IDENTIFICATION OF AROMATIC HYDROCARBONS IN HIGH-BOILING FRACTION OF PYROLYSIS OIL BY CAPILLARY GAS–LIQUID CHROMATOGRAPHY AND MASS SPECTROMETRY

Jan Novrocík[a], Marta Novrocíková[a] and Antonín Čapek[b]

[a] *Research Institute of Coke Chemistry, Urxovy závody, 757 27 Valašské Meziříčí and*
[b] *Spolana, 277 11 Neratovice*

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Capillary gas chromatography and mass spectrometry have been used for identification of most main high-boiling components of fraction of pyrolysis oil (boiling point 250 to 350°C under normal pressure) especially those boiling above the b.p. of acenaphthene. All methyl homologues of acenaphthene, phenanthrene, some isomeric methylfluorenes, trimethyl- and methylethyl naphthalenes, phenylnaphthalenes, dimethylbiphenyls, benzindans, methylbenzindans and other aromatic hydrocarbons have been prepared as standards. In connection with the preparation of some trimethyl- and methylethylnaphthalenes a discussion is presented of the course of chloromethylation and acetylation of 1- and 2-methyl- and 2-ethylnaphthalenes. Content of methylhomologues of some hydrocarbons (acenaphthene, fluorene, phenanthrene, and anthracene) in the high-boiling fraction of pyrolysis oil has been compared with that present in similar fraction of coal tar.

Pyrolysis oil is a coproduct formed in production of ethylene and propylene by pyrolysis of gasolines. According to technological arrangement of the process the pyrolysis oil boils within the range 200 to 400°C under atmospheric pressure. Considerable attention has been paid recently to identification of the components present in pyrolysis oil, because this coproduct could become an important source of aromatic hydrocarbons in near future. The pyrolysis oil was found to be a varied mixture of aromatic hydrocarbons, their methyl, ethyl, dimethyl, methylethyl, trimethyl and/or further polyalkyl homologues. Mostecký and coworkers[1] carried out a mass spectrometric group analysis of the hydrocarbons present in pyrolysis oil. Kuraš and Hála[2] determined composition of pyrolysis oil by mass spectrometry using the Fitzgerald method and dividing the components into the following categories: alkylbenzenes, indans and tetrahydronaphthalenes, indenes and dihydronaphthalenes, naphthalene and alkylnaphthalenes, acenaphthenes and biphenyls, acenaphthylenes and fluorenes. Other authors[3] deal with mass spectrometry of the components present in the high-boiling fractions obtained from pyrolysis of kerosene fraction of Romashkino crude oil and of a similar product obtained from gasoline pyrolysis. Hála and coworkers[4] described identification of tricyclic fraction of pyrolysis oil containing mostly methylhomologues of acenaphthene, fluorene and the parent tricyclic hydrocarbons (boiling range from 145 to 217°C/1·733 kPa); they also obtained alkyladamantanes by hydrogenation of the aromates and rearrangement of the obtained perhydroaromatic hydrocarbons in the presence of aluminium chloride. Soják and Barnoky[5] used the capillary gas-liquid chromatography for

investigation of composition of the pyrolysis oil fraction boiling within 130 to 160°C/2·666 kPa. It was found that the fraction contained methyl, dimethyl and ethyl homologues of naphthalene, biphenyl and its methyl homologues, diphenylmethane and acenaphthen. Also Mostecký and coworkers[6] described determination of these hydrocarbons in the same fraction by capillary gas chromatography using three different columns with various polarity of stationary phase; UV spectrometry was used for determination of 2,6- and 2,7-dimethylnaphthalene content.

However, the hydrocarbons boiling above b.p. of acenaphthene were not identified in this way. Cosyns and coworkers[7] dealt with identification of the components present in the fraction boiling within 40 to 200°C at atmospheric pressure. Synthetic approach was also applied for more detailed structure determination of methyl, ethyl and dimethyl homologues of biphenyl. Kříž and coworkers[8] prepared these hydrocarbons by the Gomberg reaction using suitable combinations of aromatic amine and aromatic hydrocarbon. The elution data of the biphenyls prepared (using three capillary columns with various polarities of stationary phases) were given in another communication of the same authors[9]. An interesting group of components present in the pyrolysis oil is represented by azulene and its methyl homologues. Their isolation from the pyrolysis oil and identification was described by Popl and coworkers[10]. These compounds were isolated with the use of phosphoric acid and were purified by column chromatography and identified by GLC and MS. Popl and coworkers[11] dealt with investigation of non-distillable portion of pyrolysis oil; they stated that this fraction was a mixture of polymers of isomeric benzindenes and their methyl homologues. Bajus and coworkers studied pyrolysis of methylcyclohexane[12] and n-heptane[13] in the presence of water vapour at 700 to 900°C in a through-flow reactor using GLC and MS for analysis of the products. Kusý[14] described GLC analysis of pyrolysis oil with two packed columns using different polarities of stationary phases, the investigation being especially focused on higher-boiling components of this product.

For the purpose of our investigation it is important to mention further papers dealing with identification of higher-boiling hydrocarbons in various materials. Aczel and Bartz[15] used MS for analysis of benzindans present in the portion obtained by percolation of the product of light pyrolysis with alumina gel; the products were identified also by UV, NMR, and IR spectrometry. Dembrovskaya[16] determined composition of gas oil with special respect to the presence of dimethyl- and trimethylnaphthalenes. A more recent paper of other authors[17] deals with identification of many dimethyl-, trimethyl-, tetramethylnaphthalenes and other alkylnaphthalenes in kerosene fraction boiling within 200 to 280°C at atmospheric pressure with the use of capillary GLC (polyethylene glycol adipate as stationary phase) and UV spectrometry. Shiyachov and coworkers[18] developed a chromatographical method for determination of group and individual composition of a mixture of aromatic hydrocarbons present in a crude oil fraction with the use of capillary GLC (Apiezon L as stationary phase) at several temperatures. Other authors[19] studied conditions of separation of alkyl homologues of fluorene, anthracene and phenanthrene with capillary column wetted with a silicon elastomer E-301. Severson and coworkers[20] analyzed polynuclear aromatic hydrocarbons isolated from cigarette smoke. The gas-chromatographical analyses were carried out with a column packed with Chromosorb W a.w. wetted with 5% Dexsil 300 GS. MS could identify methylacenaphthenes, methylphenanthrenes, methylfluorenes, methylacenaphthylenes, methylpyrenes, and benz[*f*]indan besides other hydrocarbons. Preparation of methylfluorenes, methylacenaphthenes, and methylphenanthrenes by bromomethylation of the parent hydrocarbons and subsequent reduction with zinc and acetic acid and MS of these hydrocarbons are dealt with in a paper by Schiller[21]. However, position of the substituent in these products could not be determined. Relation between connectivity indexes and elution indexes of methylphenanthrenes, methylanthracenes, and further 44 polynuclear hydrocarbons is treated in a paper by Kaliszan and Lamparczyk[22]. The Kováts elution indexes measured with capillary columns wetted with the silicone phases OV-101 and OV-17 were taken from

