

Short Communication

Thin-layer chromatographic study of the lipophilicity of triazine herbicides

Influence of different organic modifiers

G. L. Biagi, A. M. Barbaro and A. Sapone

Dipartimento di Farmacologia, Università di Bologna, Via Irnerio 48, 40126 Bologna (Italy)

M. Recanatini

Dipartimento di Scienze Farmaceutiche, Università di Bologna, 40126 Bologna (Italy)

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ABSTRACT

The R_M values of a series of triazine herbicides were measured using a reversed-phase TLC system with acetone, methanol or acetonitrile as the organic modifier of the mobile phase. The overlapping of the extrapolated R_M values from three different systems shows that they are not dependent on the nature of the organic solvent. However, a more interesting point arises from a comparison of the b values of the TLC equations. The slopes of the straight lines describing the relationship between R_M values and composition of the mobile phase are related to the solvent strength of the solvents.

INTRODUCTION

In a previous paper we considered the study of lipophilicity indices of a series of triazine herbicides [1]. Very good correlations were shown between chromatographic indices and $\log P$ data. The usefulness of TLC and HPLC techniques as complements to the classical octanol–water partition coefficients was pointed out.

This paper reports a study of the lipophilicity of triazine herbicides in order to investigate more gen-

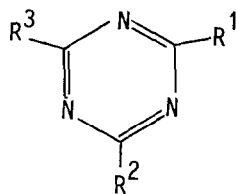
eral aspects of the chromatographic determination of R_M values as lipophilicity indices.

EXPERIMENTAL

The R_M values were obtained using a reversed-phase TLC technique, where the non-polar stationary phase was a silica gel G layer impregnated with silicone DC 200 (350 cSt) from Applied Science Labs. (State College, PA, USA), and the mobile phase was an aqueous buffer (sodium acetate–1/7 *M* Veronal at pH 7.0) alone or mixed with acetonitrile in different proportions. The details of the chromatographic technique for the determination

Correspondence to: G. L. Biagi, Dipartimento di Farmacologia, Università di Bologna, Via Irnerio 48, 40126 Bologna, Italy.

TABLE I
STRUCTURES OF TRIAZINE HERBICIDES



No.	Compound	R ¹	R ²	R ³
1	Terbutylazine	NHC(CH ₃) ₃	Cl	NHCH ₂ CH ₃
2	Cyanazine	NHC(CH ₃) ₂	Cl	NHCH ₂ CH ₃
3	Desisopropylatrazine	Cl	NHCH ₂ CH ₃	NH ₂
4	Atrazine	Cl	NHCH ₂ CH ₃	NHCH(CH ₃) ₂
5	Simazine	Cl	NHCH ₂ CH ₃	NHCH ₂ CH ₃
6	Sebumenton	CH ₃	OCH ₃	NHCH ₂ CH ₃
7	Terbumeton	NHCHCH ₂ CH ₃	OCH ₃	NHCH ₂ CH ₃
8	Terbutryn	NHC(CH ₃) ₃	SCH ₃	NHCH ₂ CH ₃
9	Trietazine	NHCH ₂ CH ₃	N(CH ₂ CH ₃) ₂	Cl
10	Anilazine	Cl	NHC ₆ H ₄ Cl- <i>o</i>	Cl
11	Aziprotryne	SCH ₃	N ₃	NHCH(CH ₃) ₂
12	Propazine	Cl	NHCH(CH ₃) ₂	NHCH(CH ₃) ₂
13	Ametryn	NHCH ₂ CH ₃	NHCH(CH ₃) ₂	SCH ₃
14	Desmetryn	NHCH ₃	SCH ₃	NHCH(CH ₃) ₂
15	Desethylatrazine	Cl	NH ₂	NHCH(CH ₃) ₂
16	Dipropetryn	NHCH(CH ₃) ₂	SCH ₂ CH ₃	NHCH(CH ₃) ₂
17	Atraton	NHCH ₂ CH ₃	NHCH(CH ₃) ₂	OCH ₃
18	Methoprotryne	NH(CH ₂) ₃ OCH ₃	SCH ₃	NHCH(CH ₃) ₂
19	Prometon	NHCH(CH ₃) ₂	OCH ₃	NHCH(CH ₃) ₂
20	Simetryn	NHCH ₂ CH ₃	SCH ₃	NHCH ₂ CH ₃

of the R_M values have been described previously [1–3].

