

Pyrolytic Disintegration of selected Tobacco Constituents and Pyrosynthetic Formation of Aromatic Hydrocarbons from Cleavage Products formed by Pyrolysis*

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SUMMARY

A rapid pyrolysis technique, combined with gas chromatographic separation and interpretation of mass spectra obtained from the resulting pyrolysis-pyrosynthesis products, has been used in the study of three different compounds present in processed tobacco: *n*-C₂₅ alkane, neophytadiene and phytol. The compounds are representative for a homologous series of *n*-alkanes and for a series of branched-chain compounds including neophytadiene, phytol, solanesol and esters of solanesol (tobacco constituents).

At temperatures below 600 °C the pyrolysis in the absence of oxygen, but in a helium flow gives only slight aromatization when *n*-alkanes are treated. For the isoprenoid compounds neophytadiene and phytol aromatization starts between 500 and 600 °C. The products formed tend to develop more-condensed ring structures at increasing temperature, although benzene and toluene are dominating even at temperatures as high as 800 to 900 °C.

Aromatization leading to relatively less methyl substitution results with increasing temperature. Previous pyrolysis work and recent interpretations point to the formation of structures such as acenaphthylene, acenaphthene, cyclopenta[*cd*]pyrene, 3,4-dihydrocyclopenta[*cd*]pyrene and probably similar structures derived from three and four-membered condensed ring structures produced.

ZUSAMMENFASSUNG

Zur Untersuchung der drei Substanzen *n*-C₂₅-Alkan, Neophytadien und Phytol, die in verarbeitetem Tabak vorkommen, wurde eine schnelle Pyrolysemethode in Verbindung mit gaschromatographischer Auftrennung und massenspektrometrischer Analyse der Pyrolyse/Pyrosynthese-Produkte angewendet. Die Substanzen stehen stellvertretend für eine homologe Reihe von *n*-Alkanen sowie für verzweigte Verbindungen wie Neophytadien, Phytol, Solanesol und Solanesolester (Tabakinhaltsstoffe).

Bei Temperaturen unter 600 °C führt die Pyrolyse von *n*-Alkanen im Heliumstrom unter Ausschluß von Sauerstoff nur in geringem Ausmaß zu Aromatisierung. Bei den Isopren-Verbindungen Neophytadien und Phytol beginnt die Aromatisierung bei Temperaturen zwischen 500 °C und 600 °C. Die Pyrolyseprodukte neigen bei ansteigender Temperatur zur Bildung höher kondensierter Ringsysteme, obwohl Benzol und Toluol noch bei 800 °C bis 900 °C dominieren.

Mit ansteigender Temperatur werden im Verhältnis weniger methylsubstituierte Aromaten gebildet. Frühere Pyrolyseversuche und Interpretationen aus jüngerer Zeit deuten auf die Bildung von Substanzen wie Acenaphthylen, Acenaphthen, Cyclopenta[*cd*]pyren und 3,4-Dihydrocyclopenta[*cd*]pyren sowie auf das Entstehen wahrscheinlich strukturell ähnlicher Verbindungen hin, welche sich von Strukturen ableiten, die aus kondensierten Systemen mit drei und vier Ringen bestehen.

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RÉSUMÉ

L'examen de trois substances: n -C₂₅-alcane, néophytadiène et phytol, que l'on trouve dans le tabac traité industriellement, a été réalisé au moyen d'une méthode de pyrolyse rapide associée à la séparation par chromatographie en phase gazeuse et à l'analyse par spectrométrie de masse des produits de la pyrolyse/pyrosynthèse. Les substances étudiées représentent une série homologue de n -alcane ainsi que des composés à chaîne ramifiée tels que néophytadiène, phytol, solanésol et esters du solanésol (constituants du tabac).

Lorsque la température est inférieure à 600 °C, la pyrolyse de n -alcane dans un courant d'hélium et en l'absence d'oxygène ne conduit qu'à une formation restreinte de carbures aromatiques. Dans le cas des composés isoprénoides, néophytadiène et phytol, l'aromatization commence à une température comprise entre 500 et 600 °C. Lorsque la température s'élève, les produits de la pyrolyse ont tendance à former des combinaisons cycliques plus condensées bien que le benzène et le toluène dominent encore vers 800–900 °C.

