

SOME C₆ HYDROCARBONS OF THE GAS PHASE OF CIGARETTE SMOKE

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INTRODUCTION

In a previous publication¹ we reported the identification of twenty hydrocarbons of cigarette smoke. The main fractionation was obtained by gas-solid chromatography on partially deactivated alumina. The rather long retention times of the various fractions, by gas-liquid chromatography standard at least, may be considered as a drawback of this technique. It is indeed much less versatile, and for that reason much less popular, than gas-liquid chromatography but has definite advantages in some special circumstances. Cigarette smoke, even after filtration of its particulate phase, still contains a considerable number of substances characterized by a great diversity of functional groups. A simple glance at the recent literature on the subject²⁻⁸ shows that, besides hydrocarbons, quite a variety of substances have been detected in the gas phase of cigarette smoke: alkyl halides, alcohols, sulfur compounds, amines, carbonyl compounds, nitriles, carboxylic acids, esters, etc.; some low boiling aromatic and heterocyclic compounds have also been reported. Most of these substances are strongly, if not permanently, adsorbed by alumina. This property of alumina, extensively relied on in liquid-adsorption chromatography, has been put to work in this investigation as well as in the previous one¹. Out of thirty peaks observed after a period of 10¹/₂ h, in the corresponding fractions of which more than fifty compounds were identified, only three non-hydrocarbon components were found, namely, nitrous oxide, methyl chloride, and furan. The primary objective of these investigations was the study of the hydrocarbon fraction of cigarette smoke gases. The near absence of other functional-group-containing compounds was especially valuable since infrared and mass spectra were used as identification criteria.

EXPERIMENTAL

Apparatus and procedure

The smoking apparatus and technique, the handling of the condensed gases before analysis, the gas chromatographic equipment and methods, the infrared spectrophotometer and associated cells, and the mass spectrometer have been described in a previous publication¹.

King size cigarettes (85 mm) of a cased commercial blend of tobaccos were selected in a weight range of 1.20 to 1.24 g and conditioned at 74° F and 60 % relative

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humidity. A total of 535 cigarettes were smoked in 20 groups, the number of cigarettes per group varying arbitrarily from 23 to 33. Eight puffs were taken on each cigarette leaving an average butt length of 44 mm. The smoke gases from each of the 20 groups of cigarettes were individually processed and chromatographed on alumina. Recovery of the eluted components was started after 5 h 30 min and was discontinued after an additional 5 h period. The eluates from each group of cigarettes were individually transferred to the vacuum gas handling apparatus, helium was pumped out and the compounds stored at liquid air temperature. The pooled eluates recovered from the 20 groups of cigarettes were rechromatographed on alumina. Five main fractions were collected and stored at liquid air temperature until they could be further separated on alumina + 3,3'-oxydipropionitrile (O.D.P.N.) and submitted to infrared and mass spectrometric analyses.

RESULTS AND DISCUSSION

Fig. 1 shows the gas chromatogram on alumina of the condensable smoke gases of 535 cigarettes after removal of carbon dioxide, water and many polar compounds, recorded from 5 h 30 min to 10 h 30 min; the two attenuation factors used during the 5 h recording period are indicated. Vertical bars show the collection time intervals of the five recovered fractions, numbered I to V. Vertical arrows under the peaks correspond to the retention times of compounds (Table I) positively identified in the smoke gases. The number under each arrow refers to the corresponding number in the legend of Fig. 1 listing these compounds in order of elution from alumina. The presence of three hydrocarbons which had been tentatively identified previously¹, namely, methylcyclopentane, cyclohexane and 3,3-dimethylbutene-1 has been re-confirmed. The smoke gases from a separate lot of 57 commercial cigarettes (85 mm

