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New polar polysiloxane stationary phases containing cyano, nitrophenyl and 8-quinolinyl units attached to diethylene oxide side groups

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ABSTRACT

A series of polysiloxane stationary phases containing 4-cyanophenyl, 4-nitrophenyl, 2,4-dinitrophenyl or 8-quinolinyl units at the ends of diethylene oxide side groups has been prepared by hydrosilylating the appropriate polar alkene onto a well-defined polymethylhydrosiloxane polymer. The polar alkenes were prepared by connecting together eugenol, 2-chloroethyl ether and the polar-substituted phenol or 8-hydroxyquinoline. These stationary phases with silicone backbone and differently substituted eugenol moieties were found to possess both polar and polarizable characteristics. The properties of the phases could be tuned by varying the end groups of the polysiloxane side arms, thereby gaining unique selectivities.

INTRODUCTION

Polysiloxanes have been shown to be the best phases for capillary column gas chromatography (GC). These materials have excellent thermostabilities and provide good diffusion of solutes [1]. A great variety of substituted polysiloxanes have been studied as stationary phases for GC. Recent studies include polysiloxanes containing polar cyanophenyl [2,3], methoxyphenyl [2,4] and nitrophenyl [2,5] as well as polarizable biphenyl [6] and liquid crystalline [7–9] substituents.

We have recently reported the synthesis and chromatographic properties of polysiloxane stationary phases containing oligoethylene oxide side groups [10,11]. The phase containing the 3-[4-(2-methoxyethoxy)ethoxyphenyl]propyl substituent was found to be useful in a temperature range of 20–280°C and it had a selectivity similar to

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that of Carbowax 20M but a much broader working temperature range. New cyanophenyl- and nitrophenyl-substituted polysiloxane stationary phases exhibited a unique blend of polar and polarizable characteristics that resulted in excellent selectivities for solutes having delocalized π-electrons [3,5]. These phases provide unique polarities that have not been achieved with other types of polar phases.

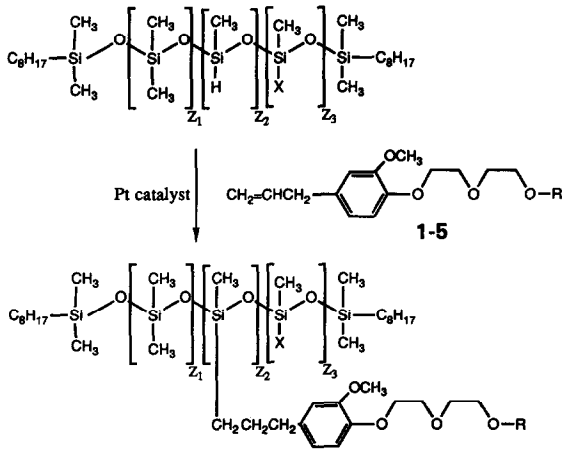
In this paper, the synthesis of new phases containing polar cyanophenyl and nitrophenyl groups as well as the stable diethylene oxide moiety are described. A phase containing a polar 8-quinolinyl group was also prepared. These new phases have polar as well as polarizable characteristics because they are based on the substitution of a phenyl ring [3,5]. The polarizable feature of the phases produces a net higher polarity, and greater selectivity with lower substitution than conventional polar phases. The various functional groups on the stationary phase produce different types of interactions (dispersive, acid–base, dipole–induced dipole, etc.). Therefore, samples having components covering a broad polarity range can be analyzed using these phases. The 8-quinoline-substituted stationary phase fills the long-time need for an efficient basic phase for open tubular columns. All of these new phases have unique selectivity properties, some of which are demonstrated in this work.

EXPERIMENTAL

Preparation of polar-substituted diethylene oxide-containing polysiloxane stationary phases

The new polar-substituted diethylene oxide-containing polysiloxane stationary phases (Fig. 1) were prepared by hydrosilylating the appropriate alkene (**1–5**) onto a previously prepared polymethylhydrosiloxane as reported [11]. The preparation of the polymethylhydrosiloxanes has also been reported [10,12]. The polar-substituted diethylene oxide-containing alkenes were prepared as outlined below

