

TERPENOIDS

LXXXV. EVALUATION OF POLYESTERS AS STATIONARY PHASES IN GLC COLUMNS*

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In previous communications¹ on the evaluation of the polyesters as stationary phases we have reported the results of the investigation on polyesters derived from different $1,\omega$ -dicarboxylic acids, $\text{HOOC}-(\text{CH}_2)_n-\text{COOH}$, ranging from malonic acid ($n = 1$) to 1,16-hexadecanedicarboxylic acid ($n = 16$) with diethylene glycol.

It was observed that the number of methylene groups in the acidic fragment of the polyester has a profound influence on the retention time, on the basis of which a clear arithemathical relationship was developed. Retention time was found to be an integral characteristic of the number of methylene groups between the two groups of the acidic fragment of the polyester.

It was then felt desirable to determine whether a similar relationship would hold good if a change was brought about in the glycol fragment of the polyester, keeping the acid fragment unchanged. The present work deals with this investigation and other related matters.

A series of polyesters were synthesised from adipic acid (constant acid fragment) and $1,\omega$ -glycols, $\text{HO}-\text{CH}_2-(\text{CH}_2)_n-\text{CH}_2-\text{OH}$, ranging from ethylene glycol to 1,15-pentadecanediol.

In this series of polyesters, it was observed that a change in the number of methylene groups in the glycolic fragment also similarly influenced the degree of separation of compounds in GLC analyses. In order to have a clear idea of the behaviour of these polyesters, three more series of polyesters were synthesised.

(I) Ethylene glycol (constant) and succinic acid, adipic acid, sebacic acid.

(II) 1,5-Pentanediol (constant) and succinic acid, adipic acid and sebacic acid.

(III) Hexadecane-1,16-dicarboxylic acid (constant) and 1,4-butanediol, 1,10-decanediol, and 1,15-pentadecanediol.

Several terpenic and a few non-terpenic compounds were analysed on GLC columns using these polyesters as stationary phases with very interesting results which are dealt with in the discussion.

EXPERIMENTAL

The modified Griffin & George Model MK-II VPC apparatus has been used as described in our earlier communication¹.

* Communication No. 873 from the National Chemical Laboratory, Poona-8, India.

Preparation and general properties of the polyesters

The preparation was carried out according to the previously described procedure¹, with minor modifications*. The polyester derived from ethylene glycol and adipic acid is a viscous liquid, while that derived from 1,4-butanediol and adipic acid is a semi-solid; the others obtained from 1,5-pentanediol onwards up to 1,15-pentadecanediol and adipic acid are low-melting solids. Polyesters derived from hexadecane-1,16-dicarboxylic acid, as well as sebacic acid, are all low-melting solids.

The approximate molecular weight determinations of some of the polyesters were carried out by end group titrations in alcoholic solution. The results are shown in Table I.

TABLE I

MOLECULAR WEIGHTS OF THE POLYESTERS AS DETERMINED BY THE END GROUP TITRATIONS

<i>Components of the polyester</i>		<i>Molecular weights</i>
<i>Acid</i>	<i>Glycol</i>	
Adipic acid	Ethyleneglycol	433, 420
Adipic acid	1,3-Propanediol	442, 466
Adipic acid	1,4-Butanediol	1021, 978
Adipic acid	1,5-Pentanediol	—
Adipic acid	1,6-Hexanediol	7563, 6730
Adipic acid	1,9-Nonanediol	insoluble
Adipic acid	1,10-Decanediol	insoluble
Adipic acid	1,13-Tridecanediol	insoluble
Adipic acid	1,15-Pentadecanediol	insoluble
Succinic acid	Ethyleneglycol	333, 286
Adipic acid	Ethyleneglycol	433, 420
Sebacic acid	Ethyleneglycol	1138, 1008
Hexadecane-1,16-dicarboxylic acid	1,4-Butanediol	insoluble
Hexadecane-1,16-dicarboxylic acid	1,10-Decanediol	insoluble
Hexadecane-1,16-dicarboxylic acid	1,15-Pentadecanediol	insoluble
Succinic acid	1,5-Pentanediol	insoluble
Adipic acid	1,5-Pentanediol	insoluble
Sebacic acid	1,5-Pentanediol	insoluble

The following terpenic and non-terpenic samples were employed for the comparative evaluation of the polyesters:

(I) α -Pinene, (2) β -pinene, (3) Δ^3 -carene, (4) limonene, (5) tricyclene, (6) camphene, (7) 1:8-cineole, (8) *p*-cymene, (9) cyclohexane, (10) methyl alcohol and (11) ethyl alcohol.