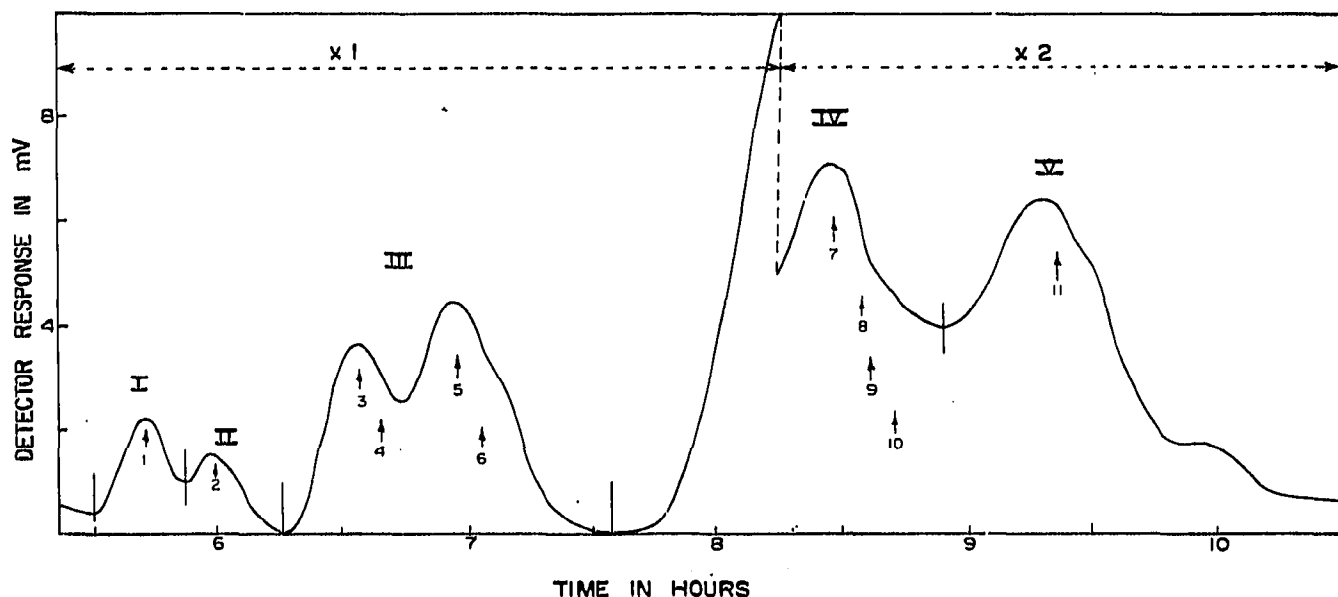


Fig. 1. Gas chromatogram on alumina of the liquid air condensable fraction of the gas phase of cigarette smoke recorded from 5 h 30 min to 10 h 30 min. I = 3-Methylcyclopentene-1; 2 = 3-methylpentene-1; 3 = 4-methylpentene-1; 4 = *trans*-4-methylpentene-2; 5 = 1-methylcyclopentene-1; 6 = 2,3-dimethylbutene-1; 7 = hexene-1; 8 = cyclohexene; 9 = 2-methylpentene-1; 10 = *trans*-hexene-2; 11 = 2-methylpentene-2.

TABLE I

RETENTION TIMES ON ALUMINA AND ON ALUMINA + O.D.P.N.

Approximate Compound b.p. (°C)		Retention time	
		On alumina	On alumina + 18.7% 3,3'-oxydipropionitrile (min)
72	Methylcyclopentane	3 h 45	11.5
81	Cyclohexane	4 h 10	16.5
41	3,3-Dimethylbutene-1	4 h 50	6.8
67	3-Methylcyclopentene-1	5 h 40	17.5
54	3-Methylpentene-1	6 h 01	8.3
54	4-Methylpentene-1	6 h 35	8.3
55	<i>trans</i> -4-Methylpentene-2	6 h 43	8.6
75	1-Methylcyclopentene-1	6 h 56	27.0
56	2,3-Dimethylbutene-1	7 h 01	10.0
76	4-Methylcyclopentene-1	—	31.2*
63.5	Hexene-1	8 h 29	11.2
83	Cyclohexene	8 h 35	41.5
63	2-Methylpentene-1	8 h 37	11.7
68	<i>trans</i> -Hexene-2	8 h 44	11.9
67	<i>trans</i> -Hexene-3	9 h 03	11.0
66	2-Ethylbutene-1	9 h 03	13.0
66	2-Methylpentene-2	9 h 28	13.0
69.5	<i>cis</i> -Hexene-2	9 h 50	14.0
73	2,3-Dimethylbutene-2	10 h 31	18.5