1-(4-Allyl-2-methoxyphenoxy)-5-phenoxy-3-oxapentane (1) (Fig. 2). Potassium hydroxide pellets (34.07 g, 0.61 mol) were dissolved in a small amount of water and slowly added to 57.08 g (0.61 mol) of phenol to form the phenoxide salt. The water was removed under vacuum, 2.67 g (0.16 mol) of 2-chloroethyl ether were added, and the mixture was heated at 120°C for 4 h. After filtering and rinsing the solution with toluene, the oil was distilled to give 1-phenoxy-5-chloro-3-oxapentane; b.p. 155–160°C/0.1 mmHg; NMR (δ): 3.60–3.80 (2H,m), 3.80–4.00 (4H,m), 4.10–4.25 (2H,m), 6.85–7.10 (3H,m), 7.20–7.40 (2H,m). Potassium hydroxide pellets (1.71 g, 0.03 mol) were dissolved in a small amount of water and added slowly to 4.99 g (0.03 mol) of eugenol to form eugenoxide. After removing the water under vacuum, 6.11 g (0.03 mol) of 1-phenoxy-5-chloro-3-oxapentane and 20 ml of dimethylformamide (DMF) were added and the solution was heated at 120°C for 5 h. The resulting mixture was extracted with 150 ml of diethyl ether. The ether layer was washed with two 100-ml portions of 5% aqueous sodium bicarbonate and then 100 ml of water, making sure that the final aqueous layer was neutral. The ether layer was dried over anhydrous magnesium sulfate and vacuum distilled to give 9.98 g (69%) of alkene **1**, b.p. 170°C/0.1 mmHg; NMR (δ): 3.30–3.40 (2H,d), 3.82 (3H,s), 3.90–4.00 (4H,m), 5.00–5.20 (2H,m), 5.75–6.20 (1H,m), 6.60–6.80 (2H,dd), 6.80–6.90 (1H,m), 6.90–7.00 (2H,m), 7.15–7.40 (3H,m). Analysis for $C_{20}H_{24}O_4$; calculated: C, 73.15; H, 7.37; found: C, 72.93; H, 7.48.



Compound	R	Z_1(%)	Z_2(%)	Z_3(%)	X
1a	Phenyl	0	>99	<1	C_2H_5
2a	4-Cyanophenyl	57	37	6	C_8H_{17}
3a	8-Quinoline	58	36	6	C_8H_{17}
4a	4-Nitrophenyl	60	36	4	C_8H_{17}
5a	2,4-Dinitrophenyl	54	33	13	C_8H_{17}

Fig. 1. Polar-substituted diethylene oxide-containing polysiloxane stationary phases.

1-(4-Allyl-2-methoxyphenoxy)-5-(4-nitrophenoxy)-3-oxapentane(4) (Fig. 3). Potassium hydroxide pellets (9.22 g, 0.16 mol) were dissolved in a small amount of water and added slowly to 27.01 g (0.16 mol) of eugenol to form the eugenoxide. Water was removed under vacuum and 58.89 g (0.41 mol) of 2-chloroethyl ether with 100 ml of dimethylsulfoxide (DMSO) were added and the mixture was heated at 120°C for 3 h. The solution was extracted as above and distilled to give 35.01 g (79%) of

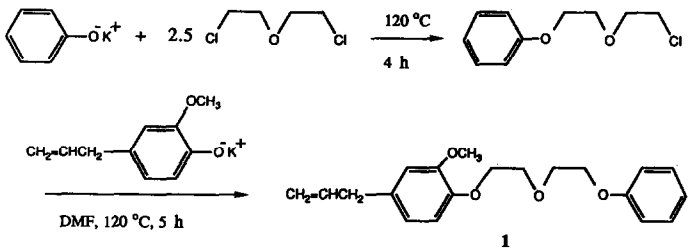
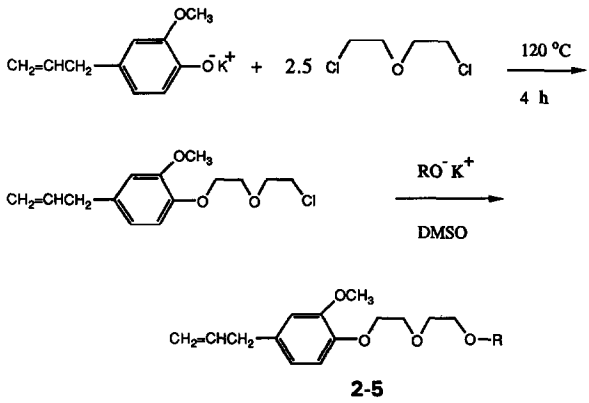


Fig. 2. Preparation of phenyl-substituted diethylene oxide-containing alkene (1).



