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EVALUATION OF 4-(2′-PHENYLISOPROPYL)PHENOL ESTERS AS STATIONARY PHASES FOR GAS–LIQUID CHROMATOGRAPHY[a]

NAGARAJ R. AYYANGAR*, AMRUTA S. TAMBE and SUJATA S. BISWAS
National Chemical Laboratory, Division of Organic Chemistry II, Pune 411 008 (India)

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SUMMARY

Five 4-(2′-phenylisopropyl)phenol esters were synthesized and their properties as stationary phases in gas–liquid chromatography were investigated. Their McReynolds' constants were determined. To investigate their selectivity, different aromatic positional isomers were used as solutes. Quantitative analyses were carried out for some of these isomers. These new esters may offer some advantages for gas chromatography.

INTRODUCTION

4-(2′-Phenylisopropyl)phenol (PIP) is a by-product in the manufacture of phenol by the cumene hydroperoxide route. A possible use for esters of PIP is as stationary phases in gas–liquid chromatography (GLC), particularly if they show superior properties to other esters. Tricresyl and trixylenyl phosphates have been used for the separation of hydrocarbons, esters, ketones, alcohols[1], sulphur compounds[2] halogenated compounds[3], cresols[4], xylenols, fluorophenols and chlorophenols[5]. We have undertaken the syntheses and GLC evaluation of some PIP esters with respect to their resolving abilities, McReynolds' values[6] and use for quantitative studies.

EXPERIMENTAL

4-(2′-Phenylisopropyl)phenyl acetate (PIPA), 4,4′-isopropylidenebisphenol diacetate (IPBPDA), butyl phenylisopropylphenyl maleate (BPIPM), di(phenylisopropylphenyl) maleate (DPIPM) and tri[4(2′-phenylisopropyl)phenyl] phosphate (TPIPP) were synthesized in the laboratory; the syntheses will be published elsewhere. Their purities were ascertained by NMR and IR spectroscopy, mass spectrometry and elemental microanalysis.

The PIP esters were used as GLC substrates at a concentration of 5% (w/w) on Chromosorb W AW DMCS. Chloroform was used as the solvent for the maleates and phosphate and acetone for the acetate and diacetate to disperse the esters on the Chromosorb support. The coated supports were packed in aluminium columns

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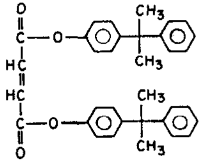
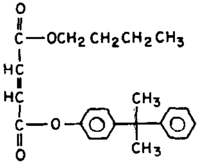
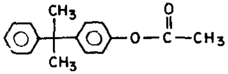
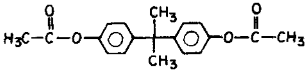
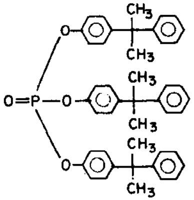
[a] NCL Communication No. 4501.

TABLE I

STRUCTURES AND PHYSICAL PROPERTIES OF PIP ESTERS

Ester	*Structure*	*B.p. (°C)*		*M.p. (°C)*	
		Observed	*Reported*	*Observed*	*Reported*
Di[4-(2′-phenylisopropyl)phenyl] maleate (DPIPM)[a]		220 (1 mmHg)	–	Liquid	–
n-Butyl-[4-(2′-phenylisopropyl)phenyl] maleate (BPIPM)[a]		180 (2 mmHg)	–	Liquid	–
[4-(2′-Phenylisopropyl)phenyl] acetate (PIPA)		120 (0.05 mmHg)	170–173 (3 mmHg)[9]	Liquid	–
(4,4′-Isopropylidenebisphenol) diacetate (IPBPDA)		–	–	76	79.5–81.5[10]
Tri[4-(2′-phenylisopropyl)phenyl] phosphate (TPIPP)		–	390–400 (0.1 mmHg)[11]	144	145[12]

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[a] These esters are not reported in the literature.

(1.8 m × 6 mm I.D.). The DPIPM, BPIPM and IPBPDA columns were conditioned at 140°C and the PIPA and TPIPP columns at 120 and 200°C, respectively.

A Hewlett-Packard 700 gas chromatograph with a flame ionization detector and an HP 3800A integrator was used. The experimental details are given in Tables II and III.