* Retention time of the smoke fraction identified as 4-methylcyclopentene-1.

long) were used in this experiment. The fifteen hydrocarbons reported for the first time as being present in cigarette smoke are, in order of elution from alumina: methylcyclopentane, cyclohexane, 3,3-dimethylbutene-1, 3-methylcyclopentene-1, 3-methylpentene-1, 4-methylpentene-1, *trans*-4-methylpentene-2, 1-methylcyclopentene-1, 2,3-dimethylbutene-1, 4-methylcyclopentene-1, hexene-1, cyclohexene, 2-methylpentene-1, *trans*-hexene-2 and 2-methylpentene-2. Presented in Table I are the approximate boiling points and the retention times, on alumina and on alumina + O.D.P.N., of these compounds and of some additional hexenes available as authentic compounds. These retention times and the infrared and mass spectra of the isolated fractions were used as identification criteria. These criteria will be reviewed and discussed for each newly identified smoke gases component.

Methylcyclopentane and cyclohexane

It was mentioned in an earlier publication¹ that one, and possibly both these compounds, had been tentatively detected in cigarette smoke. After retention times consideration (Table I) the smoke gases of 57 commercial cigarettes were chromatographed on alumina and the fraction corresponding to peaks No. 22 and 23 (Fig. 2 of ref. 1) was collected between 3 h 30 min and 4 h 30 min. This fraction was passed over a 3 in. column of 25% mercuric perchlorate on Chromosorb P 80-100 mesh to remove isoprene and furan and was chromatographed on alumina + O.D.P.N. Four major peaks were observed with the following retention times: 5.8, 6.8, 11.5 and 16.6 min. The first two peaks correspond to 2- and 3-methylpentanes as reported previously¹. The next two peaks had retention times identical with those of authentic methylcyclopentane and cyclohexane respectively (Table I). The fractions corre-

sponding to these last two peaks were collected but the amounts of samples available were too small to hope for useful infrared spectra. The mass spectrum of the first fraction compared well with the spectrum of known methylcyclopentane: molecular ion peak at m/e 84, base peak at m/e 56 and relatively high abundance (30 % or more) of ions of masses 27, 39, 41, 42, 55 and 69. The mass spectrum of the next fraction was extremely weak and was still contaminated with some isoprene (R.T.: 16.0 min on alumina + O.D.P.N.). It had, however, all of the most important ion fragments of the known cyclohexane spectrum: molecular ion peak at m/e 84, prominent peak at m/e 69, the sequence of peaks at m/e 54, 55 and 56, the last one being the base peak, and relatively high abundance of ions of masses 27, 39, 41 and 42.

3,3-Dimethylbutene-1

This low boiling hexene was also tentatively identified previously¹. Confirmation of its presence was obtained from fraction No. 24 (Fig. 2 of ref. 1) trapped from 4 h 30 min to 5 h 20 min and rechromatographed on alumina + O.D.P.N. The collection from this last column was carefully timed to trap only the first half of the hexane peak in an effort to enrich this fraction with 3,3-dimethylbutene-1. A mass spectrum of this fraction, after a slight correction for the presence of *n*-hexane, was in good agreement with the mass spectrum of authentic 3,3-dimethylbutene-1. The molecular ion appeared at m/e 84 (20 %) as well as a very high abundance (94 %) of ion (M-15)⁺ at m/e 69; the base peak was at m/e 41 besides lower intensity peaks at m/e 27 and 29.