2-5

Compound	R	Rxn Time	Yield (%)
2	4-Cyanophenyl	4 h	26
3	8-Quinoline	9 h	36
4	4-Nitrophenyl	4 h	35
5	2,4-Dinitrophenyl	7 Days	18

Fig. 3. Preparation of polar-substituted diethylene glycol-containing alkenes (**2–5**). Rxn = reaction.

1-(4-allyl-2-methoxyphenoxy)-5-chloro-3-oxapentane; b.p. 150–160°C/0.078 mmHg; NMR (δ): 3.30–3.40 (2H,d), 3.60–3.70 (2H,m), 3.70–3.90 (4H,m), 4.10–4.20 (2H,m), 5.00–5.15 (2H,m), 5.85–6.10 (1H,m), 6.65–6.75 (2H,m), 6.80–6.90 (1H,m). Potassium hydroxide pellets (2.49 g, 0.044 mol) were dissolved in water and added to 6.18 g (0.044 mol) of 4-nitrophenol and the mixture was heated until the salt was dissolved. The water was removed under vacuum and then 12.0 g (0.044 mol) of the above chloride and 100 ml of DMSO were added and the solution was heated at 120°C for 4 h. The solution was extracted as above to give a solid which was recrystallized twice from 95% aqueous ethanol. The solid was then chromatographed through silica gel (hexane–ethylacetate, 2:1) to give 5.65 g (35%) of alkene **2**; NMR (δ): 3.30 (2H,d), 3.80 (3H,s), 3.90–4.00 (4H,m), 4.15–4.30 (4H,m), 5.00–5.10 (2H,dd), 5.80–6.05 (1H,m), 6.65–6.75 (2H,d), 6.80–6.90 (1H,d), 6.90–7.00 (2H,dd), 8.10–8.20 (2H,dd). Analysis for $C_{20}H_{23}NO_6$; calculated: C, 64.33, H, 6.21; found: C, 64.09; H, 6.19.

*1-(4-Allyl-2-methoxyphenoxy)-5-(4-cyanophenoxy)-3-oxapentane (**2**) (Fig. 3)*
Alkene **2** was prepared as above for **4** from 4.11 g (0.037 mol) of 4-cyanophenol and 10.00 g (0.037 mol) of 1-(4-allyl-2-methoxyphenoxy)-5-chloro-3-oxapentane to give 3.34 g (26%), b.p. 217–230°C/0.070 mmHg which solidified upon cooling, m.p. = 44–46°C; NMR (δ): 3.30 (2H,d), 3.70 (3H,s), 3.90–4.00 (4H,m), 4.10–4.20 (4H,m), 5.00–5.10 (2H,m), 5.80–6.00 (1H,dd), 6.60–6.70 (2H,d), 6.80 (1H,d), 6.90–7.00

(2H,dd), 7.50–7.60 (2H,dd). Analysis for $C_{21}H_{23}NO_4$; calculated: C, 71.37; H, 6.56; found: C, 71.47; H, 6.56.

*1-(4-Allyl-2-methoxyphenoxy)-5-(8-quinolinoxy)-3-oxapentane (**3**) (Fig. 3).* Alkene **3** was prepared as above for **4** from 2.42 g (0.015 mol) of 8-hydroxyquinoline and 4.10 g (0.015 mol) of 1-(4-allyl-2-methoxyphenoxy)-5-chloro-3-oxapentane to give 2.02 g (36%); NMR (δ): 3.30 (2H,d), 3.80 (3H,s), 4.00 (2H,m), 4.10–4.25 (4H,m), 4.40–4.50 (2H,m), 5.00–5.10 (2H,m), 5.80–6.05 (1H,m), 6.60–6.70 (2H,m), 6.80–6.90 (1H,m), 7.10 (1H,dd), 7.30–7.50 (3H,m), 8.00–8.10 (1H,dd), 8.90 (1H,dd). Analysis for $C_{23}H_{25}NO_4$; calculated: C, 72.80; H, 6.64; found: C, 72.79; H, 6.59.

