely by air oxidation. If they were, some unoxidized thiols should also be present. Thus it seems likely that a portion if not all of the disulfides in skunk occur naturally.

The unaggressive skunk possesses large amounts of a putrid musk containing low molecular weight S compounds; it can be used effectively to repel predators. The mink, weasels, and ferrets, possess relatively small amounts of putrid musk which also contains low molecular weight S compounds but these are structurally distinct from those in the skunk; these musks seem to be used primarily but not exclusively for marking.<sup>19,20</sup> The nonvolatile portion of skunk scent may contain precursors of the volatile compounds or perhaps they are metabolites produced in unrelated processes. In any event, they may contribute to the scent's repellent effectiveness.

Examination of other musteline musks may reveal low molecular weight sulfur compounds similar but not necessarily identical in structure to those already found. The quantity and nature of these substances may correlate with the animals use of its musk. In addition, a knowledge of how these compounds are biosynthesized might yield some insight into taxonomic relationships among mustelids.

#### EXPERIMENTAL

The mass spectra reported below were obtained using a DuPont Model 102 mass spectrometer equipped with a glass capillary column GC-MS interface. The 60 M glass capillary column (WCOT with SP-1000) was temperature programmed from 80 to 200° at 2° min<sup>-1</sup> and from 200 to 220° at 0.3 min<sup>-1</sup> with an injector temp of 235°. Skunk musk was obtained from various skunks—some live and some recently killed. The volatile components were obtained by bulb-to-bulb distillation at 80° (0.2 mm). The collection bulb was cooled in liquid N<sub>2</sub>. No particular difference among samples from different skunks was noticed in the chromatograms obtained using packed columns. All capillary GC work was done on the same sample. Some of the mass spectra corresponding to the chromatographic peaks shown in Figs. 2 and 3 are as follows where the first numbers refers to the figure and the second to the peak. 2-4 *m/e* (rel intensity) 76 (65), 61 (10), 47 (100), 43 (95), 42 (80), 41 (85), 39 (25). 2-5 *m/e* 90 (35), 75 (5), 56 (55), 49 (40), 48 (40), 43 (75), 41 (100). 2-6 *m/e* 90 (35), 61 (20), 56 (90), 48 (30), 41 (100). 2-8 *m/e* 102 (40), 87 (10), 68 (70), 55 (80), 41 (100). 2-9 *m/e* 118 (20), 84 (10), 69 (15), 61 (15), 56 (100), 43 (35), 41 (70). 2-10 *m/e* 102 (10), 87 (15), 69 (30), 68 (40), 53 (25), 41 (100). 2-11 *m/e* 132 (45), 103 (2), 89 (10), 74 (30), 70 (100), 61 (20), 55 (60), 48 (30), 43 (50). 2-12 *m/e* 118 (5), 84 (5), 69 (20), 56 (100), 43 (50). 2-13 *m/e* 116 (50), 101 (5), 87 (25), 73 (5), 61 (10), 55 (100), 47 (15), 45 (20). 2-16 *m/e* 158 (15), 143 (2), 115 (2), 103 (15), 87 (15), 70 (30), 61 (20), 55 (100), 47 (10), 41 (30). 2-17 *m/e* 142 (10), 127 (3), 113 (6), 108 (4), 95 (5), 87 (25), 71 (4), 61 (10), 55 (100), 45 (40). 2-19 *m/e* 142 (5), 127 (4), 113 (10), 109 (4), 95 (5), 87 (30), 71 (2), 55 (10), 55 (100), 45