3-Methylcyclopentene-1 (Fraction I of Fig. 1)

Fraction I, eluted from alumina between 5 h 30 min and 5 h 55 min, was rechromatographed on alumina + O.D.P.N. and a fraction Ia corresponding to the major peak with retention time of 17.5 min was collected between 16.5 and 20 min. The amount of sample available was too small to observe any detailed structure in its infrared spectrum; the presence of unsaturation was, however, clearly shown at 3100 cm⁻¹. A mass spectrum of fraction Ia compared well with the mass spectrum of authentic 3-methylcyclopentene-1: molecular ion peak at m/e 82, sizable peak corresponding to the (M-1)⁺ ion, base peak at m/e 67, relatively intense peaks at m/e 27, 39 and 41, and a cluster of relatively low abundance ions from m/e 49 to 56.

3-Methylpentene-1 (Fraction II of Fig. 1)

Collected from alumina between 5 h 55 min and 6 h 15 min, fraction II was submitted to chromatography on alumina + O.D.P.N. and yielded one major peak of 8.5 min retention time. The corresponding fraction IIa was trapped between 7 and 10 min. An infrared spectrum of this fraction, although very weak, indicated the presence of an unsaturated hydrocarbon from the 3100 and 1640 cm⁻¹ spectral regions. The 1460 cm⁻¹ -CH₃ and -CH₂ deformation vibration bands appeared also as well as the characteristic out of plane vibration bands of the vinyl group at 1000 and 910 cm⁻¹. The mass spectrum of fraction IIa agreed with the mass spectrum of known 3-methylpentene-1: molecular ion peak at m/e 84, base peak at m/e 55, high abundance of ions of masses 27, 29, 39, 41, 42, 56 and 69 and the series of medium intensity peaks from m/e 50 to 54; relatively low abundance ions (5 % or less) of masses 30, 31, 45, 73 and 75 must be attributed to the presence of impurities.

4-Methylpentene-1, trans-4-methylpentene-2, 2,3-dimethylbutene-1 and 1-methylcyclopentene-1 (Fraction III of Fig. 1)

This fraction, collected between 6 h 15 min and 7 h 35 min, was divided in two subfractions, IIIa and IIIb, on alumina + O.D.P.N. The gas chromatogram of fraction IIIa showed two major peaks with retention times of 8.5 and 10.1 min which, in conjunction with retention times of fraction III on alumina, suggested the presence of 4-methylpentene-1, *trans*-4-methylpentene-2 and 2,3-dimethylbutene-1 (Nos. 3, 4 and 6 of Fig. 1).

Fraction III a (1) was collected between 7.5 and 9.5 min. Besides unsaturation at the usual infrared frequencies of 3100 and 1650 cm^{-1} , the vinyl type bands appeared at 1000 and 910 cm^{-1} , as well as the 970 cm^{-1} band characteristic of a *trans*-isomer. The mass spectrum of fraction III a (1) confirmed the presence of both 4-methylpentene-1 and *trans*-4-methylpentene-2. The molecular ion peak at m/e 84 indicated the presence of at least one C_6H_{12} hydrocarbon. The relatively high intensity of peaks at m/e 56 (31 %) and 43 (70 %) confirmed the presence of 4-methylpentene-1, whereas the relatively high abundance of ions at m/e 69 (58 %) was due to the spectrum of *trans*-4-methylpentene-2. The marked difference in the mass spectra of these two hexenes was used to calculate their relative amounts in fraction III a (1). The quantitative analysis was carried out using the intensities of peaks at m/e 43 and 69 recorded for the two authentic compounds, for a standard 50/50 mixture of these two hexenes and for fraction III a (1). This fraction contained 60 % 4-methylpentene-1 and 40 % *trans*-4-methylpentene-2.

Fraction III a (2) was collected between 9.5 and 11.0 min. Its infrared spectrum had bands at 3100 and 1640 cm^{-1} and the strong band at 890 cm^{-1} indicated the presence of an asymmetric disubstituted ethylene molecule. The mass spectrum of fraction III a (2) agreed with the spectrum of authentic 2,3-dimethylbutene-1: molecular ion peak at m/e 84, intense peak at m/e 69 (80 %), base peak at m/e 41, prominent peaks at m/e 27 and 39 and a cluster of medium intensity peaks from m/e 50 to 56.