Si l'on fait croître la température, il se forme proportionnellement moins de composés aromatiques méthyl-substitués. Des expériences de pyrolyse réalisées précédemment et des interprétations de date récente attirent l'attention sur la formation de substances telles que acénaphthylène, acénaphtène, cyclopenta[cd]pyrène, dihydro 3,4-cyclopenta[cd]pyrène ainsi que de structures vraisemblablement similaires dérivées de systèmes condensés à trois ou quatre noyaux aromatiques.

INTRODUCTION

Previously (in the period 1953–1956) pyrolysis experiments were carried out with dotriacontane [C₃₂H₆₆] (named dicetyl) (1, 2) and with an unspecified mixture of aliphatic tobacco hydrocarbons isolated from tobacco leaves (2). The experiments were carried out at various temperatures in agreement with data obtained by measurements of temperatures existing in the combustion zones of cigarettes, cigars, and pipes (3). These and related pyrolysis experiments deal with the formation of aromatic hydrocarbons (4–11). The presence of polycyclic aromatic hydrocarbons in tobacco smoke indicates that insufficient combustion reactions take place during smoking. It has been recognized for a long period that monocyclic and polycyclic aromatic hydrocarbons are generally formed by incomplete combustion at high temperatures from many organic compounds originating from fuel oil, fats, phytosterols, tobacco leaves and other organic materials.

The aim of the present research is to study the products resulting from pyrolysis of single compounds, isolable from tobacco leaves, the pyrolysis being carried out at various temperatures. The compounds are of the unbranched, normal alkane type and of a branched isoprenoid type.

As the occurrence of both normal alkanes and isoprenoid compounds is widespread in plants and in fuel oil the results of the pyrolysis may be of interest beyond the field of tobacco research. Normal alkanes are present in the aerial parts of most plants. Phytol is a part of chlorophyll bound as an ester. Neophytadiene may be formed from phytol by an enzymatic elimination procedure (12).

Normal C₂₅ alkane, phytol and neophytadiene have been chosen for the pyrolysis experiments as they all occur in tobacco leaves. Although the three compounds are representative examples from nature, many other naturally occurring compounds may be expected to be converted into aromatic hydrocarbons under similar pyrolytic conditions. Thus, for instance fatty acids often occur in great amounts in fats from plants and in animal tissues. They contain aliphatic hydrocarbon chains, hence they should also be expected to form aromatic hydrocarbons by pyrolysis at high temperatures.

INSTRUMENTS AND EXPERIMENTAL

A laboratory-built microfurnace of a similar type to the one described by *Larter, Solli and Douglas* (13) was connected to a GC-MS system consisting of a VG-Micromass MM 7070 mass spectrometer and a Carlo Erba Fractovap Linea 2150 gas chromatograph. Most of the analytical work has been carried out with a packed OV-101 column or with a capillary column coated with OV-101. The carrier gas flow of helium protects the pyrolysis products against oxidation (conditions similar to those of earlier work (1955) where pyrolysis took place in nitrogen flowing through a quartz tube packed with quartz chips). For the present pyrolysis work microgram quantities of material, adhering to a syringe needle, were inserted into the temperature-controlled microfurnace and a series of experiments was carried out at 500, 550, 600, 650, 700, 750, 800, 825, 850, 875, 900 and 950 °C. A great number of mass spectra were recorded on the basis of gas chromatograms obtained during the separation of the very complex mixture of pyrolysis products from each single experiment. The mass spectra were interpreted and in many cases compared with reference spectra of pure, commercially available compounds. A Hewlett-Packard 3380A integrator was used for the semi-quantitative determinations from the gas chromatograms.