The McReynolds' solute probes used were benzene, *n*-butanol, 2-pentanone, nitropropane and pyridine (McReynolds' A, B, C, D and E) at 120°C and 1-butylbenzene, benzyl alcohol, acetophenone, nitrobenzene and aniline at 180°C. The column dead time was determined by a graphical method[7] and also by the iterative method given by Guardino *et al.*[8]. The reference aliphatic alkanes were taken from a standard hydrocarbon kit (Analabs).

The values of these ester phases for quantitative GLC analysis were studied by using the internal standard method. Chlorobenzene, *o*-chloroaniline and *m*-cresol were used as internal standards for dichlorobenzenes (DCB), nitrochlorobenzenes (NCB) and chlorophenols (CP), respectively. Standards of different concentrations ranging from 0.1 to 0.5% were prepared. The injection volume was 2 µl. Two calibration graphs were drawn for each series: weight ratio *versus* peak-area ratio and peak-area ratio *versus* percentage composition.

RESULTS AND DISCUSSION

The structures of the five esters and their physical properties are given in Table I. Table II lists the retention times for some aliphatic alcohols and aromatic hydrocarbons studied on packed columns of these new esters. Fig. 1 shows the separation of

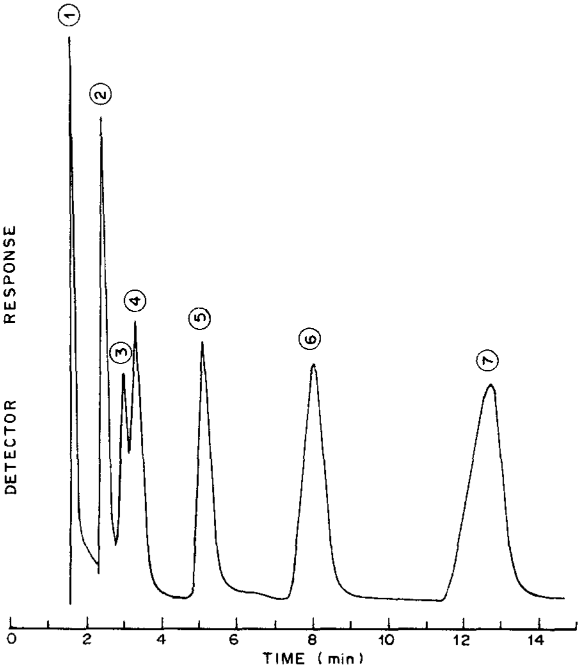

Fig. 1. Separation of aliphatic alcohols on PIPA (5%) at 50°C. Peaks: 1 = methanol; 2 = ethanol; 3 = isopropanol; 4 = *tert.*-butanol; 5 = *n*-propanol; 6 = isobutanol; 7 = *n*-butanol.

TABLE II

RETENTION TIMES (min) FOR ALIPHATIC ALCOHOLS AND AROMATIC HYDROCARBONS ON PIP ESTER PHASES

Carrier gas, nitrogen at a flow-rate of 30 ml min^{-1}. Injection temperature, 140°C; detection temperature, 200°C.

Stationary phase (5%)	*Alcohols at 50°C*						
	CH_3OH	*C_2H_5OH*	*i-C_3H_7OH*	*n-C_3H_7OH*	*t-C_4H_9OH*	*i-C_4H_9OH*	*n-C_4H_9OH*
DPIPM	1.60	1.85	1.99	3.39	2.14	4.50	6.63
BPIPM	1.28	1.82	2.10	3.41	2.39	5.71	8.70
PIPA	1.69	2.51	3.07	5.20	3.40	8.11	12.83
IPBPDA	—	—	—	—	—	—	—

[a] Xylene isomers at 80°C.