Fraction III b was trapped between 25 and 30 min, a retention time interval in agreement with the presence of 1-methylcyclopentene-1 (Table I). An infrared spectrum of this fraction agreed with the trace of known 1-methylcyclopentene-1. Unsaturation was clearly indicated at 3100 and 1665 cm^{-1} ; the $-\text{CH}_2$ and $-\text{CH}$ deformation band appeared at 1460 cm^{-1} as well as a characteristic doublet at 1005–1015 cm^{-1} . The complex band centered at about 800 cm^{-1} , with two Q-type branches at 820 and 790 cm^{-1} , could still be detected in spite of the low transmittance of the irtran-2 windows in this region of the spectrum. The mass spectrum of fraction III b confirmed the presence of 1-methylcyclopentene-1: molecular ion peak at m/e 82 and relatively abundant $(\text{M}-1)^+$ ions, base peak at m/e 67, relatively high abundance of ions at m/e 27, 39, 41 and medium intensity peaks from m/e 50 to 55. The retention time of known 1-methylcyclopentene-1 on alumina (No. 5 of Fig. 1) confirms its presence in fraction III.

Hexene-1, 2-methylpentene-1, trans-hexene-2, 4-methylcyclopentene-1 and cyclohexene (Fraction IV of Fig. 1)

Fraction IV was collected between 7 h 35 min and 8 h 55 min. Except for 4-methylcyclopentene-1 which was not available as an authentic sample, the compounds

listed above may be expected to be present in fraction IV (Nos. 7, 8, 9 and 10 of Fig. 1). This fraction was divided in four subfractions on alumina + O.D.P.N.

Fraction IVa was collected from 11.0 to 13.0 min; the peak retention time was 11.4 min with an inflection at about 12.0 min, showing the presence of more than one compound. The main features of the infrared spectrum of fraction IVa, besides indication of unsaturation at 3100 and 1640 cm⁻¹, were the vinyl-type bands at 990 and 910 cm⁻¹, this last band with its overtone at 1820 cm⁻¹, which pointed to hexene-1 as the major component of this subfraction. The relatively high intensity of the 1380 cm⁻¹ band as compared to the intensity of the 1460 cm⁻¹ band, and an inflection at 890 cm⁻¹, characteristic of an asymmetrical disubstituted ethylene, accounted for the presence of 2-methylpentene-1. The *trans*-hexene band at 970 cm⁻¹ was also clearly seen in this spectrum. The mass spectrum of fraction IVa confirmed the conclusions arrived at by infrared spectrometry. The molecular ion peak at *m/e* 84 showed that this fraction is composed of hexenes. The base peak at *m/e* 41 and the high abundance of ions of masses 27, 39, 42, 43, 55 and 56 all indicated a high percentage of hexene-1 in this fraction. The relative intensity of the *m/e* 69 peak was, however, too high, which could be explained by the presence of 2-methylpentene-1, and the high ratio of peak *m/e* 55 to peak *m/e* 56 agreed with the presence of *trans*-hexene-2 in fraction IVa. The relative amounts of hexene-1, 2-methylpentene-1 and *trans*-hexene-2 in fraction IVa were obtained by mass spectrometry. This determination was made using the intensities of peaks at *m/e* 43, 55 and 56 for the three known compounds, for a standard 1/3:1/3:1/3 mixture and for fraction IVa. The results were as follows: 73 % hexene-1, 19 % *trans*-hexene-2 and 8 % 2-methylpentene-1.

Fraction IVb, trapped between 13.5 and 17.0 min, with a peak retention time of 14.5 min, was too small to give any meaningful infrared trace. A mass spectrum of this fraction indicated a compound of molecular weight 84 and giving high abundance fragment ions (> 50 %) at *m/e* 27, 39, 41, 42, 55 (base peak) and 69. Although not specifically identified, this compound is most probably a hexene, one of those not available as pure compounds for retention times studies.

