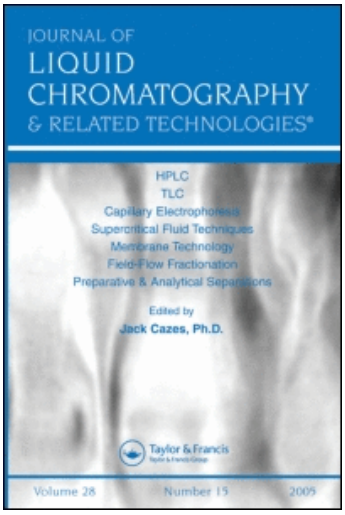

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High Performance Liquid Chromatography of Benzyl Derivatives of ES-Silanates

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Abstract: Presented in this paper are results of investigations concerning optimization of conditions of separation and determination of two newly obtained hyper coordinated silicates, which belong to the group of ES-silanates. To this process were subjected: 1-[N-(phenylmethyl)aminiomethyl]spirobi(sila-2,5-dioxa-4,4-dimethylcyclopentane-3-on)ate and 1-[N-(phenylmethyl)aminiomethyl]spirobi(sila-2,5-dioxacyclopentane-3-on)ate. The analyzed compounds show biological activity. Three stationary phases (octadecyl, octyl and naphthylpropyl), two mobile phases (acetonitrile, dichloromethane) with various flow were tested. The highest selectivity and separation factors ($\alpha = 1.27$) were obtained using the naphthylpropyl column and the mobile phase consisting of pure acetonitrile. The octadecyl (which is recommended as standard) phase did not enable satisfactory results.

Keywords: Hyper coordinated organosilicon compounds, Separation, Determination, HPLC

INTRODUCTION

Obtaining more and more complex organosilicon structures forces one to look for new methods of organic synthesis and to improve applied methods. This is

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connected with the immediate need to elaborate optimum conditions for separation and probable determination of analyzed compounds. It is advisable because these compounds are mainly analogues of natural substance or/and show pharmacological activity. Some of these compounds easily hydrolyze; this causes additional difficulties during their synthesis as well as during the chromatographic analysis.

Organosilicon compounds have a remarkable place among other groups of organic chemistry. They have been applied in numerous branches of industry (e.g., in the building trades, metallurgy, polymer, and cosmetic production) and agriculture due to differentiated and advantageous properties. Some of them are used as hydrophobic agents, high boiling oils, heat carriers, dielectrics, or elastomers.[1–4]

Organosilicon compounds are widely applied in medicine. Silatranes, discovered in 1962 by Voronkow,[5] can serve as an example. They show biological activity.[6–9] Numerous organosilicon compounds are effective agents taking part in bioregulation of the plant organism[10,11] Morpholinio-derivatives of ES-silanates, e.g., show such activities. Also silatranes belong to growth stimulating compounds. But they also belong to the class of chloroorganic compounds; therefore, there is a possibility of formation of products toxic to the environment.

The negative influence on the environment is, for many organic chemists, the main reason of synthesis of new compounds, which exhibit desired properties. Optimum compounds stimulates the growth of plants, but does not possess the disadvantages of silatranes. They should have a wide spectrum of activity, low toxicity for the environment, and should be efficient towards basic species of cultivated plants (the efficiency means increase of germination, increase of plant development rate, and generally increase of crops).

