

Examination of the Properties of Different 20% Phenyl-Substituted Polymethylsiloxane Stationary Phases for Capillary Chromatography

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Abstract. Three polysiloxanes, each having 20% phenyl substitution, have been evaluated for use as stationary phases in fused silica open tubular columns for gas and supercritical fluid chromatography. The columns were coated with PS-090 which had been treated in an aluminum pan in order to improve immobilization properties, OV-7, and a newly synthesized phase, Polymer S.

Excellent columns were prepared with PS-090; however, treatment in the aluminum pan was an uncontrolled process, and the reproducibility of polarity may be questioned. For comparison, OV-7 could not be immobilized, but columns coated with this phase showed good thermal stability. The silanol terminated Polymer S was immobilized via a mechanism involving scission of phenyl groups; thus polarity was decreased after immobilization. However, columns for which Polymer S was immobilized in the presence of a cross-linking reagent maintained their polarity. Such columns showed very good chromatographic performance. These columns were applied to the separation of polynuclear aromatic compounds by GC and to the analysis of extracts from a thermomechanical pulping white water and lichen by SFC.

Key words: *gas chromatography, supercritical fluid chromatography, open tubular columns, methylphenyl polysiloxanes, stationary phase immobilization, polycyclic aromatic compounds, triacylglycerols*

INTRODUCTION

Phenyl silicones are of great value as stationary phases for chromatography. In principle, they can be considered as stationary phases for general purpose, suitable for a variety of solutes. Further, phenyl silicones are among the most heat resistant. A silicone oil, OV-7, having 20% phenyl and 80% methyl substitution has been commercially available for many years. This polymer is composed of methylphenyl and dimethyl siloxane units and it is trimethylsiloxy terminated. Its viscosity is only 500 cSt and it has been used as a stationary phase in

packed column GC, *e.g.*, for the separation of polycyclic aromatic hydrocarbons [1].

Blum and Eglinton [2] used a silicone, PS-090, which has the same gross composition as OV-7, for the preparation of glass capillary columns. This polymer is methoxy terminated and the substituents occur as dimethyl and diphenyl units. Its viscosity is low, 650-700 cSt; however, it can be slightly increased by heat treatment in an aluminum pan. Glass capillary columns coated with this phase could be used at very high temperatures, and they

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showed good selectivity for analytes capable of π - π interactions.

Immobilization of silicones by means of thermal methods often proceeds *via* scission of substituent groups, and this results in decreased polarity [3]. Reproducibility of polarity from column to column is thereby decreased. In order to avoid this problem, alternative immobilization mechanisms have been sought. One approach involves the addition of a cross-linking reagent to the stationary phase. In this case the content of substituent groups remains largely unchanged after immobilization. Different types of cross-linkers have been used for this purpose. Methyltrimethoxysilane was used for PS-089 [4,5], phenyltrimethoxysilane for PS-086 [6], cyanopropyltriethoxysilane for OV-225-OH [7], and tetramethoxydimethyldisiloxane for OV-240-OH [8]. In the present work, immobilization has been attempted with a similar reagent, tetramethoxydivinyldisiloxane.

EXPERIMENTAL

Three types of silicones, each having 20% phenyl and 80% methyl substitution, have been evaluated for use as stationary phases. One of these, PS-090 (Petrarch, Bristol, PA), was first modified by heat treatment in an aluminum pan according to Blum [2,9]. Briefly, the polymer was heated for 4 h at 200°C, followed by 2 h at 250°C. At 30-min intervals, the fluid was stirred with a Teflon spatula. Another polymer, OV-7 (Ohio Valley, Marietta, OH), was used as received. Polymer S was synthesized in house; octamethyldimethoxytetrasiloxane and diphenyldimethoxysilane in appropriate amounts were first cohydrolyzed and then polymerized using tetramethylammonium hydroxide (TMAH) as a catalyst at 100°C for about 1 h. The methods used were similar to those used by Lee and co-workers [10].

Polymer characterization. NMR analysis of the polymers using the phenyl hydrogen peaks at δ 7.1-7.6 and the methyl hydrogen peaks at δ -0.2-0.2 were made in order to determine the composition. Thermal properties were investigated by TG. Average molecular weight was measured by GPC.