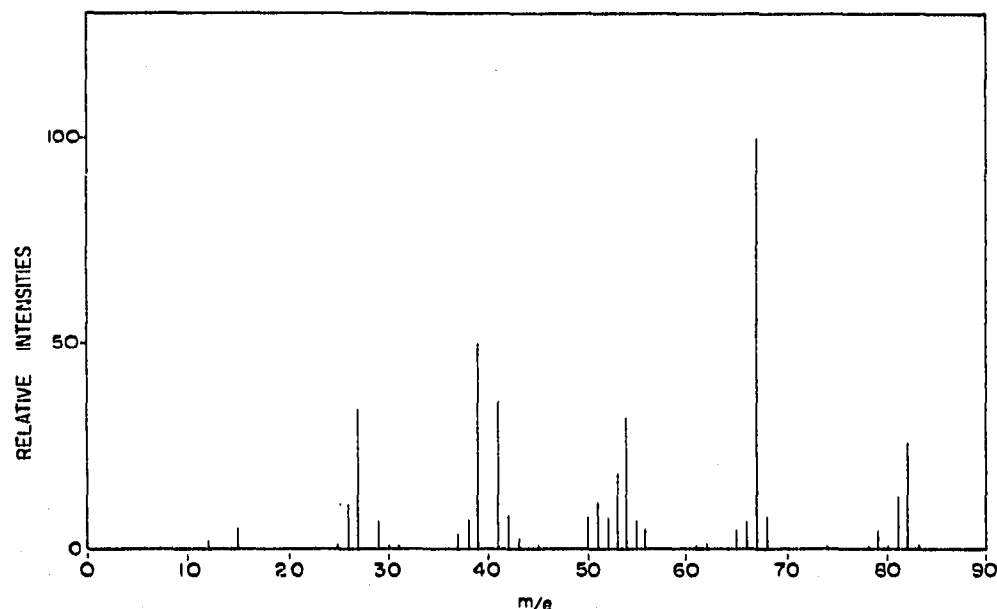


Fig. 2. Mass spectrum of fraction IVc identified as 4-methylcyclopentene-1.

Fraction IVc was collected between 29.5 and 34.0 min, the peak retention time being 31.2 min. No infrared spectrum could be obtained, the amount of sample recovered being too small. A mass spectrum of fraction IVc showed the presence of a compound of molecular weight 82, and gave no indication as to the presence of heteroatoms. The empirical formula of this hydrocarbon is therefore C_6H_{10} and the most probable structures to consider from previous experience¹ are a straight or branched chain hexadiene, a methylcyclopentene or cyclohexene. Cyclohexene was ruled out by retention times consideration and was in fact identified in the next fraction. It was found in the C_6 series¹ that alumina retained the aliphatic dienes, especially those of allene-type or conjugated structures, considerably longer than the cyclic hydrocarbons of equal molecular weight. The lowest boiling hexadiene, 1,5-hexadiene, was indeed found to have a retention time in excess of 10 h 30 min on alumina. This leaves only one possibility: 4-methylcyclopentene-1. No authentic sample of this compound was available for retention times studies and no mass spectrum was found in the literature. A mass spectrum of fraction IVc is presented in Fig. 2. This mass spectrum is similar to those of the two other isomers 1- and 3-methylcyclopentene-1: molecular ion peak at m/e 82, sizable m/e 81 peak, base peak at m/e 67 and relatively abundant fragments of masses 27, 39 and 41. A slight difference seems to be a higher relative intensity of the m/e 54 peak in the spectrum of fraction IVc.

Fraction IVd, collected between 39.0 and 47.0 min had a peak retention time of 41.5 min as does authentic cyclohexene. An infrared spectrum of fraction IVd showed unsaturation at 3100 cm^{-1} , the $-CH_2$ deformation band at 1460 cm^{-1} and the medium-strength Q-type branches at 1145 and 925 cm^{-1} ; strong continuous absorption by the irtran-2 windows prevented, however, detection of the intense 723 cm^{-1} Q branch of cyclohexene. A mass spectrum of fraction IVd compared very well with the mass spectrum of authentic cyclohexene: molecular ion peak at m/e 82, base peak at m/e 67, high abundance (90 %) of ions of mass 54, series of medium size peaks from m/e 50 to 55 and relatively high abundance of ions at m/e 27, 39 and 41.