*1-(4-Allyl-2-methoxyphenoxy)-5-(2,4-dinitrophenoxy)-3-oxapentane (**5**) (Fig. 3).* Alkene **5** was prepared as above for **4** from 7.49 g (0.041 mol) of 2,4-dinitrophenol and 11.10 g (0.041 mol) of 1-(4-allyl-2-methoxyphenoxy)-5-chloro-3-oxapentane to give 2.96 g (18%) of an oil; NMR (δ): 3.30 (2H,d), 3.80 (3H,s), 3.90 (2H,m), 4.00 (2H,m), 4.10 (2H,m), 4.40 (2H,m), 5.00–5.10 (2H,m), 5.80–6.05 (1H,m), 6.60–6.70 (2H,d), 6.75–6.85 (1H,d), 7.20–7.30 (1H,m), 8.25–8.35 (1H,m), 8.70 (1H,d). Analysis for $C_{20}H_{22}N_2O_8 \cdot 0.70\ H_2O$; calculated: C, 55.73; H, 5.47; found: C, 55.75; H, 5.53.

Column preparation and evaluation

Fused-silica capillaries were preconditioned at 250°C for 5 h under a dry nitrogen gas stream. Columns were deactivated using a cyanopropylhydrosiloxane dehydrocondensation procedure [13]. The stationary phases were dissolved in dichloromethane at concentrations to give a film thickness of 0.15 μm, filtered through a 2-μm pore stainless-steel filter, and coated in the capillary columns at 25°C using a static coating procedure.

Cross-linking was performed statically by purging the columns slowly with azo-*tert.*-butane (ATB) in argon vapor at room temperature for 1 h, sealing the ends, heating the columns from 40 to 220°C at 4°C min^{-1}, and holding the upper temperature for 35–40 min [14]. The columns were then conditioned by heating from 40 to 200°C at 1°C min^{-1} and holding the upper temperature for 8–10 h under a nitrogen purge. The ATB-treated columns were tested before and after cross-linking.

Dynamic cross-linking with dicumyl peroxide (DCP) was performed [14,15] by weighing out DCP (5–6%, w/w, of the total amount of stationary phase polymer) and dissolving it with the polymer in dichloromethane before coating. After coating, the columns were purged with nitrogen for 30 min, placed in an oven under a very slow hydrogen purge (0.1 ml min^{-1}), heated from 40 to 170°C at 5°C min^{-1}, and held at the upper temperature for 40 min. The columns were then rinsed with 3 ml of dichloromethane and conditioned under a nitrogen purge from 40 to 200°C at 1°C min^{-1}, holding the upper temperature for 8–10 h. These columns were then evaluated at 120°C for thermal stability, polarity, efficiency and acid–base properties using a mixture of biphenyl, alcohols, diols, alkanes, 2,6-dimethylaniline and 2,6-dimethylphenol.

Testing for column thermal stability was performed as follows. The polarity and efficiency were measured after the initial conditioning. The column conditioning temperature was then raised by 10°C and kept at this temperature for 8–10 h. The same test solutes were then injected (<20 ng on-column), and chromatographic measurements for loss of polarity, loss of efficiency, and increase in activity were then made. If no significant changes in these parameters occurred (loss of efficiency or capacity

factors of 10% or less, and no change in peak shape), the columns were taken 10°C higher by the same conditioning process. When losses occurred, 10°C lower than the temperature at which the losses occurred was taken to be the thermal stability limit, defined as the maximum allowable operating temperature (MAOT). Bleed tests were also performed. This method gives a much better evaluation of the stability of the column than does a simple bleed test [9]. Normally, the bleed test does not indicate, for example, oxidation or droplet formation in the stationary phase.

Instrumentation

A Carlo Erba 5160 Mega gas chromatograph with flame ionization detector was used for evaluation of the columns. Hydrogen was used as carrier gas at a linear velocity of approximately 50 cm s^{-1}. The split injector and detector were maintained at 280 and 300°C, respectively. A Hewlett-Packard Model 3390A integrator was interfaced to the chromatograph for data collection.

