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## EVALUATION OF THE PROPERTIES OF "APIEZON" GREASES AS STATIONARY PHASES IN GAS-LIQUID CHROMATOGRAPHY

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## SUMMARY

The gas chromatographic behaviour of the widely used "Apiezon" stationary phases was evaluated, taking into account several parameters. Paraffins and other homologous series were analysed at temperatures ranging from 50° to 300°, on Apiezon L, M and N, at liquid phase concentrations ranging from 2.5 to 20%, and a carrier gas flow rate from 20 to 40 ml/min. Linear retention plots were obtained, and characteristic parameters for all the homologous series, phase concentration and temperature were calculated. The use of these parameters will permit the identification of many compounds without the use of standard samples.

## INTRODUCTION

From the early days of gas chromatography (GC), "Apiezon"\* greases have been widely used as liquid phases for the separation of many classes of compounds. Literature reviews report over 300 papers where Apiezon greases have been used as the liquid phase. In spite of this, no systematic evaluation of the separation characteristics of the various types of Apiezon has been made with respect to analytical parameters, such as temperature and liquid phase concentration on the support.

## MATERIALS AND METHODS

*Instruments*

The analyses were accomplished by means of a Varian Aerograph Model A 350 gas chromatograph, equipped with a thermal conductivity detector and linear temperature programmer. The temperature readout was made with a standard thermocouple pyrometer and with high precision thermometers installed in different positions in the column oven. The inlet pressure was measured directly at the injector septum by a Bourdon type pressure gauge connected by means of a hypodermic needle. Due to the large diameter of the tubing connecting the detector to the

\* Apiezon is a registered trade mark of Shell Chemicals.

atmosphere, the outlet of the column was practically at atmospheric pressure, which was frequently monitored with a barometer.

The flow of the carrier gas was measured with a bubble flow meter and corrected to standard pressure and temperature.

### Columns

Copper tubing of  $\frac{1}{8}$  in. O.D. was used for the preparation of columns. The wall thickness was 0.5 mm, and therefore the internal bore had a cross-section of about 3.8 mm<sup>2</sup>. The tubing was thoroughly washed with hexane, acetone and ethyl alcohol, and warmed under a flow of nitrogen to clean the inner surface. The columns were coiled in a helix, 10 cm in diameter, and packed under vacuum by connecting one end to a rotary vacuum pump and gently tapping the coiled column while the stationary phase was added from the other end by means of a funnel. 150-cm long columns were used.

### Packing

The support used was Chromosorb W (Johns-Mansville), acid washed, 60-80 mesh. The product was screened before and after impregnation, in order to ensure constant mesh size. The true density of this support was 2.2 g/cm<sup>3</sup>, and the packed density was 0.24 g/cm<sup>3</sup>. Apiezon L, M and N were used as liquid phases. The physical characteristics of these three greases are given in Table I. The liquid phases were used without purification or previously purified by column chromatography on activated alumina. The effect of purification will be discussed later.

TABLE I

PROPERTIES OF APIEZON GREASES AND RECOMMENDED MAXIMUM TEMPERATURE FOR USE AS STATIONARY PHASES

<i>Apiezon grade</i>	<i>Melting point (°C)</i>	<i>Vapour pressure (torr)<sup>a</sup></i>	<i>Max. temp. (°C)<sup>b</sup></i>
L	47	10 <sup>-11</sup> at 20°C 10 <sup>-3</sup> at 300°C	325
M	44	10 <sup>-8</sup> at 20°C 10 <sup>-3</sup> at 200°C	275
N	43	10 <sup>-9</sup> at 20°C 10 <sup>-3</sup> at 250°C	300

<sup>a</sup> From Shell Chemicals.

<sup>b</sup> From Varian Aerograph.

The support was impregnated using methylene chloride as solvent, and the slurries were dried at 70° in large beakers, with manual agitation. A rotary evaporator was not used in order to minimize the crushing of the support after impregnation. Liquid phase percentages of 20, 10, 5 and 2.5 in weight were used. The filled columns contained 0.226, 0.113, 0.056 and 0.028 g of liquid phase, respectively.

### Samples

Pure paraffins were obtained from Chemical Samples Co. and from Fluka AG. Other products were obtained from Carlo Erba, Fluka and BDH.

The liquid samples were injected directly by means of Hamilton microsyringes, and a synchronized signal was given to the recorder to mark the time of the injection exactly. Solid samples were dissolved in ethylbenzene.

In order to compare the performances of different types of Apiezon greases, a comparison was made between the results of analyses of *n*-paraffins at various temperatures. Naturally, due to the well known dependence of retention time on column temperature, the analyses had to be accomplished with different blends of paraffins, in order to avoid too long an analysis time or too short a retention time, which are difficult to measure exactly. Table II gives the range of carbon numbers analysed on each column at various temperatures.

TABLE II

NUMBER OF CARBON ATOMS OF *n*-PARAFFINS ANALYSED AT VARIOUS CONCENTRATIONS OF LIQUID PHASE AND AT DIFFERENT TEMPERATURES

Apiezon grade	Liquid phase concentration (%w/w)	Column temperature (°C)											
		50	75	100	125	150	175	200	225	250	275	300	
J, M, N	20	1-10	1-11	5-12	5-12	5-12	8-17	10-19	10-22				
"	10	5-12	5-12	5-15	5-15	7-18	10-18	10-19				17-28	
"	5							10-19	18-24	18-28	18-32		
"	2.5										18-32	22-36	

The analysis of heavy products has to be made at high temperatures on columns with a low percentage of stationary phase, and therefore *n*-paraffins with 10 to 36 carbon atoms were analysed on columns with 2.5 to 10% of Apiezon L, at temperatures ranging from 175 to 300°. Only Apiezon L was used for low-concentration columns, due to its lower vapour pressure, which makes this grease very useful for high-temperature analysis (see Table I).

The results of the columns at 20% concentration can be easily extrapolated for Apiezon M and N columns at a lower concentration, by comparison with the properties of Apiezon L.

#### Calculations

The calculations were performed on the IC 10070 computer installed in the Centre for Automatic Calculation of the University of Genoa, using Fortran IV programs<sup>1</sup>.

