Thin Layer Chromatography for Some Derivatives of 1,4-Naphthoquinone

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Introduction

Amino derivatives of 1,4-naphthoquinone exhibit certain types of biological activity, in particular antibacterial, antifungal, as well as chelating activity for the transport of trace elements due to the presence in the structure of the quinone fragment and the corresponding substituents. The modification of chloro derivatives of 1,4-naphthoquinone by amine-containing compounds uses the nucleophilic substitution of chlorine atoms on the R-amine fragment. Synthesis and study of biological activity of derivatives of 1,4-naphthoquinone continue. In particular, antitumor activity of various derivatives of 1,4-naphthoquinone is investigated [1]. Although many works that deal with the synthesis of 1,4-naphthoquinone derivatives, have been reported to use thin-layer chromatography (TLC) to control the completion of the reaction, but the conditions for TLC and separation results are not given. In papers [2, 3] the effect of the composition of the eluent on retention for series of amino acid and cyclic derivatives of 1,4-naphthoquinone under conditions of TLC was investigated.

The purpose of this work is to investigate the chromatographic behavior of six derivatives of 1,4-naphthoquinone by means of normal-phase TLC, as well as to establish the relationship between the retention and structure of these compounds.

Experimental

In Table the structures are presented for investigated derivatives of 1,4-naphthoquinone I-VI which were synthesized at the Department of Technology of Biologically Active Compounds, Pharmacy and Biotechnology of the National University "Lviv Polytechnic" using the mentioned above reaction and provided for research by the TLC method. For compounds I-VI as the investigated derivatives of 1,4-naphthoquinone Table 1 also shows the relative area A_S, which was calculated according to the Snyder algorithm described in the monograph [4]. Relative area A_S is occupied by one molecule of compound that is adsorbed on the surface of the stationary phase. The measurement unit of the calculated area (A_S) corresponds to 8.5 square Ångström, for example, for the benzene ring is taken $A_S = 6$ or 51 square Ångström. TLC was performed using Silufol plates (manufacturer Kavalier) with broad-pores silica gel named as Silpearl. The solutions concentration of solutes in dimethylsulfoxide (DMSO) was 2-5 mg/ml, and the volume of the solution applied to the starting line was 1 µl. The solvents used in this work were chosen according to Snyder's classification [4]. In all binary systems, benzene formed the basis, and the elution ability was increased using polar components (chloroform, acetone, acetonitrile, methanol, propan-2-ol) in the range of 2.5 to 10 % vol. Chromatograms were obtained by the method of solvent movement from the bottom to the top.

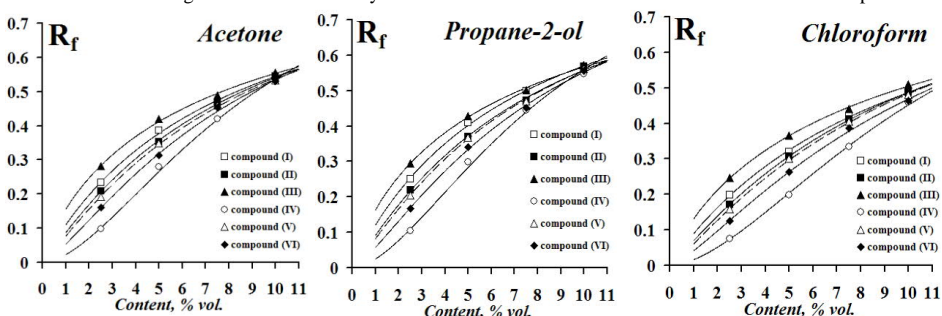| Number of compound	Compound structure	Number of compound	Compound structure
(I)	$A_S=51.9$	(II)	$A_S=52.7$
(III)	$A_S=45.0$	(IV)	$A_S=75.6$
(V)	$A_S=54.1$	(VI)	$A_S=61.6$

