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Short Communication

Prediction of the lipophilicity of some plant growth-stimulating amido esters of ethanolamine using reversed-phase thin-layer chromatography

Simion Gocan*, Florin Irimie, Gabriela Cîmpan

Analytical Chemistry Department, "Babeş-Bolyai" University, 11 Arany Janos Street, 3400 Cluj-Napoca, Romania

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Abstract

Using reversed-phase high-performance thin-layer chromatography with octadecylsilane-bonded silica gel as the stationary phase and methanol–water as the mobile phase, several new compounds (amido esters of ethanolamine) were studied. The R_M values were plotted *versus* methanol molar fraction (x) and a linear correlation was obtained, $R_M = a_0 + a_1X$, characterized by high values of the correlation coefficient, r . The R_M values for $X=0$ (organic solvent content), $(R_M)_{X=0} = a_0$, can be used to elucidate the lipophilicity of the studied compounds. The $\log P$ values were calculated using fragmental constants. A good correlation was found between a_0 and $\log P$, with $r = 0.929$.

1. Introduction

Lipophilicity can be determined by the traditional partition method between *n*-octanol and water [1,2]. The octanol–water system is used in most partition studies but the determination of the partition coefficient by equilibration methods [3] is difficult. The difficulties can be overcome by using chromatographic methods, especially reversed-phase thin-layer chromatography (RP-TLC) [4–7]. Martin and Synge [8] and Consden *et al.* [9] derived a relationship between the partition coefficient P and R_F values in partition chromatography. Bate-Smith and Westall [10] introduced the term $R_M = \log(1/R_F - 1)$, which

leads to a linear correlation between the partition coefficient ($\log P$) and R_M values. The correlations between $\log P$ and $\log k'$ or R_M are frequently linear for non-ionic and ionic compounds [11–13]. When a compound contains one or more dissociable polar substituents, the pH [14,15] and the ionic strength of the eluent [16–18] modify the apparent lipophilicity. The hydrophobic properties of seventeen aniline and phenol derivatives were characterized by Gullner *et al.* [19] by means of RP-TLC and RP-HPTLC retention data. Cserhádi *et al.* [20] studied the lipophilicity of aniline and 36 ring-substituted aniline derivatives by RP-TLC. The R_M values were determined under different experimental conditions, including the addition of salt solutions to the silica gel or to the eluent. Two linear

* Corresponding author.

correlations between the R_M and $\log P$ values [21] and between R_M and the sum of the lipophilicity values of the substituents $\Sigma\pi$ [22] were obtained. These correlations were in all instances inferior to those obtained in salt-free systems.

The purpose of this study was to determine the lipophilicity for fourteen new plant growth-stimulating amido esters of ethanolamine using RP-HPTLC and to establish the correlation between the R_M values for a zero organic solvent content of the eluent and the calculated $\log P$ values.

2. Experimental

The structures of the amido esters of ethanolamine studied are shown in Fig. 1. These compounds were synthesized in our laboratory (De-

partment of Organic Chemistry) [23] and they are new plant-growth stimulators. The compounds showed growth-stimulating activity in the Moewus test with *Lepidium sativum* similar to that of the reference substance indoleacetic acid [24].

HPTLC plates (10 × 10 cm) precoated with silica gel (RP-F_{254s}) were obtained from Merck (Darmstadt, Germany). Methanol for chromatography was obtained from Reactivul (Bucharest, Romania).

Solutions of the compounds in methanol (1 mg/ml) we prepared and 2 μ l per spot were applied to the starting line, 1.5 cm from the bottom edge of the plate. The applied spots were dried in a gentle stream of air. The plates were developed in a previously equilibrated glass chromatographic chamber for 30 min. The migration distances of the eluent between start and the front was 8 cm in all instances.

The spots were revealed under UV light at 254 nm (Camag universal UV lamp).

3. Results and discussion

C₁₈-bonded silica gel was used as a non-polar stationary phase and methanol–water as a polar mobile phase. The experimentally measured R_M values with different concentrations of methanol (in terms of the molar fraction X) in the mobile phase are presented in Table 1.

It is well known that in binary aqueous organic eluents, e.g., methanol–water, methanol has a decisive influence on the overall chromatographic distribution equilibria reflected in the R_M values of the investigated solutes.

A good linear correlation ($R_M = a_0 + a_1X$) was found between R_M and X , characterized by high values for the correlation coefficient, r . The R_M values extrapolated to zero organic solvent content, $(R_M)_{X=0} = a_0$, are different and depend on the structures. The intercept value a_0 can be correlated with the lipophilicity of the compound, and the slope a_1 can be considered as a measure of the strength of the mobile phase or, in other words, a_1 is the mobile phase contribution to the solute retention (Table 1).