a study by Grimmer and Böhnke[23]. Lee and coworkers[24] determined elution indexes of 209 polynuclear aromatic hydrocarbons and their alkyl homologues (*inter alia* methylphenanthrenes, methylfluorenes, dimethylbiphenyls, methylanthracenes, methyl- and ethylbiphenyls) with a capillary column wetted with SE-52 at a programmed temperature. Separation and identification of a number of polynuclear aromatic hydrocarbons and their methyl homologues from coal tar were described by Borwitzky and Schomburg[25]; the authors used capillary GLC-MS, the columns were wetted with stationary phases OV-7 or Poly S 179. In this case, however, position of methyl group in the aromatic hydrocarbons were not given.

None of the above-mentioned communications, however, deals with detailed identification of the aromatic hydrocarbons and their alkyl homologues in the higher-boiling fractions of pyrolysis oil (boiling range above b.p. of acenaphthene). Available chromatographical data of these hydrocarbons were obtained with columns wetted with various stationary phases and cannot be fully used for identification. The aim of the present paper is identification of most main components present in the pyrolysis oil fraction boiling within 250 to 350°C at atmospheric pressure using capillary GLC-MS complemented by detailed identification and determination of position of alkyl group by means of chromatographical standards commercially available or synthetically prepared.

EXPERIMENTAL

Sample

Content of carbon, hydrogen, nitrogen, and sulphur in the high-boiling fraction obtained by discontinuous distillation of pyrolysis oil (Chemické závody ČSSP, Litvínov) was determined by elemental analysis.

Hydrogenation

With respect to possible presence of unsaturated compounds a 20 g sample of the high-boiling fraction of pyrolysis oil was submitted to hydrogenation with a Pd/C catalyst in 98% acetic acid at 40°C at hydrogen pressure 980·6 kPa. The sample was then rid of the catalyst and acetic acid by filtration and distillation, respectively, and was analyzed by capillary GLC under the below-given conditions.

Capillary GLC of High-Boiling Portion of Pyrolysis Oil

The high-boiling sample was analyzed in a glass capillary column (50 m length, 0·25 mm inner diameter) whose surface, before wetting (dynamic method) with 3% Apiezon L solution (Carlo Erba, Milano) in benzene, was etched with hydrogen fluoride liberated by pyrolysis of 1,1,2-trifluorchlorethylmethyl ether and silanized with hexamethyldisilazane. Number of theoretical plates of the column was 65 000 for $k = 2{\cdot}5$. The column was placed in a gas chromatograph Fractovap 2 400T (Carlo Erba, Milano) equipped with an inlet splitter (the ratio was adjusted at 1 : 100), flame ionization detector, and temperature programmer. Further conditions of the analysis: injection 0·1 μl, $t_c = 100°C$, after 10 min the temperature of the column was increased at a rate of 1°C min^{-1} up to 180°C, argon flow rate 1·0 ml min^{-1}. The commercial and the

synthetized standards were analyzed under the same conditions. The same chromatograph was also used for the analysis in combination with a stainless steel capillary column (45 m length, 0·25 mm inner diameter) dynamically wetted with 7% Apiezon L solution (Carlo Erba, Milano), $t_c = 160°C$, after 26 min the temperature was increased at a rate of 1°C min^{-1} up to 230°C, argon flow rate 0·5 ml min^{-1}. For separation of methylethyl-, trimethyl- and dimethylnaphthalenes prepared synthetically we also used a stainless steel capillary column (50 m length, 0·25 mm inner diameter) wetted with 7% solution of *m*-bis(*m*-phenoxyphenoxy)benzene, $t_c = 150°C$, the argon flow rate 0·6 ml min^{-1}.

Capillary GLC-MS

For the analyses we used a gas chromatograph connected with a mass spectrometer type GC-MS Mat 111 (Varian) with magnetic expansion of data. The sample was analyzed on the glass capillary column wetted with Apiezon L under the above-mentioned conditions. Conditions of the mass spectrometry: ionisation energy 80 eV, anodic current 270 μA, temperature of the ionic source 250°C, resolution power 600, sensitivity 0·1 to 1·0 V, accelerating voltage 850 V, SEV voltage 1 000 V, rate of recording of spectra 50 amu s^{-1}. The spectra were recorded by means of a moving-coil oscillograph, UV light beam and polarographic paper, chart drive 10 cm s^{-1}. The gas chromatograph was connected to the mass spectrometer by means of an adjustable slot separator of the carrier gas.

Preparation of the Chromatographic Standards

All the analytical standards prepared as chemically pure substances were identified by IR spectroscopy (Unicam SP 200G, England) and by capillary GLC; the standard mixtures were analyzed under the above-mentioned conditions.

Syntheses by the Gomberg reaction. According to ref.[26] methyl-, ethyl-, and dimethylbiphenyls were prepared by the classic Gomberg reaction either as pure substances or as mixed standards. The individual methylbiphenyls were prepared by combination of *o*-, *m*- or *p*-toluidine with benzene, 2-ethyl- and 4-ethylbiphenyls were prepared from benzene and 2- and 4-ethylaniline, respectively, the mixed standard of all three ethylbiphenyls was prepared by combination of aniline and ethylbenzene. Some individual dimethylbiphenyls were prepared by combination of benzene with respective dimethylanilines: 2,3-, 3,4-, 3,5-, 2,4-. 2,5-Dimethylbiphenyl was prepared by combination of aniline with *p*-xylene. The remaining isomeric dimethylbiphenyls were prepared as mixed standards by combination of toluene with *o*-, *m*- or *p*-toluidine, or combination of aniline with *m*-xylene. In similar way we prepared also the following aromatic hydrocarbons: 1-phenylnaphthalene (from 1-naphthylamine and benzene), 2-phenylnaphthalene (from 2-naphthylamine and benzene), 5-phenylindan (from 5-aminoindan prepared according to ref.[27] and benzene), 4-phenylindan (from benzene and 4-aminoindan obtained by nitration of indan and vacuum distillation of mixture of nitroindans[28] and subsequent catalytic hydrogenation of 4-nitroindan). In the same way we prepared 5- and 6-phenyltetrahydronaphthalenes from 5-aminotetrahydronaphthalene (which was obtained from tetrahydronaphthalene in the same way as 4-aminoindan) and 6-aminotetrahydronaphthalene (prepared similarly as 5-aminoindan), respectively.

