

time of 230. Thus with relative retention times of 194 and 206 respectively, *p,p'*-DDT and *p,p'*-TDE appear on an otherwise long flat part of the chromatogram between these earliest and later avian compound peaks. Although not completely separated one from the other, they can be easily detected and their levels estimated in extracts which contain avian compounds.

Coupled with its reversal of the usual dieldrin and *p,p'*-DDE retention times, this column is a very useful addition to the usual silicone and Apiezon columns already in operation. It has been used for the detection and estimation of small amounts of endrin in a series of samples containing much larger amounts of *p,p'*-DDE, normally impossible on existing systems without resort to the thin-layer method referred to above.

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- 1 J. ROBINSON AND A. RICHARDSON, *Chem. Ind. (London)*, (1963) 1460.
- 2 *Laboratory of the Government Chemist Annual Report 1965*, H.M. Stationery Office, London, p. 86.
- 3 J. RICHARDSON, *Chem. Ind. (London)*, (1965) 1337.
- 4 R. B. HARRISON, *J. Sci. Food Agr.*, 17 (1966) 10.
- 5 R. GOULDEN, E. S. GOODWIN AND L. DAVIES, *Analyst*, 88 (1963) 941.
- 6 *Laboratory of the Government Chemist Annual Report 1964*, H.M. Stationery Office, London, p. 64.

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### Gas chromatography of 3,4-methylenedioxyphenyl carbamates

The gas chromatographic behavior of simple and N-substituted carbamates<sup>1-3</sup> and of 3,4-methylenedioxyphenyl derivatives<sup>4</sup> has been previously described. Several groups of workers have investigated the efficacy of uniting the herbicidal activity of carbamates with the synergistic action observed in the presence of 3,4-methylenedioxyphenyl (MDO-phenyl) derivatives via the preparation of 3,4-MDO-phenyl carbamates<sup>5-10</sup>. Analysis of such compounds utilizing thin-layer chromatography has been reported earlier<sup>11</sup>. The documentation of analysis of 3,4-MDO-phenyl derivatives via various colorimetric means and by infrared spectrophotometry, and of 3,4-MDO-phenyl synergists by paper and thin-layer chromatographic techniques are given in this latter reference.

The present study describes the gas chromatographic behavior of a selection of 3,4-MDO-phenyl carbamates and the relation of elution data to structural features of the aryl carbamate substituents.

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### Experimental

The N-substituted 3,4-MDO-phenyl carbamates were prepared by the reaction of sesamol with the appropriate isocyanate in a pyridine medium<sup>12</sup>. N-Isopropoxypropyl-, N-butoxyethoxyethyl- and N-butyl-3,4-MDO-phenyl carbamates, and N-methyl-3,4-MDO-benzyl carbamates were obtained from Dr. H. I. THAYER, New Products Division, Gulf Research and Development Co., Pittsburgh, Pa., U.S.A.

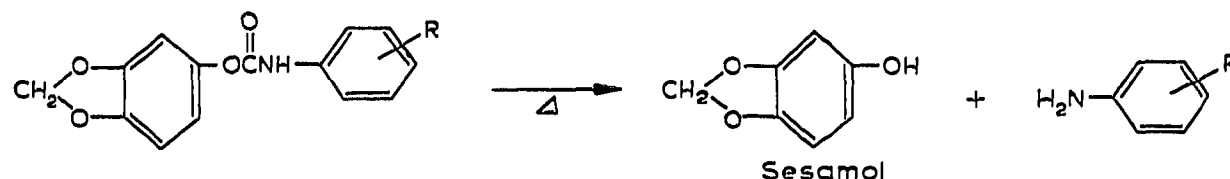
Gas chromatography was carried out utilizing a 6 ft. by 0.25 in. O.D. pyrex glass coil column packed with 4% QF-1 fluorosilicone on 80-100 mesh HMDS-pretreated Chromosorb W, housed in an F & M model 1609 flame ionization gas chromatograph.

Melting point determinations were made on a Fisher-Johns Melting Point Apparatus (Fisher Scientific Company, Silver Spring, Md., U.S.A.).

### Results and discussion

The gas chromatographic elution data of the 3,4-MDO-phenyl carbamates are presented in Table I. Separations were obtained for several of the isomeric aryl derivatives, although the N-*meta*- and *para*-tolyls were not resolvable under the conditions employed here. The column substrate (fluorosilicone) is of relatively low polarity and dipole-dipole interactions of this phase with the solute molecules would be expected to be almost completely absent. Elution order is roughly related to increasing molecular weight with the exception of (a) the N-methoxyphenyl isomers which exhibited a prolonged elution time, and (b) the N-*m*-trifluoromethyl-phenyl derivative which eluted prior to N-phenyl-3,4-MDO-phenyl carbamate.

