

## Mass Spectra of Trifluoroacetyl Derivatives of Carbaryl and Its

## Aglycone Metabolites

The *N*-trifluoroacetyl derivatives of carbaryl and the *N,O*-ditrifluoroacetyl derivatives of hydroxycarbaryl (4-, 5-, 6-, and 7-) were analyzed by gas-liquid chromatography-mass spectrometry. All derivatives possessed parent ions and easily interpretable fragmentation patterns confirming the proposed

structures. The derivatives readily lose  $-\text{CH}_3\text{NCO}$  through a rearrangement to form the base ions which subsequently fragment further. *N*-Hydroxymethylcarbaryl did not form a stable trifluoroacetyl derivative and only trifluoroacetyl 1-naphthol was observed.

Many carbamate pesticides are used commercially to regulate insect populations or undesirable plants. Carbaryl (1-naphthyl *N*-methylcarbamate), an economically important insecticide, is converted by both plants and animals to various hydroxylated metabolites, which usually are present as glycosides or sulfates (Dorough and Casida, 1964; Kuhr and Casida, 1967; Paulson *et al.*, 1970; Mumma *et al.*, 1971). The *N*-methylcarbamates are thermally unstable and are in general not capable of being directly analyzed by gas-liquid chromatography (glc). Recently it was shown that the trifluoroacetyl derivatives of carbaryl (Seiber, 1972) and its hydroxylated metabolites or potential metabolites are thermally stable and can be analyzed by glc (Khalifa and Mumma, 1972). We now report the mass spectra of the trifluoroacetyl derivatives of 1-naphthol, carbaryl, 4-hydroxy-1-naphthyl *N*-methylcarbamate (4-hydroxycarbaryl), 5-hydroxy-1-naphthyl *N*-methylcarbamate (5-hydroxycarbaryl), 6-hydroxyl-1-naphthyl *N*-methylcarbamate (6-hydroxycarbaryl), and 7-hydroxyl-1-naphthyl *N*-methylcarbamate (7-hydroxycarbaryl) to confirm their structure and elucidate their degradation pattern.

## EXPERIMENTAL PROCEDURE

**Instrumentation.** Mass spectra were obtained at 70 eV with an LKB (Model 9000) mass spectrometer employing the direct glc inlet system.

**Derivatization.** The derivatization and glc were essentially the same as previously reported (Khalifa and Mumma, 1972). Carbaryl, 4-, 5-, 6-, and 7-hydroxycarbaryl, and 1-naphthol were dissolved in anhydrous benzene (1 mg per 6 ml) and placed in a centrifuge tube. To this was added 0.2–0.4 ml of anhydrous pyridine and 0.3 ml of 10% trifluoroacetic anhydride in benzene. The contents of the centrifuge tube were mixed in a Vortex and let stand for 15 min at 25°C. The reaction mixture was then washed with three 5-ml portions of water and the remaining benzene solution containing the trifluoroacetyl derivatives was directly analyzed by glc-mass spectrometry, employing a 3% SE-30 column at 200°C (Khalifa and Mumma, 1972).

## RESULTS AND DISCUSSION

The mass spectra of the various trifluoroacetyl derivatives of carbaryl and its metabolites or potential metabolites were obtained by employing a direct glc inlet system and are given in Table I. Carbaryl forms an *N*-trifluoroacetyl derivative which has a prominent parent ion at *m/e* 297. Hydroxy-