### EXPERIMENTAL AND RESULTS

#### Carrier gas flow rate

The dependence of the flow of the carrier gas on column temperature and concentration of the stationary phase was examined. The inlet pressure necessary for a constant flow depends linearly on temperature, as can be seen from Fig. 1, where the complete lines show the behaviour of the inlet pressure *P* at a concentration of 20% of stationary phase, and the dotted lines the behaviour at 10%. Black circles represent experimental values obtained at a 20% concentration of Apiezon.

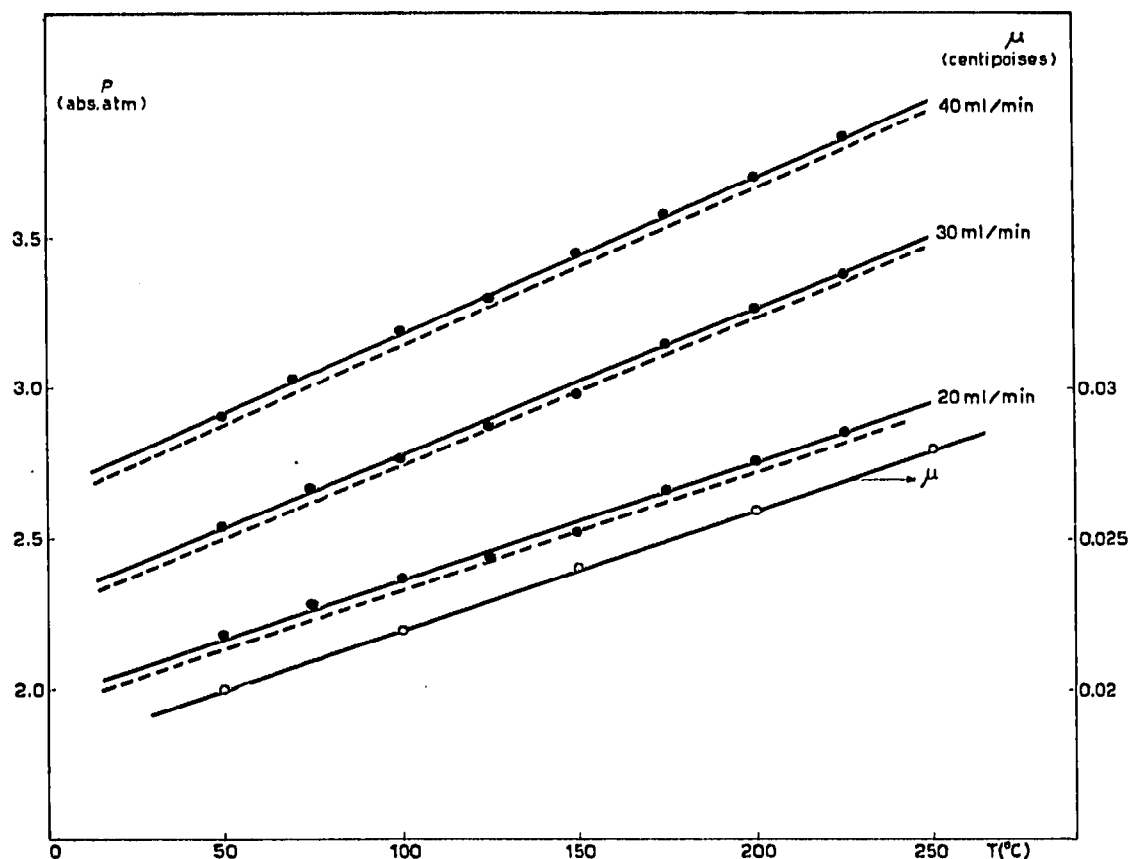


Fig. 1. Inlet pressure for three flow rates (outlet at atmospheric pressure) with 10% and 20% of Apiezon L, and absolute viscosity  $\mu$  (white circles) as a function of absolute temperature. ---, 10%; ———, 20%.

In Table III the coefficients are given of the equation:

$$P = c_0 + c_1 T \quad (1)$$

where

$P$  = inlet pressure of the column (absolute atm) and  
 $T$  = column temperature ( $^{\circ}\text{K}$ ).

TABLE III

COEFFICIENTS OF THE EQUATION  $P = c_0 + c_1 T$ , WHICH SHOWS THE DEPENDENCE OF THE INLET PRESSURE OF THE CARRIER GAS ON THE TEMPERATURE OF THE COLUMN, AT A CONCENTRATION OF 10% AND 20% OF APIEZON L

Helium flow rate (ml/min)	$c_1 (\times 10^3)$		$c_0$		$c_0 (20\%) - c_0 (10\%)$
	10%	20%	10%	20%	
20	3.94	3.93	0.861	0.895	0.034
30	4.88	4.85	0.922	0.954	0.032
40	5.20	5.19	1.202	1.239	0.037

Both  $c_0$  and  $c_1$  increase with the flow.  $c_1$  has the same value for columns containing

both 10% and 20% of liquid phase (*i.e.*, the pressure behaviour is parallel), while  $c_0$  shows a constant difference of about 0.03, because the lower concentration of stationary phase causes a smaller pressure drop in the column.

The increase of  $P$  with temperature depends mainly on the increase of the viscosity of the carrier gas. Fig. 1 also indicates, with white circles, the values of  $\mu$  (absolute viscosity) in centipoises, and one can see that the behaviour of the inlet pressure closely follows the viscosity. This dependence of the column resistance on temperature makes careful control of the carrier gas flow rate necessary at every change in column temperature, in order that the retention times for an analysis may be compared at different temperatures without errors due to flow variation.

### *Separation of paraffins*

A first evaluation of the separation properties of the different types of Apiezon was made by plotting the logarithm of the adjusted retention times  $t_s$  (given by total retention time minus the gas hold-up time  $t_m$ )<sup>2</sup> as a function of the number of carbon atoms in the paraffin. This kind of representation gives a straight-line equation of the type:

$$\log t_s = a_0 + a_1 n \quad (2)$$

where

$n$  = number of carbon atoms and

$a_0$  and  $a_1$  = constants dependent on flow, temperature and concentration of stationary phase.

The graphical representation of eqn. 2 gives a series of straight lines with a decreasing slope when the column temperature increases.  $a_1$  therefore depends on the temperature; this will be discussed later.