RESULTS AND DISCUSSION

Pyrolysis of the organic material studied does not result in aromatization until the temperature exceeds 500 to 600 °C, starting with formation of benzene, toluene and xylenes and with increasing amounts produced at higher temperatures. At a first glance, the normal alkanes seem to indicate that a special reaction occurs at

the disintegration of the molecules since a series of normal alkenes (C_4 to C_{22} alkenes from n - C_{25} alkane) is produced at about 600 °C (see Fig. 1). There is, however, a similar breakdown taking place for the isoprenoid substances neophytadiene and phytol starting at even lower temperature (about 500 °C).

The branched isoprenoid compounds produce unsaturated elements of alkene, alkadiene and alkatriene or unsaturated ring structures, particularly compounds formed by cleavage at the branched sites of neophytadiene (see Fig. 2 and Table 1) and of phytol. The clearest pattern of this is best studied by correlating the gas chromatograms from the pyrolysis of neophytadiene at 550 °C with Table 1. The phytol eliminates water forming branched diene molecules of the same molecular weight as that of neophytadiene. They react as neophytadiene does by breaking down to smaller unsaturated molecules, and they also react by forming aromatic hydrocarbons at generally lower temperatures than normal alkanes.

By inspection of Figures 1 and 2 it may be noticed that breakdown of the molecules leading to total disintegration and start of aromatization occurs at slightly lower temperature for the isoprenoid compound neophytadiene than for normal alkanes. Traces of benzene, toluene and xylenes were produced by pyrolysis of n - C_{25} alkane at 600 °C, whereas for neophytadiene pyrolysis at 550 °C leads to formation of traces of the same aromatic hydrocarbons.

By study of the gas chromatogram from the pyrolysis of n - C_{25} alkane at 650 °C (see Fig. 1) it is obvious that the decomposition has increased with only a faint alkene pattern left and with increased formation of other compounds, namely benzene and toluene and minor amounts of styrene and xylenes. At even higher temperatures (700 °C), the resulting pattern of the gas chromatogram almost entirely agrees with the aromatic hydrocarbon formation.

Figure 2 presents the gas chromatograms resulting from the pyrolysis of neophytadiene at 500, 550 and 600 °C. At 500 °C a slight disintegration takes place, strongly increasing by 550 °C, with a slight aromatization leading to the formation of benzene, toluene and xylenes, and with an even higher degree of aromatization occurring at 600 °C. The amounts of recovered neophytadiene, branched alkenes and alkadienes produced during pyrolysis are decreased at 600 °C compared to 500 °C.

When phytol is pyrolysed at 550 °C at least five phytadienes seem to be formed with different retention times in the gas chromatogram (all with the molecular weight of 278 corresponding to that of neophytadiene). The gas chromatogram moreover is very much like that of neophytadiene from the pyrolysis of this compound at 550 °C with respect to the "fragments" appearing with increasing molecular weight up to the order of magnitude of $C_{15}H_{30}$, an isoprenoid alkene.

The possibility of thermal isomerization of neophytadiene during the smoking process is discussed by Alan Rodgman (14). We have not observed a preformation of

isomeric phytadiene molecules by the pyrolysis of neophytadiene. It is thus more realistic to expect the formation of different phytadienes to be derived from phytol or phytol bound as an ester in the tobacco. This is supported by the fact that chlorophyll-bound phytol yields several phytadienes, when specific geological material containing chlorophylls is pyrolysed at 610 °C (15).

The increase in temperature for normal alkane pyrolysis as well as for pyrolysis of the isoprenoid compound generally leads to more-condensed aromatic ring structures. However, a competition between decomposition and pyrosynthesis seems to occur (cf. the formation of benzo[*a*]pyrene at various temperatures) (16). A quite clear picture of the reactions which are taking place cannot be given at present as a series of radical mechanisms appears to be involved in the building of aromatic hydrocarbons at various temperatures. Furthermore, it seems likely that slightly different building blocks are taking part in the aromatization, when the compounds are produced either from normal alkanes or from isoprenoid compounds.

Aromatic hydrocarbons may react mutually, under suitable conditions. Two molecules of naphthalene may form perylene or benzofluoranthenes. Naphthalene plus benzene may give rise to fluoranthene (16, 17).