The structures of triazine herbicides are shown in Table I.

RESULTS

In the reversed-phase TLC system, the range of

the linear relationship between the R_M values and the organic modifier concentration in the mobile phase allowed the calculation of extrapolated R_M values at 0%. The TLC equations obtained with acetonitrile in the mobile phase and those previously calculated using acetone or methanol systems are reported in Table II.

$$R_{M \text{ methanol}} = 0.030 (\pm 0.064) + 1.002 (\pm 0.046) R_{M \text{ acetone}} \quad (1)$$

($n = 20$; $r = 0.981$; $s = 0.076$; $F = 467.0$; $P < 0.005$)

$$R_{M \text{ methanol}} = -0.019 (\pm 0.065) + 0.999 (\pm 0.046) R_{M \text{ acetonitrile}} \quad (2)$$

($n = 20$; $r = 0.982$; $s = 0.075$; $F = 478.5$; $P < 0.005$)

$$R_{M \text{ acetone}} = -0.013 (\pm 0.076) + 0.971 (\pm 0.053) R_{M \text{ acetonitrile}} \quad (3)$$

($n = 20$; $r = 0.974$; $s = 0.087$; $F = 334.7$; $P < 0.005$)

TABLE II

TLC EQUATIONS FOR THE ACETONE, METHANOL AND ACETONITRILE SYSTEMS

 $R_M = a + b$ (% organic modifier).

No.	$R_{M\text{extrap}} = a$	b	r	Organic modifier	Concentration range (%)
1	1.588	-0.042	0.993	Acetone	12-60
2	0.970	-0.034	0.991		0-60
3	0.546	-0.071	0.965		0-8
4	1.273	-0.036	0.993		4-60
5	1.035	-0.034	0.979		0-60
6	1.348	-0.036	0.989		4-60
7	1.525	-0.042	0.989		12-60
8	2.003	-0.045	0.993		16-60
9	1.485	-0.040	0.992		12-60
10	1.627	-0.037	0.993		4-60
11	1.223	-0.033	0.979		4-60
12	1.620	-0.040	0.990		12-60
13	1.454	-0.037	0.991		4-60
14	1.117	-0.038	0.991		4-60
15	0.637	-0.062	0.966		0-8
16	1.986	-0.045	0.989		16-60
17	1.101	-0.035	0.991		0-60
18	1.552	-0.038	0.992		12-60
19	1.349	-0.037	0.992		4-60
20	1.252	-0.042	0.995		4-60
1	1.540	-0.028	0.998	Methanol	20-70
2	0.985	-0.026	0.998		0-70
3	0.588	-0.026	0.999		0-8
4	1.252	-0.027	0.995		4-70
5	1.003	-0.026	0.995		0-70
6	1.495	-0.029	0.997		16-70
7	1.491	-0.027	0.998		20-70
8	1.950	-0.027	0.979		20-70
9	1.595	-0.027	0.987		20-70
10	1.623	-0.031	0.987		20-70
11	1.301	-0.023	0.989		12-70
12	1.711	-0.031	0.994		28-70
13	1.465	-0.027	0.994		12-70
14	1.239	-0.026	0.996		12-70
15	0.599	-0.021	0.987		0-70
16	2.100	-0.030	0.996		24-70
17	1.188	-0.025	0.991		0-70
18	1.498	-0.029	0.999		20-70
19	1.522	-0.029	0.996		20-70
20	1.210	-0.026	0.987		4-70
1	1.679	-0.036	0.995	Acetonitrile	20-60
2	1.019	-0.037	0.995		0-55
3	0.568	-0.033	0.998		0-8
4	1.302	-0.033	0.992		4-60
5	1.049	-0.033	0.995		0-55
6	1.521	-0.039	0.994		12-55
7	1.561	-0.037	0.993		16-60
8	1.872	-0.040	0.996		20-60
9	1.542	-0.034	0.995		12-60
10	1.631	-0.038	0.996		16-60