It was observed that at the same temperature, flow and concentration, the three stationary phases tested (L, M and N) give very similar values of  $a_0$  and  $a_1$ . The small variations are completely random and probably due to small differences in experimental conditions. The largest difference observed between the three Apiezon is of the same order of magnitude as that which would be given by a difference of temperature of 3–4°, or by a variation in the concentration of the stationary phase from 20% to 19.5%. As these variations are normal between analyses made in different laboratories or at different periods of the column life, it can be deduced that the three Apiezon are completely interchangeable from the point of view of their separation properties. As Apiezon L has a lower vapour pressure and allows higher operating temperatures, it seems reasonable to employ mainly this type of grease.

The majority of the published works that report separations on Apiezon greases confirm that Apiezon L is the one most widely used. (In 280 papers examined, 213 used Apiezon L, 33 Apiezon M, 11 Apiezon N, 1 each Apiezon C, H and Q. Other authors do not specify the grade of Apiezon used.)

Eqn. 2 gives values of  $a_0$  and  $a_1$  quite independent of the type of Apiezon, but the dependence on carrier gas flow rate and on the percentage of stationary phase still remains. Differences in flow and variation of the stationary phase concentration cause a change in  $a_0$ , *i.e.*, a parallel shift of the plot, while variation in temperature produces a change in  $a_1$ . For example, Fig. 2 shows the plots of  $\log t_s$  as a function

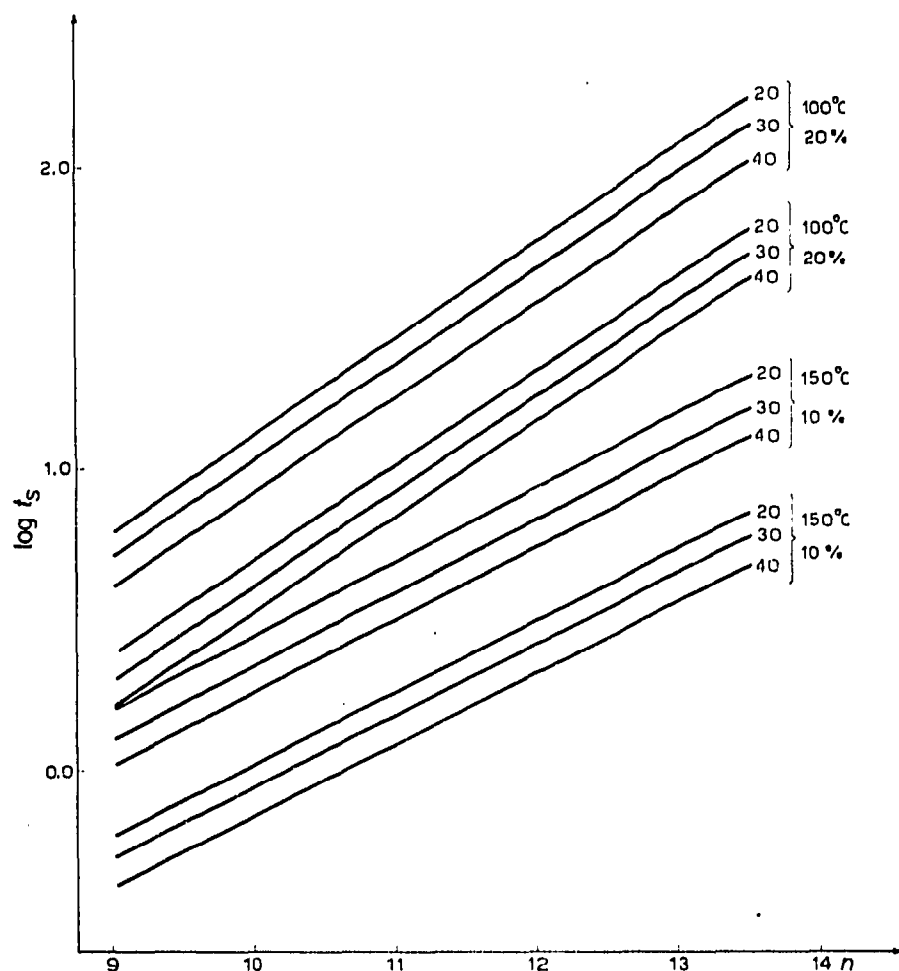


Fig. 2. Logarithm of adjusted retention time of *n*-paraffins versus the number of carbon atoms, temperature, carrier gas flow rate and percentage of Apiezon L.

of *n* for 20% and 10% concentrations of Apiezon L with three different flow rates at 100° and 200°C. To determine the dependence of retention time on temperature (without the influence of flow rate and concentration),  $V_g$ , the specific retention volume, was used instead of  $t_s$  (ref. 3). The specific retention volume  $V_g$  is given by the equation:

$$V_g = \frac{273 \cdot V_r^{PT}}{W_L \cdot T_s} \quad (3)$$

where

$W_L$  = grams of liquid phase;

$T_s$  = temperature of separation in °K and

$V_r^{PT}$  = retention volume corrected for temperature and pressure.

$V_r^{PT}$  can be calculated with the formula:

$$V_r^{PT} = t_s \cdot f \cdot F_m \cdot \frac{T_s}{T_m} \quad (4)$$

where

$t_s$  = adjusted retention time (see eqn. 2);

$f$  = pressure correction factor;

$F_m$  = linear gas flow rate, measured at  $T_m$  in ml/min;

$T_s$  = column temperature in °K and

$T_m$  = temperature of the flow meter in °K.

The calculation of  $V_g$ , which is very difficult to achieve exactly, due to the high precision required for the measurement of the variables involved, gives interesting results. All the infinite parallel lines represented by eqn. 2 and dependent on the variation in flow rate and concentration are replaced by a single straight line of equation:

$$\log V_g = d_0 + d_1 n \quad (5)$$

At constant temperature, the largest difference in  $\log V_g$  of a given substance is about 0.02 for a flow variation from 20 to 30 or 40 ml/min, and about 0.04 for a decrease of concentration of stationary phase from 20% to 10%.

