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Note

Thin-layer and gas chromatography of the glycol esters of phenoxy acids

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Phenoxy acids and their esters with aliphatic alcohols are actually used as herbicides. The chromatographic methods of separation and identification have been described both for the formulations and for the residues. This group of herbicides was analysed by thin-layer chromatography (TLC)[1–3], gas chromatography[4–12] and high-performance liquid chromatography (HPLC)[13–15].

In our work, new herbicides prepared by esterification of polyethyleneglycol 300 with selected phenoxy acids were separated and identified using TLC and GC.

EXPERIMENTAL

Preparation of phenoxy esters

Polyethyleneglycol 300 was azeotropically esterified with the selected phenoxy acids in a molecular ratio of 2:1. After distillation of benzene which was applied as an azeotropic agent, the excess of polyethyleneglycol 300 was removed after reaction of the mixture, by extraction, with a 5% solution of sodium bicarbonate. The following mixtures of ethylene glycol monoesters were made with the selected phenoxy acids: 4-chloro-2-methylphenoxyacetic acid (MCPA), 4-chloro-2-methylphenoxy-α-propionic acid (MCPP), 4-chloro-2-methylphenoxy-γ-butyric acid (MCPB), 2,4-dichlorophenoxyacetic acid (2,4-D).

Standards were obtained by similar esterification of the glycols having the summary formula $HO(CH_2–CH_2–O)_nH$, where $n = 1–5$ with phenoxy acids.

Thin-layer chromatography

Separation of the glycol monoesters of phenoxy acids was performed using TLC glass plates pre-coated with silica gel 60 F_{254} with concentrating zone (E. Merck, Darmstadt, G.F.R.). Plates were activated at 110° for 30 min immediately before use. On the above-mentioned plates, 5 μl of the 5% phenoxy acid esters in acetone were developed. The mobile phase was composed of *n*-hexane–acetone (1:1). Visualisation of the separated substances was accomplished with a 5% solution of ammonium molybdate in 30% sulphuric acid or in UV light at 254 nm. The results of this separation are given in Table I and Fig. 1.

Gas–liquid chromatography

The qualitative identification performed on a thin layer was confirmed by the

TABLE I

R_F VALUES FOR THE GLYCOL MONOESTERS OF PHENOXY ACIDS

Polyethyleneglycol 300 monoesters	R_F			
	MCPP	*MCPA*	*2,4-D*	*MCPB*
Ethylene	0.55	0.51	0.48	0.46
Diethylene	0.47	0.43	0.41	0.39
Triethylene	0.40	0.36	0.34	0.32
Tetraethylene	0.33	0.29	0.27	0.25
Pentaethylene	0.26	0.23	0.22	0.20