All of the derivatives were observed to cleave thermally upon chromatography, liberating sesamol and a secondary peak, tentatively believed to be the aniline derivative as follows:



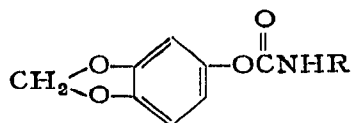
The elution of *o*-chloroaniline matched that of the secondary peak from N-*o*-chlorophenyl-3,4-MDO-phenyl carbamate, as did several other substituted anilines coincide with the elution of the secondary peak of the respective carbamate. The secondary peak from N-*p*-nitrophenyl derivative was not detected.

N-substituted 3,4-MDO-benzyl derivatives were prepared by reaction of piperonyl alcohol with the same isocyanate reagents in the presence of pyridine and subjected to chromatography. The results obtained were identical to those reported herein for the 3,4-MDO-phenyl carbamates with the exception that a piperonyl alcohol peak was detected in each case, which had an elution 1.67 relative to sesamol.

The carbamates obtained from Dr. THAYER (see Experimental) were chromatographed on a 10% SE-30 column in an F & M model 720 gas chromatograph containing a hot-wire bridge detector. The lower N-alkyl members, *i.e.*, N-propyl- and N-butyl-3,4-MDO-phenyl, as well as N-methyl-3,4-MDO-benzyl carbamates exhibited no cleavage during chromatography. However, the comparatively bulky N-

TABLE I

GAS CHROMATOGRAPHY OF 3,4-METHYLENEDIOXYPHENYL CARBAMATES



Compound No.	R	Mol. wt.	m.p. (°C)	Relative elution <sup>a</sup>
1	Phenyl	245	121-122	0.18, 1.00
2	Cyclohexyl	251	130-132	0.19, 1.00
3	<i>o</i> -Tolyl	259	142-143	0.19, 1.00
4	<i>m</i> -Tolyl	259	84-85	0.22, 1.00
5	<i>p</i> -Tolyl	259	151-153	0.22, 1.00
6	<i>o</i> -Methoxyphenyl	275	78-79	0.53, 1.00
7	<i>p</i> -Methoxyphenyl	275	164-165	0.59, 1.00
8	<i>o</i> -Chlorophenyl	279	96-97	0.31, 1.00
9	<i>m</i> -Chlorophenyl	279	90-91	0.29, 1.00
10	<i>p</i> -Chlorophenyl	279	170-171	0.32, 1.00
11	<i>p</i> -Nitrophenyl	290	187-189	— <sup>b</sup> , 1.00
12	$\alpha$ -Naphthyl	295	157-158	0.42, 1.00
13	<i>m</i> -Trifluoromethylphenyl	313	129-130	0.17, 1.00
14	<i>p</i> -Bromophenyl	324	178-179	0.50, 1.00
	Sesamol			1.00

<sup>a</sup> Relative to sesamol as 1.00. Column: 6 ft. by 0.25 in. O.D. pyrex glass coil, 4% QF-1 on 80-100 mesh HMDS-pretreated Chromosorb W. Conditions: column 115°; injection port 70 V (cartridge-heated block); detector 225°; range 1000; nitrogen carrier 88 ml/min; hydrogen 123 ml/min; air 300 ml/min.

<sup>b</sup> No secondary peak observed.

TABLE II

MOIETY VALUES OF ARYL SUBSTITUENTS IN 3,4-METHYLENEDIOXYPHENYL ARYL CARBAMATES

Compound No.	R	Moiety value
13	<i>m</i> -CF <sub>3</sub>	—0.025
1	H	+0.000
3	<i>o</i> -CH <sub>3</sub>	+0.024
4	<i>m</i> -CH <sub>3</sub>	+0.111
5	<i>p</i> -CH <sub>3</sub>	+0.111
8	<i>o</i> -Cl	+0.236
9	<i>m</i> -Cl	+0.207
10	<i>p</i> -Cl	+0.250
14	<i>p</i> -Br	+0.444
6	<i>o</i> -CH <sub>3</sub> O	+0.469
7	<i>p</i> -CH <sub>3</sub> O	+0.516

alkoxy derivative, *i.e.*, N-butoxyethoxyethyl-3,4-MDO-phenyl carbamate decomposed on chromatography. A composite chromatogram is given in Fig. 1.