TABLE II (continued)

No.	$R_{M\text{extrap}} = a$	b	r	Organic modifier	Concentration range (%)
11	1.416	-0.031	0.997	Acetonitrile	8–60
12	1.553	-0.035	0.995		16–60
13	1.460	-0.035	0.993		12–60
14	1.278	-0.034	0.995		4–60
15	0.655	-0.029	0.995		0–55
16	2.135	-0.044	0.993		20–60
17	1.130	-0.036	0.993		0–60
18	1.640	-0.042	0.998		16–55
19	1.532	-0.040	0.997		12–55
20	1.217	-0.035	0.995		0–55

The slopes and intercepts of eqns. 1, 2 and 3, very close to 0 and 1 respectively, show the overlapping of the R_M values extrapolated from three solvent systems.

In fact, if the extrapolated R_M values represent the partitioning of the compounds between the silicone oil of the stationary phase and a mobile phase constituted only by water, then we expect the same R_M values whether the organic modifier is acetone, methanol or acetonitrile. These findings are in agreement with earlier results for series of dermorphin-related oligopeptides [4], prostaglandins [5] and quinolines and naphthalenes [6]. This shows that the linear relationship between R_M values and mobile phase composition yields extrapolated R_M values that are not dependent on the nature of the organic solvent.

However, a more interesting point arises from the analysis of the b values in Table II. Their mean values in the acetone, acetonitrile and methanol systems are reported in Table III. The low standard deviations are due to the strong parallelism existing in each chemical class among the straight lines describing the relationship between R_M values and composition of the mobile phase. The more negative slopes in the acetone compared with the other systems are related to the higher eluting power of acetone and indicate that the same decrease in R_M value is given by a smaller increase in the acetone concentration. In Table III are also reported previous data obtained with series of dermorphin-related oligopeptides [4], prostaglandins [5], and quinolines and naphthalenes [6], together with the solvent strength parameters (E_o) of acetone, acetonitrile

TABLE III
RATIOS BETWEEN SLOPES IN DIFFERENT TLC SYSTEMS

Compounds	Slopes in solvent systems			Ratios		
	Acetone	Acetonitrile	Methanol	Acetone/ acetonitrile	Acetone/ methanol	Acetonitrile/ methanol
Triazines	-0.041 (±0.002)	-0.036 (±0.001)	-0.027 (±0.001)	1.14	1.52	1.33
Prostaglandins	-0.071 (±0.002)	–	-0.042 (±0.002)		1.69	
Dermorphin-related oligopeptides	-0.089 (±0.002)	–	-0.055 (±0.002)		1.62	
Quinolines and naphthalenes	-0.046 (±0.002)	–	-0.030 (±0.002)		1.53	
Solvent strength (1/ E_o)	1.78	1.54	1.05	1.15	1.70	1.47

and methanol, when considered in a reversed-phase chromatographic system ($1/E_0$) [7,8].

The ratios between the mean slopes in different solvent systems, and the corresponding ratios between the solvent strengths, are also given in Table III. It can be seen that the ratios between the slopes are very close to the ratios between the $1/E_0$ values for the corresponding solvent pairs.

DISCUSSION AND CONCLUSIONS

The results show the reliability of the TLC system for determining the lipophilic character of molecules. As the R_M values extrapolated to 0% organic solvent are not dependent on the nature of the modifier of the mobile phase, they actually measure the partitioning of the compounds between silicone oil and water. As a consequence, the TLC system shows versatility. In fact, one can choose the most convenient solvent for a given series of compounds and obtain extrapolated R_M values measuring the lipophilic character in the same standard system.

In each solvent system the R_M values change with the composition of the mobile phase at a rate that is correlated with the solvent strength of the organic

modifier as expressed by its $1/E_0$ value. In fact, the ratios between the slopes in different solvent systems follow the ratios between the corresponding $1/E_0$ values.

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