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Note

Gas chromatographic behaviour of mono- and dihydroxybiphenyls on various silicone phases

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Phenolic substances are widespread in nature as components of various plant and animal products and are introduced into the biosphere in pesticides, herbicides, etc.

From the point of view of environmental protection it is important to determine traces of phenol and its derivatives. For this purpose, titration and spectrophotometric methods, *e.g.*, refs. 1 and 2, and various chromatographic methods, *e.g.*, refs. 3 and 4, especially gas chromatography (GC)[5–20] have been employed. However, the analysis is usually complicated, because of the character of phenols (high polarity, weakly acidic, low vapour pressure).

Many stationary phases have been recommended for GC separations of phenols, such as Apiezon L[5], Porapak P[6], tricresyl phosphate[7,8], Carbowax 20M[9], silicone stationary phases SE-30, OV-225[10], XE-60[11–13], etc. Good results have been obtained with graphitized carbon black coated with a small amount of an acidic polar phase, *e.g.*, FFAP[14] or a mixture of H_3PO_4 with Carbowax 1500[15]. Mixed stationary phases have been recommended for separation of complex mixtures of phenols.

To prevent tailing of phenols, acid-washed supports must be used, whose active sites are blocked by silanization. When using capillary columns, surfactants are added to suppress adsorption of phenols on the column walls which results in peak broadening.

A number of authors have attempted to solve the problems of quantitative analysis of phenols by converting phenols into volatile derivatives, esters or ethers. Silanization has most often been used, *e.g.* refs. 16–19. Davis *et al.*[20] determined mono- and dihydroxybiphenyls in biological materials as heptafluorobutyrates.

In a study of the sensitized photodecomposition of phenol, dihydroxybenzenes and biphenyls were found[21] as the main products. Therefore, the GC behaviour of

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some hydroxylated biphenyls (HBPs), considered as possible photodecomposition products of phenols, has been investigated.

EXPERIMENTAL

2-HBP, 4-HBP, 2,2′-DHBP and 4,4′-DHBP were kindly provided by Dr. P. van der Jagd (Vrije Universiteit, Amsterdam, The Netherlands). 3-HBP, 3,3′-DHBP, 2,5-DHBP and 3,4-DHBP were kindly donated by Dr. P. J. Davis, the Drug Dynamic Institute, University of Texas, Austin, TX, U.S.A. 2,4′-DHBP was synthetized by Dr. B. Černý (Isotope Laboratory, Czechoslovak Academy of Sciences, Prague, Czechoslovakia), according to a described procedure[22] and its structure was confirmed by mass spectrometry. The hydrocarbons required for the determination of the retention indices were supplied by Applied Science Labs. (State College, PA, U.S.A.).

The measurements were performed on a Varian Model 3700 gas chromatograph equipped with a flame-ionization detector and a Varian 9176 recorder. The results were evaluated using the Varian CDS-111C Data System. Glass column (200 cm × 2 mm I.D.) were packed with OV-101, OV-17, OV-210, OV-225 and XE-60 stationary phases coated (3%) on Varaport 30 (100–120 mesh) support. An XE-60 stationary phase coated on Chromaton N-Super (0.125–0.16 mm) was also used. The column and injection block temperatures were 197 and 230°C, respectively. The nitrogen flow-rate was 20 ml/min.

RESULTS AND DISCUSSION

Gas chromatographic behaviour of nine mono- and dihydroxybiphenyls was studied on five stationary phases, OV-101, OV-17, OV-210, OV-225 and XE-60. The retention indices at 197°C are given in Table I. Symmetrical elution curves were obtained for all the compounds studied, on all the stationary phases.

The retention indices on the OV-101 phase are about 150–500 units lower than on the OV-17 and OV-210 phases, and about 500–1500 units lower than on the OV-

TABLE I

RETENTION INDICES OF MONO- AND DIHYDROXYBIPHENYLS ON VARIOUS STATIONARY PHASES AT 197°C

	Retention index				
	OV-101	*OV-17*	*OV-210*	*OV-225*	*XE-60*
2-HBP	1622	1808	1784	2180	2167
3-HBP	1677	2021	1978	2598	2604
4-HBP	1683	2034	1980	2624	2632
2,2′-DHBP	1655	2004	1950	2611	2605
2,5-DHBP	1805	2202	2189	2919	2937
2,4′-DHBP	1820	2226	2204	–	–
3,4-DHBP	1918	2318	2314	–	3154
3,3′-DHBP	1976	2426	2414	–	3419
4,4′-DHBP	1979	2441	2442	–	3432

225 and XE-60 phases. On OV-101, 3- and 4-HBP are poorly separated and 3,3'- and 4,4'-DHBP are not separated at all.

Although the OV-17 and OV-210 phases differ considerably in their polarity when evaluated in terms of $\Sigma \Delta I$[23] ($\Sigma \Delta I$ = 884 for OV-17 and 1520 for OV-210), the retention indices for the hydroxylated biphenyls are similar. The relatively high retention indices on the OV-17 phase are due to the considerably higher solubility of these substances in the phenolic stationary phase.

All nine compounds studied can be separated on the OV-17 phase, as shown in Fig. 1.

