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Short Communication

Study of dihydroxy-substituted saturated urushiol crown ether as a stationary phase in capillary gas chromatography

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ABSTRACT

A new way of cross-linking glass capillary columns with dihydroxy-substituted saturated urushiol crown ether stationary phase is described. The columns were evaluated by determining the column efficiency, phase transition temperature, thermal stability and polarity. It was shown that they have good chromatographic characteristics and unique selectivity in separating phenols, nitro compounds and monsaccharides. The average polarity of these columns was comparable to those of SE-52 and FFAP. The mechanism of separation is discussed.

INTRODUCTION

As most crown ethers have a polar ring formed by heteroatoms, they are useful as chromatographic stationary phases because of the good selectivity resulting from the cavity structure and the strong electronegative effect of heteroatoms on the crown ether ring [1–5]. However, their poor column efficiency and thermal stability prevent the practical usage of small crown ethers, and many attempts have therefore been made to increase their molecular weights [3–5]. Two approaches have been used. One is the synthesis of crown ether-substituted polysiloxane stationary phases. In 1988, Rouse *et al.* [3] first substituted 18-crown-6 onto a polysiloxane backbone with a polymer spacing of 3. Later, we developed an 18-crown-6-substituted polysiloxane with a polymer spacing of 11 [5]. The crown ether–polysiloxane gave a good performance as a stationary phase in capillary gas chromatography and it has sufficient efficiency to achieve many separations, such as those of alcohols, ketones and aromatic hydrocarbons, and especially some polar positional isomers.

The other approach is to cross-link the crown ether directly with SE-54 inside a column [4]. This crown ether–polymer phase also gave good results. However, all these methods are carried out by free-radical cross-linking.

In this work, a new crown ether, dihydroxy-substituted saturated urushiol crown ether (DHSU14C4), shown in Fig. 1, was investigated. It

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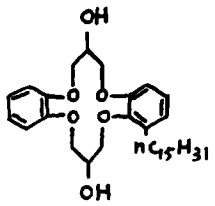

Fig. 1. Structure of dihydroxy-substituted saturated urushiol crown ether.

not only has a long polar alkyl, easily polarizable benzene ring and a polar polyether ring, but also two hydroxyl groups which are convenient for condensation reactions. Capillaries were coated with a mixture of DHSU14C4, OH-terminal silicone oil (GY-202) and γ-chloropropyltriethoxysilane (as coupling agent), and then heated at 60–110°C, so that the crown ether formed a high-molecular-weight immobilized phase on the wall of the glass capillary column by the condesation reaction of the OH-terminated phase on the silica surface [6–8].

Test made with these immobilized crown ether columns showed that the moderately polar phase has a high operating temperature and good selectivity for polar compounds.

EXPERIMENTAL

Apparatus and materials

An SC-7 gas chromatograph (Sichuan Analytical Instrument Factory) equipped with a capillary split injection system and flame ionzation detector, was used with nitrogen as the carrier gas. Capillaries were prepared with a Model GDM glass-drawing machine (Shimadzu).

DHSU14C4 (m.p. 77–78°C) was kindly provided by the Department of Environment Science, Wuhan University). GY202 OH-terminal silicone oil was obtained from the Chendu Centre for Applied Reasarch of Silicone (Ministry of Chemical Industry) and γ-chloropropyltriethoxysilane from Wuhan University Chemical Factory).

Synthesis of DHSU14C4

The dihydroxy-substituted saturated urushiol crown ether was prepared by reaction of saturated urushiol with 1,1′-(*O*-phenyl) bis (2,3-epoxypropyl) ether (Fig. 2). The structure of the new compound was determined by IR, ^{1}H NMR and mass spectrometry and elemental analysis [9].

Capillary column preparation

Glass tubes (7.5 mm O.D, 2.4 mm I.D.) were drawn into capillary columns (0.3 mm I.D.). The columns were filled with 20% hydrochloric acid to 92% of their volume and heated at 180°C for 12 h. They were then rinsed with water and acetone and dried with nitrogen at 150°C for 3 h. The capillaries were statically coated with 0.5% (w/v) mixed stationary phase (DHSU14C4 with GY-202 in different proportions) and γ-chloropropyltriethoxysilane [1% (w/w) of the stationary phase] in methylene chloride. On completion of coating, the column were purged with nitrogen for 5 min, then both ends of the column were flame sealed under vacuum and heated in a gas chromatographic oven at 60°C for 15 h. Finally, the ends were opened and the column was conditioned at 250°C for 8 h. The columns were tested for efficiency. Subsequently, they were rinsed with ten column volumes of methylene chloride and reconditioned at 300°C for 10 h.