Monoterpenic oxygenated compounds. (1) α -Terpineol, (2) linalool, (3) *l*-borneol, (4) isoborneol, (5) menthol, (6) isopulegol, (7) camphor, (8) carvone, (9) bornyl acetate.

Sesquiterpenic hydrocarbons. (1) Tetrahydroelemene, (2) β -selinene, (3) caryophyllene, (4) humulene, (5) longifolene, (6) longicyclene, (7) cyclopentadecane.

* The temperature for the ester formation in the present case is 145–150° as against 135–140° employed previously, as this slightly higher temperature was necessary to ensure homogeneity of the reaction mass.

All the samples of the dicarboxylic acids were obtained from the laboratory stock and the $1,\omega$ -glycols, wherever necessary, were synthesised by the known procedures available in the literature², mainly by the reduction of the respective diesters with lithium aluminium hydride.

As usual, their purity was ascertained by m.p./b.p., elemental analyses and also GLC analyses in the case of volatile samples.

Impregnation and filling

These were performed as described previously¹.

RESULTS AND DISCUSSION

The weight of the column liquid was 1.980 g in all the cases. Retention times of the above mentioned compounds were recorded as before¹.

A column temperature of 80° was used for monoterpenic hydrocarbons and 163–164° was used for sesquiterpenic hydrocarbons and monoterpenic oxygenated compounds. Results are recorded in Tables II and III.

The arithmetical relationship

$$\frac{t_{R^x} - t_{R^y}}{x - y} = C$$

observed in our previous series of polyesters, was applied in the case of the $1,\omega$ -glycols and adipic acid polyester series. The results are recorded in Tables IV A and B. It was clear that the linear relationship was valid for the present series as well. The arithmetical pattern of the relationship of the retention time has been further indicated in Table V, in which the average ratio of the retention time for six monoterpenes and six sesquiterpenes on different polyesters have been shown against the expected values. It can be seen that the maximum deviation is about 9%. When the retention times of these monoterpenic and sesquiterpenic hydrocarbons are plotted against the number of intervening methylene groups in the alcoholic fragment of the polyester, fairly straight lines are obtained (Figs. 1 a and b).

TABLE II

RETENTION TIME IN MINUTES AT 80°; ACIDIC COMPONENT (ADIPIC ACID) CONSTANT

Compound	Number of methylene groups in the glycolic fragment of the polyester					
	2	3	4	5	6	9
α -Pinene	2.95	4.10	5.47	6.35	8.30	11.9
β -Pinene	5.05	7.23	9.50	10.75	14.35	19.5
Δ^1 -Carene	6.70	9.08	12.10	13.86	18.10	25.5
Limonene	9.13	12.70	17.00	19.26	25.3	35.0
Tricyclene	2.833	3.93	5.10	5.75	8.20	10.6
Camphene	4.280	5.80	7.50	8.66	11.10	15.3
<i>p</i> -Cymene	15.25	20.000	26.0	28.40	37.0	41.3
Cyclohexane	0.366	0.460	0.66	0.666	1.00	1.40
Methyl alcohol	1.366	—	1.42	1.50	1.15	1.10
Ethyl alcohol	1.783	—	2.10	2.00	1.70	1.60
1:8-Cineole	13.70	—	22.1	24.0	27.6	33.9