RESULTS AND DISCUSSION

The polar-substituted diethylene oxide-containing polysiloxanes used in this study were prepared by hydrosilylating the appropriate diethylene oxide-containing alkene onto polymethylhydrosiloxanes of known composition (Fig. 1). This technique has been used for the preparation of polysiloxanes with complicated side chains such as those containing liquid crystalline [7,9] and chiral carboxamide [16] units. Indeed, the structurally similar oligoethylene oxide-containing polysiloxanes, which are suggested as a substitute for Carbowax 20M, were prepared in the same manner [10,11]. This procedure allows for the preparation of polysiloxane phases of known composition in a reproducible manner. The yields of these hydrosilylation reactions are usually greater than 90%. The molecular weight of the final polymer and the percent substitution can be fixed by using a starting hydro polymer of the appropriate size and with the appropriate number of Si–H groups. The hydro polymers were readily prepared from 1,3,5,7-tetramethylcyclotetrasiloxane, dimethyldiethoxysilane and the appropriate amount of octylmethyldimethoxysilane (or vinylmethyldimethoxysilane if one wants a vinyl cross-linking group) in the presence of trifluoromethylsulfonic acid [10,12]. The octyl group was used in these polymers for cross-linking the polymer chains after the material had been coated onto the capillary column [17].

Polysiloxane phases **2a**–**5a** were prepared containing approximately 30% of the polar-substituted diethylene oxide function (see Fig. 1). These were prepared from a hydro polymer where about one-third of the silanes contained a hydrogen. The hydrosilylation reaction was carried out until nearly all of the Si–H groups had reacted; then 1-octene was added. The final percentages of polar functionality and octyl groups were determined from the NMR spectrum of the polymer.

The diethylene oxide-containing alkenes used to form the polymers were prepared by reacting eugenol with 2-chloroethyl ether and the substituted phenol or 8-hydroxyquinoline. Initially, it was thought that the order of combining these three materials was not important. Alkene **1** (Fig. 2) was prepared in a 69% yield by first reacting potassium phenoxide with an excess of 2-chloroethyl ether, followed by reacting the resulting monochloro product with the potassium salt of eugenol. The reaction of the potassium salts of the substituted phenols and 8-hydroxyquinoline with

2-chloroethyl ether gave the disubstituted diethylene oxide rather than the monosubstituted product, even though the phenoxide was in a 2.5 molar excess. Evidently, the monochloro intermediate is more reactive towards the phenoxide than is the dichloro starting material. Alkenes **2–5** were prepared by first reacting the potassium salt of eugenol with 2-chloroethyl ether, followed by reacting the resulting monochloride with the potassium salt of the substituted phenol or 8-hydroxyquinoline. These reactions gave moderate yields of **2–5** (see Fig. 3) when compared to the 69% yield of alkene **1**. It is possible that the electrons on the phenoxide oxygen atoms are less available for nucleophilic substitution reactions because of the electron withdrawing effect of the nitro, cyano or annelated pyridine ring.

The main characteristic chromatographic features of the stationary phases are summarized in Table I. The measurements listed were made on at least two columns of the same type, and 3–5 consecutive runs were averaged. An alkane, *n*-hexadecane (C_{16}), was used to measure column efficiencies and dispersion interactions; an alcohol, 1-dodecanol ($C_{12}OH$), was used to indicate the tendency of each column to retain polar solutes; and an aromatic compound, biphenyl (PhPh), was used to test for dipole-induced dipole interactions. The 2,6-dimethylphenol (DMP) and 2,6-dimethylaniline (DMA) were used to investigate the acid–base characteristics of the phases. Data were obtained for comparison on the well-known Carbowax 20M stationary phase.

The measured efficiencies indicate that the phases produced uniform films during coating; all gave efficiencies above 4200 plates m^{-1}. The low percentage of substitution ensured high diffusity properties of the primarily methylsiloxane backbone. The three-carbon spacer between the backbone and the phenyl ring was long enough to preserve the helical structure of the silicone backbone. The diethylene glycol unit served as a flexible joint between the two aromatic functionalities, which also helped preserve high solute diffusity.

The ethyleneoxy spacer would have an advantage of thermostability, but it is not long enough to preserve the flexibility of the backbone structure. The working temperature ranges of the phases are rather broad as desired. The phenyl ring prevents the functional group from back-biting on the polymer backbone. The 250°C MAOT value of the 8-quinoline phase is lower than desirable, however no other highly basic

TABLE I

RETENTION CHARACTERISTICS OF THE SUBSTITUTED-EUGENOL POLYSILOXANE STATIONARY PHASES

All measurements were done at 120°C on 10 m × 200 μm I.D. fused-silica columns coated with 0.15-μm films. k' = Capacity factor; N = plate number; I = retention index.