All the analyses on different columns at various temperatures can therefore be plotted as a series of straight lines of different slopes  $d_1$  (see Fig. 3). It must be pointed out that the values of  $d_1$  are the same as those previously calculated for  $a_1$ ,

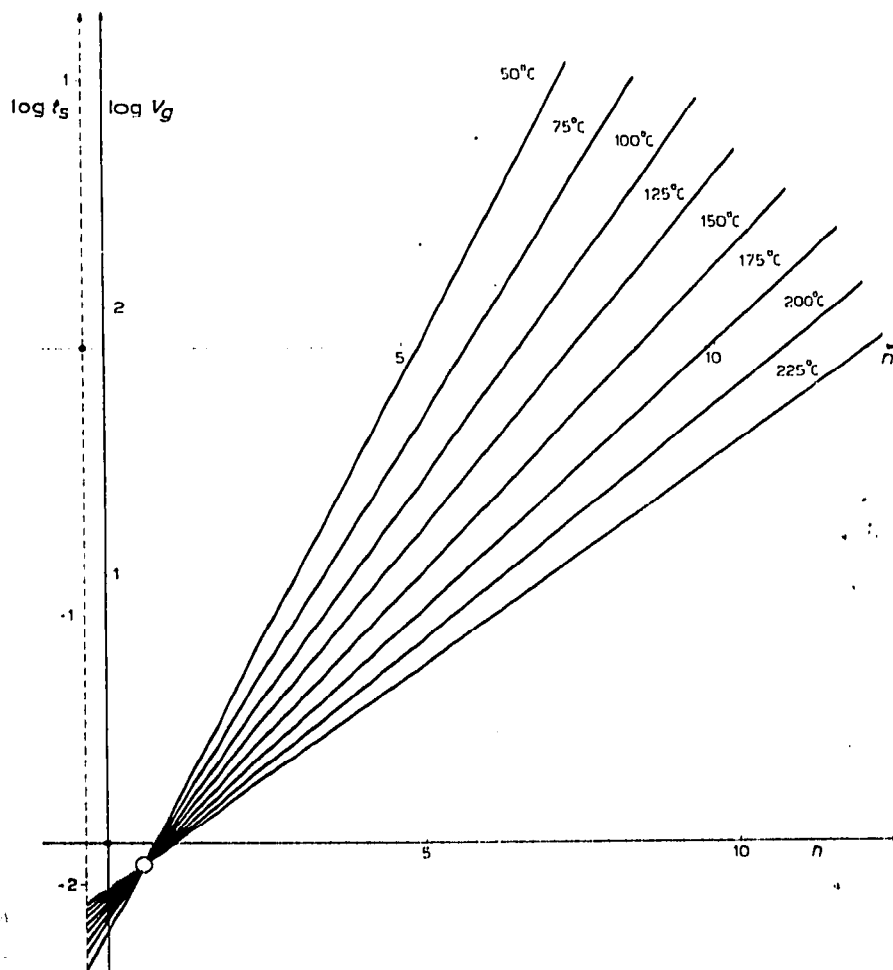


Fig. 3. Logarithm of specific retention volume  $V_g$  and of adjusted retention time  $t_s$  versus the number of carbon atoms for the  $n$ -paraffins at different temperatures (column, Apiezon L 20%; flow rate, 40 ml/min).

and therefore the new lines representing eqn. 5 have, on the same scale, a behaviour parallel to the lines representing eqn. 2. Thus, it can be seen in Fig. 3 that both eqn. 2 and eqn. 5 can be represented by the same series of lines, simply by changing the ordinate.

$a_0$  and  $d_0$  show small and irregular variations with temperature, which may be due to errors of extrapolation by the least squares method.

It is interesting to observe that all the lines have a common point, with approximate coordinates  $\log t_s = -1.9$  at  $n = 0.8$ , and  $\log V_g = -0.1$  at  $n = 0.5$ . This behaviour of the plots indicates that methane is also retained on Apiezon columns, and if it were not retained on the stationary phase,  $V_g = 0$  would be obtained at all temperatures. On the other hand,  $\log V_g$  for methane is inversely proportional to temperature (see Fig. 4).

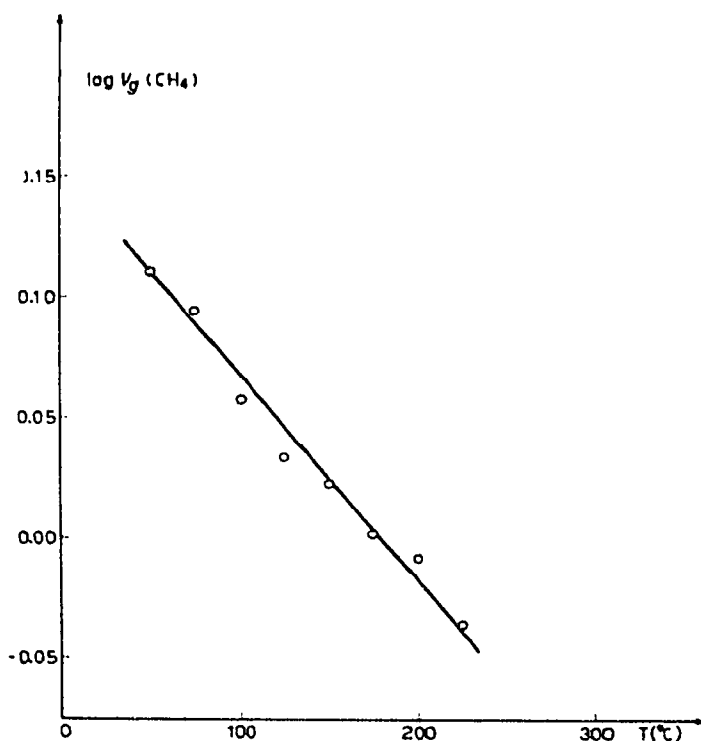


Fig. 4. Logarithm of the specific retention volume of methane *versus* column temperature.

Sometimes the retention time of methane is taken as a measure of the gas hold-up time  $t_m$ , especially when a flame ionization detector, insensitive to air, is used. Measuring  $t_m$  in this manner can produce errors that increase when the temperature of analysis decreases, due to the fact that  $V_g$  for methane is not equal to zero.