Syntheses of methyl derivatives by chloromethylation and subsequent hydrogenolysis. A number of further methyl homologues of aromatic hydrocarbons were prepared as mixed standards by chloromethylation and subsequent hydrogenolysis of the chloromethyl derivatives formed using Pd/C catalyst in acetic acid and hydrogen pressure 490 kPa at room temperature. The

hydrogenolysis products were always purified by chromatography on a silica gel column deactivated with 5% water (20 cm column length), eluent system n-hexane–acetone (2 : 1 by vol.).

Phenanthrene (99% purity, 0·06 mol) was dissolved in 300 ml 99% acetic acid saturated with gaseous hydrogen chloride, and the solution was treated with 60 ml 85% phosphoric acid and 20 ml 40% aqueous formaldehyde added drop by drop with stirring. The mixture was heated at 80°C (water bath) for 3 hours and was continuously saturated with gaseous hydrogen chloride with intensive stirring. Then the reaction mixture was poured in 800 ml water, and the chloromethylated product was isolated by three extractions with benzene (3 × 50 ml). The extract was concentrated to 50 ml and submitted to hydrogenation. The hydrogenolysis product was rid of acetic acid and purified in the above-mentioned way. The experiment was repeated under the same conditions except for the chloromethylation time which was increased to 4 h.

Fluorene (98·5% purity, 0·05 mol) was dissolved in 150 ml 99% acetic acid and submitted to chloromethylation by addition of 4·1 g finely powdered paraformaldehyde and gaseous hydrogen chloride which was introduced with intensive stirring for 2 h.

The product was processed in the same way as before. Chloromethylation of acenaphthene had to be carried out in a modified way: 0·05 mol 98·6% acenaphthene was dissolved in 50 ml tetrachloromethane and chloromethylated with intensive stirring under reflux condenser at 68 to 70°C by addition of a mixture of 35% aqueous formaldehyde and 65 ml 35% hydrochloric acid *p.a.* After 1·5 h the reaction mixture was treated with 12 ml 85% phosphoric acid added drop by drop during 12 min, and the chloromethylation was finished within further 30 min. The product was obtained in the above-mentioned way after removal of tetrachloromethane by distillation of the organic layer.

Chloromethylation with monochlordimethyl ether (Spolek pro chemickou a hutní výrobu, Ústí nad Labem) in the presence of 1% w/w tin tetrachloride and subsequent hydrogenolysis (similar to the above cases) were applied to preparation of the following trimethylnaphthalenes: 1,2,3- from 2,3-dimethylnaphthalene (Loba Chemie, Wien), 1,4,5- from 1,8-dimethylnaphthalene (Aldrich Chem. Comp., U.S.A.), 1,2,7- from 2,7-dimethylnaphthalene (ICN Pharm., N.Y., U.S.A.), 1,2,6- from 2,6-dimethylnaphthalene (Loba Chemie, Wien), 1,2,4- from 1,3-dimethylnaphthalene (Fluka AG, Buchs, Austria), 1,4,6- mixed with 1,5,6- from 1,6-dimethylnaphthalene (BDH Ltd., Poole, England), 1,4,7- and 1,3,5- from 1,7-dimethylnaphthalene (ICN Pharm., N.Y., U.S.A.). General procedure of the chloromethylation: $5 \cdot 10^{-3}$ mol of the respective dimethylnaphthalene was dissolved in 4 ml benzene, the solution was treated with $8 \cdot 5 \cdot 10^{-3}$ mol monochlordimethyl ether and 0·03 ml tin tetrachloride. The mixture was left to stand at room temperature for 24 h, then it was poured in 10 ml 20% hydrochloric acid, thoroughly mixed, the organic layer was separated, dried with anhydrous sodium sulphate, and the unreacted monochlordimethyl ether was distilled off, and the distillation residue was submitted to hydrogenolysis. The same procedure was also used for chloromethylation of 2-ethylnaphthalene (Pfaltz Bauer, Conn., U.S.A.) and, for determination of the substitution position, also of 1- and 2-methylnaphthalene. The obtained chloromethyl derivatives were submitted to hydrogenolysis.

1-*Methylacenaphthene*: 0·3 mol 1-naphthylacetic acid (Lachema, Brno) was boiled with 4·15 mol thionyl chloride (Lachema, Brno) for 5 h to give the corresponding chloride. The excess thionyl chloride was distilled off at normal pressure and then at reduced pressure. The distillation residue was diluted with 120 ml 1,2-dichloroethane and the solution was added drop by drop into a mixed suspension of 60 g anhydrous aluminium chloride at 0—3°C. The reaction mixture was stirred for another 4 h, the temperature increasing spontaneously to 20°C. The next day, the reaction product was poured onto a mixture of ice and 200 ml 20% hydrochloric acid, the organic layer was separated, boiled with charcoal, and hot filtered. The filtrate was concentrated to give a yellow substance whose IR spectrum proved the presence of two structurally different carbonyl groups,

one of them being bound to five-membered ring. The substance was chromatographically uniform (TLC with Silufol and hexane–acetone 3 : 1 v/v), but its high melting point excluded the possibility to identify the substance as 1-acenaphthenone (m.p. 274—275°C corr., ref.[29] gives m.p. of 1-acenaphthenone 119°C). The mother liquor after crystallization of this substance was concentrated to 20 ml to give further 3·7 g chromatographically pure substance (TLC with Silufol, hexane–benzene–acetone 2 : 1 : 1 by vol.) whose IR spectrum indicated the presence of only one type of carbonyl group bound to a five-membered ring (m.p. 118—119°C corr.). 1-Acenaphthenone was dissolved in 200 ml dry diethyl ether and added drop by drop to a solution of methylmagnesium iodide prepared under nitrogen from 5·23 g methyl iodide and 0·80 g magnesium in 50 ml anhydrous diethyl ether. The organomagnesium compound was stirred for 2 h and then decomposed by addition of 80 ml water and 100 ml 10% hydrochloric acid. The organic layer was separated, dried with anhydrous calcium chloride, and evaporated until dry. The residue was heated at 160—180°C (oil bath) with introduction of nitrogen, whereby the water of reaction was removed. The dehydrated product containing 1-methylacenaphtylene was purified on a silica gel column (20 cm, hexane–acetone 3 : 1 by vol.) and then hydrogenated to 1-methylacenaphthene in 100 ml ethanol with Pd/C catalyst under atmospheric pressure of hydrogen.