Although the attempts to correlate the formation of aromatic hydrocarbons quantitatively have not been very successful it is obvious from the integration of the gas chromatograms that benzene plus toluene constitute more than 50% of the total amount of aromatic hydrocarbons formed, when n -alkanes and branched-chain alkanes are pyrolysed at about 700 °C, in good agreement with the results obtained by Badger et al. (6, 18). The relative amount of styrene is about 9, 25 and 32% when n - C_{25} alkane, neophytadiene, and phytol are pyrolyzed at 750 °C, respectively. At 825 °C the corresponding values are 29, 31 and 32%, and at 900 °C the pyrolysis yields 29, 20 and 15%, respectively, of the total amount of aromatic hydrocarbons formed. The relative percentage values were obtained by integration of the gas chromatograms. The observation that the aromatization processes are progressing at slightly lower energy with the branched-chain compounds than with the normal alkanes and that competition between aromatization and decomposition changes in favour of decomposition at increasing energy seems to agree well with the above-mentioned results.

Although there is a general increase in the amount of naphthalene formed with increasing temperature from 750 to 900 °C in all three cases, and although generally with higher temperature more-condensed ring systems are formed, there is still an increasing amount of benzene from the pyrolysis of neophytadiene and phytol, whereas the relative amount of benzene decreases in the case of normal alkanes. The amount of toluene and xylenes is decreasing relatively with increasing pyrolysis temperature in all three cases (n -alkanes, neophytadiene and phytol).

Whereas the formation of methyl-substituted aromatic

hydrocarbons such as toluene, xylenes, methylnaphthalene and methylphenanthrene seems to decrease with increasing temperature, the formation of acenaphthene, acenaphthylene and similar products should perhaps not be neglected (1). After pyrolysis of all three compounds, *n*-alkanes and the two isoprenoids, at high temperatures (700–950 °C) the mass spectra reveal the presence of compounds with molecular weights of (190), 192, 202, 204, 216, 226, 228, (240), 242, 250, 252, 254, 276 and 278. The molecular weights of 202, 204, 226, 228 and 252 are all represented in more than one peak of the gas chromatogram, and thus they represent two or more compounds formed for each figure. Corresponding to the molecular weights of 226 and 228 several possible structures exist, however cyclopenta[*cd*]pyrene and 3,4-dihydrocyclopenta[*cd*]pyrene are compounds isolated (especially the cyclopenta[*cd*]pyrene) from a selected carbon black in a relatively great amount (60 times as much as benzo[*a*]pyrene) (19).

Figure 3 shows possible structures for the molecular weights listed above; many other structures are possible, which is also indicated by the repeated appearance of certain molecular weight values obtained by mass spectrometry (GC-MS in high-temperature pyrolysis experiments). Structures I and II, characterized in previous research (1953–1956), may be the basis of the development of fused ring structures at increasing temperature.

Benzo[*a*]pyrene and benzo[*e*]pyrene are frequently reported to be present in tobacco smoke and they could possibly give rise to the formation of compounds analogous to cyclopenta[*cd*]pyrene and a corresponding dihydro compound, but derived from the benzopyrenes. The molecular weights of such compounds would be 276 and 278, respectively, in agreement with those recorded in our pyrolysis experiments at high temperature (800–900 °C) with *n*-alkane, with neophytadiene, and also with phytol.

Doubly charged ions in the mass spectra are very informative in the interpretation of the spectra of aromatic hydrocarbons. Some of the spectra contain several molecular weight figures. Characteristic mass spectral patterns correspond to the molecular weight recordings of stable aromatic structures. Each molecular weight figure may represent more than one structure. It may therefore be a future challenge to study on a greater scale pyrolysis products in detail, when pyrolysis of specific compounds is performed at high temperature (900–1000 °C).