Column preparation. Fused silica capillary tubing, 0.25-mm i.d. (Chrompack, Middelburg, The Netherlands), was used as column material in lengths of 10 m for GC. For SFC, capillary tubing, 10-m x 0.050-mm i.d. x 0.375-mm o.d. (Poly-micro Technologies, Phoenix, AZ), was used as column material. Before coating, the capillaries were flushed with nitrogen for several hours at room temperature. The stationary phase was dissolved in dichloromethane for GC columns and

in a 1:1 mixture of dichloromethane and pentane for SFC columns. All columns were statically coated at room temperature. In some cases, the coating solution contained a cross-linking reagent, tetramethoxydivinyldisiloxane (TMDVDS), at 1 or 0.1% (w/w) of the stationary phase. After coating, the columns were flushed with dry nitrogen. The calculated stationary phase film thickness was 0.15 μm in the GC columns and 0.25 μm in the SFC columns. The columns were mounted in a Carlo Erba Mega gas chromatograph equipped with a hydrogen safety system. Prior to making a preliminary test, the columns were conditioned at 220°C for 1 h. Several columns were treated with azo-*t*-butane according to Lee *et al.* [11] before the preliminary test. Heat curing was performed under a slow flow of hydrogen at 300°C, 350°C, and 370°C. Heating rates were 0.5°C min⁻¹ for Polymer S and 5°C min⁻¹ for OV-7 and PS-090.

Column evaluation. All GC columns were evaluated on the same instrument, which was a Carlo Erba Mega gas chromatograph connected to an ELDS 900 data system (Chromatography Data Systems, Kungshög, Stenhamra, Sweden). The columns were evaluated under isothermal conditions by the use of two test mixtures. These were split-injected at 100°C and 125°C, respectively, with the injector temperature at 280°C and the flame ionization detector at 300°C. Hydrogen was used as mobile phase at a linear velocity of 50 cm s⁻¹. Column dead time values were calculated by the iterative method of Guardino *et al.* [12]. The first test mixture consisted of C₁₁-C₁₅ *n*-alkanes, phenol, aniline, 2,6-dimethylphenol, 2,6-dimethylaniline, decanol, decylamine, 2-methylnaphthalene, and nicotine. The second test mixture consisted of C₁₂-C₁₇ *n*-alkanes and biphenyl. Tailing factors were calculated according to McNair [13]. Calculations of the degree of immobilization were based on a decrease in *k* of the C₁₇ *n*-alkane at 125°C.

A Suprex 200A SFC (Suprex, Pittsburgh, PA) was used for column evaluation in SFC. SFC grade CO₂ (Scott, Plumsteadville, PA) was used as mobile phase and a frit restrictor (Lee Scientific, Salt Lake City, UT) was applied.

RESULTS AND DISCUSSION

The phenyl content of PS-090 was reported to be 18-21% [14]. Examination of the batch used here indicated a phenyl content of 23.5%. After heat treatment in the aluminum pan, the phenyl content decreased to 19.5%. An appreciable number of phenyl groups were, therefore, cleaved. Such cleavage, in general, leads to the formation of branched structures [15]. Reactions between silanol