5-*Ethylacenaphthene*: the substance was prepared according to ref.[30] by reaction of acenaphthene with ethyl bromide in carbon disulphide with anhydrous aluminium chloride as catalyst.

9-*Methylfluorene*: the substance was prepared by decomposition of sodium salt of 9-ethoxalylfluorene by boiling with aqueous sodium hydroxide[31]. 9-Ethoxalylfluorene was prepared according to ref.[32] by reaction of fluorene with diethyl oxalate (VCHZ Synthesia, Semtín) using sodium ethoxide as catalyst.

9,10-*Dihydrophenanthrene*: the substance was prepared by reduction of phenanthrene with sodium in 1-pentanol[33] and crystallized from the same alcohol.

The mixed standard 2-, 3-, and 4-*methyldiphenylmethane* was obtained by reaction of benzyl chloride with toluene in the presence of tin tetrachloride as catalyst[26].

1-*Methyl*-3-*phenylindane* was prepared by dimerization of styrene[34] by boiling with 63% sulphuric acid and purified by vacuum distillation (the fraction boiling at 106—112°C/66 Pa was taken).

1,3-*Diphenyl*-1-*butene* (with admixture of 5% 1,3-diphenyl-2-butene) was prepared by dimerization of styrene according to ref.[35].

Benz[e]*indans*: the substance was prepared by reduction of a mixture of 65% benz[*e*]indan--1-one and 35% benz[*e*]indan-3-one (analyzed by GLC, 1 m column with Chromosorb W wetted with 5% OV-17, $t_c = 165°C$, $p_{Ar} = 83·4$ kPa) with zinc amalgam. The product was purified by column chromatography under the same conditions as those used for 1-methylacenaphthylene. The mixture of the two isomeric benz[*e*]indanones was prepared by acylation of naphthalene with maleic anhydride[36], subsequent cyclization of the formed mixture of 2-(2-naphthoyl)-acrylic and 2-(1-naphthoyl)acrylic acids, and decarboxylation of the obtained mixture of benz[*e*]-indan-1-one-3-carboxylic acid and benz[*e*]indan-3-one-1-carboxylic acid[37]. The mixture of the two isomeric benz[*e*]indanones was converted[38] into a mixture of 1-methyl-1*H*-benz[*e*]indene and 3-methyl-3*H*-benz[*e*]indene which on hydrogenation (Pd/C catalyst, atmospheric pressure of hydrogen) gave a mixture of 1- and 3-methylbenz[*e*]indans. According to ref.[38] we also prepared 1-methyl-1*H*-benz[*e*]indene and then 1-methylbenz[*e*]indan. Chloromethylation of benz[*e*]-indan with monochlordimethyl ether and subsequent hydrogenolysis gave 5-methylbenz[*e*]indan, which was purified in the same way as 1-methylacenaphthylene.

Benz[f]indan was prepared[39] by acylation of tetrahydronaphthalene with 2-chloropropionyl chloride (BASF, Ludwigshafen, FRG), subsequent cyclization to 5,6,7,8-tetrahydrobenz[*f*]indan--1-one, and reduction with zinc amalgam to 5,6,7,8-tetrahydrobenz[*f*]indan. Its dehydrogenation on Pd/C catalyst[40] at 280—290°C gave benz[*f*]indan.

1-*Methyl*-4-*ethylnaphthalene* was prepared by acetylation of 1-methylnaphthalene with acetyl chloride in nitrobenzene with anhydrous aluminium chloride as catalyst[41]. The raw product obtained after distillation off of nitrobenzene was rid of tary substances by pouring into an excess of ethanol and filtration with charcoal. The acetyl derivative was reduced with zinc amalgam, and the product was purified by column chromatography as in the case of 1-methylacenaphthylene.

2-*Methyl*-6-*ethylnaphthalene* with admixtures of other isomeric methylethylnaphthalenes was prepared by reduction of corresponding mixture of acetyl derivatives with zinc amalgam. The acetyl derivatives were prepared by acetylation of 2-methylnaphthalene with acetyl chloride catalyzed with anhydrous aluminium chloride in nitrobenzene[42], and they were purified from tary admixtures as in above cases. An attempt was made of selective chloromethylation of 1- and 2-acetylnaphthalenes with monochlordimethyl ether in anhydrous acetic acid with anhydrous zinc dichloride as catalyst; subsequent hydrogenolysis and reduction with zinc amalgam gave further isomeric methylethylnaphthalenes. 1- and 2-Acetylnaphthalenes were prepared according to ref.[43] and ref.[44], respectively.

2,3-*Dihydro*-1H-*phenalene* was prepared as a mixed standard with benz[*e*]indan acording to ref.[45,46] by reaction of 1-chloromethylnaphthalene with diethyl malonate (Pfaltz Bauer, Conn., U.S.A.), subsequent hydrolysis and decarboxylation of the obtained ester to 2-(1-naphthyl)propionic acid, which on cyclization with phosphoric acid and phosphorus pentoxide gave a mixture of perinaphthindan-1-one and benz[*e*]indan-3-one; reduction of the latter mixture with zinc amalgam gave a mixture of 2,3-dihydro-1*H*-phenalene and benz[*e*]indan.

1-*Methyl*-2,3-*dihydro*-1H-*phenalene* was prepared from perinaphthindan-1-one by reaction with methylmagnesium iodide, subsequent dehydratation and hydrogenation and final purification as in the case of 1-methylacenaphthylene.