RESULTS AND DISCUSSION

When DHSU14C4 was directly coated on a glass capillary column it was found that the capacity factor did not remain constant ($k' = 2.1$–3.4) and the efficiency was especially low ($N < 100$), because the crown ether has poor wettebility on the surface of

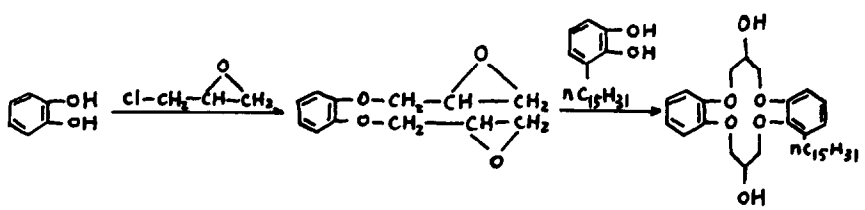

Fig. 2. Preparation of DHSU14C4.

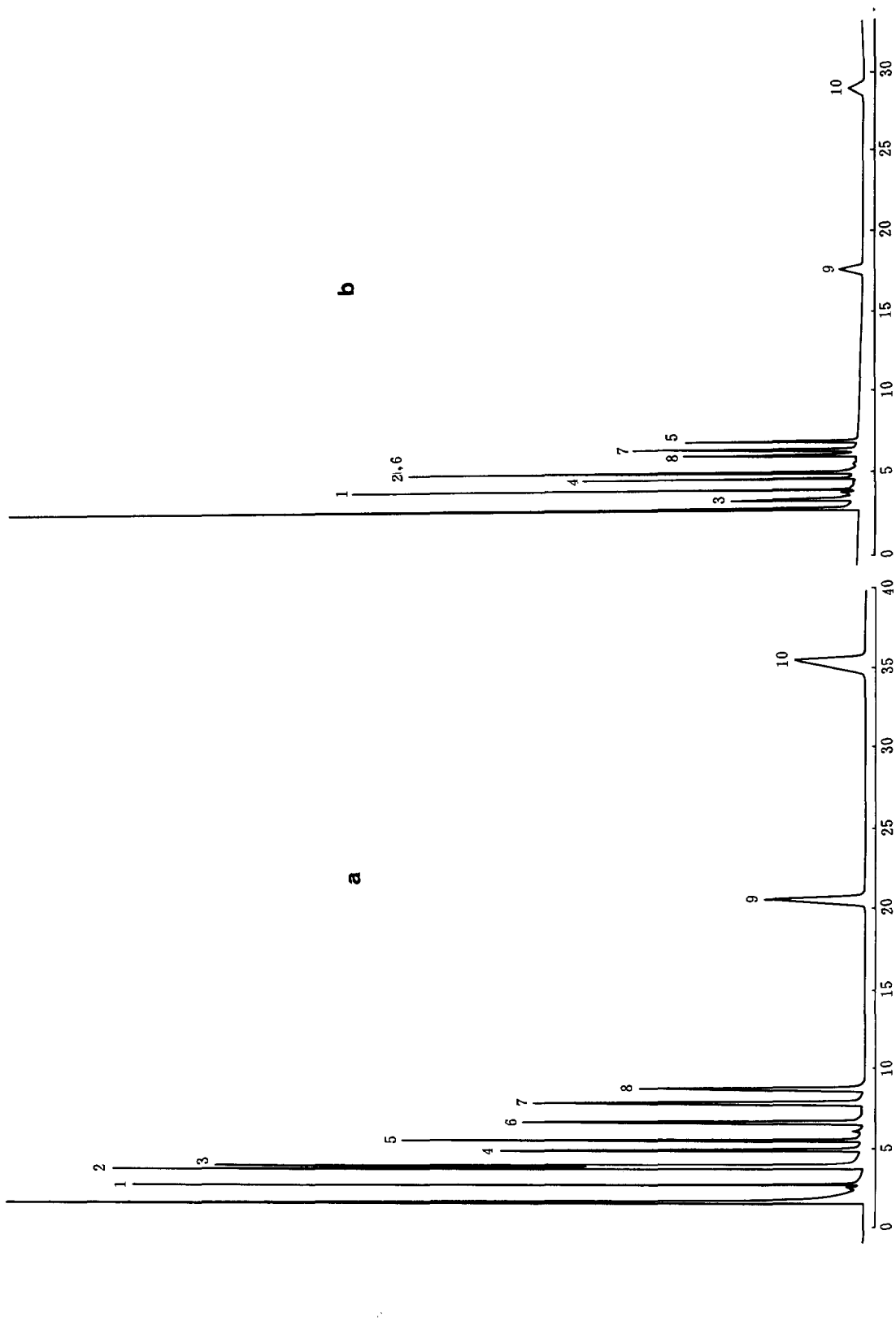

Fig. 3. Chromatogram of the Grob test mixture. (a) On DHSU14C4–GY202 column 2; (b) on GY202 column 5. Temperature, 120°C; flow rate, 13 cm/s. Peaks: 1 = *n*-decane; 2 = *n*-undecane; 3 = 1,3-butanediol; 4 = octanol; 5 = *n*-dodecane; 6 = 2,6-dimethylphenol; 7 = naphthalene; 8 = 2,4-dimethylaniline; 9 = methyl undecanoate; 10 = methyl dodecanoate.

TABLE I

CHARACTERISTICS OF DHSU14C4–GY202 AND GY202

Column No.	Column dimensions [length (m) × I.D. (mm)]	Stationary phase	Capacity factor, k'[a] (naphthalene at 120°C)	Efficiency (plates/m)
1	14 × 0.30	DHSU14C4–GY202	4.1	2141
2	17 × 0.30	DHSU14C4–GY202	3.8	2614
3	17 × 0.30	DHSU14C4	3.9	2185 (3002)[b]
4	18 × 0.30	DHSU14C4–GY202	4.3	2280 (3200)[b]
5	15 × 0.30	GY202	2.1	2950

[a] $k' = (t_r - t_o)/t_o$; t_o was determined directly with methane.
[b] After use at 300°C for 1 month.

an untreated glass capillary. The mixing of a OH-terminal silicone oil (GY202) can help to spread the stationary phase on the glass surface. However, even at a ratio of DHSU14C4 to GY202 of 50:50, the column efficiency is not high ($N = 1000$), but at 30:70 the theoretical plate number increased to 2000–3000, which is better than that with similar urushiol crown ethers [10]. The chromatographic characteristics of these crown ether columns (DHSU14C4–GY202) are summarized in Table I.