TABLE III

RETENTION TIME IN MINUTES AT 163-164°: ACIDIC COMPONENT (ADIPIC ACID) CONSTANT

Compound	Number of methylene groups in the glycolic fragment of the polyester														
	Silicone	Apiezon	2	3	4	5	6	9	10	13	15				
α -Terpineol	4.30	4.80	7.55	9.20	9.20	10.60	—	12.00	—	12.40	11.75				
Linalool	2.53	3.70	3.40	4.00	4.15	4.95	4.50	4.60	4.75	4.90	4.60				
Borneol	3.95	9.20	6.75	8.75	8.60	9.70	10.40	10.93	11.06	11.45	10.75				
Isoborneol	3.70	3.47	5.90	7.33	7.30	8.95	—	9.75	10.25	10.00	9.75				
<i>l</i> -Menthol	3.86	9.33	5.20	7.00	7.15	8.17	8.80	9.66	9.86	9.75	10.00				
Carphor	3.35	7.75	4.70	5.40	5.50	6.10	6.80	6.85	7.10	7.35	7.00				
Carvone	5.37	14.10	10.00	11.57	11.50	12.80	13.60	15.10	14.80	13.80	13.50				
Isopulegol	3.66	10.00	4.80	5.86	6.0	6.87	7.93	9.10	8.30	8.13	9.40				
Bornyl acetate	6.10	13.60	5.00	5.80	6.20	7.00	8.25	9.77	9.83	9.81	9.70				
Tetrahydrofuran	10.90	27.35	3.40	4.05	4.90	6.60	8.10	11.50	12.70	15.13	14.65				
β -Selinene	16.13	45.50	8.0	9.63	11.35	15.00	17.80	23.90	26.13	29.56	28.75				
Longifolene	11.65	33.00	4.66	5.53	6.93	8.70	10.80	15.00	16.00	19.16	18.60				
Caryophyllene	12.66	34.00	5.40	6.00	7.43	9.60	10.90	15.90	16.90	19.26	19.10				
Humulene	14.30	30.50	6.93	8.17	9.90	12.25	15.00	21.13	21.85	25.41	26.00				
Longicyclene	10.33	32.80	3.50	4.40	5.26	6.75	9.00	11.80	13.00	14.15	15.40				
Cyclopentadecane	27.60	—	7.25	10.00	12.40	18.00	22.00	31.56	33.83	43.50	—				

TABLE IVA

EVALUATION OF C AT 80°

$t_{R^x} - t_{R^y}$	$x - y$	C	$t_{R^x} - t_{R^y}$	$x - y$	C
<i>α-Pinene</i>			<i>β-Pinene</i>		
8.95	9 - 2 = 7	1.26	14.45	9 - 2 = 7	2.06
7.80	9 - 3 = 6	1.30	12.27	9 - 3 = 6	2.05
6.43	9 - 4 = 5	1.29	10.00	9 - 4 = 5	2.00
<i>Δ^3-Carene</i>			<i>Limonene</i>		
18.80	9 - 2 = 7	2.70	25.87	9 - 2 = 7	3.70
16.42	9 - 3 = 6	2.74	22.30	9 - 3 = 6	3.71
13.40	9 - 4 = 5	2.68	18.00	9 - 4 = 5	3.60
<i>Tricyclene</i>			<i>Camphene</i>		
7.77	9 - 2 = 7	1.11	11.02	9 - 2 = 7	1.57
6.67	9 - 3 = 6	1.11	9.50	9 - 3 = 6	1.58
5.50	9 - 4 = 5	1.10	7.80	9 - 4 = 5	1.56
<i>Cyclohexane</i>					
1.034	9 - 2 = 7	0.148			
0.940	9 - 3 = 6	0.157			
0.740	9 - 4 = 5	0.148			

TABLE IVB

EVALUATION OF C AT $163-164^\circ$

$t_{R^x} - t_{R^y}$	$x - y$	C	$t_{R^x} - t_{R^y}$	$x - y$	C
<i>Tetrahydroelemene</i>			<i>β-Selinene</i>		
9.30	10 - 2 = 8	1.16	18.15	10 - 2 = 8	2.27
8.65	10 - 3 = 7	1.23	16.52	10 - 3 = 7	2.36
7.80	10 - 4 = 6	1.30	14.80	10 - 4 = 6	2.46
6.11	10 - 5 = 5	1.22	11.14	10 - 5 = 5	2.23
<i>Longifolene</i>			<i>Caryophyllene</i>		
12.36	10 - 2 = 8	1.54	11.50	10 - 2 = 8	1.45
10.47	10 - 3 = 7	1.49	10.90	10 - 3 = 7	1.56
9.07	10 - 4 = 6	1.51	9.47	10 - 4 = 6	1.58
7.30	10 - 5 = 5	1.46	7.30	10 - 5 = 5	1.46
<i>Humulene</i>			<i>Longicyclene</i>		
14.92	10 - 2 = 8	1.87	9.50	10 - 2 = 8	1.33
13.68	10 - 3 = 7	1.95	8.60	10 - 3 = 7	1.23
11.95	10 - 4 = 6	1.99	7.74	10 - 4 = 6	1.29
9.63	10 - 5 = 5	1.92	6.25	10 - 5 = 5	1.25