The mixed standard of methylazulenes and azulene was isolated from high-boiling portion of pyrolysis oil by means of 85% phosphoric acid and purified by column chromatography[10]. The following analytical standards were commercially available: 1,2-dimethylnaphthalene, 1-methylfluorene (the both Aldrich-Europe, Beerse, Belgium), 1,4-dimethylnaphthalene, 2-methylphenanthrene, 9-methylanthracene, 2,3,5- and 2,3,6-trimethylnaphthalene, 1-ethylnaphthalene (all ICN Pharm., N. Y., U.S.A.), 2-methylfluorene, 2-methylanthracene (the both Pfaltz Bauer, Conn., U.S.A.), 1,3,7-trimethylnaphthalene (Fluka AG, Basel, Switzerland), symmetrical indacene and mixed standard of symmetrical and asymmetrical indacenes (both Research Institute of Pharmacy and Biochemistry, Prague). Also used as standards were isomeric trimethyl- and methylethylbiphenyls prepared in the work[26].

RESULTS AND DISCUSSION

By elemental analysis of the high-boiling fraction of pyrolysis oil it was found: 92·8% C, 6·9% H, 0·3% S. Heterocyclic compounds are not present in this product in significant amounts and need not be considered, hence attention must be focused to identification of aromatic hydrocarbons. Hydrogenation of a sample of the high-boiling fraction under the conditions unfavourable for hydrogenation of aromatic rings revealed

that the product did not contain significant concentrations of compounds of indene or dihydronaphthalene types.

Capillary Gas–Liguid Chromatography

The capillary GLC with the glass column wetted with 3% Apiezon L enabled separation into 105 components. The said column wetted with a low concentration of the stationary phase failed in separation of some components, however, its advantage lies in its enabling to use a temperature program in the region of lower temperatures (with respect to service life of the column) with good results of elution and separation of the high-boiling components. The mentioned disadvantage of imperfect separation of some lower-boiling components is due to low (and not suitable for separation of these compounds) initial temperature of analysis. Hence the temperature conditions of the analysis must be chosen to make a compromise with respect to the above-mentioned facts. From Fig. 1 it is seen that biphenyl and 2-methylbiphenyl are not separated, insufficient separation being also between the peaks of benz[*e*]indan, 3-methylacenaphthene and 4,4'-dimethylbiphenyl. These drawbacks can be removed by application of the capillary column wetted with a higher concentration of Apiezon L and, consequently, of another temperature program. This column, however, failed to separate diphenylmethane from 1-ethylnaphthalene, and 5-methyl-acenaphthene from 3,4-dimethylbiphenyl which are perfectly separated in the glass capillary column wetted with the lower concentration of stationary phase. These changes in elution behaviour can be explained by the fact that Apiezon L is not a quite non-polar stationary phase, which results in operation of weak polar interactions between the stationary phase and a polar solute; this phenomenon is observed at different temperatures. Neither of the two columns, however, could separate some isomeric dimethylnaphthalenes (2,7- from 2,6-; 1,3- from 1,6-) whose separation is better accomplished in columns wetted with more polar stationary phases[6]; the latter ones, on the contrary, are not suitable for analysis of higher-boiling compounds.

Capillary Gas–Liquid Chromatography – Mass Spectrometry

This method was used for orientation identification of some unknown aromatic hydrocarbons present in concentrations above 0·1% (w/w). In this way we identified the peaks denoted in Fig. 1 by the following numbers: 22, 26, 27, 30, 41, 50, 52–54, 57, 60, 62, 63, 71, 72, 74, 75, 77, 89, 91, 95, 99–103. The results of GLC-MS are given in Table I; the numbers of peaks agree with those in Fig. 1. From the results it follows that mass spectra of the individual isomers are so similar that it is impossible (in most cases) to assign the position of alkyl group in aromatic ring. The similarity of spectra is due to high stability of aromatic compounds (as well as their fragments *e.g.* tropylium cation) and, hence, poor fragmentation, the effects of substituents (or their position) being not much distinct. Detailed identification

and determination of substituent position was only possible by means of capillary GLC with added standards which were prepared on the basis of data about structure of unknown components obtained from capillary GLC-MS. Results of the identification along with analysis of a typical sample are summarized in Table II (numbers

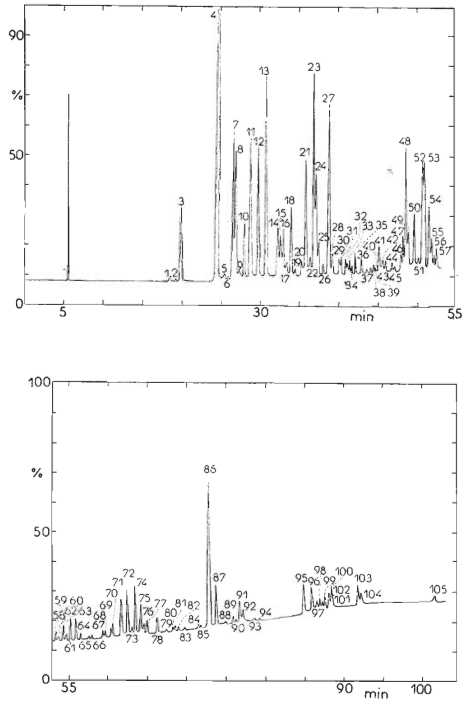

FIG. 1

Analysis of a sample of high-boiling portion of pyrolysis oil. Conditions: glass capillary column, 50 m length, 0·25 mm inner diameter, wetted with 3% Apiezon L, $t_{col} = 100°C$ was increased (after 10 min) at a rate of 1°C min^{-1} up to 180°C, argon flow rate 1 ml min^{-1}. The numbers of peaks are identical with those in Tables I and II

