

## TERPENOIDS

## LXIV. EVALUATION OF POLYESTERS AS STATIONARY PHASES IN GAS-LIQUID CHROMATOGRAPHY OF TERPENOIDS\*

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Essential oils are generally intricate mixtures of a variety of terpenic and non-terpenic compounds including hydrocarbons, carbonyl compounds, alcohols, esters, acids etc. In recent years, gas-liquid chromatographic (GLC) techniques have been widely employed for the evaluation of such oils<sup>1</sup>. It has been observed that substrates of medium polarity are most suitable for analyses of these substances, on gas chromatography (GC) columns, considering their nature. Polyesters which fall in this category have been widely used for this purpose<sup>2-9</sup>. They show sufficient thermal stability and capability of resolving compounds of wide polarity and boiling range. Recently VON RUDLOFF<sup>10</sup> prepared a few polyesters from glycols and fatty acids, and also from dicarboxylic acids (succinic, adipic, azelaic), and evaluated their solvent capability in GLC columns.

We have been interested in the GLC evaluation of essential oils for quite some time, and to find suitable phases, a systematic study of the polyesters from different  $1,\omega$ -dicarboxylic acids  $\text{HOOC} \cdot (\text{CH}_2)_n \cdot \text{COOH}$  was undertaken.

The dicarboxylic acids ranging from malonic acid ( $n = 1$ ) to hexadecane-1,16-dicarboxylic acid ( $n = 16$ ) were tested and analyses of several typical terpenic and non-terpenic compounds were carried out using these polyesters. The results are quite interesting and will be discussed in detail later.

The number of methylene groups separating the two carboxylic acid groups have been found to have a profound influence on the retention time, which follows a clear arithmetical relationship which holds up to brassylic acid ( $n = 11$ ) and only deviates slightly in the case of higher dicarboxylic acids.

Thus it has been found that if  $t_R^x$  is the retention time in minutes and  $x$  is the number of methylene groups present in the acidic component of the polyester, and if  $t_R^y$  be the retention time on another polyester containing  $y$  methylene groups, then:

$$\frac{t_R^x - t_R^y}{x - y} = c \quad (1)$$

where  $c$  is a constant for a particular compound at a particular temperature and is the individual contribution of a single methylene group.

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This relationship seems to be an integral characteristic of the number of methylene ( $\text{CH}_2$ ) groups between the two carboxylic groups and is valid for non-polar terpenic and other hydrocarbons and is nearly so for the aromatic hydrocarbons.

The large difference in retention times observed for the higher polyester stationary phases ( $n = 9$  to 16) would render them specially useful for preparative separation.

#### EXPERIMENTAL

A Griffin & George Model MK-II VPC apparatus, which employed a system with nitrogen under reduced pressure, was converted to a system with hydrogen under pressure, resulting in higher efficiency and sensitivity. It can now be worked with any desired flow rates. The instrument is provided with a thermal conductivity detector, which along with the injection port is heated to the same temperature as that of the oven. The recorder range is 0.0–1.0 mV and has a chart speed of 6 in. per hour.

#### PREPARATION OF POLYESTERS

For the preparation of the polyesters the method described by CRAIG AND MURTY<sup>5</sup> has been followed essentially, with minor modifications.

Diethylene glycol and the corresponding dicarboxylic acids were placed in molar proportions in a round-bottom flask and to this *p*-toluenesulphonic acid (0.2 g) and diglycerol (0.5 g) were added. This mixture was heated carefully at 135–140° (bath)/2 mm for 4 h. The resulting viscous material was dissolved in methylene chloride and washed repeatedly with water, dried (sodium sulphate), the solvent removed and the residue dried to a constant weight under vacuum at room temperature. The polyesters from different dicarboxylic acids were prepared under almost identical conditions. In the case of the malonic acid polyester preparation ( $n = 1$ ), instead of heating directly at 135° (bath), the mixture was initially heated slowly below 100° (bath) for 1 h and then at the usual temperature of 135–140° (bath) for 4 h.

Polyesters up to azelaic acid ( $n = 7$ ) are viscous liquids, while higher polyesters are low melting solids (m.p. below 60°). The approximate molecular weights were determined in duplicate by end group titration. The results are shown in Table I.