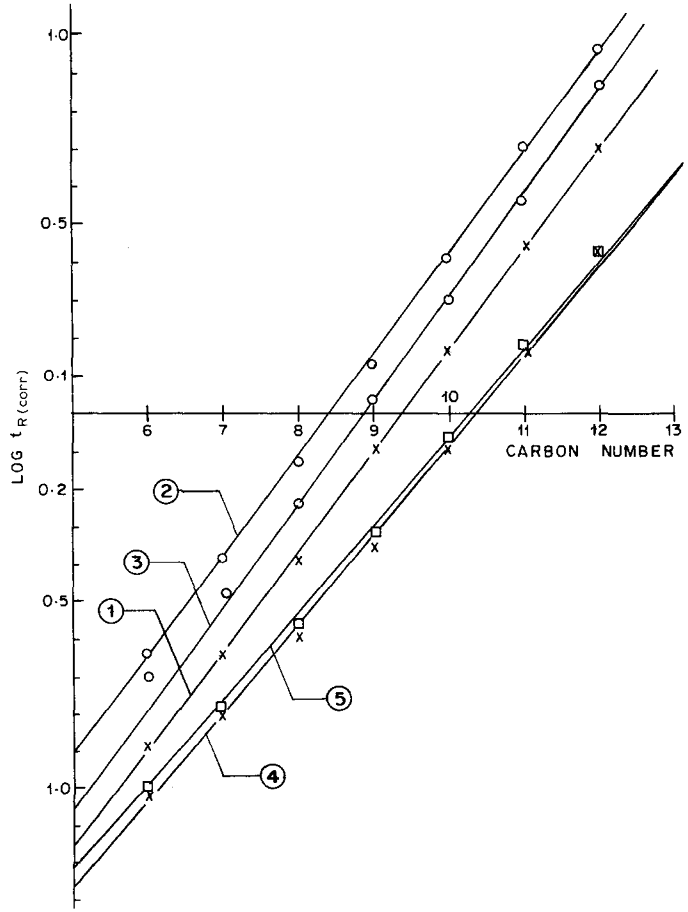

Fig. 2. Graphs of log $t_{R(corr)}$ (corrected retention time) *versus* number of carbon atoms in *n*-alkanes. Stationary phase: 1 = DPIPM; 2 = BPIPM; 3 = PIPA; 4 = IPBPDA; 5 = TPIPP.

Aromatic hydrocarbons at 50°C					
Benzene	*Toluene*	*Ethylbenzene*	*o-Xylene*[a]	*m-Xylene*[a]	*o-Xylene*[a]
5.37	12.45	26.30	15.87	12.65	12.12
6.05	13.09	28.80	16.08	12.75	12.14
5.02	11.65	24.13	18.57	14.17	14.48
–	–	–	9.64	7.91	7.13

some aliphatic alcohols on PIPA. Graphs of the logarithm of corrected retention times *versus* carbon number for *n*-alkanes plotted for all five phases were linear (Fig. 2).

Although TPIPP is a solid at 120°C, a linear graph was obtained with TPIPP. As the retention index concept utilizes this plot for *n*-alkanes and the retention index of a substance is simply the number of carbon atoms (conveniently multiplied by 100) of a hypothetical *n*-alkane that would have identical retention characteristics[13], we decided to determine McReynolds' constants for TPIPP at 120°C and to compare these with the values for the other ester phases. When the esters IPBPDA and TPIPP were used below their melting points, the principle of separation is by adsorption and not by partition. In most instances, the shapes of the peaks and separations on these ester phases were satisfactory and no peak tailing was observed.

Table III indicates a good separation between *o*- (slowest) and *p*-nitrochlorobenzenes on DPIPM and TPIPP but the *meta* (fastest) and *para* isomers were poorly resolved. On the other hand, with BPIPM and PIPA *o*- and *p*-nitrochlorobenzenes were poorly resolved and the *meta* and *para* isomers showed a near baseline separation. These results suggest that the presence of two or more diaromatic phenylisopropyl groups in an ester helps to resolve the *ortho* and *para* isomers. The IPBPDA column gave a complete separation of *o*-, *m*- and *p*-nitrochlorobenzene. A near baseline separation of *o*-, *m*- and *p*-dichlorobenzene was obtained on IPBPDA. Unfortunately, the separation of *m*- and *p*-chloroaniline and of *m*- and *p*-cresol and the separation between 2,5- and 2,4-xylenols could not be achieved on any of the columns.

Of all the esters, TPIPP showed exceptional thermal stability and could be used for the separation of high-boiling compounds. Thermogravimetric analysis (STA 409 apparatus from Netzsch Gerätebau, Selb, F.R.G.) shows that the decomposition starts after 200°C and is complete at 480°C. Hence the column can be safely used up to 200°C. This is an improvement over similar phosphate esters such as tricresyl phosphate (maximum 125°C) and tri(2,4-xylenyl) phosphate (maximum 150°C). The separation of *o*-chloro-, *p*-chloro- and 2,4-dichlorophenol was baseline on TPIPP. This column also separated α- and β-naphthol, but the naphthylamine isomers were only partially resolved. Table IV gives the experimental and retention time data.