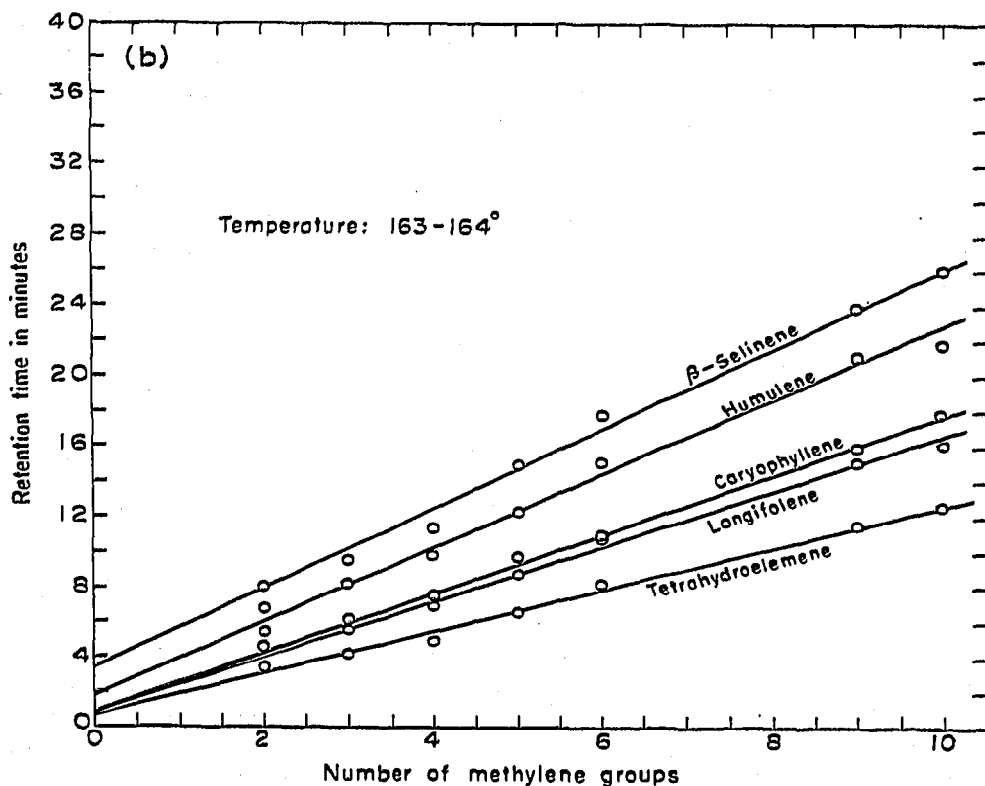
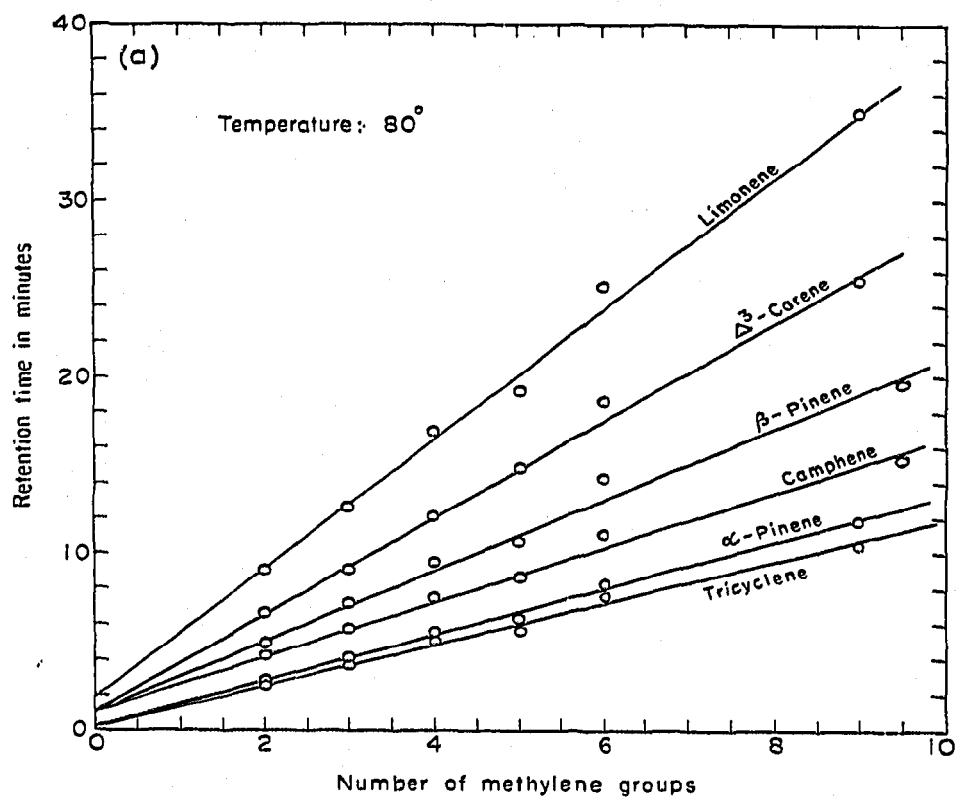