The other reason of organosilicon compounds synthesis is their success in the area of chemotherapy. They caused elaboration of unusual valuable synthetic drugs with many-sided activities. Drugs of this type are applied in therapy of the gastric ulcer, tuberculoses, and cancer.[5] Some organosilicon derivatives increase effectiveness of a drug and elongate the time of its activity.[1]

Recently, extensive investigation concerning pent and six coordinated silicon compounds were carried out.[6,7,12] These compounds are interesting because of their structure, which enables activation of bonds situated near to the central silicon atom. Pent coordinated silicon compounds are organic bicyclic systems; both rings are condensed by only one common silicon atom.[13,14]

Information enclosed in the literature showed that hyper coordinated siliconorganic complexes could be formed in biologically connected liquids.[15] Also, proof of an existence of transition organosilicon complex, generated during the cycle of the organism life was reported. It was confirmed that hyper coordinated organosilicon compounds play an important part in assimilation and transport of silica through biological systems. The existence of such complexes can explain other questions concerning biogeochemistry of

silicon, i.e., stability of dissolved silica in concentrated biological liquids, biofractionation of silicon isotopes, and fractionation of germane from the mixture with silicon. Organosilicon compounds containing pent coordinated silicon can effectively increase solubility of silicon, transport this element through tissues, and accumulate it in chosen utilization places.[15]

Considering the above mentioned rudimental information, it seems to be advisable to elaborate methods of determination of this type of hyper coordinated compounds. That is why the aim of our work was to obtain optimum data of separation and determination of two newly synthesized benzyl derivatives, which belong to the group of ES-silanates: 1-[N-(phenylmethyl)aminiomethyl]spirobi (sila-2,5-dioxa-4,4-dimethylcyclopentane-3-on)ate and 1-[N-(phenylmethyl) aminiomethyl]spirobi(sila-2,5-dioxacyclopentane-3-on)ate.

EXPERIMENTAL

HPLC Analysis of ES-Silanates

Samples of 1-[N-(phenylmethyl)aminiomethyl]spirobi(sila-2,5-dioxa-4,4-dimethylcyclopentane-3-on)ate and 1-[N-(phenylmethyl)aminiomethyl] spirobi(sila-2,5-dioxacyclopentane-3-on)ate (Figure 1)[16] were dissolved in DMSO (HPLC purity, Fluka AG, Buchs, Switzerland); to obtain a concentration at about 20 $\mu g \cdot mL^{-1}$. Analyses were performed at 326 nm and at a temperature of 20°C. Three stationary phases were examined: octadecyl (S. Witko – J.T. Baker, Łódź, Poland), octyl (S. Witko – J.T. Baker, Łódź, Poland), and naphthylpropyl (RP Si–NAF, Figure 2).[17] Dimensions of steel columns were: RP Si-C_{18}-250 × 4.6 mm, RP Si-C_8 and RP Si-NAF – 125 × 4.6 mm (Table 1). Two anhydrous systems of mobile phase were applied: acetonitrile and dichloromethane.

The of ES-silanate compounds were prepared by the method described in the literature (Figure 1).[16]

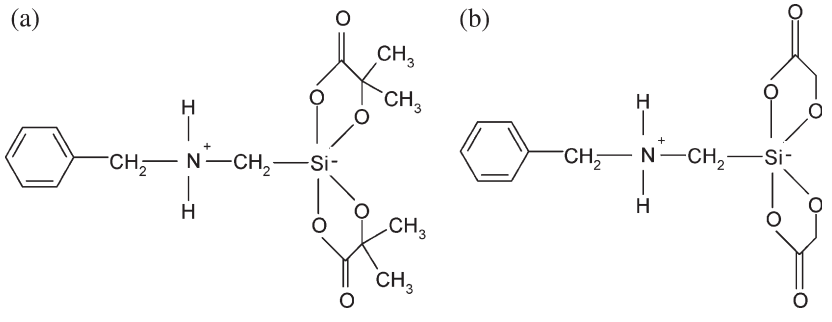

Figure 1. Structures of: (a) 1-[N-(phenylmethyl)aminiomethyl]spirobi(sila-2,5-dioxa-4,4-dimethylcyclopentane-3-on)ate, and (b) 1-[N-(phenylmethyl)aminiomethyl] spirobi(sila-2,5-dioxacyclopentane-3-on)ate.