Values were obtained for aryl substituent moieties for the N-aryl-3,4-MDO-phenyl carbamates by determining  $[\log (i \cdot 10) - \log (\phi \cdot 10)]$ , where *i* and  $\phi$  represent the relative elution values in Table I of any aryl substituted carbamate and the

N-phenyl-3,4-MDO-phenyl carbamate, respectively. The values are given in Table II. The relative influence of the various substituents towards chromatographic elution may be readily discerned. The elution influence of halogen is in the order of  $F > Cl > Br$ , while it is likewise apparent that the position of ring attachment in isomers is important. A more detailed structure-elution study was reported earlier for diverse simple and N-substituted carbamates<sup>2</sup>.

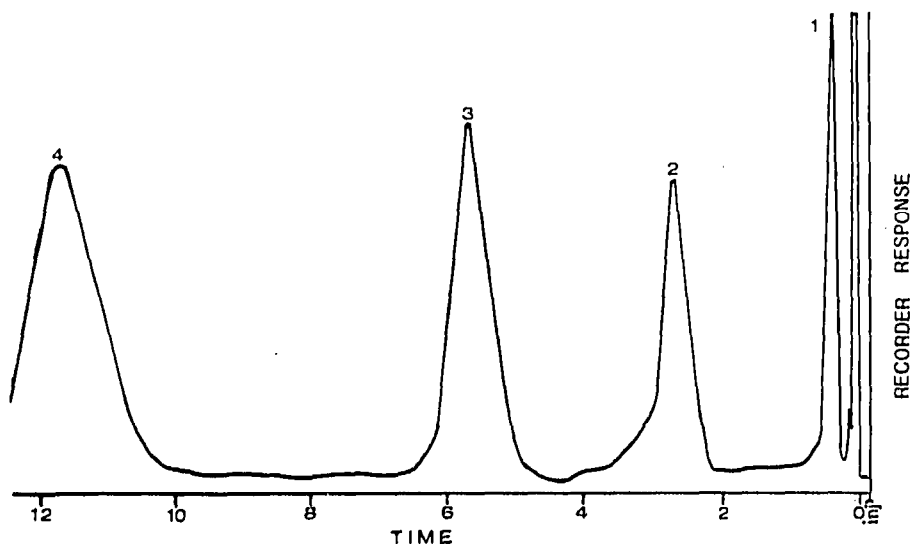


Fig. 1. Composite chromatogram of synergistic 3,4-MDO-phenyl carbamates. Peak identity: (1) break-down product of 3,4-MDO-phenyl-N-butoxyethoxyethyl carbamate; (2) N-methyl-3,4-MDO-benzyl carbamate; (3) N-butyl-3,4-MDO-phenyl carbamate; (4) N-isopropoxypropyl-3,4-MDO-phenyl carbamate.

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- 1 W. L. ZIELINSKI, JR. AND L. FISHBEIN, *J. Gas Chromatog.*, 3 (1965) 142.
- 2 W. L. ZIELINSKI, JR. AND L. FISHBEIN, *J. Gas Chromatog.*, 3 (1965) 260.
- 3 W. L. ZIELINSKI, JR. AND L. FISHBEIN, *J. Gas Chromatog.*, 3 (1965) 333.
- 4 W. L. ZIELINSKI, JR. AND L. FISHBEIN, *Anal. Chem.*, 38 (1966) 41.
- 5 E. A. PRILL, *U.S. Pat.*, 2,773,062 (Dec. 4, 1956).
- 6 E. A. PRILL, *U.S. Pat.*, 2,856,411 (Oct. 14, 1958).
- 7 M. BEROZA, *J. Agr. Food Chem.*, 4 (1956) 49.
- 8 M. BEROZA AND W. F. BERTHEL, *J. Agr. Food Chem.*, 5 (1957) 855.
- 9 W. A. GERSDORFF, P. G. PIQUETTE AND M. BEROZA, *J. Agr. Food Chem.*, 4 (1956) 858.
- 10 H. I. THAYER, R. J. HARTLE AND A. MALLIS, *J. Agr. Food Chem.*, 13 (1956) 43.
- 11 L. FISHBEIN AND J. FAWKES, *J. Chromatog.*, 20 (1965) 521.
- 12 M. BEROZA, *J. Agr. Food Chem.*, 4 (1956) 49.

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