Fig. 1. Number of methylene groups in the glycolic fragment of the polyester (keeping adipic acid constant) vs. retention time. (a) Monoterpenes at 80°; (b) sesquiterpenes at 163-164°.

TABLE V

RELATIONSHIP BETWEEN THE RATIO OF THE NUMBER OF METHYLENE GROUPS AND THE RATIO OF THE RETENTION TIMES IN THE RESPECTIVE SUBSTRATES

Ratio of the number of methylene groups	Average ratio of observed retention times at 163°	Calculated ratio	Error (%)	Average ratio of observed retention times at 80°	Calculated ratio	Error (%)
10/4	2.36	2.50	5.6	—	—	—
10/6	1.50	1.66	9.6	—	—	—
9/4	2.19	2.25	3	2.09	2.26	7
9/6	1.42	1.50	5	1.37	1.50	8
6/3	1.91	2.0	5	1.99	2.0	< 1
6/4	1.58	1.5	5	1.51	1.50	< 1
4/3	1.21	1.33	9	1.31	1.33	2
3/2	—	—	—	1.39	1.50	7

In this series it appears that the linearity breaks down near the 1,10-decanediol-adipic acid polyester. This is similar to previous observations in the case of the diethylene glycol- $1,\omega$ -dicarboxylic acid polyesters series, where the linearity breaks at the brassylic acid polyester, which contains eleven methylene groups in the acid chain.

In order to confirm the deviation of the constant C and its root cause, some more polyesters were tested under exactly the same conditions as before.

Ethylene glycol (constant) and succinic acid, adipic acid, sebacic acid polyesters

The retention time data recorded on the above mentioned columns are tabulated in Table VI.

TABLE VI

RETENTION TIME IN MINUTES: GLYCOLIC FRAGMENT (ETHYLENE GLYCOL) CONSTANT

Compound	Number of methylene groups in the acidic fragment of the polyester		
	8	4	2
α -Terpineol	3.80	7.55	1.066
Linalool	4.70	3.40	2.00
<i>l</i> -Borneol	10.70	6.75	4.40
Isoborneol	—	5.90	0.700
<i>l</i> -Menthol	—	5.20	3.20
Camphor	6.80	4.70	3.10
Carvone	14.10	10.0	6.85
Isopulegol	8.30	4.80	3.0
Bornyl acetate	8.60	5.0	2.83
Tetrahydroelemene	9.00	3.40	1.83
β -Selinene	19.83	8.0	3.90
Longifolene	11.66	4.66	2.20
Caryophyllene	12.10	5.40	2.50
Humulene	16.30	6.93	3.40
Longicyclene	9.60	—	2.20
Cyclopentadecane	—	7.25	3.50

Calculation of the average ratio of the retention times of sesquiterpenic hydrocarbons on sebacic acid polyester and succinic acid polyester shows that the ratio is 5.083 instead of 4, and in the case of adipic acid polyester and succinic acid polyester, it is 2.42 instead of 2.0. However, it is interesting to note that in both cases the values are almost exactly 25 % higher when compared to the expected values, and the ratio of the observed and the expected values is nearly constant, though not in the form of a multiple of unity. This can be attributed to the difference in the nature of the glycols (diethylene glycol in the previous series and ethylene glycol in this series). This probably indicates that only diethylene glycol, having ethereal oxygen is responsible for the exact unitary nature of the arithmetical relationship in the polyester series prepared from 1, ω -dicarboxylic acids and diethylene glycol. This, however, is merely incidental.