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TABLE I

Results of capillary GLC-MS

Peak No[a]	Molecular ion, amu	Characteristical fragments found, amu	Molecular formula	Suggested structure
22	170	M^+-29,. M^+-59	$C_{13}H_{14}$	propylnaphthalene
26	182	M^+-15, M^+-27	$C_{14}H_{14}$	methyldiphenylmethane
27	168	M^+-15, double charged M^+-15, double charged M^+, double charged M^+-2 H, double charged M^+-4 H and $C_6H_4^+$	$C_{13}H_{12}$	methylbiphenyl
30	170	M^+-15, M^+-29, $M^+-29-26$	$C_{13}H_{14}$	methylethylnaphthalene
41	170	M^+-15, other fragments little distinct	$C_{13}H_{14}$	trimethylnaphthalene
50	180	M^+-15, M^+-28, double charged M^+-15, and double charged M^+-28	$C_{14}H_{12}$	methylfluorene
52	168 + 182	M^+-15, other fragments are combined with other compounds	$C_{13}H_{12}$ $C_{14}H_{14}$	methylacenaphthene dimethylbiphenyl
53	168	M^+-1, M^+-3, M^+-15	$C_{13}H_{12}$	methylacenaphthene
54	168	the same fragments as with the peak 53	$C_{13}H_{12}$	methylacenaphthene
60	182	M^+-15, $C_6H_4^+$ typical of biphenyl	$C_{14}H_{14}$	dimethylbiphenyl
62	182	the same fragments as with the peak 60	$C_{14}H_{14}$	dimethylbiphenyl
63	182	the same fragments as with the peak 60	$C_{14}H_{14}$	dimethylbiphenyl
71	180	M^+-1, M^+-15, M^+-28, M^+-91, double charged M^+-15, $C_6H_4^+$	$C_{14}H_{12}$	methylfluorene
74	180	the same fragments as with the peak 71	$C_{14}H_{12}$	methylfluorene
75	180	the same fragments as with the peak 71	$C_{14}H_{12}$	methylfluorene
77	182	M^+-15, M^+-17	$C_{14}H_{14}$	dimethylacenaphthene
89	194	M^+-15, further record of poor quality (low conc.)	$C_{15}H_{14}$	dimethylfluorene
91	204	M^+-1. M^+-2, M^+-103	$C_{16}H_{12}$	phenylnaphthalene
95	192	M^+-1, M^+-2, M^+-3, these ions double charged	$C_{15}H_{12}$	3-methylphenanthrene
99	192	the same fragments as with the peak 95	$C_{15}H_{12}$	methylphenanthrene
100	190	M^+-1, M^+-94, M^+-95, double charged M^+-1, these and other fragments identical with those of ref.[46]	$C_{15}H_{10}$	4,5-methylenephenanthrene
101	192	the same fragments as with the peak 99	$C_{15}H_{12}$	methylphenanthrene
102	192	the same fragments as with the peak 99	$C_{15}H_{12}$	methylphenanthrene or methylanthracene
103	204	the same fragments as with the peak 91	$C_{16}H_{12}$	phenylnaphthalene

[a] The numbers of peaks are the same as those in Fig. 1 and Table II.

TABLE II

Composition of high-boiling portion of pyrolysis oil

Peak No[a]	Component	Content %, w/w
1	2-methylnaphthalene	0·09
2	azulene	0·01
3	1-methylnaphthalene	1·39
4	biphenyl + 2-methylbiphenyl	6·80[b]
5	unidentified	0·12
6	unidentified	0·05
7	2-ethylnaphthalene	3·46
8	1-ethylnaphthalene	2·35
9	2,6-dimethylbiphenyl	0·14
10	diphenylmethane	1·29
11	2,6- and 2,7-dimethylnaphthalenes	4·29
12	1,7-dimethylnaphthalene	2·81
13	1,3- and 1,6-dimethylnaphthalene	5·94
14	2,3-dimethylbiphenyl	1·38
15	1,4-dimethylnaphthalene	1·11
16	1,5-dimethylnaphthalene	1·20
17	unidentified	0·48
18	1,2-dimethynaphthalene	1·56
19	2,3′-dimethylbiphenyl	0·45
20	2,5-dimethylbiphenyl	0·14
21	3-methylbiphenyl	4·05
22	2-propylnaphthalene	0·96
23	acenaphthene	6·13
24	4-methylbiphenyl	2·34
25	2-methyl-6-ethylnaphthalene	0·86
26	2,3-dimethylbiphenyl	0·27
27	1-methylacenaphthene	3·90
28	1-methyl-7-ethyl- and 1-ethyl-7-methyl-naphthalenes	0·39
29	4-methyldiphenylmethane	0·14
30	x,y-methylethylnaphthalene	0·61
31	unidentified	0·31
32	1-methyl-4-ethylnaphthalene	0·23
33	unidentified	0·26
34	unidentified	0·15
35	1,3,7-trimethylnaphthalene	0·52
36	1-methyl-2-ethylnaphthalene	0·40
37	unidentified	0·06
38	unidentified	0·11
39	1,2,5- or 1,4,6-trimethylnaphthalene	0·13
40	unidentified	0·04

TABLE II
(*Continued*)

Peak No[a]	Component	Content %, w/w
41	2,3,6-trimethylnaphthalene	0·62
42	1,2,7-trimethylnaphthalene	0·36
43	2,3,5-trimethylnaphthalene	0·34
44	1,2,6-trimethylnaphthalene	0·57
45	unidentified	0·18
46	3,5-dimethylbiphenyl	0·23
47	3,3′-dimethylbiphenyl	0·54
48	fluorene	3·46
49	4-methylacenaphthene	0·69
50	9-methylfluorene	1·77
51	1,2-diphenylethane	0·42
52	3-methylacenaphthene and 4,4′-dimethylbiphenyl	3·67
53	benz[*e*]indan	3·35
54	5-methylacenaphthene	1·32
55	1,2,3-trimethylnaphthalene	0·82
56	3-methylbenz[*e*]indan	0·38
57	3,4-dimethylbiphenyl	0·49
58	unidentified	0·23
59	unidentified	0·24
60	aromatic hydrocarbon $C_{14}H_{14}$	0·37[c]
61	unidentified	0·20
62	1-methylbenz[*e*]indan	0·56
63	aromatic hydrocarbon $C_{14}H_{14}$	0·60
64	unidentified	0·08
65	1,3-diphenyl-1-butene	0·08
66	9,10-dihydroanthracene	0·07
67	9,10-dihydrophenanthrene	0·23
68	4-ethylacenaphthene	0·11
69	3-ethylacenaphthene	0·26
70	5-ethylacenaphthene and 4-phenylindan	0·16
71	3-methylfluorene	0·94
72	2-methylfluorene	1·65
73	unidentified	0·28
74	1-methylfluorene	1·28
75	4-methylfluorene	1·05
77	5,6-dimethylacenaphthene	0·57
78	unidentified	0·54
79	1-methyl-3-phenylindan	0·20
80	unidentified	0·19

