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Akihiro Ohta,[*1,*2] **Yukio Ogihara,**[*1] **Kiyoshi Nei,**[*3] **Nobuo Ikekawa,**[*2] **and Shoji Shibata**[*1] : On Methyl-1-phenylnaphthalenes. II.[*4]
The Gas Chromatography of Methyl-1-phenylnaphthalenes.

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As has been shown by Solo and Pelletier,[1] gas chromatography is employed as an useful tool for identification of alkyl derivatives of polycyclic aromatic compounds which are obtained by dehydrogenation of natural products.

In the present study it has been reported the gas chromatographic separation of nine monomethyl- and nine dimethyl-1-phenylnaphthalenes which have been prepared as reference compounds in some connection with the natural products studies.

The gas chromatography using SE-30 as the stationary phase has shown a correlation between the retention time and the location of methyl group on the phenylnaphthalene nucleus.

Experimental

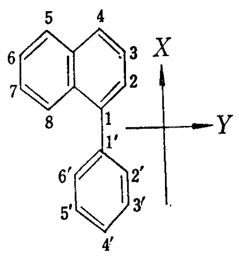
Apparatus——The Shimadzu Seisakusho Model GC-1B Gas-chromatograph attached with a hydrogen flame detector (dual column and differential flame) was employed in the experiment (A) and (B), and the Barber-Colman Co., Model 10 Gas-chromatograph attached with Argon ionization detector in the experiment (C).

A) Column : Stainless steel tube (225 cm. × 4 mm.); packing : 1.0% SE-30 (G.E. Methylsilicon gum) on Chromatosorb W (60~80 mesh); column temperature : 160°, detector temperature : 200°, sample heater temperature : 220°; carrier gas : N_2, 35 ml./min.; sensitivity : 1000; range : 0.8.

B) Column : Stainless steel column (225 cm. × 4 mm.); packing : 0.5% SE-30 on Chromatosorb W (60~80 mesh); column temperature : 160°, detector temperature : 230°, sample heater temperature : 270°; carrier gas : N_2, 28 ml./min.; sensitivity : 1000; range : 1.6.

C) Column : Pyrex-glass tube (U-type) (270 cm. × 8 mm.); packing : 1% SE-30 on Chromatosorb W (60~80 mesh); column temperature : 183°, detector temperature : 165°, sample heater temperature : 280°; carrier gas : Argon, inlet pressure 1 kg./cm^2.

Samples : 1-phenylnaphthalene; 2-, 3-, 4-, 5-, 6-, 7-, 2′-, 3′- and 4′-monomethyl-1-phenylnaphthalenes, and 2,2′-, 2,3′-, 3,2′-, 3,7-, 3,6- 4,7- 4,6-, 4,4′- and 3′,4′-dimethyl-1-phenylnaphthalenes. The numbering of substitution used in this study is shown in the formula.



Results

The retention times and the relative retention times of the methyl substituted phenylnaphthalenes are listed in Table I, and an example of separation of a mixture of eight samples is shown in Fig. 1.

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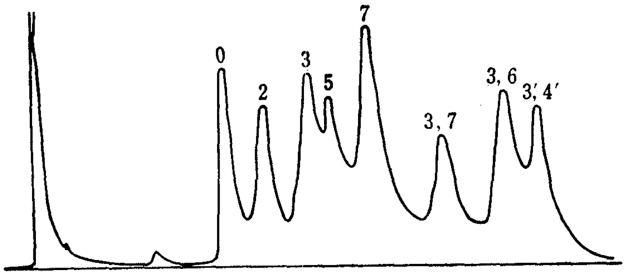

Fig. 1.

Table I.[a]

Compound 1-Phenylnaphthalene	The position of substitution	A Time (min.)	A Relative time	B Time (min.)	B Relative time	C Time (min.)	C Relative time
		7.7	1.00	4.10	1.00	4.37	1.00
Monomethyl derivatives	2′	7.7	1.00			4.45	1.01
	2	8.55	1.11	4.90	1.20	5.00	1.19
	3′	10.25	1.33			6.05	1.43
	3	10.60	1.38	6.40	1.56	6.11	1.44
	4′	11.10	1.44			6.45	1.48
	4	11.85	1.54			6.75	1.53
	5	12.00	1.56	7.20	1.76		
	6	11.05	1.44			6.45	1.48
	7	9.50	1.23	5.90	1.44	5.71	1.29
Dimethyl derivatives	2,2′	8.60	1.12			5.10	1.20
	2,3′	11.50	1.49			6.67	1.52
	3,2′	11.90	1.55			6.10	1.44
	3,7	14.30	1.88	8.90	2.17	8.25	1.93
	3,6	15.90	2.07	10.30	2.52	9.37	2.18
	4,7	16.30	2.12			8.95	2.03
	4,6	16.40	2.13				
	4,4′	17.20	2.24			10.10	2.38
	3′,4′	18.30	2.38	11.00	2.68		

a) The detail experimental condition : see Experimental part.

Discussion

It has been shown that on employing SE-30 as the stationary liquid phase the retention time corresponds to the polarity and the size of molecule to be separated.

In the case of methyl derivatives of 1-phenylnaphthalene, the retention time is varied not only by the number of methyl groups but also by the position of methyl on the 1-phenylnaphthalene nucleus, and an experimental rule can be seen between them.

The retention times of monomethyl derivatives of 1-phenylnaphthalene have been shown in the following sequence : $2'<2<3'<3<4'<4<5>6>7$ (The figures show the position of methyl group.). The retention time is much affected by the methyl substitution in the naphthalene moiety than that in the phenyl moiety when it occupies the corresponding position. A similar tendency can be seen in the dimethyl derivatives of 1-phenylnaphthalene, whose retention times are in the following sequence : $2,2'<2,3'<3,2'<3,7<3,6<4,7<4,6<4,4'<3',4'$.

This result would be expected by the additive effect of mono-substitution.

It would be noted that the methyl substitution at 2- or 2′-position gives no remarkable effect to the retention time. The retention time of 2′-methyl derivative is the same of that given by 1-phenylnaphthalene, while 2,2′-dimethyl- and 3,2′-dimethyl-1-phenylnaphthalenes show the retention times almost same as those given by 2-methyl and 3-methyl derivatives, respectively. This would be resulted by the steric hindrance of 2- or 2′-substitution which prevents the planarity of the phenylnaphthalene ring system.

The longer retention times given by 4′-, 4- or 5′-substitution would be resulted by the higher polarities of these compounds whose molecules are extended to the X-direction.

By the present investigation it has been shown that the measurement of retention times by the gas chromatography can provide an available evidence for the structures of methyl substituted 1-phenylnaphthalenes.

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Summary

The gas chromatography of monomethyl- and dimethyl-1-phenylnaphthalenes were carried out. A correlation between the retention time and the position of methyl substitution in 1-phenylnaphthalene nucleus was found.

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