The dependence of the retention times on temperature can be expressed in terms of slope variation. Fig. 5 shows the values of slope  $d_1$  (equal to  $a_1$ , as previously seen) as a function of column temperature. The coincidence between the values for columns with different concentrations of stationary phase is very satisfactory. The dependence of  $a_1$  and  $d_1$  on absolute temperature  $T$  is given with good approximation by the following equation:

$$d_1 = b_0 + b_1 \frac{1}{T} \quad (6)$$



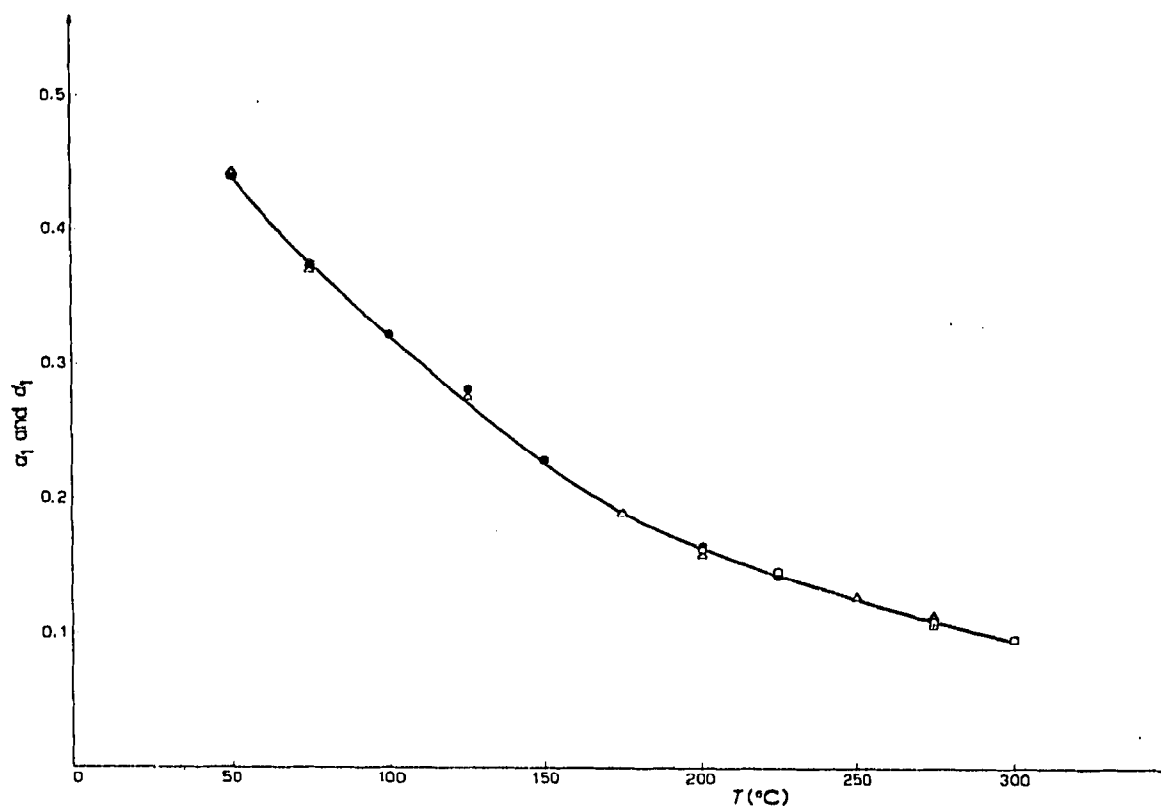


Fig. 5. Values of the slope  $d_1$  (equal to  $a_1$ , see text) versus column temperature at different concentrations of Apiezon L. □, 2.5%; ○, 5%; △, 10%; ●, 20%.

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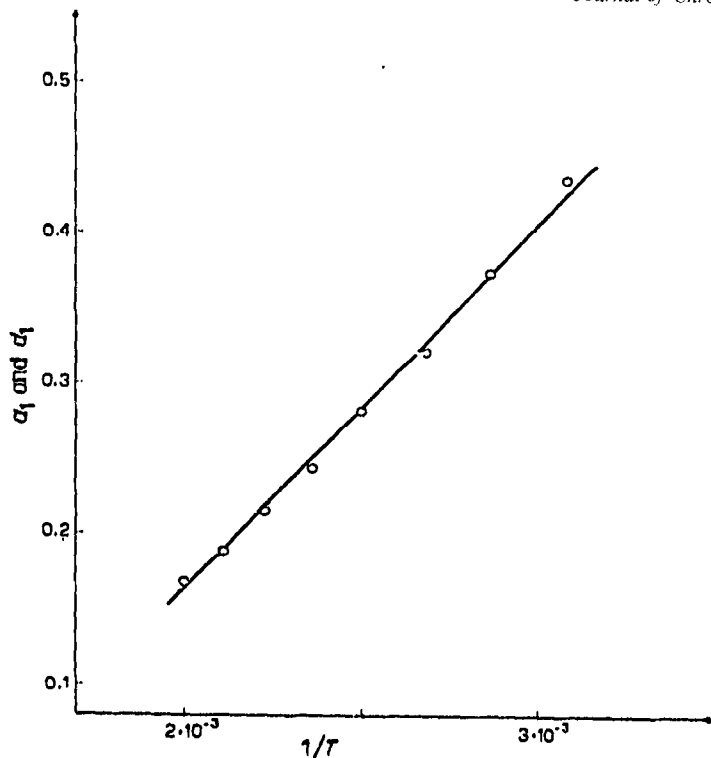


Fig. 6. Values of the slope  $d_1$  and  $a_1$  as a function of the reciprocal of the absolute temperature of the column.

*i.e.*, the plot of  $a_1$  and  $d_1$  vs. the reciprocal of absolute temperature is linear (Fig. 6)

Eqns. 2 and 5 can therefore be modified to:

$$\log t_s = b_0 n + b_1 \frac{n}{T} + a_0 \quad (7)$$

$$\log V_g = b_0 n + b_1 \frac{n}{T} + d_0 \quad (8)$$

The general equation proposed by AMBROSE *et al.*<sup>4</sup> and PURNELL<sup>5</sup>, allows the theoretical calculation of  $V_g$ :

$$V_g = \frac{273 R}{\gamma p_0 M_l} \quad (9)$$

where

$273 R = 1.7 \times 10^7$  if  $R$  (gas constant) =  $6.3 \times 10^4$  ml·mm·mole<sup>-1</sup>·deg<sup>-1</sup>;

$p_0$  = saturation vapour pressure of the analysed substance (torr) at the temperature of analysis;

$M_l$  = molecular weight of the analysed substance and

$\gamma$  = activity coefficient.