It is interesting to note that the polyesters containing an even number of methylene groups in the acidic component have higher molecular weights compared to those obtained from acids containing an odd number of methylene groups.

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

(1) Tricyclene; (2)  $\alpha$ -pinene; (3) camphene; (4)  $\beta$ -pinene; (5)  $\Delta^3$ -carene; (6) limonene; (7) ocimene; (8) 1,8-cineole; (9) cyclohexane; (10) *p*-cymene; (11) benzene; (12) toluene; (13) cyclopentanone; (14) cyclohexanone; (15) methyl alcohol; (16) ethyl alcohol; (17) isopropyl alcohol; (18) longifolene; (19) humulene; and (20) caryophyllene.

Compounds 1 to 7 are monoterpenes and compounds 18 to 20 are sesquiterpenes.

All the samples and the requisite dicarboxylic acids were obtained in a pure state from the laboratory stock and their purity was ascertained by m.p./b.p. determinations, elemental analyses, equivalent weights and also GLC analyses in the case of volatile samples.

TABLE I.

MOLECULAR WEIGHTS OF THE POLYESTERS AS DETERMINED BY END GROUP TITRATION

<i>Number of methylene groups in the acidic fragments</i>	<i>Molecular weights</i>
1	545, 567
2	1246, 1253
3	344, 336
4	1129, 1180
7	399, 398
8	2166, 2143
9	689, 698
11	968, 947
13	646, 633
14	953, 936
15	866, 875
16	— —

#### *Impregnation and filling the column*

The Indian fire-brick support (60–100 mesh) and the polyesters were weighed accurate to a milligram. The polyester was dissolved in methylene chloride, applied to the support and the solvent was removed by careful evaporation at 60°. It was then dried at 110° for several hours to constant weight. The impregnated material was packed in the column in the usual way. In order to have uniformity of filling every time, the same column was used and the identical amount of filling material was taken. The column was tested for gas flow rates with an identical inlet pressure in every case (within the limits of  $\pm 3$  mm pressure of mercury).

In order to compare the retention time- or volume-data from column to column, all the column variables were normalised according to LITTLEWOOD<sup>11</sup>. The following constants were maintained for all the columns:

- (1) Column length, 6 ft.
- (2) Weight of the column liquid, 2.95 g  $\pm$  0.005 g.
- (3) Carrier gas flow rate (hydrogen), 4 l/h.
- (4) Inlet pressure, 126  $\pm$  3 mm of mercury.
- (5) Temperature of the column, 80°, 100°, 120° and 162°.
- (6) Bridge current, 150 mA.
- (7) Sample size, 1  $\mu$ l.

Retention times were recorded with the help of a stop-watch up to the third place of decimals and rounded off to the nearest second place as a matter of convenience. Several concordant readings were taken in each case.

TABLE IIa

RETENTION TIME IN MIN AT 80°

Compound	Number of methylene groups in the acidic fragment of the polyester				
	1	2	3	4	7
$\alpha$ -Pinene	1.38	2.73	3.92	5.40	9.67
$\beta$ -Pinene	2.52	4.83	7.27	9.73	16.90
$\Delta^3$ -Carene	3.18	6.18	9.02	12.87	22.03
Limonene	4.57	8.83	13.12	17.83	30.90
Ocimene	6.71	12.53	18.55	24.80	41.73
Tricyclene	1.25	2.40	3.63	4.92	9.13
Camphene	1.73	3.70	5.63	7.50	13.13
Benzene	1.61	2.50	3.10	3.55	4.48
Toluene	2.83	4.52	5.80	7.00	9.35
<i>p</i> -Cymene	9.60	15.70	22.80	29.90	45.30
Cyclohexane	0.20	0.36	0.56	0.77	1.23
Cyclohexanone	26.60	34.00	39.10	41.00	47.70
Cyclopentanone	15.80	20.60	22.00	21.80	23.50
Methyl alcohol	1.77	2.22	2.63	2.36	2.25
Ethyl alcohol	1.85	2.72	3.32	3.03	3.26
Isopropyl alcohol	1.56	2.40	3.20	2.94	3.45
1,8-Cineole	7.60	12.33	18.90	22.10	42.10