In Table 2 is recorded a typical list of molecular weights corresponding to pyrolysis products as they appear in our high-temperature experiments (700–950 °C) with *n*-alkanes and isoprenoid compounds and as they are known from tobacco smoke and from various pyrolysis studies at high temperatures (800–950 °C) (20, 21) based on MS data. Pyrolysis of toluene at 850 and 950 °C has revealed that a certain degree of decomposition occurs leading to the formation of benzene, indene, naphthalene, acenaphthene, acenaphthy-

lene, fluorene and many other aromatic substances, which are apparently the same as those produced from *n*-alkanes and isoprenoid compounds by pyrolysis. The major part of the toluene came out unchanged under the present conditions which were not ideal as the toluene (being a liquid) had to be injected into the pyrolysis unit.

Similarly acenaphthylene, which is another compound abundantly formed by pyrolysis of *n*-alkanes and isoprenoid compounds at high temperature (2, 11, 18), was pyrolysed. The pyrolysis products from acenaphthylene resulted in a similar series of compounds to those produced by the aliphatic hydrocarbons, apparently showing a cleavage of the bonds in the five-carbon ring of acenaphthylene.

The pyrolysis experiments with toluene and acenaphthylene were carried out in order to study the further decomposition and pyrosynthesis of aromatic hydrocarbons which are typical examples of aromatics formed by pyrolysis and pyrosynthesis of *n*-alkanes and branched-chain hydrocarbons at high temperature (6, 18).

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(P.t.o. for figures and tables.)

Table 1.
Pyrolysis of neophytadiene at 550 °C.

GC peak registration	Molecular weight (MS)	Molecular formula	Number of double bonds or ring equivalents *
1	56	C ₄ H ₈	1
	70	C ₅ H ₁₀	1
2	56	C ₄ H ₈	1
	70	C ₅ H ₁₀	1
3	68	C ₆ H ₈	2 (isoprene?)
	70	C ₅ H ₁₀	1
4	82	C ₆ H ₁₀	2
	84	C ₆ H ₁₂	1
5	78	C ₆ H ₈	benzene
	80	C ₆ H ₈	3
	98	C ₇ H ₁₄	1
6	96	C ₇ H ₁₂	2
	98	C ₇ H ₁₄	1
7	92	C ₇ H ₈	toluene
	94	C ₇ H ₁₀	3
	96	C ₇ H ₁₂	2
	112	C ₈ H ₁₆	1
8	92	C ₇ H ₈	toluene
	94	C ₇ H ₁₀	3
	112	C ₈ H ₁₆	1
9	106	C ₈ H ₁₀	xylene
	108	C ₈ H ₁₂	3
	110	C ₈ H ₁₄	2
	126	C ₉ H ₁₈	1
10	122	C ₉ H ₁₄	3
	124	C ₉ H ₁₆	2
	140	C ₁₀ H ₂₀	1
11	136	C ₁₀ H ₁₆	3
	138	C ₁₀ H ₁₈	2
	154	C ₁₁ H ₂₂	1
12	154	C ₁₁ H ₂₂	1
14	182	C ₁₃ H ₂₆	1
15	196	C ₁₄ H ₂₈	1
16—18	210	C ₁₅ H ₃₀	1
20—22	278	C ₂₀ H ₃₈	2 (neophytadiene)

Table 2.
Compounds assumed to be obtained after high-temperature pyrolysis (700—950 °C) of *n*-alkanes and isoprenoids.

Molecular weight	Compound	Molecular formula
66	cyclopentadiene?	C ₅ H ₆
78	benzene	C ₆ H ₆
92	toluene	C ₇ H ₈
102	phenylacetylene	C ₈ H ₆
104	styrene	C ₈ H ₈
118	indane	C ₉ H ₁₀
116	indene	C ₉ H ₈
130	dihydronaphthalene?	C ₁₀ H ₁₀
128	naphthalene	C ₁₀ H ₈
142	β- and α-methylnaphthalenes	C ₁₁ H ₁₀
154	acenaphthene	C ₁₂ H ₁₀
152	acenaphthylene	C ₁₂ H ₈
166	fluorene	C ₁₃ H ₁₀
180	dihydrophenanthrene?	C ₁₄ H ₁₂
178	phenanthrene + anthracene	C ₁₄ H ₁₀
192*		C ₁₅ H ₁₂
190*		C ₁₅ H ₁₀
204*		C ₁₆ H ₁₂
202*		C ₁₆ H ₁₀
216*		C ₁₇ H ₁₂
228*		C ₁₈ H ₁₂
226*		C ₁₈ H ₁₀
242*		C ₁₉ H ₁₄
240*		C ₁₉ H ₁₂
250*		C ₂₀ H ₁₀
252*		C ₂₀ H ₁₂
254*		C ₂₀ H ₁₄
276*		C ₂₂ H ₁₂
278*		C ₂₂ H ₁₄

* Molecular weights corresponding to gas chromatograms from high-temperature pyrolysis, often representing more than one possible structure.