Stationary phase	Working range (°C)	Efficiency (N m^{-1})	k'			I			
			C_{16}	PhPh	$C_{12}OH$	PhPh	$C_{12}OH$	DMA	DMP
Carbowax 20M	60–225	5000	3.0	15.9	17	1935	1951	1814	1876
3a	50–250	4800	5.8	14.4	18.6	1740	1790	1594	1671
4a	55–260	4970	3.8	8.0	9.9	1732	1779	1629	1629
2a	60–260	4400	4.7	13.2	12.5	1791	1781	1652	1626
5a	70–200	4200	4.7	13	13	1788	1789	1632	1612

phase exists with as good a performance as this phase in open tubular column GC. The 200°C MAOT value of the dinitrophenyl-substituted phase was a result of the chemical reactivity of the nitro group [5]. The phases were all easily cross-linked. The octyl moiety was a good choice for free radical cross-linking, because it is long, and not hindered for the free radical reaction. The phase with the dinitro substituent required cross-linking by the dynamic procedure using dicumyl peroxide [5]. All of the other phases gave good results with the static method using azo-*tert.*-butane [14].

The eugenol-substituted phases have larger dispersive interactions than Carbowax 20M, which is obvious from the k' values of C_{16} in Table I. This ability to interact well with both polar and non-polar compounds is useful for the analysis of essential oils (see Fig. 4). These mixtures contain compounds covering a broad polarity range. The cyanophenyl-substituted phase has the highest polarizability because biphenyl gives a higher retention index (I) value than dodecanol. The acid–base properties of the phases were tested using the DMA/DMP test pair. The most basic phase is the 8-hydroxyquinoline-substituted phase, and the 4-cyanophenyl-containing phase produces the strongest interactions (see Fig. 5). The 8-hydroxyquinoline phase is a much better alternative than columns treated with potassium hydroxide, because basic solutes elute with good peak shapes (Fig. 6). The slightly acidic cyanopropylhydrosiloxane deactivation was used, however no peak tailing can be observed. More basic compounds can be analyzed using the Carbowax deactivation method. All

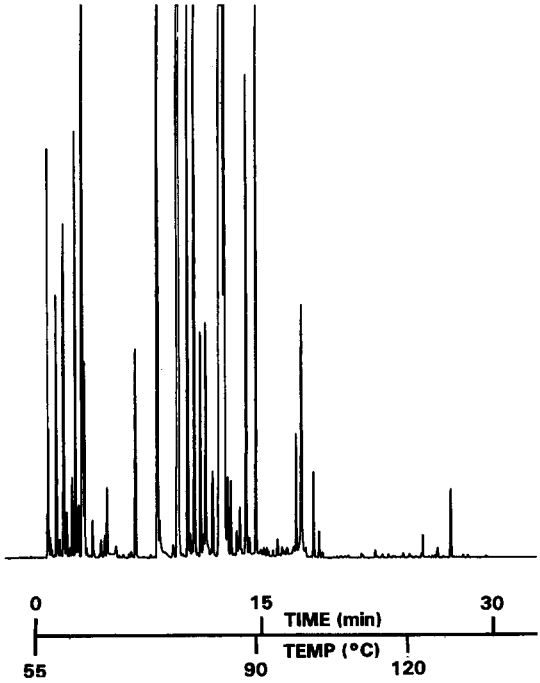


Fig. 4. Capillary column gas chromatogram of Peppermint essential oil. Conditions: 15 m × 200 μm I.D. fused-silica column coated with a 0.15-μm film of 4-nitrophenyl-substituted poly(eugenol)methylsiloxane stationary phase (**4**); temperature programmed from 55°C (2 min) to 150°C at 3°C min^{-1}.

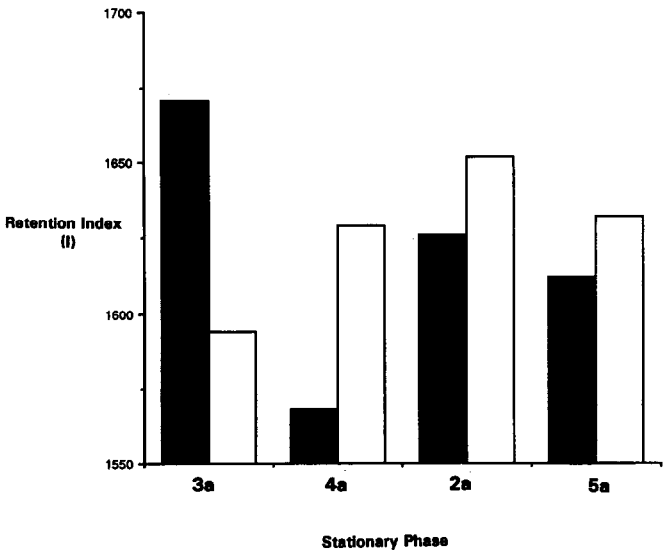


Fig. 5. Retention indices of 2,6-dimethylphenol (■) and 2,6-dimethylaniline (□), showing the acid–base characteristics of the new eugenol-substituted stationary phases. These measurements were made at 120°C.