Table V gives the retention times and percentage errors by weight and by percentage composition in the determination of dichlorobenzenes, nitrochloro-

TABLE III

RETENTION TIMES (min) FOR VARIOUS POSITIONAL ISOMERS OF BENZENE ON NEW ESTER PHASES

Carrier gas, nitrogen at a flow-rate of 40 ml min^{-1}.

Stationary phase (5%)	*Temperature (°C)*	*Nitrochlorobenzenes*			*Chloroanilines*			*Cresols*		
		o-	*m-*	*p-*	*o-*	*m-*	*p-*	*o-*	*m-*	*p-*
DPIPM	140	19.09	15.20	16.56	7.12	12.86	13.80	4.71	5.7	5.60
BPIPM	140	20.36	16.04	18.00	9.55	18.03	18.60	7.21	9.08	8.82
PIPA	120	34.20	25.60	29.60	12.99	27.00	28.00	30.35	33.00	34.35
IPBPDA	140	21.00	16.00	18.80	11.12	22.46	23.52	9.99	9.78	9.79
TPIPP	140	19.59	14.53	15.79	7.54	15.18	14.90	8.00	10.35	9.88

[a] Dichlorobenzenes at 110°C on all the esters.

benzenes and chlorophenols on two of the stationary phases using internal standards. The error limit is ±1.5%.

The McReynolds' constants for the stationary phases determined at 120°C are given in Table VI. The absolute values of the retention indices on squalane, tricresyl phosphate and other stationary phases were taken from the original reference[6]. Table VI also lists the dead times obtained by graphical and iterative methods; these values are in good agreement.

The ΔI values in Table VI show that the polarity of IPBPDA is comparable to that of cyclohexanedimethanol succinate (CHDMS). Of the five test probe values for CHDMS, four of them (A, B, D and E) are very close to those of IPBPDA and the latter retains ketones more strongly than the former. PIPA and Ucon-50-HB-280X differ in their polarity towards ketones (C) and alcohols (B): ketones are retained more strongly on the former whereas alcohols are retained more strongly on the latter. Compared with OS-124, DPIPM retains nitro compounds more strongly and the A, B,

TABLE IV

RETENTION TIMES ON TPIPP (5%)

Carrier gas, nitrogen at a flow-rate of 40 ml min^{-1}.

Solute	*Temperature (°C)*	*Retention time (min)*
α-Naphthylamine	190	14.40
β-Napthylamine		15.80
α-Naphthol	190	21.60
β-Naphthol		24.20
o-Chlorophenol	165	2.18
p-Chlorophenol		6.48
2,4-Dichlorophenol		12.80

Xylenols				*Dichlorobenzenes*[a]		
2,4-	*2,5-*	*2,6-*	*3,4-*	*o-*	*m-*	*p-*
7.83	7.86	6.04	10.89	9.20	6.84	7.92
14.87	14.58	10.22	22.88	11.81	9.19	9.97
–	–	–	–	6.63	5.08	5.60
14.08	13.38	9.63	19.81	13.26	9.55	11.04
14.16	14.16	8.88	22.40	7.20	6.14	6.16

C and E values are comparable. BPIPM and OV-17 are comparable for all other test probes except benzene (A). With TPIPP, three values (B, C and D) are very close to those for tricresyl phosphate and it retains aromatic and proton-accepting compounds more strongly than the latter. As can be seen from the sum of ΔI values, BPIPM is the least polar and IPBDA is the most polar of the new ester phases. PIPA, TPIPP and DPIPM esters are of intermediate polarity.

Table VII gives McReynolds' constants for TPIPP at 120 and 180°C. The retention indices on Apiezon MH at 180°C were taken from the original reference[14]. It can be seen that overall polarity of TPIPP at 180°C is greater than that at 120°C, *i.e.*, below its melting point. Alcohols, ketones, nitro compounds and proton acceptor compounds are retained much more strongly at 180°C, as can be seen from the McReynolds' constants. Nitro compounds are most strongly retained at 120°C whereas alcohols are most strongly retained at 180°C, as is evident from the relative differences in the McReynolds' constants. This means that at 180°C forces between TPIPP and solutes with proton donor and proton acceptor groups are more significant than the dipole orientation forces between TPIPP and solutes with weak proton acceptor groups (*e.g.* NO_2).

CONCLUSION

PIP esters such as PIPA, IPBPDA and TPIPP have shown promising results as GLC stationary phases. TPIPP is more strongly polar than tricresyl phosphate and thermally the most stable. It is suggested as an improvement over other phosphate esters that can be used only up to 125°C. TPIPP has McReynold's constants for B, C and D similar to those for tricresyl phosphate and it retains aromatics and proton acceptor compounds more strongly than the latter when used below its melting point.