Fig.1. Retention dependencies (R_f) from the content (% vol.) of the polar component in the eluent for the compounds I to VI (lines correspond to model of Soczewinski equation)

$$R_f = \frac{L}{L_0} \qquad R_M = \lg\left(\frac{1}{R_f} - 1\right) \qquad R_M = A - B \cdot \lg(N_B)$$

L – the retention distance of the solute; $L_0 = 120$ mm – the distance that passed the front of the mobile phase;
N_B – mole fraction of the polar component in the binary mixture of the mobile phase;
in Soczewinski equation there are A and B – constants whose values depend on the properties of the solute and the mobile phase composition.

Results and discussion

In Fig. 1 there are examples of dependences of the R_f values on the volume fraction of the polar component in the eluent. In all cases according to Soczewinski equation good correlations are obtained, since the values of R^2 are in the range of 0.997 to 0.999. Constant A has negative values, their absolute values lie in the range from 0.807 to 1.710 and depend on both the solute and the polar component of the mobile phase. The values of B lie in the range from 0.8311 to 1.7058 and are appreciably dependent on solute, and also almost do not change from the qualitative composition of the eluent. The correlation between the mean values of inclination B and the areas of A_S occupied adsorbed molecules of compounds I-VI on the stationary phase is shown in Fig. 2. With an increase in the area of A_S an increase in the slope B is observed, which is well in agreement with the theory of retention in the normal phase chromatography, which is described in detail in the monograph [4]. In Fig. 3 shows the relationship between the values of the slopes B and the intercepts A in Soczewinski equation for the polar components of the mobile phase and compounds I-VI. Within each polar component of the mobile phase are well described by straight lines with close slopes.
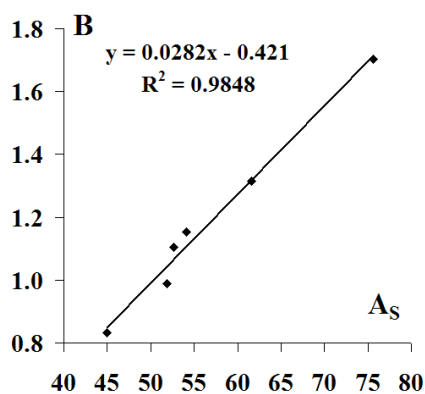
Fig.2. The correlation between the mean values of slopes B and A_S areas occupied by adsorbed molecules of compounds I-VI on a stationary phase.
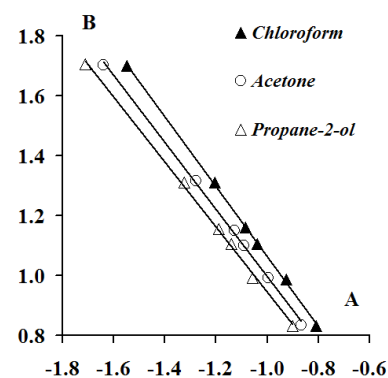
Fig.3. The relationship between the values of the slopes B and the intercepts A in the Soczewinski equation for the polar components of the mobile phase and compounds I-VI.

Conclusions. The retention was studied for six derivatives of 1,4-naphthoquinone, compounds I-VI under conditions of normal-phase TLC with silica gel, as a stationary phase, and benzene binary eluents with a volume fraction of the corresponding polar components within the range of 2.5-10% vol. When using the volumetric particle (%), as the coordinates of the abscissa axis, for all compounds I-VI, the growth of R_f values is determined for the replacement of the polar component of the mobile phase in the following series: chloroform - acetone - propane-2-ol. It is shown that the slopes of rectilinear dependences in accordance with the Soczewinski equation between the R_M values as retention parameter and the logarithm of the molar part of the polar modifier $\lg(N_B)$ is well correlated with the area (A_S) occupied by the adsorbed molecule of solute on a stationary phase, For eluents with a certain polar component, the linear correlations were found between the intercepts and slopes in the Soczewinski equation.

References

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