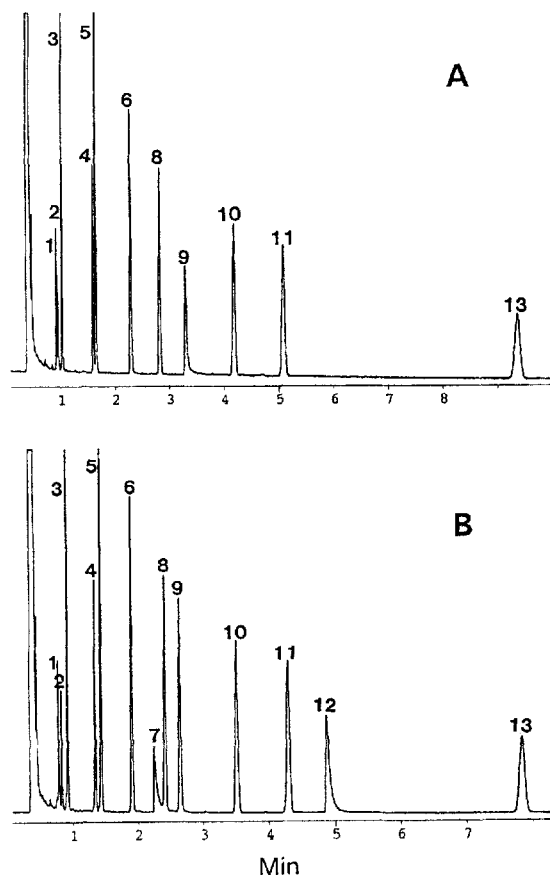


Figure 1. Gas chromatograms (FID) of a test mixture on fused silica open tubular columns. Conditions: 10-m x 0.25-mm i.d. columns coated with aluminum pan treated PS-090; split injection; isothermal at 100°C; (A) after column conditioning at 100°C for 1 h; and (B) after conditioning at 370°C for 12 h. Peak identifications: (1) phenol, (2) aniline, (3) *n*-undecane, (4) 2,6-dimethylphenol, (5) *n*-dodecane, (6) 2,6-dimethylaniline, (7) decylamine, (8) *n*-tridecane, (9) decanol, (10) 2-methylnaphthalene, (11) *n*-tetradecane, (12) nicotine, (13) *n*-pentadecane.

terminated polysiloxanes and aluminum may lead to the incorporation of aluminum in the polymer as discussed by Andrianov [16]. Furthermore, it was suggested that the presence of aluminum in a silicone increases the rate of elimination of phenyl substituents [17].

The weight average molecular weight of PS-090 after the aluminum pan treatment was 1.5×10^5 . Part of the aluminum pan treated polymer was fractionated by precipitation in 50:50 methanol/methylene chloride. A relatively viscous oil, comprising 10% of the polymer was precipitated. The soluble fraction consisted of a low viscous oil.

Polymer S was a true gum. Its weight average molecular weight was 8×10^5 , and its phenyl content was 20.0%. Furthermore, its glass transition temperature, T_g , was -86°C , which is in accordance with data reported by Babu *et al.* [18]. The phenyl content of OV-7, determined by ^1H NMR, was found to be 20.0%, and GPC analysis indicated a weight average molecular weight of 8×10^3 .

Column adsorptive activity. In general, newly prepared columns showed some acidity (see Figure 1A). High temperature treatment of the columns, however, resulted in greatly improved deactivation for the elution of basic compounds (see Figure 1B). Addition of 1% TMDVDS to Polymer S resulted in decreased acidity (Column 3b, Table I). Addition of 0.1% TMDVDS had no such effect (Column 5, Table I). The symmetry of the decanol peaks was also improved by thermal treatment (Table I). The *n*-alkane peaks showed good symmetry, which is an indication that the cross-link density was suitable for chromatography at the temperature tested. Thermal treatment at 330°C for 10 h resulted in a symmetrical alcohol peak, and the acidity was decreased (Column 7, Table I).

Polarity, separation efficiency, and immobilization. From the results given in Table I, columns coated with OV-7 showed high efficiency, which was maintained after conditioning at 370°C . The retention index of biphenyl was not shifted after the conditioning steps. The degree of immobilization was only 2%.

The aluminum pan modified PS-090 was 78% immobilized, and the biphenyl index was only slightly decreased after the immobilization process. It seems that the necessary cross-linking sites were formed during the aluminum pan treatment. Furthermore, excellent separation efficiency was attained.

Polymer S was 81% immobilized. During the heat treatment, the index for biphenyl was decreased by 14 units, which indicates that immobilization in this case proceeds *via* scission of phenyl groups. According to Grassie *et al.* [15], scission of phenyl groups is catalyzed by silanol groups. These silanol groups occur as terminal groups in the polymer and on the fused silica surface. It is clear from the index data in Table I that the scission of phenyl groups in this case took place mainly at temperatures above 350°C .