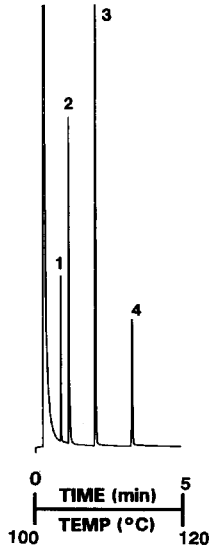


Fig. 6. Capillary column gas chromatogram of basic standard compounds. Conditions: 10 m × 200 μm I.D. fused-silica column coated with a 0.15-μm film of 8-quinoline-containing poly(eugenol)methylsiloxane stationary phase (3); temperature programmed from 100 to 120°C at 4°C min^{-1}. Peaks: 1 = phenylethylamine; 2 = amphetamine; 3 = dicyclohexylamine; 4 = nicotine.

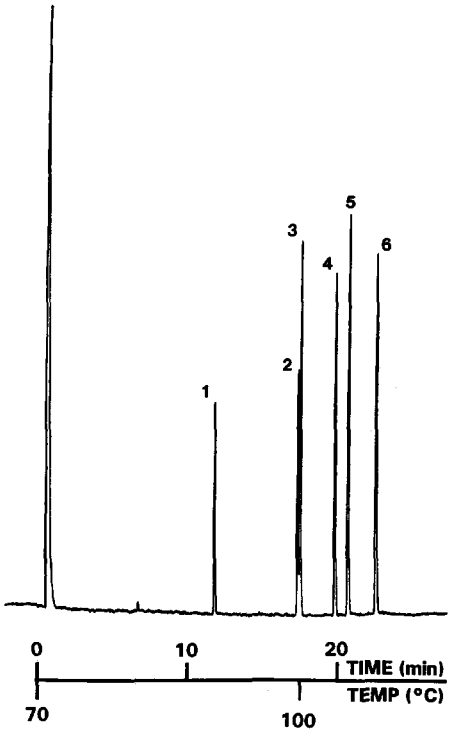


Fig. 7. Capillary gas chromatogram of the dimethylphenol isomers. Conditions: 10 m × 200 μm I.D. fused-silica column coated with a 0.15-μm film of 4-cyanophenyl-containing poly(eugenol)methylsiloxane stationary phase (**2**); temperature programmed from 70°C (2 min) to 120°C (10 min) at 4°C min^{-1}. Peaks: 1 = 2,6-; 2 = 2,5-; 3 = 2,4-; 4 = 2,3-; 5 = 3,5-; 6 = 3,4-dimethylphenol.

isomers of the acidic dimethylphenols were separated on the cyano-substituted stationary phase (Fig. 7). It is interesting to note that the retention order of the 2,5- and the 2,4-dimethylphenol isomers were reversed when using the 4-nitrophenyleugenol phase. The eugenol phases containing cyano or nitro groups have some amphoteric character; both DMA and DMP have strong retention on the cyanophenyleugenol phase (see Fig. 5).

The structural arrangement of the functional groups in the stationary phases also adds a degree of selectivity. The strengths of the solute–stationary phase interactions are influenced not only by the polarities and polarizabilities of the solute molecules and stationary phase substituents, but also by their steric arrangements. By comparing the test solute retention data on the nitro and dinitro phases it can be seen that the second nitro substituent does not increase significantly the acidity of the stationary phase, but instead increases the H-bonding ability of the phase. This can be seen in Figs. 8 and 9.The relatively low H-bonding tendency of the 4-nitrophenyl-substituted phase becomes obvious. The combination of the unique features of the nitro-substituted phases makes possible the separation of all of the dimethylaniline isomers (Fig. 10).