1,5-Pentanediol (constant) and succinic acid, adipic acid, sebacic acid

The retention time data recorded on the above mentioned columns are tabulated in Table VII.

In this case, calculation of the average ratio of the retention times of the same samples of hydrocarbons on sebacic acid polyester and adipic acid polyester shows that the ratio is 1.45 instead of 2 and in the case of adipic acid polyester and succinic acid polyester it is 1.48 instead of 2. These values are nearly 26 % lower than the calculated value of 2.

TABLE VII

RETENTION TIME IN MINUTES AT 163-164°: GLYCOLIC FRAGMENT (1,5-PENTANEDIOL) CONSTANT

Compound	Number of methylene groups in the acidic fragment of the polyester		
	8	4	2
α -Terpineol	11.45	10.60	8.75
Linalool	5.23	4.95	3.90
<i>l</i> -Borneol	10.45	9.70	8.17
Isoborneol	8.66	8.95	7.17
<i>l</i> -Menthol	8.66	8.17	6.70
Camphor	6.40	6.10	5.40
Carvone	12.60	12.80	11.40
Isopulegol	8.50	6.87	5.60
Bornyl acetate	8.00	7.00	5.70
Tetrahydroelemene	9.56	6.66	4.40
β -Selinene	20.80	15.00	10.50
Longifolene	12.70	8.70	5.70
Caryophyllene	14.20	9.60	6.70
Humulene	18.00	12.25	8.70
Longicyclene	10.00	6.75	4.33
Cyclopentadecane	—	18.00	10.90

This transition from higher values in the case of the ethylene glycol and 1, ω -dicarboxylic acid series to lower values in the case of pentanediol polyester series is most probably connected with structural features associated with the chain length and conformational features of the glycol part. This aspect is receiving our special attention and will form the subject of a separate communication.

Polyester from long-chain dicarboxylic acids and long-chain glycols

After careful observation of the retention data in the case of above mentioned polyester series, it was felt necessary to investigate the behaviour of the polyesters synthesised from very-long-chain dicarboxylic acids and long-chain glycols. Therefore polyesters were prepared from hexadecane-1,16-dicarboxylic acid (constant) and 1,4-butanediol, 1,10-decanediol and 1,15-pentadecanediol. Retention time data are presented in Table VIII.

TABLE VIII

RETENTION TIME IN MINUTES: ACIDIC FRAGMENT (HEXADECANE-1,16-DICARBOXYLIC ACID) CONSTANT

Compound	Number of methylene groups in the glycolic fragment of the polyester		
	4	10	15
α -Terpineol	17.60	4.00	4.10
Linalool	7.66	4.60	4.83
<i>l</i> -Borneol	15.60	10.70	10.90
Isoborneol	13.50	2.50	2.60
<i>l</i> -Menthol	14.20	10.00	9.80
Camphor	9.20	6.90	7.30
Carvone	18.10	12.70	13.83
Isopulegol	11.50	8.10	7.93
Bornyl acetate	13.60	10.20	10.30
Tetrahydroelemene	17.81	16.40	19.00
β -Selinene	34.50	32.50	37.50
Longifolene	22.00	22.30	24.10
Caryophyllene	23.10	20.50	22.83
Humulene	29.20	27.00	30.10
Longicylene	18.00	18.50	19.50
Cyclopentadecane	—	—	—

Surprisingly it was found that there are some cases of a saturation point being reached in the retention times of hydrocarbons on these polyesters. While going from a polyester derived from 1,4-butanediol and hexadecane-1,16-dicarboxylic acid to a polyester derived from 1,15-pentadecanediol and the same dicarboxylic acid, it was observed that the retention times of hydrocarbons recorded on both these polyesters are almost the same, being only slightly higher in the latter case.

Comparative assessment of related factors

Relative retention time data* show that polyesters synthesised from the long chain, 1, ω -glycols and adipic acid exhibit very high solubilities for sesquiterpenic hydrocarbons. These results can also be conveniently used for the separation of monoterpenic oxygenated compounds and sesquiterpenic hydrocarbons.