In order to achieve immobilization without decreasing the retention index, immobilization was attempted by means of a cross-linking reagent, tetramethoxydivinylsiloxane. This reagent can block silanol groups and at the same time provide

Table I. Column properties.

Column no.	Stationary phase	Thermal treatment and extraction ^a	d _f (μm)	k (C ₁₇ , 125°C)	Theoretical plates m ⁻¹	Tailing factors at 100°C		Kováts index (biphenyl, 125°C)	% Immobilization (calculated from C ₁₇)	Column bleed (pA)
						Decanol	Nicotine			
1	PS-090	A	0.15	23.8	4,400	1.88	-	1,473.6	78	1.7
		B		23.0	4,220	1.21	14.6	1,472.7		
		C		21.5	4,470	1.28	6.58	1,472.4		
		D		20.0	4,180	1.29	4.24	1,471.8		
		E		18.6	4,580	1.39	3.17	1,471.8		
2	OV-7	A	0.15	18.9	3,780	2.16	21.3	1,457.6	2	2
		B		18.0	4,060	1.39	5.42	1,458.2		
		C		17.3	4,090	1.25	2.23	1,457.8		
		D		15.9	3,720	1.25	2.23	1,456.6		
		E		0.4	-	-	-	-		
3	Polymer S	A	0.15	17.9	3,500	-	-	1,479.3	81	4.9
		B		18.8	3,370	-	13.2	1,478.2		
		C		18.0	3,830	2.81	7.85	1,475.7		
		D		15.7	3,940	2.81	4.52	1,467.7		
		E		14.5	3,970	1.46	2.38	1,464.2		
4	Polymer S + 1% TMDVDS	A	0.15	17.6	4,040	1.90	-	1,469.4	62	4.0
		B		17.1	3,920	1.20	2.75	1,468.2		
		C		15.1	3,930	1.30	2.20	1,463.1		
		D		12.7	3,760	1.17	2.29	1,459.1		
		E		10.9	3,650	1.32	2.86	1,459.2		
5	Polymer S + 0.1% TMDVDS	A	0.15	18.7	3,680	1.39	8.04	1,468.1	66	3.7
		B		18.0	3,950	2.21	13.6	1,469.3		
		C		16.9	3,930	2.65	7.91	1,469.1		
		D		14.8	4,010	2.02	5.30	1,467.4		
		E		12.2	3,840	1.44	9.49 ^b	1,466.8		
6	Polymer S + 0.1% TMDVDS + ATB	A	0.15	18.4	4,210	1.74	-	1,469.0	74	3.4
		B		18.4	4,210	1.34	15.6	1,468.1		
		C		16.2	4,030	1.10	5.02	1,465.7		
		D		14.1	3,920	1.13	3.24	1,463.0		
		E		13.6	3,890	1.17	5.57	1,462.7		
7	Polymer S + 0.1% TMDVDS	A	0.15	18.3	4,200	1.91	-	1,469.2	42	-
		F		17.8	4,250	1.15	12.9	1,468.8		
		E		7.8	4,230	1.34	9.88	1,469.5		

^aA = conditioned at 220°C for 1 h; B = conditioned at 300°C for 10 h; C = conditioned at 350°C for 10 h; D = conditioned at 370°C for 10 h; E = after rinsing with methylene chloride; F = conditioned at 330°C for 10 h.

^bSymmetrical peak except for a tail.