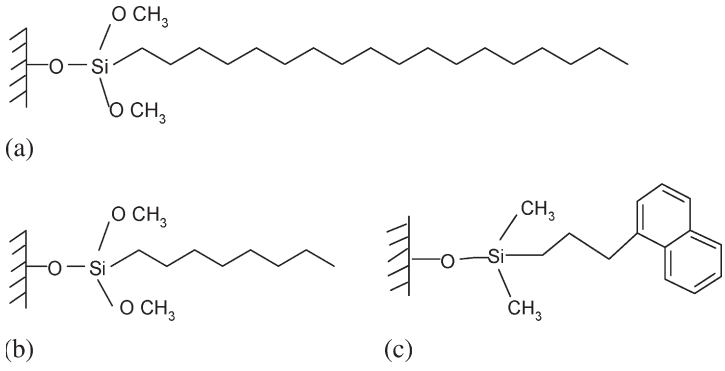

Figure 2. Scheme of chemically bonded stationary phases: (a) octadecyl (RP Si-C_{18}), (b) octyl (RP Si-C_8) and (c) naphthylpropyl (RP Si-NAF).

1-[N-(phenylmethyl)aminiomethyl]spirobi(sila-2,5-dioxa-4,4-dimethyl cyclopentane-3-on)ate: ^{13}C NMR (DMSO-d_6) δ (ppm) = 26.6 (CH_3), 27.3 (CCH_3), 35.3 ($SiCH_2$), 48.9 (NCH_2), 127, 128.6, 128.9 (α, β, γ-C), 177.7 (C═O). ^{1}H NMR, δ (ppm)[16], UV (DMSO): λ_{max} = 326, 354.5, 356.5, 457.5, 478 nm. ^{29}Si NMR (DMSO-d_6) δ (ppm) = −94.3.

1-[N-(phenylmethyl)aminiomethyl]spirobi(sila-2,5-dioxacyclopentane-3-on)ate: ^{13}C NMR (DMSO-d_6) δ (ppm) = 28.5 (OCH_2), 34.8 ($SiCH_2$), 49.4 (NCH_2), 127.1, 128.8, 129 (α, β, γ-C), 179.8 (C═O). ^{1}H NMR, δ (ppm),[16] UV (DMSO): λ_{max} = 326, 354.5, 359, 457.5 nm. ^{29}Si NMR (DMSO-d_6) δ (ppm) = −95.1

Apparatus

Chromatographic measurements were performed on a liquid chromatograph SPD-6A (Shimadzu, Kyoto, Japan) equipped with a gradient pump LC-6A, UV detector, a sampling valve Rheodyne (Berkeley, CA, USA), model 7125, with a 20 μl sample loop, and a Shimadzu C-R6 A data recorder.

^{1}H, ^{13}C, ^{29}Si NMR spectra were recorded on a Varian Mercury 400 MHz in DMSO-d_6, with TMS as internal standard. The UV/Vis spectra were

Table 1. Characteristics of bonded phase

Stationary phases	Type of packing	Manufacturer of column	Carbon content (vol. %)	Length of column (mm)
Octadecyl	RP Si-C_{18}	S. Witko–J.T. Baker	18.09	250 × 4.6
Octyl	RP Si-C_8	Home made	13.49	125 × 4.6
Naphthylpropyl	RP Si-NAF	Home made	16.10	125 × 4.6

recorded on a spectrophotometer DU-68 (Beckman, USA). The infrared (IR) spectra were recorded on a Nicollet Magna-IR 760 in bromide of potassium.[16]

RESULTS AND DISCUSSION

Results obtained during optimization of chromatographic separation are collected in Table 2. In this paper are presented optimum data of chromatographic separation and determination of two benzyl derivatives, which belong to the group of ES-silanates: 1-[N-(phenylmethyl) aminiomethyl]spirobi(sila-2,5-dioxa-4,4-dimethylcyclopentane-3-on)ate and 1-[N-(phenylmethyl) aminiomethyl]spirobi(sila-2,5-dioxacyclopentane-3-on)ate. Two mobile phases (acetonitrile and dichloromethane) in different flow intensity and three stationary phases (octadecyl, octyl, and naphthylpropyl) were tested during this research.