TABLE IIb

RETENTION TIME IN MIN AT 100°

Compound	Number of methylene groups in the acidic fragment of the polyester							
	1	2	3	4	7	8	9	11
$\alpha$ -Pinene	0.75	1.43	2.18	2.75	5.26	6.04	6.73	8.82
$\beta$ -Pinene	1.34	2.53	4.01	5.13	8.66	9.90	10.92	14.50
$\Delta^3$ -Carene	1.70	3.07	4.85	6.66	10.75	12.30	13.58	17.80
Limonene	2.28	4.30	6.71	8.50	14.65	16.30	17.38	24.00
Ocimene	3.08	5.53	8.30	11.10	18.54	20.20	21.50	27.50
Tricyclene	0.70	1.30	2.11	2.73	4.93	5.46	6.52	8.34
Camphene	1.23	1.93	3.17	4.03	7.10	7.82	8.60	11.53
Benzene	0.89	1.40	1.83	1.95	2.60	2.68	2.35	2.81
Toluene	1.48	2.30	3.18	3.81	4.90	5.30	4.75	5.90
<i>p</i> -Cymene	4.25	7.02	10.70	13.40	20.80	22.80	23.10	29.60
Cyclohexane	0.13	0.27	0.38	0.45	0.78	0.92	0.95	1.26
Cyclohexanone	11.40	17.60	18.80	18.80	20.80	21.40	20.60	22.20
Cyclopentanone	8.40	10.10	10.50	10.40	11.50	11.40	10.30	11.50
Methyl alcohol	0.97	1.23	1.48	1.27	1.32	1.15	1.01	1.05
Ethyl alcohol	1.00	1.39	1.80	1.55	1.70	1.53	1.47	1.46
Isopropyl alcohol	0.80	1.32	1.70	1.53	1.80	1.53	1.67	1.70
1,8-Cineole	3.35	5.67	9.40	10.60	18.20	19.60	22.60	25.50

TABLE IIc

RETENTION TIME IN MINUTES AT 120°

Compound	Number of methylene groups in the acidic fragment of the polyester							Apiezon
	8	9	11	13	14	15	16	
$\alpha$ -Pinene	3.45	3.80	4.60	4.75	4.85	5.23	5.75	9.80
$\beta$ -Pinene	5.43	5.90	7.45	7.30	7.33	8.00	9.00	11.30
$\Delta^3$ -Carene	6.63	7.20	8.75	8.80	8.66	9.63	10.70	16.40
Limonene	8.30	9.10	11.30	11.10	11.33	12.50	13.40	19.40
Ocimene	9.75	10.50	12.90	12.50	13.45	13.36	15.03	18.10
Tricyclene	3.30	3.70	4.48	4.48	4.80	4.95	5.58	9.50
Camphene	4.46	4.90	5.93	5.95	6.55	6.50	7.58	11.80
Benzene	1.66	1.50	1.80	1.60	1.55	1.64	1.80	1.50
Toluene	3.47	2.80	3.86	3.10	3.15	3.20	3.60	3.30
<i>p</i> -Cymene	11.65	11.80	14.53	13.90	13.45	14.30	16.60	18.10
Cyclohexane	0.62	0.63	0.80	0.76	0.83	0.87	0.95	1.60
Cyclohexanone	11.50	11.10	12.20	10.90	11.00	10.63	11.10	6.40
Cyclopentanone	6.10	5.80	6.30	5.60	5.50	5.33	5.60	—
Methyl alcohol	0.66	0.64	0.60	0.54	0.55	0.52	0.50	1.10
Ethyl alcohol	0.90	0.86	0.86	0.76	0.78	0.74	0.70	1.50
Isopropyl alcohol	0.93	0.96	0.95	0.87	0.90	0.87	0.80	1.60
1,8-Cineole	9.75	11.50	12.76	12.60	13.55	13.40	14.10	19.80

## RESULTS AND DISCUSSION

Retention times of monoterpenic hydrocarbons, 1,8-cineole, cyclohexane, benzene, toluene, *p*-cymene, cyclopentanone, cyclohexanone, methyl alcohol, ethyl alcohol and isopropyl alcohol were determined under identical conditions for all the polyester substrates. Results are presented in Table II (a, b, c) for the temperatures 80°, 100° and 120°, respectively. The operations were carried out at the different temperatures 80°, 100° and 120° to get good resolution of the different compounds. While examining the behaviour of monoterpenes on polyesters of higher dicarboxylic acids ( $n > 7$ ), low temperature ranges (80–100°) were avoided as the retention time was inordinately long to be of any practical value. Only the temperature of 120° was used.