The selectivity and polarity of DHSU14C4–GY202, GY202, SE-52 and FFAP, represented by McReynolds constants and b (the slope of the curve obtained when the logarithms of the adjusted retention times of n-alkanes are plotted against the number carbon atoms), are listed in Table II. The results indicate that DHSU14C4–GY202 has a medium polarity which is higher than that of GY202 and SE-52. However, the b value for the DHSU14–GY202 is higher than that of GY202, owing to long apolar alkyl groups of DHSU14C4.

Fig. 3a shows that the Grob test mixture is separated well on DHSU14C4–GY202, in contrast to GY202 (Fig. 3b). The relative retentions of the polar compounds 1,3-butanediol, 1-octanol, naphthalene, 2,6-dimethylphenol and 2,4-dimethylaniline on DHSU14C4–GY202 are about twice those on GY202 (see Table III). The results show that DHSU14C4–GY202 has a higher selectivity for polar compounds.

The glass transition temperature is shown in Fig. 4. A change in the slope is not apparent compared with the column directly coated with a similar crown ether [6]. This indicates that the thermodynamic properties of DHSU14C4–GY202 are very similar in the two states at the transition point of the glass transition temperature.

The thermal stability of the DHSU14C4–GY202

TABLE II

SELECTIVITY (McREYNOLDS CONSTANTS) AND POLARITY OF DHSU14C4–GY202

Test temperature, 120°C.