2-Methylpentene-2 (Fraction V of Fig. 1)

Fraction V, trapped between 8 h 55 min and 10 h 30 min, was separated in three subfractions on alumina + O.D.P.N. Fraction Va, collected from 12 to 15 min was made essentially of 2-methylpentene-2 as shown by its infrared spectrum: no resolved $=CH$ band, relatively weak $C=C$ band at 1660 cm^{-1} , bands at 1455 , 1380 , 1313 , 1260 , 1200 , 1115 , 1060 cm^{-1} and the characteristic band for a trisubstituted ethylene at 835 cm^{-1} . A band observed at 970 cm^{-1} may indicate the presence of an unidentified *trans*-hexene, possibly *trans*-3-methylpentene-2 which was not available as an authentic compound. A mass spectrum of fraction Va confirmed the presence of 2-methylpentene-2: molecular ion peak at m/e 84, high abundance of ions of mass 69 (86 %) and base peak at m/e 41. Relatively high abundance of ions at m/e 29, 42, 55 and 56 indicated the presence of another hexene, possibly *cis*-hexene-2 (retention times of 9 h 50 min on alumina and of 14.0 min on alumina + O.D.P.N.).

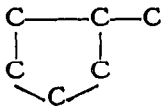
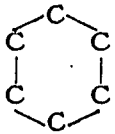
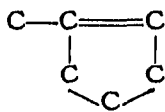
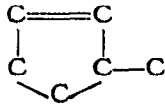
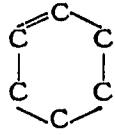
Fraction Vb was collected from 15 to 17.5 min, with peak retention time at 15.5 min, fraction Vc from 17.5 to 22 min, the peak retention time being 18.3 min. Both were small fractions and no attempt was made to record infrared spectra. Mass spectra of both fractions showed features characteristic of hexene spectra: molecular ion peak at m/e 84, prominent peak at m/e 69, base peak at m/e 41 and relatively

high abundance of ions of masses 27, 29, 39, 42, 53, 55 and 56. These fractions must be associated with unidentified hexenes, possibly the two high boiling hexenes, *cis*-3-methylpentene-2 and 2,3-dimethylbutene-2.

Although the main purpose of this investigation was the qualitative identification of the compounds discussed above, semi-quantitative data were obtained from gas chromatograms on alumina + O.D.P.N. and, in some cases, in combination with mass spectrometric analyses. Calibration curves were determined for each compound; all substances were assumed to behave like ideal gases for calculation purposes. Percentage recovery after a typical cycle of operations was determined with isoprene, hexene-1 and 2-methylpentene-2. These determinations involve the following operations: sample transfer from the vacuum apparatus to the capillary injection trap, injection into the gas chromatograph, recovery in collection trap, transfer back to the vacuum manifold and injection trap, and finally, re-injection into the gas chromatograph. An average of 70% recovery was obtained after this series of manipulations with either gas chromatograph used in this investigation. Since the quantitative estimations were performed on fractions which had been submitted to four such cycles of operations (two on each column), an overall recovery of 24% could be expected. This figure does not include the losses suffered during the carbon dioxide removal step, which were determined to be 5% at the most. A final figure of 20% recovery was therefore agreed upon; the semiquantitative data, corrected for such expected losses, are presented in Table II and expressed in mole % $\times 10^3$ of the total gas phase and in $\mu\text{g}/\text{puff}$. Only a few data from our own laboratory⁹ were available for comparison, namely, quantitative results for methylcyclopentane and 4-methylpentene-1. The agreement is not satisfactory, our results being lower by a factor of 5 to 7. Since the data used for comparison were obtained on a single puff of freshly produced smoke, without condensation prior to injection into the gas chromatograph, they potentially represent better values. This would mean that our recovery percentages determined with known compounds are too optimistic. It is possible also that serious losses are suffered during the smoking process, due to incomplete condensation. This would however require an "across the board" correction and it would be difficult to explain the relatively good agreement between the two methods for many smoke components¹. Although the high sensitivity of the flame ionization detector allows the analysis to be carried out on a puff or even a fraction of a puff, the identification of the eluted components is usually based on retention times only. With such a complex mixture as cigarette smoke, even the use of several columns always leaves the possibility of having more than one compound contribute to a single gas chromatographic peak.