From eqn. 9 the following can be deduced:

$$\log V_g = \log \frac{1.7 \times 10^7}{M_l} - \log p_0 - \log \gamma \quad (10)$$

As it is difficult to know what the activity coefficient is, theoretical values of  $\log V_g$  can only be calculated from eqn. 9 if one assumes that the solutions are ideal, that is  $\gamma = 1$  (ref. 5). The equation therefore becomes:

$$\log V_g = \frac{\log 1.7 \times 10^7}{M_l} - \log p_0 \quad (11)$$

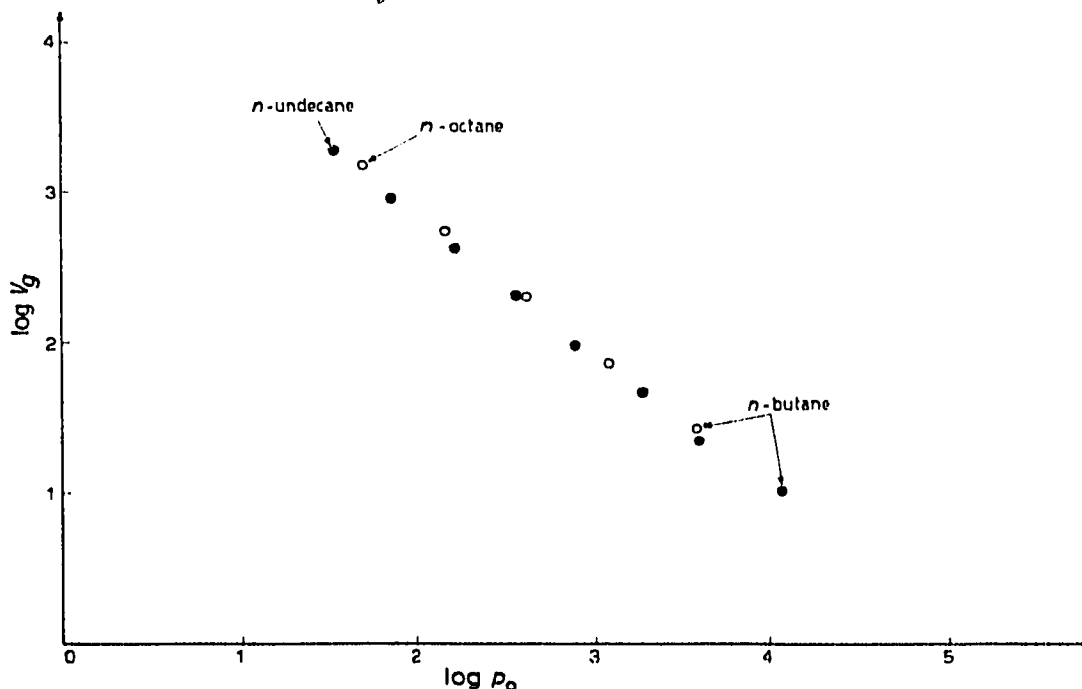


Fig. 7. Experimental  $\log V_g$  as a function of  $\log p_0$  (saturation vapour pressure) for *n*-paraffins at 50° and 100°C. O, 50°C; ●, 100°C.

This ideal solution equation is not fully verified by our experimental results. Although the plot of  $\log V_g$  vs.  $\log p_0$  (Fig. 7) is linear and, for *n*-paraffins, the values at different temperatures lie practically on the same line, a difference (decreasing with the number of carbon atoms and temperature) was observed between the calculated (from eqn. 11) and experimental values of  $\log V_g$  (see Table IV). The actual values of  $\log V_g$  are lower than those obtained from the "ideal solution equation", and the observed differences may be attributed to the fact that the term  $-\log \gamma$  differs from zero. It should therefore be possible to calculate the activity coefficient  $\gamma$  from these differences, for the various compounds at different temperatures.

TABLE IV

LOGARITHM OF THE SATURATION VAPOUR PRESSURE OF *n*-PARAFFINS AND COMPARISON BETWEEN EXPERIMENTAL  $\log V_g$  AND THOSE CALCULATED WITH EQN. 10, AT 50° AND 100°C

<i>T</i> (°C)	<i>n</i> -Paraffin	$\log p_0$	$\log V_g$		$\log V_g$ (calc.) - $\log V_g$ (exptl.)
			Exptl.	Calc.	
50	Butane	3.58	1.43	1.88	0.45
	Pentane	3.09	1.87	2.28	0.41
	Hexane	2.61	2.31	2.68	0.37
	Heptane	2.17	2.75	3.06	0.31
	Octane	1.71	3.19	3.46	0.27
100	Butane	4.07	1.02	1.39	0.37
	Pentane	3.60	1.35	1.78	0.43
	Hexane	3.29	1.67	2.01	0.34
	Heptane	2.91	1.99	2.32	0.33
	Octane	2.56	2.31	2.62	0.31
	Nonane	2.20	2.63	2.91	0.28
	Decane	1.87	2.96	3.21	0.25

The theoretical eqn. 11 is similar to the experimental eqn. 8. The first term of eqn. 11 is in fact proportional to the number of carbon atoms *n*, as for the normal paraffins:

$$M_l = 14.027 n + 2.016 \quad (12)$$

The vapour pressure  $p_0$  (second term of eqn. 11) is directly proportional to *n* and inversely proportional to the temperature. The third term ( $-\log \gamma$ ) is similar to  $d_0$ . The average of the difference between  $\log V_g$  (calc.) and  $\log V_g$  (exptl.) in Table IV is 0.36 at 50°C and 0.33 at 100°C, while the mean values of  $d_0$  taken from experimental data at the corresponding temperatures are 0.37 and 0.32, respectively.

By definition,  $d_0$  is constant if the temperature of analysis is constant, but the last column of Table IV shows a decrease of the difference between  $\log V_g$  (calc.) and  $\log V_g$  (exptl.) with the increase of *n*. It is not clear if this deviation is due to the fact that the values of  $p_0$  were calculated by interpolation<sup>6</sup> and have an increasing uncertainty when *n* decreases, or if the plots of  $\log V_g$  vs. *n* (Fig. 3) are not perfectly linear.

The former hypothesis seems to be the more reliable, as the logarithmic dependence of retention values on the number of carbon atoms of the molecule is one of the most verified correlations of GC<sup>3,5</sup>.