Stationary phase	Benzene	Butanol	1-Pentanone	Nitropropane	Pyridine	Mean	b
DHSU14C4–GY202 (30:70)	41	137	209	130	180	140	0.275
DHSU14C4–GY202 (50:50)	86	214	216	220	238	195	0.284
GY202	17	64	203	34	119	87	0.254
SE-52	32	72	65	98	67	67	0.249
FFAP	340	580	397	602	627	509	0.222

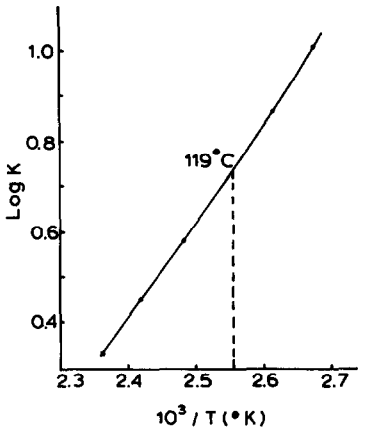

Fig. 4. Plots of log k' (capacity factor) against inverse of absolute temperature for naphthalene on DHSU14C4–GY202.

TABLE III

RELATIVE RETENTION VALUES OF SOME TEST COMPOUNDS

Compound	DHSU14C4–GY202	GY202
n-Decane	0.30	0.31
n-Undecane	0.53	0.55
n-Dodecane	1.00	1.00
Methyl undecanoate	4.88	3.49
Methyl dodecanoate	8.82	6.10
1,3-Butanediol	0.57	0.15
1-Octanol	0.84	0.46
Naphthalene	1.60	0.88
2,6-Dimethylphenol	1.28	0.55
2,4-Dimethylaniline	1.82	0.79