* Where aromatic compounds are formed the name or type is indicated.

Figure 1.
Gas chromatograms after pyrolysis of $n\text{-C}_{25}$ alkane at different temperatures.*

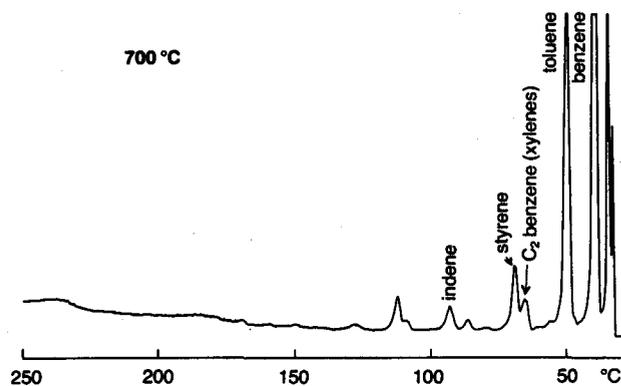
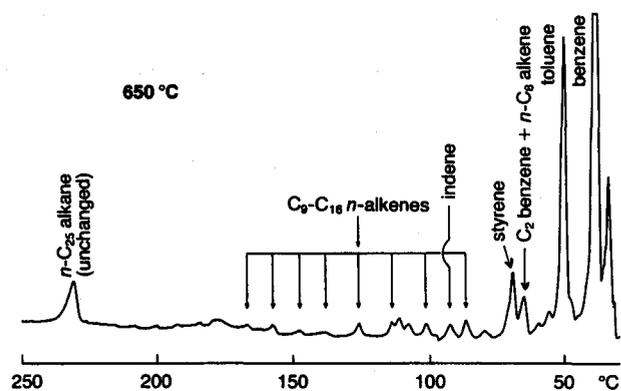
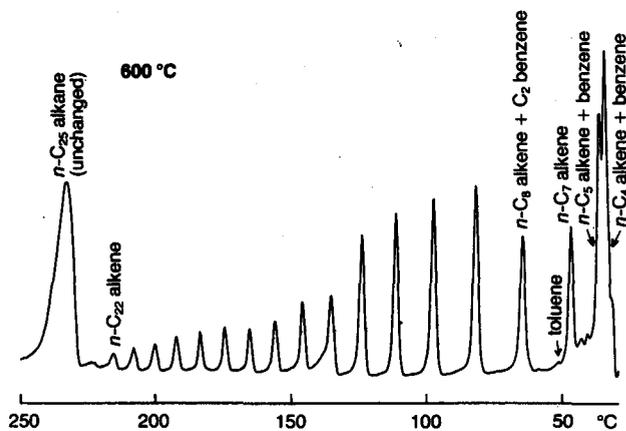
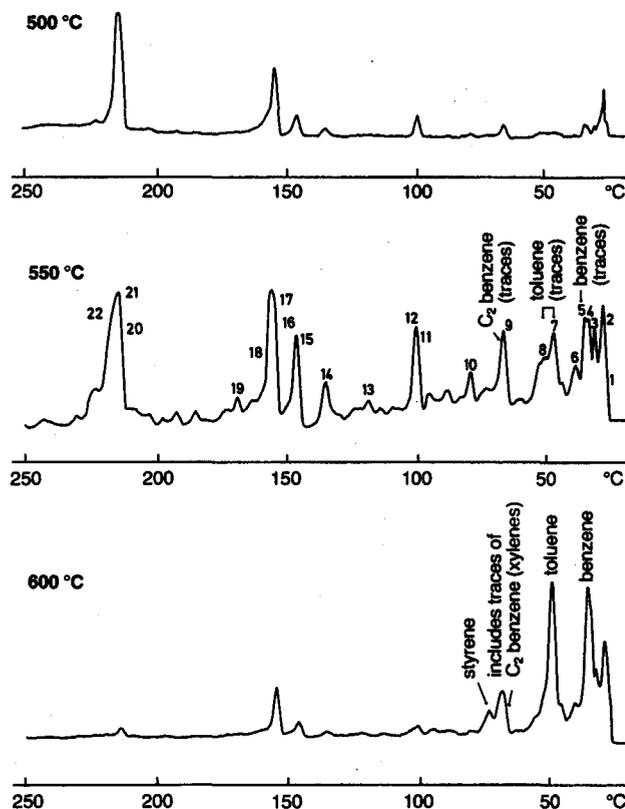