The values of α the relative volatility, N the number of theoretical plates and s the separation factor have been calculated for three typical pairs of monoterpenic hydrocarbons according to PURNELL³ and are presented in Table IX.

Thus a mixture of isopulegol and longifolene would require nearly 50,000 plates

* These can be easily calculated from the data presented in Table II and III, taking the value of camphor as unity.

TABLE IX

Components of the polyester	Compound pair	α	N	S
Adipic acid and ethylene glycol	Borneol and caryophyllene	1.250	1009	900
	Bornyl acetate and caryophyllene	1.08	7570	6560
	Isopulegol and longifolene	1.03	49840	42430
Adipic acid and 1,15-pentadecanediol	Borneol and caryophyllene	1.776	196.4	188.6
	Bornyl acetate and caryophyllene	1.969	154.8	148.6
	Isopulegol and longifolene	1.979	153.3	147.1
Hexadecane-1,16-dicarboxylic acid and 1,15-pentadecanediol	Borneol and caryophyllene	2.095	136.5	131.7
	Bornyl acetate and caryophyllene	2.217	123.7	119.5
	Isopulegol and longifolene	3.039	82.68	79.97
Silicone elastomer	Tetrahydroelemene and β -selinene	1.480	—	342.2
	Caryophyllene and humulene	1.129	—	2758
	Longifolene and longicyclene	1.128	—	2797
Adipic acid and 1,15-pentadecanediol	Tetrahydroelemene and β -selinene	1.963	—	149.5
	Caryophyllene and humulene	1.361	—	512.1
	Longifolene and longicyclene	1.208	—	1213

if it is to be resolved on a column of polyester synthesised from adipic acid and ethylene glycol, but the same mixtures can be resolved by only 83 plates if a column of polyester synthesised from hexadecane-1,16-dicarboxylic acid and 1,15-pentadecanediol is used. The case is similar with other pairs presented in Table IX.

This type of stationary phase, prepared from either long-chain $1,\omega$ -glycols or long-chain dicarboxylic acids, seems to give a very nice and distinctive cut between the oxygenated compounds and hydrocarbons. At the same time these phases will also resolve the individual components. From Table IX, it is clear that the separation of tetrahydroelemene and β -selinene would require nearly 342 plates on a silicone column, but the same mixture can be separated by only 150 plates if it is chromatographed on a polyester synthesised from adipic acid and 1,15-pentadecanediol; and similarly with other pairs of hydrocarbons.

Calculation of N , the number of theoretical plates, in the case of capillary columns used to give very high values, but the same degree of separation was also attainable by packed columns. This anomaly was clearly explained by PURNELL³. The general equation given by him is as follows:

$$N = S \left[1 + 2 \left(\frac{V_d}{V_R} \right) + \left(\frac{V_d}{V_R} \right)^2 \right]$$

In this equation full allowance is made for the dead volume of the column, which becomes significant when the retention volume is very low compared to the dead volume.

In the present series of polyesters, it can be seen from the retention time data that, while going from ethylene glycol-adipic acid polyester to the last polyester,

the retention times of hydrocarbons are increased several fold. Similarly the retention times of oxygenated compounds are also increased by nearly a factor of two; consequently the effect of dead volume should be pronounced in the case of lower polyesters and negligible in the case of higher polyesters.

The values of N , S and α calculated for typical pairs of compounds (Table IX) indicate that there is not much difference in the values of N and S in the case of long-chain polyesters and this point would strongly favour the use of these polyesters as stationary phases in capillary columns.

When a graph of relative retention times (Fig. 2) (with respect to camphor) on 1,3-propanediol-adipic acid polyester is plotted against the relative retention times on 1,10-decanediol-adipic acid polyester, two distinct straight lines are obtained.