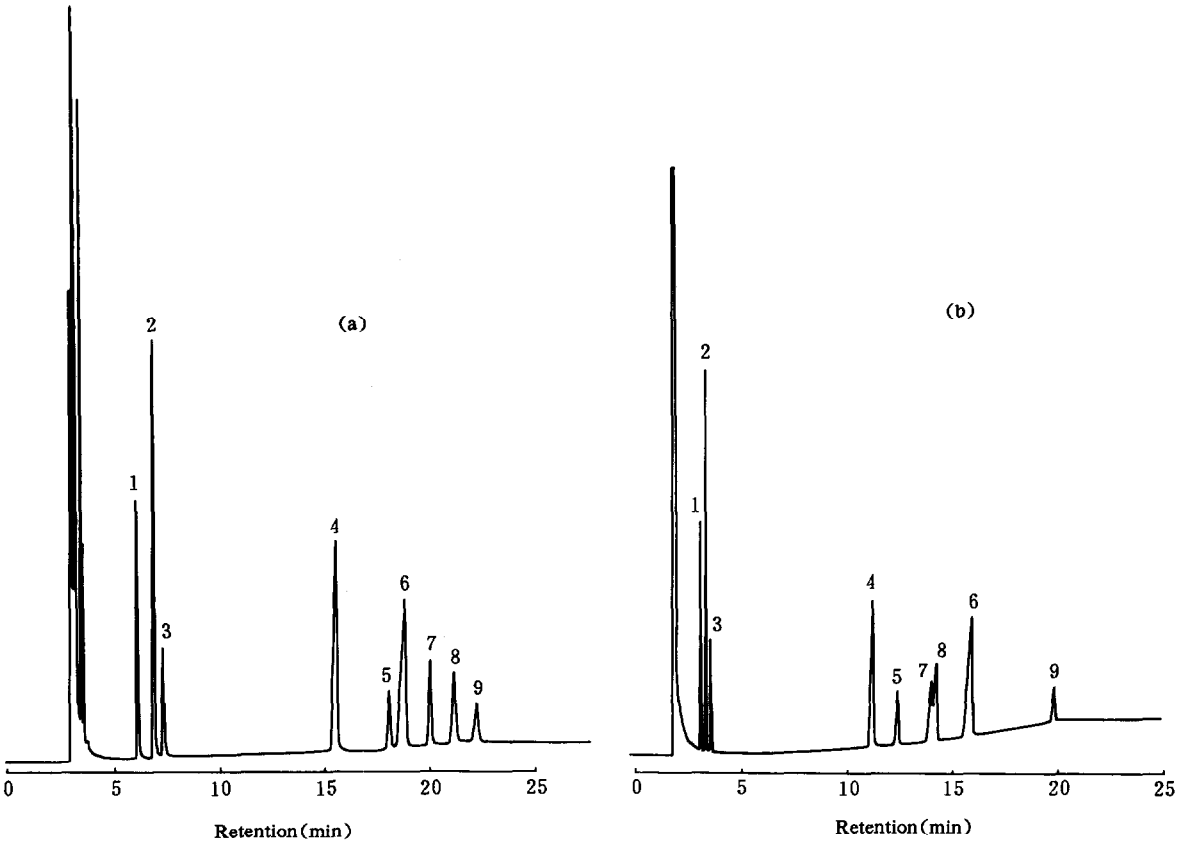

Fig. 5. Separation of a mixture of isomeric nitro compounds, (a) on DHSU14C4–GY202 column 4 and (b) on FFAP. Column temperature, programmed from 150 to 190°C at 2°C/min; flow-rate, 13 cm/s. Peaks: 1 = *o*-MNT; 2 = *m*-MNT; 3 = *p*-MNT; 4 = 2,6-DNT; 5 = 2,5-DNT; 6 = 2,3-DNT; 7 = 2,4-DNT; 8 = 3,5-DNT; 9 = 3,4-DNT (MNT = mononitrotoluene; DNT = dinitrotoluene).

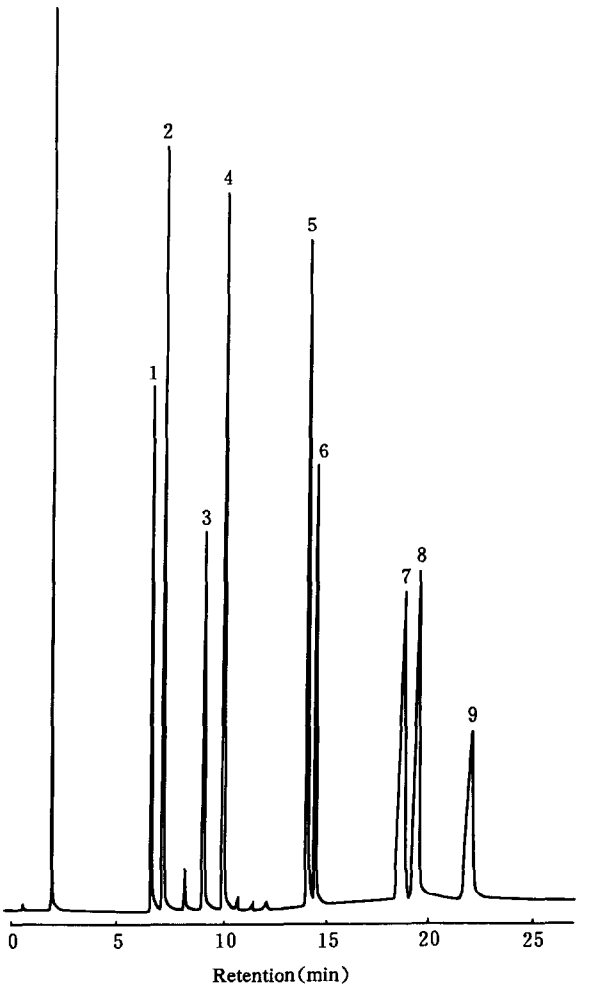

Fig. 6. Chromatogram of phenol compounds on column 3. Temperature, programmed from 90 to 210°C at 8°C/min. Peaks: 1 = *o*-chlorophenol; 2 = phenol; 3 = *o*-nitrophenol; 4 = 2,4-dimethylphenol; 5 = *p*-bromophenol; 6 = 2,4,6-trichlorophenol; 7 = 2,4-dinitrophenol; 8 = *m*-nitrophenol; 9 = *p*-nitrophenol.

column was determined by measuring the column bleed. The results show that the column begins to bleed at 210°C and the baseline drift is $1 \cdot 10^{-12}$ A at 300°C, that is, it has a high thermal stability. When the columns 3 and 4 were used at 300°C for 1 month, the capacity factor did not change and the column efficiencies tended to increase from 2100–2200 to 3000–3200 (Table I). This demonstrates that the crown ether phases have excellent thermal stability.

The DHSU14C4–GY202 column shows high selectivity, especially for nitrotoluene isomers. As shown in Fig. 5, although the polarity of DHSU14C4–GY202 is lower than that of FFAP, its separation properties are better. It is interesting that on the DHSU14C4–GY202 column, the elution of the solutes was not only dependent on the dipole–dipole reaction, but also on the steric hindrance. The sequence of dipole–dipole forces is 2,5-DNT < 2,4-DNT < 2,3-DNT < 2,6-DNT < 3,5-DNT < 3,4-DNT, but the retention times decrease in the order 2,6-DNT < 2,5-DNT < 2,3-DNT < 2,4-DNT < 3,5-DNT < 3,4-DNT (DNT = dinitrotoluene). This differential elution is possibly caused by the steric hindrance of the 2,6- and 2,3-DNT molecules.