(40). 2-20 *m/e* 103 (1), 86 (20), 70 (20), 55 (10), 43 (100). 2-22 *m/e* 130 (20), 115 (1), 97 (4), 88 (40), 76 (4), 55 (60), 43 (100). 2-23 *m/e* 142 (35), 127 (5), 113 (7), 101 (4), 87 (65), 73 (3), 60 (15), 55 (100), 45 (40). 2-24 *m/e* 142 (25), 127 (1), 108 (2), 87 (45), 71 (3), 55 (100), 45 (55). 2-25 *m/e* 122 (8), 88 (40), 75 (10), 60 (15), 55 (60), 41 (100). 2-26 *m/e* 122 (20), 120 (20), 88 (20), 73 (5), 61 (15), 59 (15), 55 (100), 47 (25). 2-27 *m/e* 156 (35), 142 (3), 127 (2), 101 (30), 88-85 (15-20), 69 (45), 59 (40), 55 (90), 41 (100). 2-29 *m/e* 120 (45), 88 (2), 71 (30), 60 (10), 55 (100), 43 (65). 3-1 *m/e* 124 (35), 91 (100), 77 (5), 65 (10), 51 (10), 45 (10). 3-6 *m/e* 138 (40), 104 (15), 91 (100), 77 (5), 65 (15), 51 (15), 47 (5). 3-7 *m/e* 174 (2), 142 (2), 120 (8), 113 (3), 95 (2), 88 (8), 87 (8), 69 (5), 55 (100), 45 (20). 3-8 *m/e* 192 (20), 159 (10), 145 (25), 89 (60), 70 (35), 61 (50), 55 (100), 47 (35), 43 (40), 41 (60). 3-9 *m/e* 176 (10), 147 (2), 129 (15), 88 (20), 87 (20), 75 (20), 55 (100), 47 (15), 45 (15). 3-10 *m/e* 176 (50), 161 (2), 147 (25), 129 (15), 120 (10), 113 (5), 89 (35), 74 (100), 61 (15), 55 (55), 41 (35). 3-11 *m/e* 192 (50), 159 (2), 145 (2), 131 (5), 121 (25), 88 (50), 75 (45), 61 (25), 55 (100), 47 (35). 3-12 *m/e* 176 (30), 161 (2), 147 (10), 129 (15), 113 (2), 105 (5), 89 (30), 74 (100), 61 (10), 55 (50), 45 (30). 3-13 *m/e* 177 (1), 121 (70), 87 (80), 79 (10), 61 (25), 55 (100), 47 (35). 3-21 *m/e* 143 (100), 128 (20), 115 (15), 101 (5), 89 (3), 77 (5), 63 (5).

*Acknowledgement*—We thank B. W. Christensen for a capillary column GC analysis and Catherine E. Costello of MIT for doing the packed column GC-MS analysis.

#### REFERENCES

- <sup>1</sup>B. J. Verts, *The Biology of the Striped Skunk*. University of Illinois Press: Urbana (1967).
- <sup>2</sup>W. T. Edmonds, Jr., *Bulletin of the State Biological Survey of Kansas*, No. 3 (1974). A bibliography of over 500 references to skunks is on file with the State Biological Survey of Kansas.
- <sup>3</sup>R. G. Van Gelder, *Animal Kingdom* **61**, 153-157 (1958).
- <sup>4</sup>R. G. Van Gelder, *Bull. Am. Museum Nat. Hist.* **117**, 229-392 (1959).
- <sup>5</sup>K. K. Andersen and D. T. Bernstein, *J. Chem. Ed.* **55**, 159-160 (1978).
- <sup>6</sup>Swarts, *Justus Liebigs Ann. Chem.* **123**, 266-270 (1862).
- <sup>7</sup>O. Low, *Artzliches Intelligensblatt von Munchen* 252-253 (June 1879).
- <sup>8</sup>T. B. Aldrich, *J. Exp. Med.* **1**, 323-340 (1896).
- <sup>9</sup>P. G. Stevens, *J. Am. Chem. Soc.* **67**, 407-408 (1945).
- <sup>10</sup>K. K. Andersen and D. T. Bernstein, *J. Chem. Ecol.* **1**, 493-499 (1975).
- <sup>11</sup>K. K. Andersen and D. T. Bernstein, *Natural Sulfur Compounds* (Edited by D. Cavallini, G. E. Gaull and V. Zappia), pp. 399-406. Plenum Press, New York (1980).
- <sup>12</sup>D. R. Crump, *J. Chem. Ecol.* **6**, 341-347 (1980).
- <sup>13</sup>D. R. Crump, *Ibid.* **6**, 837-844 (1980).
- <sup>14</sup>E. Block, *Reactions of Organosulfur Compounds*, p. 264. Academic Press, New York (1978).
- <sup>15</sup>G. Hofle and J. E. Baldwin, *J. Am. Chem. Soc.* **93**, 6307-6308 (1971).
- <sup>16</sup>E. Beckmann, *Pharm. Zentralhalle, Dsch.* **37**, 557-558 (1896).
- <sup>17</sup>G. A. Fester and F. A. Bertuzzi, *Rev. Fac. Quim. Ind. Agr. Univ. Nac. litoral* **5**, 85-87 (1937).
- <sup>18</sup>H. Schildknecht, I. Wilz, F. Enzmann, N. Grund and M. Ziegler, *Angew. Chem. Int. Ed. Engl.* **15**, 242-253 (1976).
- <sup>19</sup>C. Brinck, R. Gerell and G. Odham, *Oikos* **330**, 68-75 (1978).
- <sup>20</sup>V. E. Sokolov, E. S. Albone, P. F. Flood, P. F. Heap, M. Z. Kagan, V. S. Vasilieva, V. V. Roznov and E. P. Zinkevich, *J. Chem. Ecol.* **6**, 805-825 (1980).