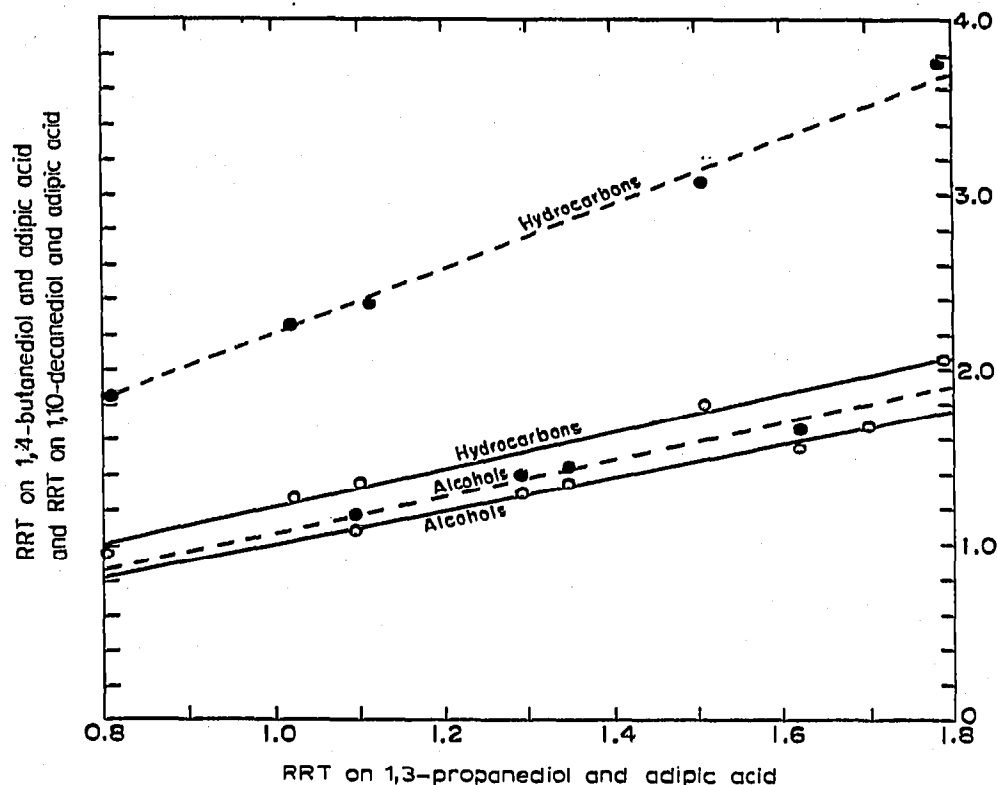


Fig. 2. $\circ-\circ$ = 1,3-propanediol and adipic acid vs. 1,4-butanediol and adipic acid; $\bullet-\bullet$ = 1,3-propanediol and adipic acid vs. 1,10-decanediol and adipic acid.

One line represents the hydrocarbons and the other one represents the alcohols. As the number of methylene groups in the alcoholic fragment of the polyester goes on increasing, these lines diverge further apart. This clearly indicates that these two groups of compounds will be separated on the polyesters synthesised from long-chain glycols. If we examine relative retention time data obtained on ethylene glycol-adipic acid polyester and 1,15-pentadecanediol-adipic acid polyester, we find that there is no apparent loss in the resolution of the individual components of the oxygenated compounds, but at the same time the hydrocarbon group is well separated also with no loss in the resolution of the individual components of the hydrocarbon group.

SUMMARY

Polyesters from different $1,\omega$ -glycols, ranging from ethylene glycol to 1,15-pentadecanediol, with adipic acid were prepared and evaluated as substrates for gas-liquid chromatography. Several terpenic and a few non-terpenic compounds were analysed. It was observed that the retention time is a characteristic of the number of methylene groups in the glycolic fragment of the polyester and, as before, follows a linear relationship, which starts deviating at 1,10-decanediol. The effect on retention times by using ethylene glycol and changing the acid fragment was also studied. Similarly, the effect on retention times by using 1,5-pentanediol (which has the same number of polyvalent atoms in the chain unit as diethylene glycol) and changing the acidic fragment was also examined. From the above mentioned observations, it was clear that the retention times of hydrocarbon-type compounds may be enormously increased by using a polyester derived from very-long-chain dicarboxylic acid and long-chain $1,\omega$ -glycol. However, the retention times of hydrocarbons reach a certain saturation point above which their solubilities do not increase appreciably. Finally, the effect of dead volume of the column was discussed with respect to the case of long-chain as well as short-chain polyesters. Some of the stationary phases described in the paper are likely to be very useful for capillary columns and for preparative gas-liquid chromatography.

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