Table 2. Chosen dependence k′ for 1-[N-(phenylmethyl)aminiomethyl]spirobi (sila-2,5-dioxa-4,4-dimethylcyclopentane-3-on)ate and 1-[N-(phenylmethyl)aminiomethyl] spirobi(sila-2,5-dioxacyclopentane-3-on)ate from on type of stationary and mobile phase. Chromatographic conditions: flow −1.0, 0.5 or 0.3 mL · min^{-1}, wavelength −326 nm, temperature −20°C

Type of stationary phase	[a]Mobile phase/	k'_1	k'_2	$\alpha = k'_2/k'_1$
RP Si-C_{18}	Acetonitrile/1.0	2.77	2.86	1.03
	Acetonitrile/0.5	6.91	6.93	1.00
	Acetonitrile/0.3	9.22	9.41	1.02
	Dichlomethane/1.0	2.81	2.87	1.02
	Dichlomethane/0.5	6.94	6.97	1.00
	Dichlomethane/0.3	9.34	9.52	1.02
RP Si-C_8	Acetonitrile/1.0	0.82	0.84	1.02
	Acetonitrile/0.5	4.34	4.45	1.03
	Acetonitrile/0.3	7.85	7.92	1.01
	Dichlomethane/1.0	1.18	1.21	1.03
	Dichlomethane/0.5	4.52	4.61	1.02
	Dichlomethane/0.3	7.78	7.91	1.02
RP Si-NAF	Acetonitrile/1.0	0.41	0.52	1.27
	Acetonitrile/0.5	2.04	2.17	1.06
	Acetonitrile/0.3	8.75	10.35	1.18
	Dichlomethane/1.0	0.45	0.51	1.13
	Dichlomethane/0.5	2.13	2.19	1.03
	Dichlomethane/0.3	9.87	10.36	1.05

[a]In the table are presented only optimum data of separation of the analyzed derivatives.

Octadecyl stationary phase is commonly recommended as a standard phase in numerous determinations performed by the use of HPLC. Different compositions of water containing solvent mixtures caused only an elongation of retention times (these results are not reported in the tables).

As results obtained on the octadecyl phase were not satisfactory, the octyl phase was applied. But it also did not yield suitable separation of the analyzed compounds. Retention times of analyzed compounds were similar for both alkyl columns. When flow intensity was 0.3 mL · min^{-1}, retention time was less than 20 min.

Then, the aryl (naphthylpropyl) column was applied. Usually, this type of phase is designed only for determination of a specific group of compounds, which contain an aromatic ring.[18–20] In the chromatographic process carried on with participation of such stationary phases and analyzed substances, interactions of $\pi-\pi$ type are predominating. Due to these interactions in numerous investigations, as well as in our work, good separation was achieved.

The use of aryl phase shortened the retention times of analyzed compounds by a half. Retention time of (benz.2) obtained due to the aryl stationary phase, did not exceed 2 min when the flow intensity was 1 mL · min^{-1} and as the mobile phase acetonitrile (100%) or dichloromethane (100%) was used. Separation effects of the three stationary phases, which were applied, were presented in Figures 3–5.

Optimum conditions of separation and determination of the two above mentioned derivatives are shown in Table 2. It has been demonstrated that the naphthylpropyl chemically bonded stationary phase is characterized by the highest selectivity ($\alpha = 1.27$). The best separation was obtained by the use of pure acetonitrile as the mobile phase (Table 2, Figures 4–5). Octadecyl and octyl phases were incapable of achieving satisfactory results.