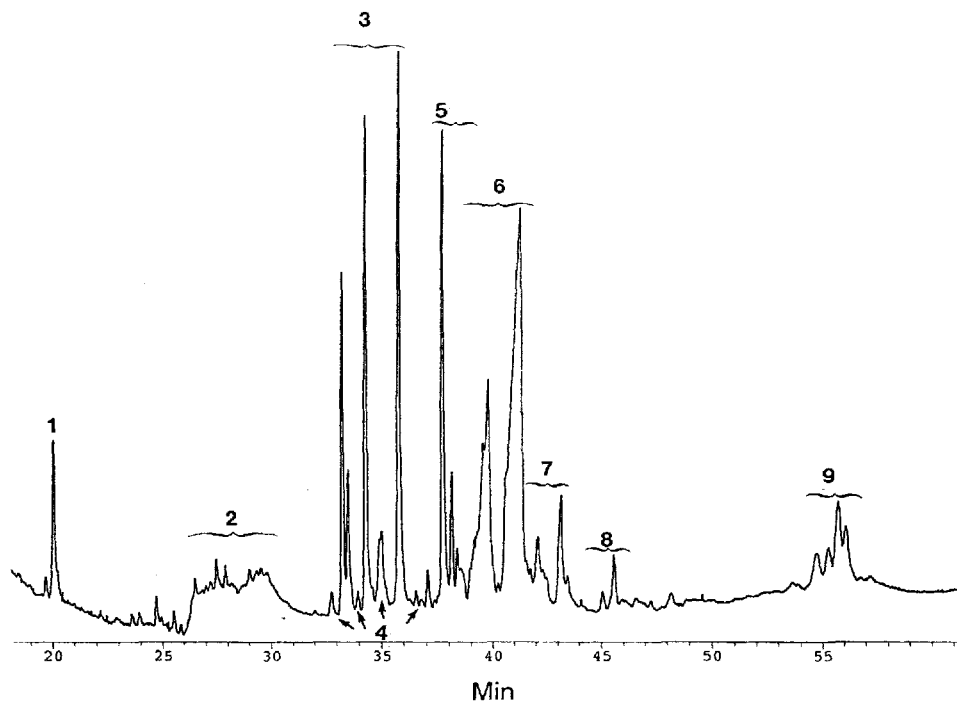


Figure 2. Gas chromatogram (FID) of a test mixture containing polynuclear aromatic compounds on an open tubular column coated with Polymer S (Column 3, Table I). Conditions: splitless injection at 68°C; 1-min hold, then temperature programmed at 20°C min⁻¹ to 120°C, then 5°C min⁻¹ to 320°C; attenuation of 2⁴. Peak identifications: (1) 2-methylfluorene, (2) dibenzothiophene, (3) phenanthrene, (4) anthracene, (5) 4-methyldibenzothiophene, (6) 3-methyldibenzothiophene, (7) 3-methylphenanthrene, (8) 2-methylantracene, (9) 1-methylphenanthrene, (10) 4- and 9-methylphenanthrene, (11) fluoranthene, (12) pyrene, (13) 1-methyl-7-isopropylphenanthrene, (14) benzo[a]fluorene, (15) 2-methylpyrene, (16) 1-methylpyrene, (17) benzo[ghi]fluoranthene, (18) cyclopenta[cd]pyrene, (19) benzo[a]anthracene, (20) chrysene/triphenylene, (21) not identified, (22) β,β-binaphthyl, (23) benzo[k]fluoranthene, (24) benzo[e]pyrene, (25) benzo[a]pyrene, (26) perylene, (27) ideno[1,2,3-cd]fluoranthene, (28) indeno[1,2,3-cd]pyrene, (29) picene, (30) benzo[ghi]perylene, (31) coronene.

a mechanism for immobilization. First, 1% TMDVDS was added to Polymer S. This represents a large molar excess of the reagent when the polymer molecular weight is considered. With such addition, the retention index of biphenyl after a short conditioning step was 10 units lower than on columns where no cross-linker had been added. A further decrease of 10 units was experienced after thermal treatment. Second, 0.1% TMDVDS was added. This amount corresponded to a threefold molar excess, assuming that two methoxy groups on each TMDVDS molecule react with a silanol group on the polymer. Again, the retention index of biphenyl, measured after a short conditioning step, was 10 units lower than for pure Polymer S. The index was, however, maintained constant during the heat treatment step. This result can be explained as a consequence of two factors: blockage of silanol groups and immobilization at lower temperatures. Such immobilization restricts chain

mobility and scission of phenyl groups at higher temperatures. Immobilization of Polymer S + 0.1% cross-linker was also attempted at 330°C (10 h). The degree of immobilization obtained was 42% (Column 7, Table I).