The arithmetical relationship mentioned previously and the constancy of the value of  $c$  at a particular temperature are also valid in this case.

For sesquiterpenic hydrocarbons, only the temperature of 162° was employed and the results are shown in Table III. The arithmetical relationship valid in the case of monoterpenes is also applicable in the case of sesquiterpenes.

The arithmetical pattern of the relationship of the retention time has been further indicated in Table IV, in which the average ratio of the retention time for seven monoterpenes on different polyesters (see Table IIa and IIb for actual values) have been shown against expected values. It will be seen from the tables that the observed and the calculated values agree extremely well.

The value of  $c$  which is a constant at a particular temperature for a particular compound and is the individual contribution of a single methylene group, has been calculated according to the formula (I) and tabulated in Tables Va and Vb for the two temperatures 80° and 100°.

TABLE III

RETENTION TIME IN MINUTES AT 162°

Compound	Number of methylene groups in the acidic fragment of the polyester		
	2	7	11
Longifolene	3.61	12.30	20.30
Caryophyllene	3.60	13.30	20.70
Humulene	5.50	17.66	26.95
Nerol	10.16	18.75	19.30
Terpineol	7.75	15.20	16.56
Camphor	5.40	9.25	10.30
Borneol	7.70	14.20	16.16
Linalool	3.40	7.07	7.70

The constant nature of the value of  $c$  is apparent from these tables.

CRAIG<sup>12</sup> and RUDLOFF<sup>13</sup> in earlier communications, based on a limited number of polyesters, felt that the number of methylene groups situated between the carboxylic groups might have some significant influence. This has now been fully justified by our present investigation.

The effect of the spacing of the methylene groups on the ester function can be appreciated up to where eleven methylene groups (brassylic acid) are involved in the acidic part of the polyesters, beyond this it seems that the retention time becomes almost constant. This is possibly due to the fact that in polyesters of higher dicarbo-

TABLE IV

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

Ratio of the number of methylene groups	Average ratio of observed retention times	Calculated ratio	Error (%)
9/2	4.40	4.50	2.23
9/3	2.82	3.00	6.00
9/4	2.17	2.25	4.47
9/7	1.24	1.29	3.55
9/8	1.10	1.13	2.65
8/7	1.12	1.16	3.57
8/4	1.96	2.00	2.00
8/3	2.53	2.66	4.89
8/2	3.96	4.0	1.00
7/4	1.73	1.75	1.37
7/3	2.24	2.33	3.98
7/2	3.54	3.50	1.17
4/3	1.31	1.33	1.90
4/2	2.05	2.00	2.70
4/1	3.81	4.00	4.87
3/2	1.54	1.50	2.30
3/1	2.90	3.00	3.20
2/1	1.90	2.00	5.00

TABLE Va

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>		
8.29	7 — 1 = 6	1.38	14.38	7 — 1 = 6	2.39
6.94	7 — 2 = 5	1.39	12.07	7 — 2 = 5	2.41
5.75	7 — 3 = 4	1.44	9.63	7 — 3 = 4	2.40
4.27	7 — 4 = 3	1.42	7.17	7 — 4 = 3	2.39
<i>Δ<sup>3</sup>-Carene</i>			<i>Limonene</i>		
18.85	7 — 1 = 6	3.14	26.33	7 — 1 = 6	4.39
15.65	7 — 2 = 5	3.13	22.07	7 — 2 = 5	4.41
13.01	7 — 3 = 4	3.25	17.78	7 — 3 = 4	4.44
9.16	7 — 4 = 3	3.05	13.07	7 — 4 = 3	4.36
<i>Ocimene</i>			<i>Tricyclene</i>		
35.02	7 — 1 = 6	5.84	7.88	7 — 1 = 6	1.31
29.20	7 — 2 = 5	5.84	6.73	7 — 2 = 5	1.35
23.18	7 — 3 = 4	5.79	5.50	7 — 3 = 4	1.37
16.93	7 — 4 = 3	5.64	4.21	7 — 4 = 3	1.40
<i>Camphene</i>			<i>Cyclohexane</i>		
11.4	7 — 1 = 6	1.90	1.03	7 — 1 = 6	0.17
9.43	7 — 2 = 5	1.89	0.97	7 — 2 = 5	0.19
7.50	7 — 3 = 4	1.87	0.67	7 — 3 = 4	0.17
5.63	7 — 4 = 3	1.88	0.46	7 — 4 = 3	0.15