TABLE II
(*Continued*)

Peak No[a]	Component	Content %, w/w
81	5-methylbenz[*e*]indan	0·21
82	unidentified	0·17
83	5-phenyltetrahydronaphthalene	0·11
84	unidentified	0·17
85	unidentified	0·23
86	phenanthrene	4·09
87	anthracene	1·42
88	unidentified	0·14
89	2,7-dimethylfluorene	0·10
90	unidentified	0·07
91	1-phenylnaphthalene	0·38
92	unidentified	0·05
93	unidentified	0·03
94	unidentified	0·03
95	3-methylphenanthrene	1·22
96	2-methylphenanthrene	0·93
97	2-methylanthracene	0·23
98	unidentified	0·38
99	4-methylphenanthrene	0·31
100	4,5-methylenphenanthrene	0·41
101	9-methylphenanthrene and 1-methylanthracene	0·44
102	1-methylphenanthrene and 9-methylanthracene	0·80
103	2-phenylnaphthalene	0·46
104	unidentified	0·36
105	fluoranthene	0·21

[a] The numbers of peaks are the same as those in Fig. 1 and Table I; [b] ratio of 2-methylbiphenyl to biphenyl is 12·64 : 87·36; [c] the hydrocarbon is probably 2-methylbenz[*e*]indan or one of methyl-2,3-dihydro-1*H*-phenalenes.

of the components agree with those in Fig. 1). Figures at the second decimal place in Table II have an only semiquantitative character. Comparison of the data given in Table II with results of the capillary GLC-MS reveals certain discrepancies which, however, can be explained. The peak 27 was identified by GLC-MS to be one of isomeric methylbiphenyls; in fact this peak corresponds to 1-methylacenaphthene with identical molecular formula, its molecule giving in MS, *inter alia*, the fragment $M^+ - CH_3$. On the contrary, the peak 53 (which, from GLC-MS, was considered

to be one of methylacenaphthenes) corresponds to one of isomeric benzindans or to 2,3-dihydro-1*H*-phenalene with the same molecular formula; in this case the presence of benz[*e*]indan was confirmed. Possible presence of some of methylacenaphthene isomers was excluded by comparison of elution data of the mixed standard of 3-, 4-, and 5-methylacenaphthene and 1-methylacenaphthene with those of this of peak. From known elution data of isomeric dimethylbiphenyls (3,4'-dimethylbiphenyl is eluted as the last of them under the given chromatographic conditions) it is possible to eliminate the suggested structures for the peaks 60, 62, and 63. In fact, these peaks belong to isomeric methyl-2,3-dihydro-1*H*-phenalenes or methylbenz[*e*]indans (benz[*f*]indan, eluted between the peaks 42 and 43, is absent, and hence the presence of its methylhomologues cannot be anticipated) which have the same molecular formula. In other cases the elution data confirmed the results of the capillary GLC-MS and assigned the substituent positions.

Further analytical standards were prepared and analyzed by the capillary GLC after evaluation of the previous results giving a relatively detailed picture of composition of the high-boiling fraction of pyrolysis oil. A number of minor components was thus identified, whereas 27 components (total content 5·15% w/w) remained unidentified.

From the identification the following conclusions can be made:

1) The high-boiling fraction of pyrolysis oil (boiling range 250 to 350°C) contains substantially greater amounts of methylhomologues of acenaphthene, fluorene, anthracene, and phenanthrene as compared with the corresponding parent hydrocarbons (ratio of the content of all isomeric methylhomologues to that of the parent hydrocarbons is 1·26), whereas in the coal tar fraction boiling within the same temperature range the above ratio is only 0·26. This difference is so distinct that it will not be markedly affected by varying conditions of coking and pyrolyse processes.

2) The highest concentration is that of dimethylnaphthalenes (total 15·35% w/w) followed by methylacenaphthenes (9·58%), methylbiphenyls (6·39%), methylfluorenes (6·69%), methylphenanthrenes and methylanthracenes (3·93%), and dimethylbiphenyls (2·26%). The other groups are not given because of incomplete identification.

3) The ratio of the methylated to the parent hydrocarbons is highest with methylfluorenes followed by methylacenapthenes, methylbiphenyls, methylphenanthrenes, methylanthracenes, and dimethylbiphenyls. Dimethylnaphthalenes could not be evaluated, because naphthalene is not present in this fraction. Only those aromatic hydrocarbons were evaluated whose concentration in the fraction is not affected by their boiling points.

4) In contrast to trimethyl- and methylethylnaphthalenes, the pyrolysis products do not contain significant concentrations of trimethyl- and methylethylbiphenyls. The dimerization products of styrene are present in traces.

Syntheses of the Analytical Standards

The preparation of analytical standards by the described procedures was complicated in may cases by formation of isomers, which was advantageous, if it was possible to identify position of the substituent from relative reactivity of the given centre or if some of the isomers were commercially available. Due to difficult separation of the individual isomers (close boiling points and other physical and chemical properties) their isolation in pure state was abandoned, and they were used as mixed analytical standards.

3-, 4-, and 5-*Methylacenaphthenes*: Chloromethylation of acenaphthene with formaldehyde and hydrogen chloride was complicated by the fact that (at conditions used for successful chloromethylation of phenanthrene or fluorene) it was accompanied by a not well understood formation of tary products, and the said methylacenaphthenes could not be isolated after hydrogenolysis. Assignment of the substituent position was relatively easy, because order of reactivity of the individual positions of acenaphthene to electrophilic aromatic substitution is $5 \gg 3 > 4$. The identity of methylacenaphthene was confirmed by capillary GLC-MS. Relative content of the individual isomers: 5- 83·6%, 3- 10·0%, 4-methylacenaphthene 6·4% (w/w).

Methylphenanthrenes: Determination of position of substituent was enabled by commercial availability of 2-methylphenanthrene. Position of methyl group in molecules of the remaining four isomers could be determined by combination of GLC-MS results, literature data[22] on elution order of isomeric methylphenanthrenes with the use of non-polar phase, and reactivity order of the individual positions to electrophilic substitution[47]. The mixture contained 9-, 1-, 3-, 2-, and 4-methylphenanthrenes at the concentrations (w/w) 55·3%, 34·2%, 7·6%, 2·6%, and 0·3%, respectively. The reaction product contained only 50·1% (w/w) methylphenanthrenes (total), and attempts to increase the conversion of phenanthrene to chloromethyl derivatives resulted in increased formation of bis(chloromethyl)phenanthrenes.