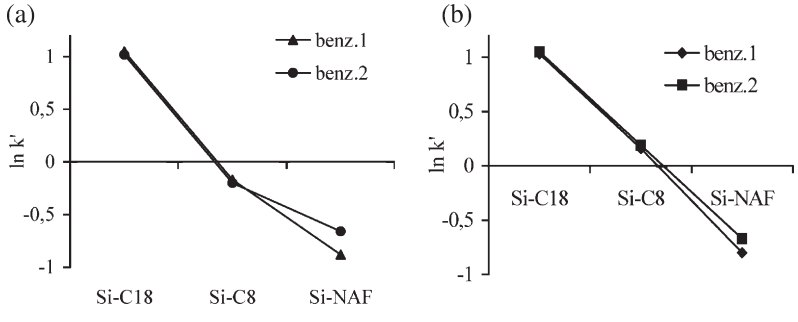

Figure 3. Effect of the separation of benz. 1 and benz. 2 with the use of stationary phases RP Si-C_{18}, RP Si-C_8 and RP Si-NAF. Mobile phase: (a) acetonitrile (vol. 100%), flow rate: 1.0 mL · min^{-1}, (b) dichloromethane (vol. 100%), flow rate: 1.0 mL · min^{-1}, detection −326 nm (see Table 2).

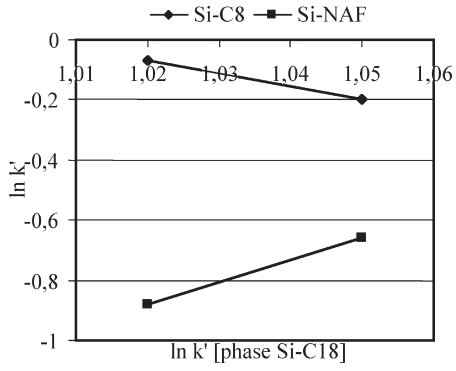

Figure 4. Dependence of ln k′ of the RP Si-C_8 and RP Si-NAF phases on ln k′ obtained for the octadecyl phase for 1-[N-(phenylmethyl)aminiomethyl]spirobi(sila-2,5-dioxa-4,4-dimethylcyclopentane-3-on)ate and 1-[N-(phenylmethyl)aminiomethyl] spirobi(sila-2,5-dioxacyclopentane-3-on)ate.

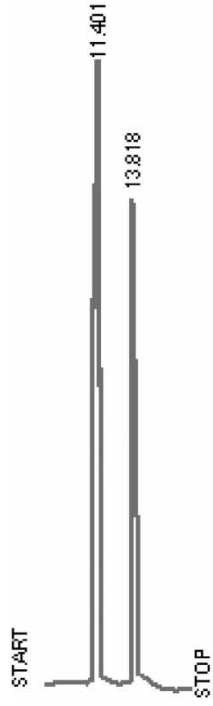

Figure 5. A chromatogram of separation of the 1-[N-(phenylmethyl)aminiomethyl]-spirobi(sila-2,5-dioxa-4,4-dimethylcyclopentane-3-on)ate (11.401 min), and 1-[N-(phenylmethyl)aminiomethyl]spirobi(sila-2,5-dioxacyclopentane-3-on)ate (13.818 min) on the stationary RP Si-NAF phase. Mobile phase: acetonitrile (100 vol. %); flow $-0.3\ \text{ml} \cdot \text{min}^{-1}$, wavelength -326 nm, temperature -20°C.

CONCLUSIONS

Suitable separation of two analyzed derivatives of ES-silanates: 1-[N-(phenylmethyl)aminiomethyl]spirobi(sila-2,5-dioxa-4,4-dimethylcyclopentane-3-on)ate and 1-[N-(phenylmethyl)aminiomethyl]spirobi(sila-2,5-dioxacyclopentane-3-on)ate was obtained only when aryl column was used. The highest separation factor (α) was achieved by the application of acetonitrile as the mobile phase. Analyses carried out on octadecyl and octyl stationary phases did not yield desired effects.

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