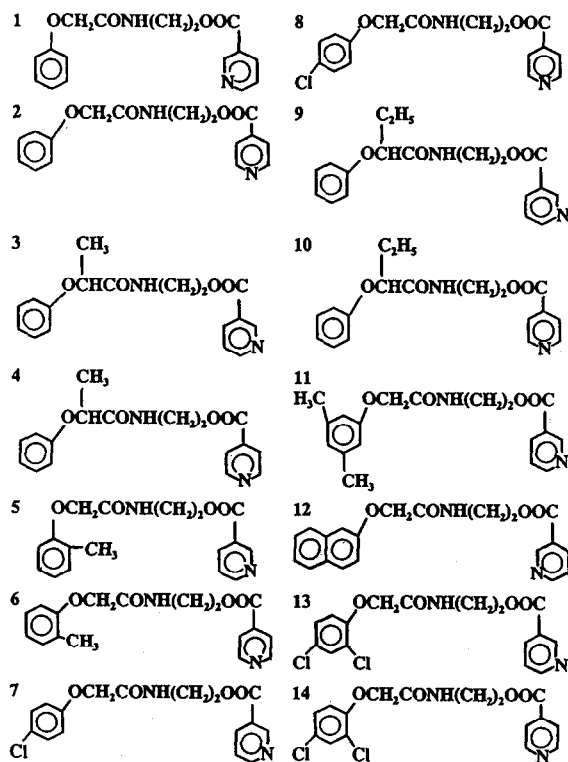


Fig. 1. Structures of the amido esters of ethanolamine studied.

Table 1

Dependence of R_F values (first row in each pair) and R_M values (second row) of some amido esters of ethanolamine on methanol molar fraction in aqueous solutions, X

Sample No. ^a	$X/(1-X)$				a_0	a_1	r	Log P
	0.800/0.200	0.640/0.360	0.509/0.491	0.400/0.600				
1	0.78 -0.549	0.62 -0.213	0.52 -0.053	0.31 0.347	1.13	-2.12	-0.981	2.090
2	0.76 -0.501	0.60 -0.176	0.50 0.000	0.29 0.389	1.17	-2.12	-0.984	2.090
3	0.78 -0.545	0.61 -0.194	0.50 0.000	0.29 0.389	1.23	-2.24	-0.988	2.497
4	0.78 -0.549	0.59 -0.158	0.48 0.035	0.29 0.389	1.25	-2.25	-0.992	2.497
5	0.73 -0.432	0.51 -0.017	0.40 0.176	0.19 0.630	1.57	-2.52	-0.985	2.594
6	0.75 -0.477	0.54 -0.070	0.40 0.176	0.20 0.602	1.58	-2.60	-0.991	2.594
7	0.73 -0.432	0.54 -0.070	0.40 0.176	0.20 0.602	1.53	-2.49	-0.988	2.814
8	0.74 -0.454	0.53 -0.052	0.39 0.194	0.20 0.602	1.57	-2.55	-0.992	2.814
9	0.76 -0.501	0.56 -0.105	0.43 0.122	0.21 0.575	1.53	-2.57	-0.987	3.027
10	0.77 -0.525	0.56 -0.105	0.41 0.158	0.21 0.575	1.59	-2.66	-0.993	3.027
11	0.70 -0.368	0.48 0.035	0.34 0.288	0.15 0.753	1.76	-2.69	-0.988	3.039
12	0.71 -0.389	0.48 0.035	0.34 0.288	0.15 0.753	1.78	-2.74	-0.989	3.374
13	0.67 -0.308	0.42 0.140	0.28 0.410	0.11 0.908	2.00	-2.92	-0.989	3.479
14	0.68 -0.327	0.42 0.140	0.27 0.432	0.10 0.954	2.11	-3.09	-0.989	3.479

^a See Fig. 1.

The log P values were calculated according to the method described by Rekker [25] using the fragmental constants and the relationship $\log P = \sum f_i n_i + \sum k_n C_m$, where f_i is fragmental constant for fragment i , n_i is the number of identical fragments, k_n is the number of identical proximity effect corrections and C_m is the proximity effect correction type m . The resulting values for the studied compounds are present in Table 1.

Arranging the compounds according to their increasing values of log P , the same trend results for the corresponding a_0 values. Exceptions were observed for certain compounds, but these were within the experimental error limits. The intercept values were correlated with log P values, and the linear regression is plotted in Fig. 2. In this way, the following linear expression was obtained: $a_0 = 0.140 + 0.603 \log P$. The statisti-

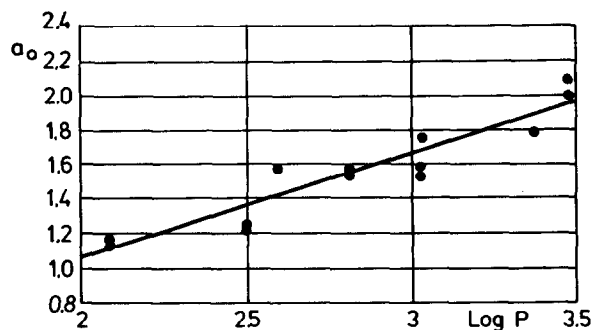


Fig. 2. Correlation between a_0 and $\log P$ values.

cally supported correlation coefficient was $r = 0.929$.

4. Conclusions

RP-HPTLC is a suitable method for the determination of the intercept values $(R_M)_{X=0} = a_0$, which may be used as lipophilicity parameter for several compounds. A good correlation between a_0 and $\log P$ with $r = 0.929$ was found.

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