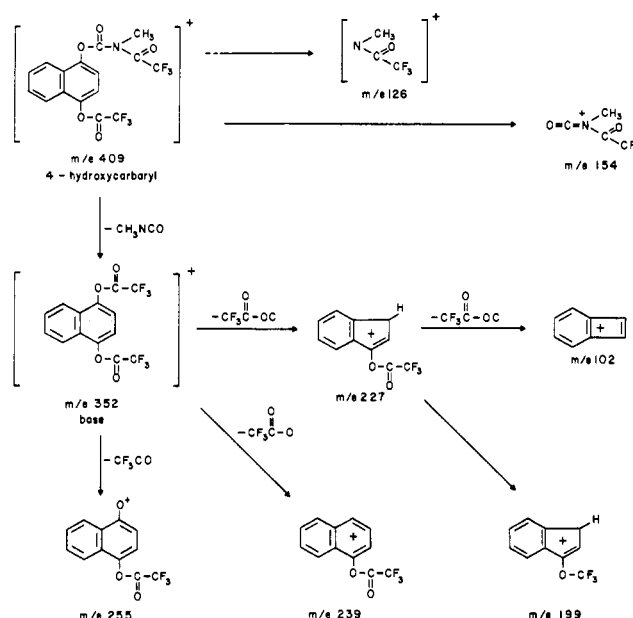


Figure 1. Mass spectral fragmentation of 4-hydroxycarbaryl

carbaryl (4-, 5-, 6-, and 7-) formed *N,O*-ditrifluoroacetyl derivatives with prominent parent ions at *m/e* 409. The carbaryl metabolite 1-naphthyl *N*-hydroxymethylcarbamate (*N*-hydroxymethylcarbaryl) did not form a stable trifluoroacetyl derivative. It is more sensitive to hydrolysis than the other carbamates and under the derivatization conditions (Khalifa and Mumma, 1972) only trifluoroacetyl 1-naphthol was formed.

The fragmentation pattern of *N,O*-ditrifluoroacetyl 4-hydroxycarbaryl is shown in Figure 1 and is typical of all the trifluoroacetyl carbamate derivatives examined. These derivatives readily lose  $-57$  ( $-\text{CH}_3\text{NCO}$ ) through a rearrangement (Damico and Benson, 1965) to form the base ion *m/e* 352 from ditrifluoroacetyl hydroxycarbaryls and *m/e* 240 from trifluoroacetyl carbaryl. Most of the intense ions arise from further fragmentation of these base ions through the loss of  $-\text{CF}_3\text{CO}$ ,  $-\text{CF}_3\text{COO}$ , and  $-\text{CF}_3\text{COOC}$ . Prominent ions of *m/e* 126 ( $\text{CF}_3\text{CONCH}_3$ ) and *m/e* 154 ( $\text{CF}_3\text{CON}(\text{CH}_3)\text{CO}$ ) were present in the spectra of all the carbamate derivatives.

The mass spectra confirm the proposed structures of the trifluoroacetyl derivatives of carbaryl and its metabolites and show predictable fragmentation patterns. These data

Table I. The Mass Spectra of Trifluoroacetyl Derivatives of Carbaryl and Metabolites

<i>m/e</i>	Compounds <sup>a</sup>					
	1-Naphthol	Carbaryl	4-Hydroxy-carbaryl	5-Hydroxy-carbaryl	6-Hydroxy-carbaryl	7-Hydroxy-carbaryl
63	7.0					
65	3.3					
69	9.5	35.10	76.9	42.6	52.4	64.8
75						3.6
76			7.1	4.3		5.2
77						4.4
78	6.5					
89	7.9					
97			9.5	6.7	7.9	11.1
102			9.1	13.4	17.5	22.0
103						3.4
105			5.9			
110			8.7	8.6	8.3	10.1
113	3.3					
114	5.9		6.7	5.9		10.1
115	100.0	55.9				
116	11.4	5.9				
126		26.5	39.4	41.5	42.1	52.4
127	9.2	14.7	3.6			3.1
130			5.9		6.3	
131				3.1	5.6	
133			3.6	27.7	9.5	15.1
144	62.9	50.0				
145	7.3	8.8				
151			4.3			
154			19.7	21.3	15.1	19.6
170				4.1		
199			20.1	3.1	13.5	20.6
227			14.2	23.4	28.6	18.1
228					3.2	
239			6.3	4.9	10.7	11.0
240	100.0 P	100.0				
241	12.4	11.7				
255			51.2	46.8	24.6	55.0
256			10.3	10.6	13.5	14.0
297		32.4 P				
298		3.9				
305					3.2	
352			100.0	100.0	100.0	100.0
353			12.2	12.8	13.5	13.7
409			21.3 P	22.1 P	20.6 P	19.6 P
410			3.2	3.4	3.2	3.0

<sup>a</sup> Ions of less than 3% intensity or less than *m/e* 50 are not included.

should be applicable to most *N*-methylcarbamates and, therefore, be of considerable use in the identification of the metabolites of other carbamate pesticides.

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