It was speculated in a previous publication¹ that if the presence in cigarette smoke of 3,3-dimethylbutene-1 was confirmed, the sixteen other isomeric hexenes could be expected. The present investigation seems to confirm this prediction although only half of these remaining sixteen aliphatic hexenes have been positively identified. It is very likely, however, that further studies in this field would indicate the presence, in cigarette smoke, of these missing hexenes as well as of traces of C₇, C₈, etc. hydrocarbons. Several of our fractions, accidentally trapped for more than 10 h 30 min had indeed a peak of *m/e* 98 in their mass spectra which could be due to some low boiling heptenes. It is, however, logical to expect that, as the boiling points of these hydrocarbons increase rather rapidly with the carbon numbers of their

TABLE II
SEMIQUANTITATIVE RESULTS.

Compound	Carbon skeleton	Mole % $\times 10^3$	$\mu\text{g}/\text{puff}$
Methylcyclopentane		0.04	0.04
Cyclohexane		trace	trace
Hexene-1	$\text{C}=\text{C}-\text{C}-\text{C}-\text{C}-\text{C}$	0.32	0.40
2-Methylpentene-1	$\begin{array}{c} \text{C} \\ \\ \text{C}=\text{C}-\text{C}-\text{C}-\text{C} \end{array}$	0.04	0.05
3-Methylpentene-1	$\begin{array}{c} \text{C} \\ \\ \text{C}=\text{C}-\text{C}-\text{C}-\text{C} \end{array}$	0.02	0.02
4-Methylpentene-1	$\begin{array}{c} \text{C} \\ \\ \text{C}=\text{C}-\text{C}-\text{C}-\text{C} \end{array}$	0.05	0.06
2,3-Dimethylbutene-1	$\begin{array}{c} \text{C} \quad \text{C} \\ \quad \\ \text{C}=\text{C}-\text{C}-\text{C} \end{array}$	0.06	0.08
<i>trans</i> -Hexene-2	$\text{C}-\text{C}=\text{C}-\text{C}-\text{C}-\text{C}$	0.09	0.12
2-Methylpentene-2	$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}=\text{C}-\text{C}-\text{C} \end{array}$	0.23	0.34
<i>trans</i> -4-Methylpentene-2	$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}=\text{C}-\text{C}-\text{C} \end{array}$	0.03	0.04
1-Methylcyclopentene-1		0.02	0.03
3-Methylcyclopentene-1		0.01	0.01
Cyclohexene		0.01	0.01

molecules, their partition between gas-vapor phase and particulate phase of the smoke will increasingly favor the latter. For further investigation on this subject, it would be very desirable to develop convenient and reliable techniques capable of evaluating these partition coefficients. Should the trend found previously and in the present study for the amounts of the C₂ to C₆ hydrocarbons continue in the same direction, only traces of higher hydrocarbons should be found in cigarette smoke. Exceptions may, however, exist for some specific hydrocarbons such as the C₁₀ dipentene^{10,11} which, like isoprene, is a thermal degradation product of higher terpenoid compounds present in tobacco. The detection of appreciable amounts of saturated aliphatic hydrocarbons of carbon numbers C₂₅ to C₃₃¹²⁻¹⁵ may also be explained by direct transfer of these hydrocarbons from tobacco to smoke stream.

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SUMMARY

Fifteen C₆ hydrocarbons have been isolated from cigarette smoke by gas chromatography. Identification was based on information derived from retention times on two different columns and from infrared and mass spectra. Semiquantitative analytical data were obtained either by gas chromatography alone or in combination with mass spectrometric analyses.

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