TABLE V  
VALUES OF  $d_1$  (EQUAL TO  $a_1$ ) FOR DIFFERENT SERIES OF COMPOUNDS AT VARIOUS FLOW RATES, CONCENTRATIONS OF STATIONARY PHASE AND TEMPERATURES

Homologous series	Temperature (°C)	10% Apiezon L			20% Apiezon L			Overall average		
		20 ml/min	30 ml/min	40 ml/min	Average at 10%	20 ml/min	30 ml/min		40 ml/min	Average at 20%
<i>n</i> -Paraffins	50	0.411	0.434	0.440	0.428	0.419	0.414	0.432	0.421	0.425
	100	0.315	0.314	0.322	0.317	0.320	0.320	0.306	0.315	0.316
	150	0.238	0.236	0.240	0.238	0.245	0.242	0.243	0.243	0.241
<i>n</i> -Alkyl iodides	50	0.409	0.392	0.427	0.409	0.406	0.397	0.396	0.400	0.404
	100	0.318	0.320	0.314	0.317	0.317	0.317	0.320	0.318	0.318
	150	0.238	0.238	0.235	0.237	0.237	0.239	0.241	0.239	0.238
<i>n</i> -Alcohols	50	0.400	0.387	0.398	0.395	0.415	0.417	0.416	0.416	0.405
	100	0.319	0.309	0.324	0.317	0.327	0.322	0.329	0.326	0.322
	150	0.247	0.240	0.238	0.242	0.251	0.249	0.247	0.249	0.245
Acetates	50	0.391	0.399	0.403	0.397	0.396	0.406	0.402	0.401	0.399
	100	0.316	0.319	0.323	0.319	0.324	0.329	0.313	0.319	0.319
	150	0.246	0.252	0.238	0.245	0.256	0.260	0.256	0.257	0.251
Methyl ketones	50	0.407	0.389	0.386	0.394	0.408	0.395	0.410	0.404	0.399
	100	—	—	—	—	0.335	0.349	0.339	0.341	—
<i>n</i> -Alkyl chlorides	150	0.244	0.240	0.238	0.241	0.241	0.244	0.239	0.241	0.241

The data reported in Fig. 7 and in Table IV show that the slope of the plot  $\log V_g$  vs.  $\log p_0$  is greater than 1. This means<sup>5</sup> that the retentions of successive homologues are greater than would be expected on the basis of their vapour pressures. The separation of paraffins on Apiezon greases is thus a sort of "superdistillation", *i.e.*, the separation obtainable is better than ideal distillation. This fact is in agreement with the well known efficiency of Apiezon in separating hydrocarbons with the same boiling points.

#### *Analyses of other homologous series*

After the paraffins, several members of other homologous series were analysed with the same columns and under the same conditions as above.

The compounds analysed were: *n*-alkyl iodides, *n*-alkyl chlorides, *n*-alcohols, methyl ketones and acetates of normal alcohols.

TABLE VI

VALUES OF  $d_0$  FOR DIFFERENT SERIES OF COMPOUNDS AT VARIOUS TEMPERATURES FOR TWO CONCENTRATIONS OF STATIONARY PHASE

<i>Homologous series</i>	<i>Temperature (°C)</i>	<i>10% Apiezon L</i>	<i>20% Apiezon L</i>
<i>n</i> -Paraffins	50	-0.552	-0.398
	100	-0.436	-0.315
	150	-0.351	-0.290
<i>n</i> -Alkyl iodides	50	1.319	1.463
	100	0.953	1.077
	150	0.771	0.882
<i>n</i> -Alcohols	50	0.585	0.593
	100	0.289	0.346
	150	0.139	0.235
Acetates	50	0.289	0.365
	100	0.107	0.149
	150	0.027	0.027
Methyl ketones	50	0.273	0.215
	100	—	0.068
<i>n</i> -Alkyl chlorides	150	0.238	0.375

Tables V and VI show the values of  $d_1$  (equal to  $a_1$ , as shown) and of  $d_0$ , respectively, for the series of compounds cited. From the reported data one can see that the slopes ( $d_1$ ) for any series are practically the same for the three flow rates and for the two concentrations tested. The differences are in the range of the experimental error. All the compounds show a regular variation of slope with the temperature, and every homologous series thus gives straight lines similar to those shown for the *n*-paraffins in Fig. 3.

The lines for the different series have a shift with respect to the *n*-paraffins, as can be seen from the different values of  $d_0$ , but at every temperature they are parallel, with the exception of the methyl ketones, the slope of which is greater. Fig. 8 shows the lines for several series at 50°C and a flow rate of 20 ml/min of carrier gas, on a column of Apiezon L with 20% of stationary phase.

TABLE VII

COMPARISON BETWEEN MOLECULAR WEIGHT AND BOILING POINT OF THE FIRST TERM OF EVERY HOMOLOGOUS SERIES AND ITS RETENTION TIME ON 20% APIEZON L (20 ml/min flow rate) AT THREE TEMPERATURES (50°, 100°, 150°C).

Compound	$M_1$	Boiling point (°C)	Retention time, $t_R$ (min)		
			50°C	100°C	150°C
Methane	16.04	-161.5	0.020	0.017	0.017
Methyl alcohol	32.04	64.6	0.18	0.09	0.06
Methyl chloride	50.49	-24.2	—	—	0.08
Dimethyl ketone	58.08	56.5	0.55	0.22	—
Methyl acetate	74.08	57.1	0.60	0.24	0.12
Methyl iodide	141.95	42.5	1.23	0.48	0.28

The alkyl chlorides are not reported in this figure, as a minimum temperature of 150°C is necessary for the analysis, but Table V shows that their values of  $d_1$  at this temperature are quite similar to those of *n*-paraffins and this means that chlorides also have parallel behaviour.

The fact that both  $d_0$  and  $d_1$  decrease with temperature for all the series examined shows that the common point of all the lines (see Fig. 3) is below  $n = 0$ . This means that in the range of temperatures normally used for GC, every member of these series can be separated from the others on Apiezon columns.

The separation of compounds belonging to different series is always possible, not only between products with the same number of carbon atoms  $n$  (as demonstrated by the difference of  $d_0$ ) but also between compounds with different  $n$ , when the lines have, along the abscissa, distances different from multiples of  $n$  (see Fig. 8). An exception can be seen in Fig. 8, due to the different slopes for the acetates and methyl ketones, whose lines intersect at  $n = 5$ . Propyl acetate has therefore the same retention time as methyl propyl ketone at this temperature and with this flow rate. Generally speaking, the differences between  $d_0$  and  $d_1$ , although small, allow the separation to be achieved by changing the temperature.

When the shift between the parallel lines of Fig. 8 is large, an identification of the chemical species can be obtained on the basis of the value of  $d_0$ , because the distance between the members of different homologous series is much greater than the experimental variation due to column flow, temperature and concentration of the stationary phase.