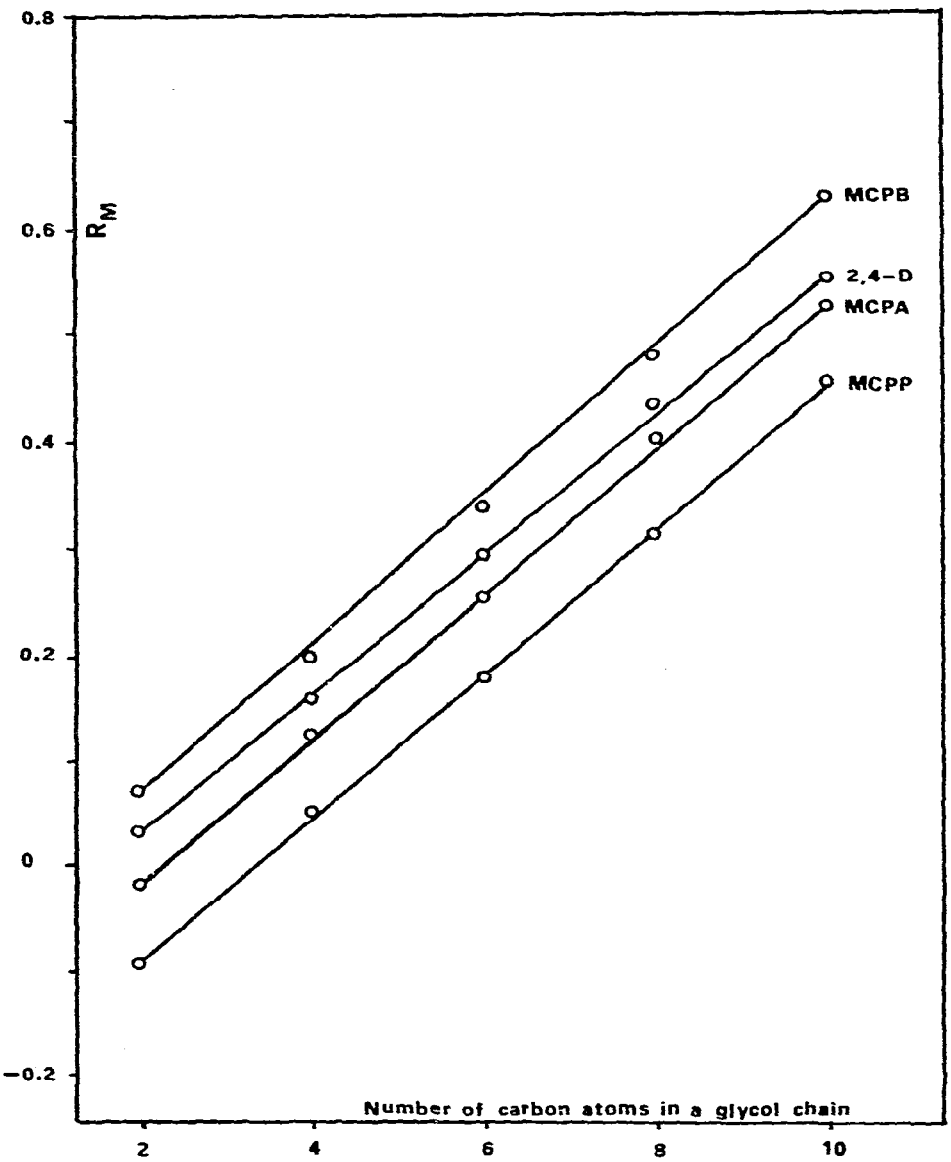

Fig. 1. R_M values *vs.* the number of carbon atoms in a glycol chain of phenoxy esters.

TABLE II

RETENTION TIMES OF THE GLYCOL MONOESTERS OF PHENOXY ACIDS

Polyethyleneglycol 300 monoesters	*Retention time (sec)*			
	MCPP	*MCPA*	*2,4-D*	*MCPB*
Ethylene	54	66	87	126
Diethylene	132	162	204	312
Triethylene	312	390	504	774
Tetraethylene	725	1010	1230	1950
Pentaethylene	1863	2512	2954	4590