TABLE Vb

EVALUATION OF  $c$  AT 100°

$t_{R^x} - t_{R^y}$	$x - y$	$c$	$t_{R^x} - t_{R^y}$	$x - y$	$c$
<i>α-Pinene</i>			<i>β-Pinene</i>		
5.98	9 — 1 = 8	0.75	9.6	9 — 1 = 8	1.20
5.3	9 — 2 = 7	0.76	8.49	9 — 2 = 7	1.21
4.55	9 — 3 = 6	0.76	6.91	9 — 3 = 6	1.15
3.98	9 — 4 = 5	0.79	5.79	9 — 4 = 5	1.16
<i>Δ<sup>3</sup>-Carene</i>			<i>Limonene</i>		
11.88	9 — 1 = 8	1.49	15.1	9 — 1 = 8	1.90
10.51	9 — 2 = 7	1.50	13.08	9 — 2 = 7	1.87
8.73	9 — 3 = 6	1.46	10.67	9 — 3 = 6	1.78
6.92	9 — 4 = 5	1.40	8.88	9 — 4 = 5	1.78
<i>Ocimene</i>			<i>Tricyclene</i>		
18.42	9 — 1 = 8	2.30	5.82	9 — 1 = 8	0.73
15.97	9 — 2 = 7	2.28	5.22	9 — 2 = 7	0.75
13.20	9 — 3 = 6	2.20	4.41	9 — 3 = 6	0.74
10.4	9 — 4 = 5	2.08	3.79	9 — 4 = 5	0.76
<i>Camphene</i>			<i>Cyclohexane</i>		
7.37	9 — 1 = 8	0.92	0.82	9 — 1 = 8	0.103
6.67	9 — 2 = 7	0.95	0.68	9 — 2 = 7	0.097
5.44	9 — 3 = 6	0.91	0.57	9 — 3 = 6	0.095
4.57	9 — 4 = 5	0.92	0.50	9 — 4 = 5	0.100

xylic acids the relative proportion of the oxygen function is greatly reduced, as a consequence of which the resulting polyester behaves increasingly like a hydrocarbon phase.

Even then, the higher polyesters still show a marked difference in their behaviour from an "Apiezon" phase (compare the retention times on these polyesters with the retention time on "Apiezon", as shown in Table IIc). In some cases, the order of the compounds emerging is altered.

The spacing of these ester groups has no marked effect on the separation factor of the hydrocarbons having different structural features.

The relationship, however, deviates slightly in the case of aromatic hydrocarbons and is not applicable to oxygenated substances. The total contribution in the case of the latter is of the order of 1:2 (Table II a, b and c). The results can very well be explained in the following manner.

As the carbon content of the polyester goes on increasing with the increase of the intervening methylene groups in the acidic component, the solubility of the hydrocarbons also increases, while that for oxygenated substances may not change appreciably. Experimental values of these solubility ratios for the hydrocarbons agree well with the theoretical interpretation based on the number of methylene groups in the acidic fragment of the polyester.

This fact can be utilised practically for the analyses of essential oils. It has been noted by earlier workers<sup>14, 15</sup> that monoterpenic oxygenated compounds often overlap sesquiterpene hydrocarbons on normal substrates. By using appropriate higher polyesters, separation of such mixtures can be achieved practically. Table III presents the retention time data under nearly identical conditions for a number of typical monoterpenic oxygenated compounds and sesquiterpenic hydrocarbons.