Similar plots, obtained with a different column of higher polarity, can confirm the nature of the compounds when the distances between the plots in Fig. 8 on Apiezon are insufficient to permit identification<sup>3</sup> but, in the majority of cases, the careful control of the analytical parameters gives small experimental errors and allows one column only to be used for identification purposes, with consequent savings in time.

The use of a computer program is now in progress to evaluate the analytical results and to allow automatic identification of the compounds analysed.

The separation of different substances depends approximately on their molecular weights, as can be seen from Table VII and Fig. 9, where the retention times for the first members of each homologous series are reported. On the other hand, the behaviour of the boiling points is very different from the retention times, due to the

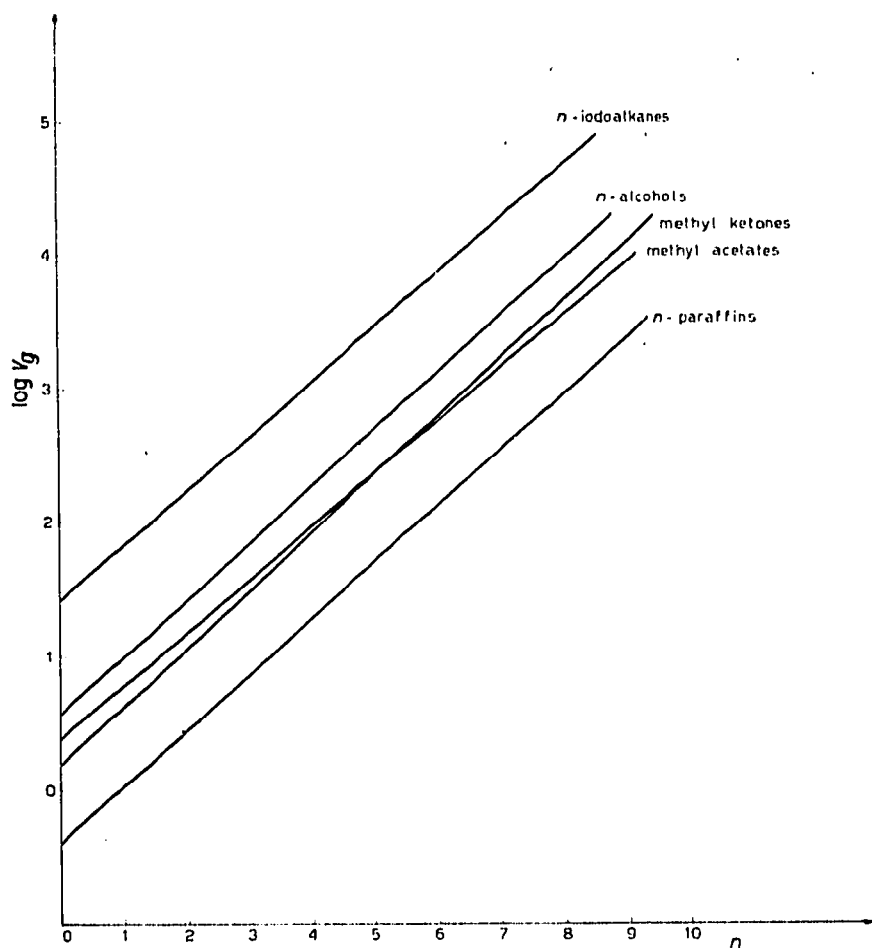


Fig. 8.  $\log V_R$  versus the number of carbon atoms in different homologous series. Column, 20% Apiezon L; temperature, 50°C; flow rate, 20 ml/min.

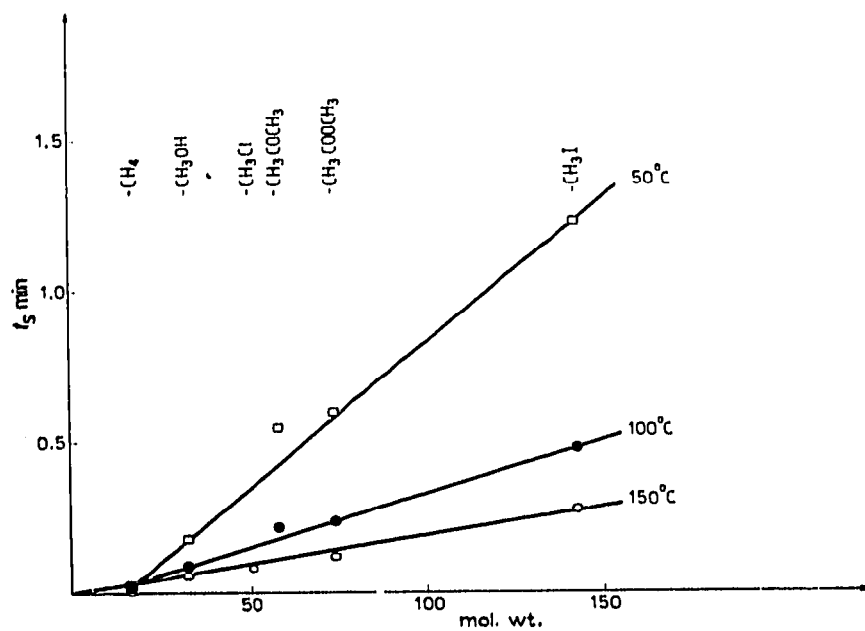


Fig. 9. Adjusted retention time of the first term of each homologous series as a function of molecular weight and temperature.

influence of hydrogen bonds. This confirms that although Apiezon is an apolar phase the phrase sometimes found in GC manuals: "On apolar columns separation takes place according to the boiling points of the substances analysed" is not correct. In fact the retention time depends chiefly on molecular weight and not on the boiling point when different chemical groups are present in the molecule.

#### *Effect of purity*

When the Apiezon was used as received, with its characteristic yellow-brown colour and without purification, some effects due to a small degree of polarity were observed (tailing and non-linearity of retention plots), but after purification by column chromatography on alumina<sup>7</sup> the colour disappeared and apolar behaviour was fully restored. It seems probable that the slight polarity is due to the presence of some impurities, as infrared spectroscopy of the original Apiezon has shown the presence of carbonyl and carboxylic compounds whose characteristic bands were completely absent from the spectra of the purified fractions.

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