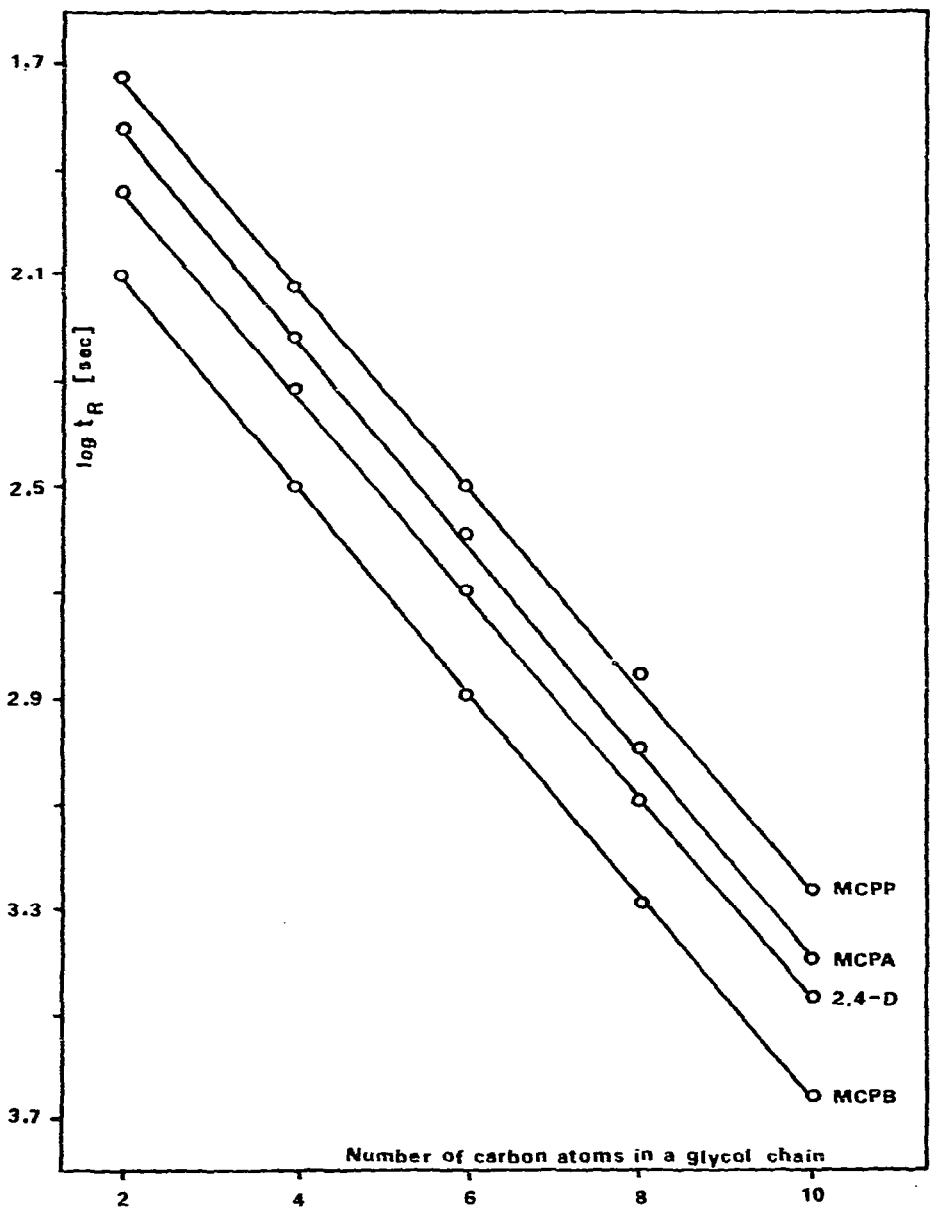

Fig. 2. Dependence of log t_R on the number of carbon atoms in a glycol chain of phenoxy esters.

results received by means of gas chromatography. The Perkin-Elmer 800 chromatograph with flame ionization detector was used equipped with the glass column (6 ft. × 3 mm I.D.). Stationary phase: 3% OV-17 on Gas-Chrom Q, 100–120 mesh. Analyses were performed with the detector temperature 200° and the injection chamber temperature 260°; hydrogen flow-rate at 40 ml/min, air flow-rate at 360 ml/min and nitrogen carrier flow-rate at 30 ml/min, were held constant. The isothermal separation was performed at 240°. The results of the separation of the phenoxy esters are given in Table II and Fig. 2.

RESULTS AND DISCUSSION

The results of TLC separation of the polyethyleneglycol 300 phenoxy monoesters are given in Table I.

The R_M values of the examined homologous series of the phenoxy acid glycol monoesters show a linear correlation based on the number of carbon atoms in a molecule or on the number of carbon atoms in a glycol chain. This dependence is given in Fig. 1 and remains unchanged for all the examined homologous series of phenoxy esters.

The linear correlation of the $R_M = f(c)$ function remains valid for the R_M values from 0.2–0.6. The proposed correlation of the R_M values gives an opportunity to determine the chromatographic behaviour of substances belonging to certain homologous series on the basis of a limited number of standard compounds. The results of the isothermal GC separation are given in Table II. The linear dependence of the logarithm of the retention times t_R from the number of carbon atoms in a glycol chain for the phenoxy esters is given in Fig. 2.

From the dependence of the functions $\log t_R = f(c)$ which are shown in Fig. 2 it is evident that the plots for various homologous sequences are parallel. It can be used for qualitative estimation of the composition of esterified polyethyleneglycol 300 on the bases of the retention times, even with an incomplete number of standards.

REFERENCES

1 C. Meinard, *J. Chromatogr.*, 61 (1971) 173.
2 P. Gruebner, *Arch. Pflanzenschutz*, 7 (1971) 309.
3 F. Geike, *J. Chromatogr.*, 72 (1972) 333.
4 J. M. Devine and G. Zweig, *J. Ass. Offic. Anal. Chem.*, 52 (1969) 187.
5 D. E. Clark and J. S. Palmer, *J. Agr. Food Chem.*, 19 (1971) 761.
6 S. F. Howard and G. Yip, *J. Ass. Offic. Anal. Chem.*, 55 (1972) 1031.
7 C. E. McKone and R. J. Hance, *J. Chromatogr.*, 69 (1972) 204.
8 J. E. Allebone and R. J. Hamilton, *J. Chromatogr.*, 109 (1974) 188.
9 S. U. Khan, *J. Ass. Offic. Anal. Chem.*, 58 (1975) 1027.
10 H. Agemian and A. S. Y. Chau, *Analyst (London)*, 101 (1976) 732.
11 A. E. Smith, *J. Chromatogr.*, 129 (1976) 309.
12 S. Mierzwa and S. Witek, *J. Chromatogr.*, 136 (1977) 105.
13 F. Eisenbeiss and H. Sieper, *J. Chromatogr.*, 83 (1973) 439.
14 T. Hanai and H. F. Walton, *Anal. Chem.*, 49 (1977) 1954.
15 J. F. Lawrence and D. Turton, *J. Chromatogr.*, 159 (1978) 207.