In a third approach, 0.1% TMDVDS was added, but the columns were treated with ATB as a first step. In this method, the vinyl groups in the TMDVDS were most likely employed in the immobilization. On such columns, the retention index of biphenyl dropped only 6 units after thermal treatment.

The stability of the columns in SFC is very high. The columns have now been in use for several months, and the performance is still excellent.

Column bleeding. All columns showed low bleeding at 370°C. However, PS-090 and OV-7 showed the lowest bleeding (Table I).

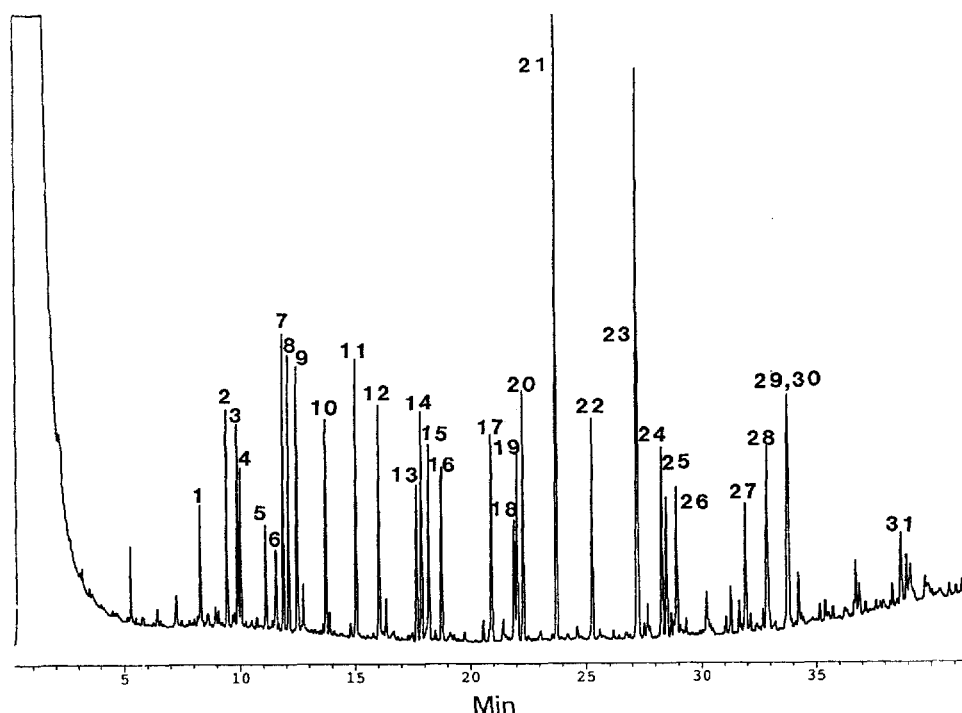


Figure 3. Supercritical fluid chromatogram (FID) of a methylene chloride extract from a thermomechanical white water system on an open tubular column coated with Polymer S. Conditions: 10-m x 0.05-mm i.d. column, 0.22- μ m film thickness; isothermal at 100°C; 100 atm pressure for 15 min, then programmed at 5 atm min⁻¹ to 300 atm. Peak identifications: (1) monoterpenes, (2) lignins, (3) diterpene alcohols, (4) fatty acids, (5) monoglycerides, (6) resins, (7) oxidized resins, (8) diglycerides, (9) sterylesters.

Comparison of treatments. In this study, the method of Blum [2] was transferred from glass capillary columns to fused silica capillary columns. Furthermore, the method was simplified since no separate deactivation step was necessary. The yield of the immobilization step was improved; on glass it was reported to be 40% [2], in this work, we achieved 78%. The columns coated with the aluminum pan treated PS-090 showed excellent chromatographic properties. The only problem with this phase seems to be reproducibility of polarity from batch to batch.

Coating with OV-7 also resulted in columns having good properties. This may be somewhat surprising since it is usually observed that silicone gums result in the most stable stationary phase films [19,20].

Polymer S was immobilized *via* cleavage of phenyl groups, which resulted in a decrease in polarity. With PS-090, the necessary cleavage of phenyl groups took place in the aluminum pan; thus the polarity remained relatively constant during the *in situ* immobilization. Columns coated

with PS-090 and Polymer S showed essentially equivalent chromatographic properties, except that PS-090 had the lowest column bleed.