TABLE V

DETERMINATION OF DICHLOROBENZENES (DCB), NITROCHLOROBENZENES (NCB) AND CHLOROPHENOLS (CP)

Stationary phase	*Temperature (°C)*	*Sample*	*Retention time (min)*	*Weight (mg)*		*Composition (%)*		*Error (%)*	
				Actual	*Exptl.*	*Actual*	*Exptl.*	*Weight*	*Composition*
IPBDA (5%)	110	*m*-DCB	9.55	27.8	27.8	0.278	0.280	0.00	−0.71
		p-DCB	11.04	16.1	16.0	0.161	0.162	+0.62	−0.62
		o-DCB	13.26	19.9	19.8	0.199	0.200	+0.50	−0.50
		Chlorobenzene (I.S.)[a]	3.46						
IPBDA (5%)	140	*m*-NCB	16.00	50.0	49.8	0.500	0.497	+0.40	+0.60
		p-NCB	18.80	36.8	36.5	0.368	0.363	+0.081	+1.35
		o-NCB	21.00	38.6	38.3	0.386	0.380	+0.77	+1.55
		o-Chloroaniline (I.S.)[a]	10.28						
TPIPP (5%)	165	*o*-CP	2.18	39.6	39.5	0.396	0.399	+0.25	−0.75
		2,4-Di-CP	6.48	48.5	48.5	0.485	0.485	0.00	0.00
		p-CP	12.80	57.6	57.5	0.576	0.580	+0.17	−0.69
		m-Cresol (I.S.)[a]	4.11						

[a] Internal standard.

TABLE VI

McREYNOLDS CONSTANTS AND DEAD TIME DETERMINATIONS FOR VARIOUS STATIONARY PHASES AT 120°C

t_m = Dead time obtained by the graphical method[7]; t'_m = dead time obtained by the iterative method[8]; I = retention index calculated considering t_m as dead time value $= I_{R\text{ test phase}} - I_{R\text{ squalane for test probe solutes}}$; I' = retention index calculated considering t'_m as dead time value $= I'_{R\text{ test phase}} - I_{R\text{ squalane for test probe solutes}}$.

Stationary phase (5%)	*McReynolds probes*										t_m *(min)*	$\sum_1^5 \Delta I$	t'_m *(min)*	$\sum_1^5 \Delta I'$
	Benzene (A)		*1-Butanol (B)*		*2-Pentanone (C)*		*Nitropropane (D)*		*Pyridine (E)*					
	ΔI	$\Delta I'$	ΔI	$\Delta I'$	ΔI	$\Delta I'$	ΔI	$\Delta I'$	ΔI	$\Delta I'$				
IPBPDA	264	265	426	426	379	379	492	492	481	481	0.63	2042	0.629	2043
CHDMS	269		446		328		493		481			2017		
PIPA	196	188	298	293	269	265	352	351	314	314	0.60	1429	0.649	1411
Ucon-50-HB-280X	177		362		227		351		302			1419		
DPIPM	166	166	219	219	226	226	334	334	294	294	0.66	1239	0.659	1239
OS-124	176		227		224		306		283			1216		
BPIPM	64	56	169	164	143	134	266	265	202	201	0.72	844	0.749	0824
OV-17	119		158		162		243		202			842		
TPIPP	203	201	311	310	255	253	379	379	328	328	0.61	1476	0.619	1471
Tricresyl phosphate	176		321		250		374		299			1420		

TABLE VII

McREYNOLDS CONSTANTS FOR TPIPP (5%)

Solute	ΔI^a	*Solute*	ΔI^b
Benzene (A)	203	1-Butylbenzene (A)	150
1-Butanol (B)	311	Benzyl alcohol (B)	438
2-Pentanone (C)	255	Acetophenone (C)	391
1-Nitropropane (D)	379	Nitrobenzene (D)	423
Pyridine (E)	328	Aniline (E)	400
$\sum_{1}^{5} \Delta I$	1476	$\sum_{1}^{5} \Delta I$	1801

[a] $\Delta I = I_{\text{TPIPP}} - I_{\text{squalane}}$ (120°C).
[b] $\Delta I = I_{\text{TPIPP}} - I_{\text{Apiezon MH}}$ (180°C).

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