The concept of resolving power technique<sup>16</sup> has been used and the resolving powers for two of our typical polyesters are noted in Table VI. These data and the chromatogram (Fig. 1) illustrate the utility of higher polyesters.

BERNHARD in his study<sup>17</sup> of the terpenic hydrocarbons on capillary columns with different phases has observed that an adipic polyester column has a better separation factor as compared with "Apiezon" or silicone columns, in spite of the low number of theoretical plates.

In our study of these polyesters, it has been seen that although the retention time goes on increasing with the increase in the number of methylene groups, the

TABLE VI

RESOLVING POWERS FOR TWO TYPICAL POLYESTERS  $n = 7$  AND  $n = 11$ 

Numbers of methylene groups in the acidic fragment of the polyester	Compound pair	$y_2 - y_1$ in mm	$\frac{y_2 + y_1}{2}$ in mm	Resolving power $y_2 - y_1 / \frac{y_2 + y_1}{2}$
7	Caryophyllene-camphor	10.00	29.0	0.3448
7	Humulene-borneol	9.00	40.50	0.2222
11	Caryophyllene-camphor	26.00	40.00	0.6500
11	Humulene-borneol	28.00	55.00	0.5090



separation factor remains the same. If these higher polyesters are used in capillary columns, it may be possible that the theoretical plate number of the column will increase many fold without any loss of resolution.

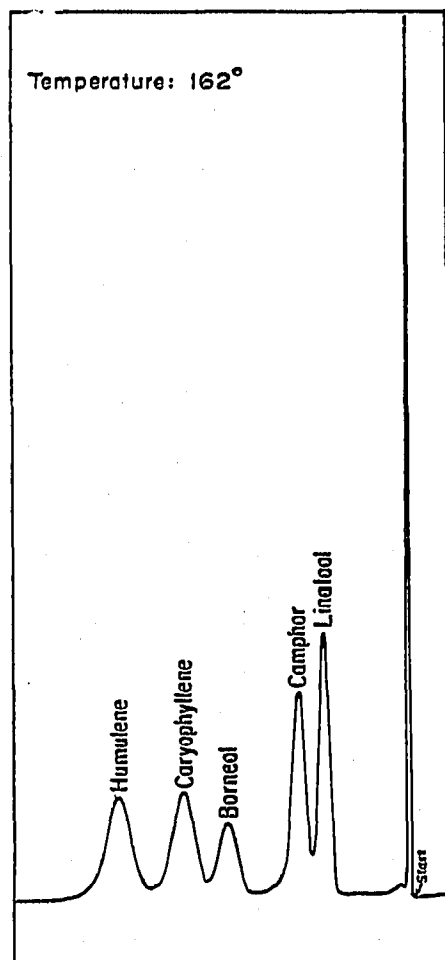


Fig. 1.

One more interesting application, though somewhat indirect, may be mentioned. In the symposium of 1957<sup>18</sup>, the point was discussed regarding the identification of substances by using them as GLC substrates. The investigation carried out above shows that  $1,\omega$ -dicarboxylic acids can be identified with considerable accuracy by preparing a polyester of the unknown acid and running the column for some hydrocarbons under standard conditions.

It has been observed that unsaturation in the acid fraction of the polyester or a methyl group side chain does not appreciably change the retention time as compared to the difference between saturated and unbranched acid polyesters.

#### SUMMARY

Polyesters from different  $1,\omega$ -dicarboxylic acids  $\text{HOOC}\cdot(\text{CH}_2)_n\cdot\text{COOH}$  ranging from malonic acid ( $n = 1$ ) to hexadecane-1,16-dicarboxylic acid ( $n = 16$ ) with diethylene glycol were prepared and evaluated as substrates for gas-liquid

chromatography. Several terpenic and non-terpenic compounds were analysed. It was observed that the number of methylene groups in the acid fragment of the polyester has a profound influence on the retention time, on the basis of which an interesting mathematical relationship has been developed. The retention time appears to be a characteristic of the number of methylene groups between the two carboxyl groups and the contribution of a single methylene group to the retention time of a particular compound at a particular temperature has been found to be a constant. This relationship holds good for aliphatic and alicyclic hydrocarbons and only slightly deviates for aromatic hydrocarbons.

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