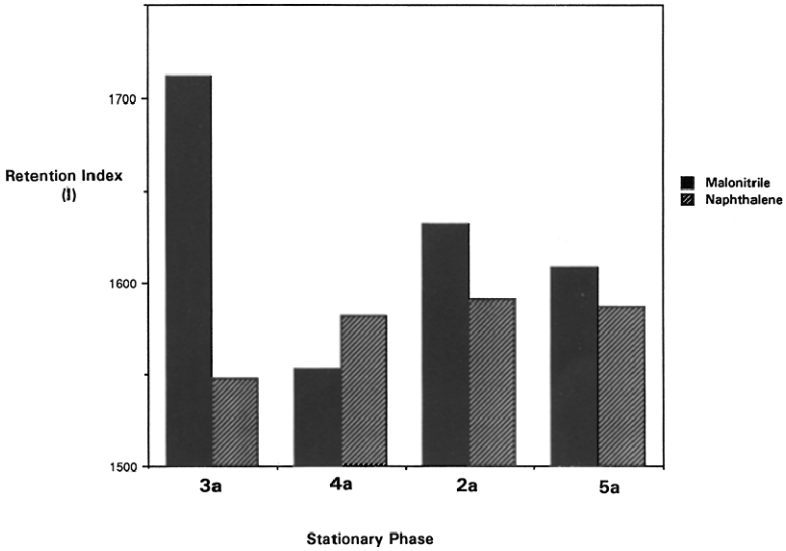


Fig. 8. Retention indices of malonitrile and naphthalene test compounds, showing the π-bond and H-bond characteristics of the substituted poly(eugenol)methylsiloxane stationary phases. The measurements were made at 120°C.

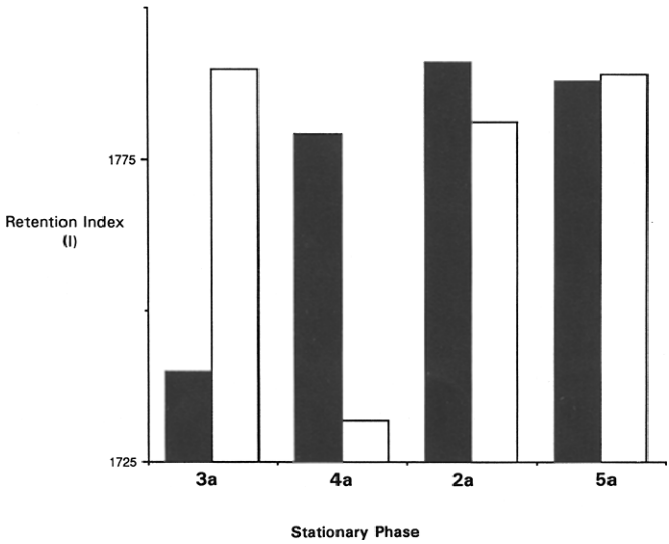


Fig. 9. Retention indices of biphenyl (■) and dodecanol (□) test compounds, showing the π-bond and H-bond characteristics of the poly(eugenol)methylsiloxane stationary phases. The measurements were made at 120°C.

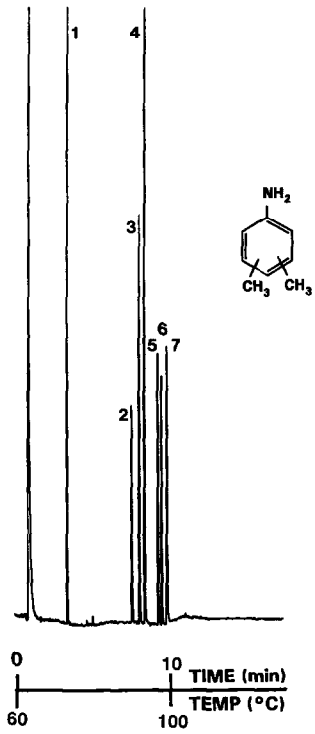


Fig. 10. Capillary column gas chromatogram of the dimethylaniline isomers. Conditions: 10 m × 200 μm I.D. fused-silica column coated with a 0.15-μm film of 8-quinoline-substituted poly(eugenol)methylsiloxane stationary phase (3); temperature programmed from 60 to 150°C (10 min) at 4°C min^{-1}. Peaks: 1 = N,N-; 2 = 2,6-; 3 = 2,5-; 4 = 2,4-; 5 = 2,3-; 6 = 3,5-; 7 = 3,4-dimethylaniline.

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