Figure 2.
Gas chromatograms after pyrolysis of neophytadiene at different temperatures.*



* The separation of pyrolysis products on OV-101 is based on programming from 30 °C to 250 °C with an increase in temperature of 4 °/min.

Figure 3.
Possible structural formulae for the molecular weights found after pyrolysis of
n-alkanes and isoprenoids.

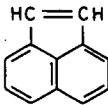
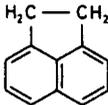
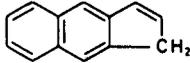
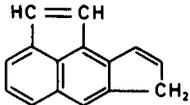
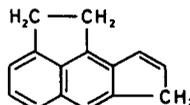
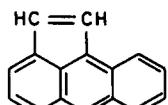
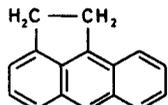
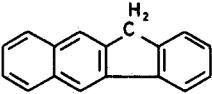
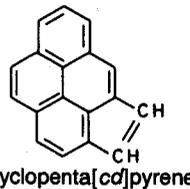
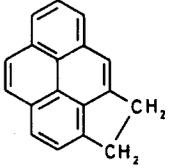
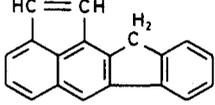
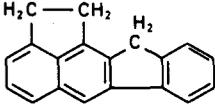
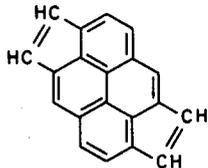
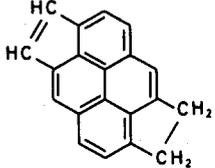
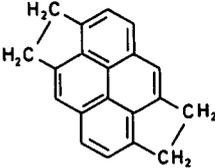
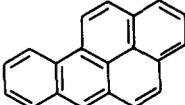
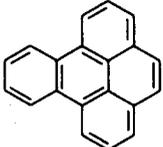
Compound No.	Molecular weight	Molecular formula	Structural formula	References
I	152	$C_{12}H_8$	 Acenaphthylene	1
II	154	$C_{12}H_{10}$	 Acenaphthene	1
III	166	$C_{13}H_{10}$		
IV	190	$C_{15}H_{10}$		
V	192	$C_{15}H_{12}$		
VI	202	$C_{16}H_{10}$		
VII	204	$C_{16}H_{12}$		
VIII	216	$C_{17}H_{12}$		
IX	226	$C_{18}H_{10}$	 cyclopenta[cd]pyrene	19, 21

Figure 3 (cont'd.).

Compound No.	Molecular weight	Molecular formula	Structural formula	References
X	228	$C_{18}H_{12}$	 <p>3,4-dihydrocyclopenta[cd]pyrene</p>	19, 21
XI	240	$C_{19}H_{12}$		
XII	242	$C_{19}H_{14}$		
XIII	250	$C_{20}H_{10}$		
XIV	252	$C_{20}H_{12}$		
XV	254	$C_{20}H_{14}$		
XVI	252	$C_{20}H_{12}$	 <p>Benzo[a]pyrene</p>	
XVII	252	$C_{20}H_{12}$	 <p>Benzo[e]pyrene</p>	