When a cross-linker was added to Polymer S, immobilization proceeded *via* another mechanism, and column polarity was not changed during immobilization. Thus, when applying this method, column polarity can be controlled. Furthermore, columns prepared in this way showed excellent chromatographic properties. Taking all factors into account, the best columns were obtained when using this last approach.

Applications. A GC chromatogram of a standard solution of polycyclic aromatic hydrocarbons on a column coated with Polymer S is shown in Figure 2, and Figure 3 shows an SFC chromatogram of a dichloromethane extract from a thermomechanical pulping white water system on the same stationary phase. Wood from Norway Spruce was used. The peaks in Figure 3 were tentatively identified by injection of standard substances. Likewise, Figure 4 demonstrates the separation of depsides in an extract from a lichen, *Avernia*

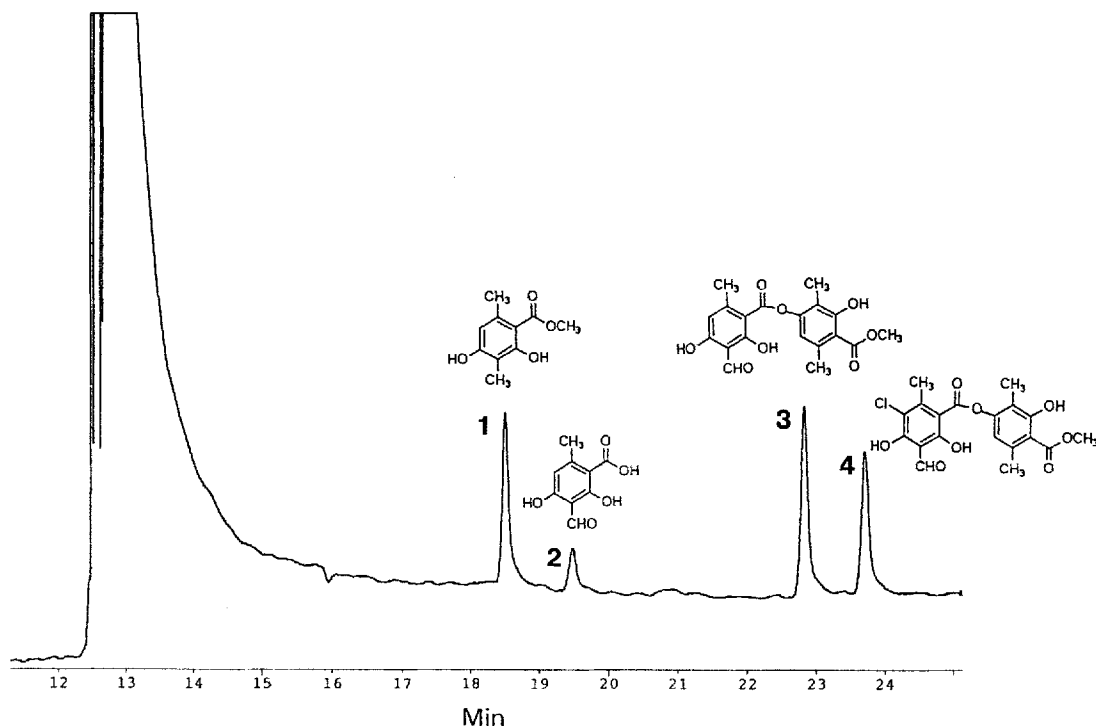


Figure 4. Supercritical fluid chromatogram (FID) of depsides extracted from the lichen, *Evernia prunastri*. Conditions: column as in Figure 3; isothermal at 70°C; 120 atm pressure for 10 min, then programmed at 10 atm min⁻¹ to 300 atm. Peak identifications: (1) methyl β-orsellinate, (2) haematomic acid, (3) atranorin, (4) chloroatranorin.

prunastri. The components of this sample were identified by GC/MS, and their retention in SFC was established by the injection of pure standards.

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