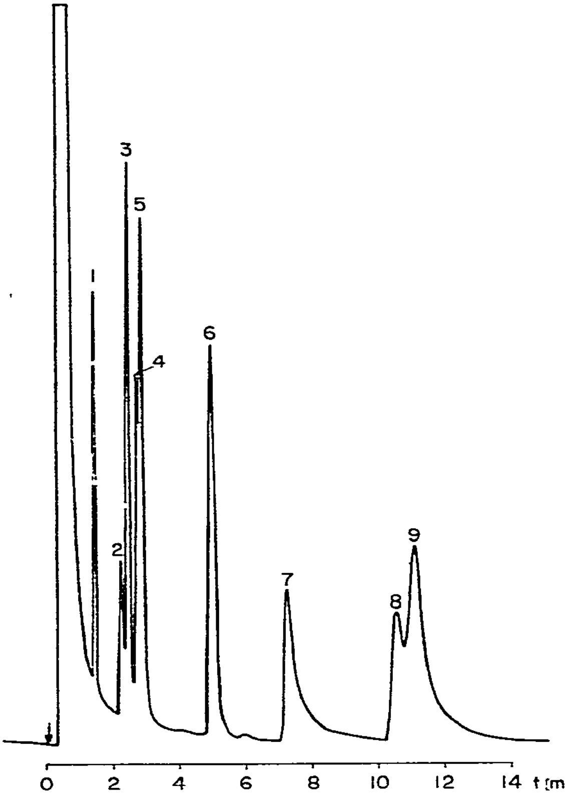
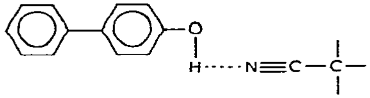


Fig. 1. Chromatogram of a mixture of mono- and dihydroxybiphenyls on OV-17 at 197°C. Peaks: 1 = 2-HBP; 2 = impurity in 2,5-DHBP; 3 = 2,2'-DHBP; 4 = 3-HBP; 5 = 4-HBP; 6 = 2,5-DHBP; 7 = 3,4-DHBP; 8 = 3,3'-DHBP; 9 = 4,4'-DHBP.

The pronounced increase in the retention indices on the OV-225 phase can be attributed to the fact that this phase contains nitrile groups, –C≡N, in addition to phenyl groups (25%). Phenols can form intermolecular hydrogen bonds with electron-donor nitrile groups, resulting in substantially increased retention of mono- and dihydroxybiphenyls:



Higher dihydroxybiphenyls were so strongly retained that they could not be eluted from the OV-225 phase.

The XE-60 phase (a silicone phase which also contains nitrile groups) is very similar in character to OV-225 and results in similar retention indices (see Table I).

The retention behaviour of phenols is chiefly dependent on their ability to form hydrogen bonds. In the monohydroxybiphenyl series, 2-HBP exhibits a substantially lower retention index as its OH group is screened by a phenyl group. The retention of 3- and 4-HBP is not very different.

Among dihydroxybiphenyls, 2,2′-DHBP is least retained as it forms intramolecular hydrogen bonds and thus has the highest vapour pressure. 3,3′-DHBP and 4,4′-DHBP have similar properties and are therefore more difficult to separate.

Silanol groups on the support surface that are not blocked by the stationary phase can also form hydrogen bonds with O and H atoms of the phenol hydroxyl groups. These interactions are important in GC and often cause tailing of chromatographic peaks. The packings coated on the Varaport support gave very good results for separations of phenols; all substances studied gave symmetrical peaks.

For the series of mono- and dihydroxybiphenyls, the retention indices on two phases, OV-101 and OV-17, were plotted. Two different straight lines were obtained for HBP and DHBP (see Fig. 2), which were used for identification of some products of phenol photodecomposition[21].

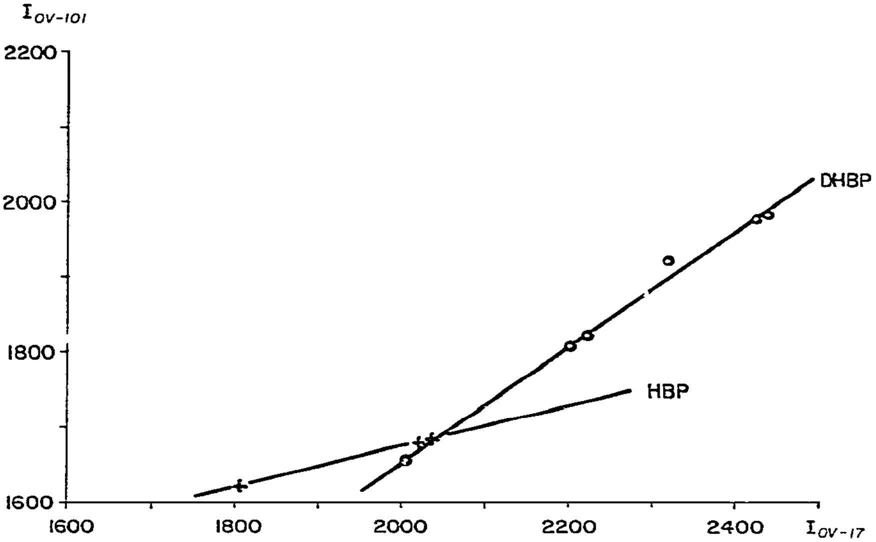


Fig. 2. Plots of retention indices I_{OV-101} vs. I_{OV-17} for mono- and dihydroxybiphenyls.

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