The column coated with the crown ether stationary provided good resolution of phenol compounds (see Fig. 6). This selectivity depends on the availability of hydrogen bonding between the hydroxylic hydrogens and the crown ether ring oxigen atoms. For instance, in Fig. 6, *p*-nitrophenol was eluted much later than *o*-nitrophenol, because the *ortho*-substituted compound forms intramolecular hydrogen bonds between the nitro oxygen atom and the phenolic hydrogen atoms, which diminishes the hydrogen-bonding interaction to crown ether oxygens, so that it elutes earlier.

Application of DHSU14C4–GY202 phase to the analysis of monosaccharides in *Mycobacterium tuberculosis* is shown in Fig. 7.

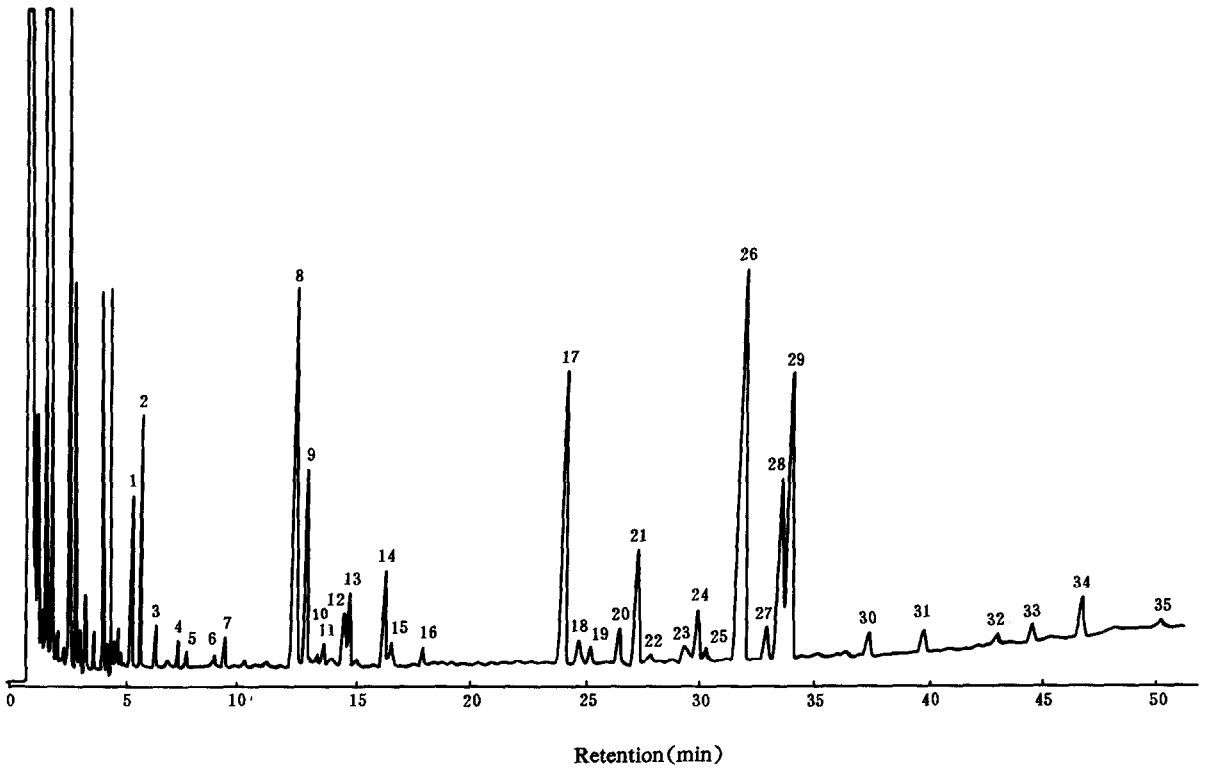

Fig. 7. Chromatogram of monosaccharides in *Mycobacterium tuberculosis* on column 2, separated as trimethylsilyl ether derivatives. Temperature, programmed from 150 to 220°C at 2°C/min. Peaks: 10,14 = ribose; 13 = rhamnose; 17 = mannose; 21 = fructose; 26 = galactose; 27,28,30 = glucose; 29 = mannitol (internal standard); 34 = myo-inositol.

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