Methylfluorenes: Chloromethylation and subsequent hydrogenolysis of fluorene gives a mixture of only two isomers, 2- and 4-methylfluorene (87·8 and 12·4% (w/w), respectively). With 70% conversion of fluorene to chloromethyl derivatives, bis(chloromethyl)fluorenes are already formed (obviously 2,7-), their concentration in the reaction mixture being 10·0% (w/w) besides 58·0% monochloromethyl derivatives. In the case of 4-methylfluorene the position of methyl group was determined from the fact that out of the possible remaining isomers, 3- and 4-methylfluorenes, the former has lower boiling point than the latter (315·5 *vs* 317·5°C at 98·066 kPa) and, hence, would have been eluted before 2-methylfluorene on a non-polar stationary phase. Since the opposite is true, the isomer is most likely 4-methylfluorene.

Chloromethylation of benz[e]indan: the reaction should produce selectively (after hydrogenolysis) 5-methylbenz[*e*]indan, since the aromatic ring connected to the aliphatic skeleton is more reactive to electrophiles than the other aromatic ring of benz[*e*]indan molecule. Experimentally it was found that the product is chromatographically uniform, hence, most likely it represents 5-methylbenz[*e*]indan.

Chloromethylation of 1- *and* 2-*methyl*- and 2-*ethylnaphthalenes*: Chloromethylation and subsequent hydrogenolysis of 1-methylnaphthalene gave a mixture of 1,4- and 1,8-dimethylnaphthalenes in the ratio 95·3% to 3·8% (w/w), respectively. The same procedure applied to 2-methylnaphthalene gave a mixture of 1,2-, 1,7-, 1,3- and 1,6-dimethylnaphthalenes (83·3%, 12·3%, 2·4%, and 2·0%, respectively). The mixture obtained by the same procedure from 2-ethylnaphthalene was identified on the basis of a certain analogy due to structural similarity between 2-methyl- and 2-ethylnaphthalenes: 47·9% (w/w) 1-methyl-2-ethylnaphthalene, 33·6% 1-methyl--7-ethyl-, 12·0% 1-methyl-3-ethyl-, and 6·5% 1-methyl-6-ethylnaphthalene. The presence of 1-methyl-7-ethyl- and 1-methyl-6-ethylnaphthalenes was proved by their independent synthesis from 2-acetylnaphthalene *via* chloromethylation, hydrogenolysis, and reduction. These results confirm the fact that chloromethylation of 1- and 2-alkylnaphthalenes attacks selectively α position, the alternating position to the alkyl group present being preferred. The substantially higher content of 1-methyl--2-ethylnaphthalene can obviously be explained by increased steric hindrance of ethyl group, which results in an easier chloromethylation at the next alternating position, *i.e.* 8. Finaly this effect results in an increased content of 1-methyl-7-ethylnaphthalene in the mixture of methylethylnaphthalenes.

Chloromethylation of isomeric dimethylnaphthalenes and subsequent hydrogenolysis gave chromatographically pure trimethylnaphthalenes in the cases of some symmetrical dimethylnaphthalenes in accordance with the above conclusions (1,2,6-trimethylnaphthalenes from 2,6-dimethylnaphthalene, 1,2,7-trimethylnaphthalene from 2,7-dimethylnaphthalene, 1,4,5-trimethylnaphthalene from 1,8-dimethylnaphththalene, and 1,2,3-trimethylnaphthalene from 2,3-dimethylnaphthalene). 1,4,5-Trimethylnaphthalene could be prepared by chloromethylation *etc.* from 1,4-, 1,5-, or 1,8-dimethylnaphthalenes. However, with the two former isomers it was found, that chloromethylation proceeds with low conversion (maximum 10%), the reason being obviously in the presence of one methyl group in *peri* position with respect to the site of substitution. 1,4,5-Trimethylnaphthalene was obtained in this way from 1,8-dimethylnaphthalene in high conversion (75% with respect to dimethylnaphthalene). The same steric reasons probably exclude the formation of 1,2,8-trimethylnaphthalene by the same reactions from 1,7-dimethylnaphthalene, the 1,4,7- or 1,5,7-isomers being preferred.

Methylethylnaphthalenes. The mixture obtained by acetylation of 2-methylnaphthalene and subsequent reduction contained 39·4% 2-methyl-6-ethyl, 47·8%

1-ethyl-7-methyl-, 6·0% 1-ethyl-6-methyl-, 4·0% 1-ethyl-3-methyl-, and 2·8% 2-methyl-7-ethylnaphthalene. These results contradict the composition of mixture of acetyl-derivatives from 2-methylnaphthalene[41]. Structure of 1-ethyl-7-methylnaphthalene was determined by combination of the elution data obtained with a capillary column wetted with Apiezon L (this isomer is eluted with the same elution time as 1-methyl-7-ethylnaphthalene) and with a column wetted with *m*-bis(*m*-phenoxyphenoxy)benzene which enables separation of the two isomers due to different polarity. This fact agrees with similar conclusions concerning elution data of isomeric methylethylbiphenyls (ref.[48]). It is obvious that the 8 position in 2-methylnaphthalene is more activated than the next alternating position 6 with respect to acylation (the remaining alternating positions 1 and 3 can be excluded due to sterical requirements of the acylating complex solvated by solvent and to a certain sterical hindrance due to methyl group), although substitution at the 8 position should be suppressed by using nitrobenzene as solvent. The same method was used to convert 1-methylnaphthalene into a mixture of 1-methyl-4-ethyl- and 1-methyl-5-ethylnaphthalenes (97·7% and 2·3%, respectively); the presence of the latter was confirmed by independent synthesis from 1-acetylnaphthalene (chloromethylation, hydrogenolysis, and reduction), the presence of 1-methyl-2-ethyl-naphthalene was excluded by comparison with the above-given elution data. Preparation of isomeric methylethylnaphthalenes from 1- and 2-acetylnaphthalenes by chloromethylation, hydrogenolysis, and reduction suffered from a low conversion degree of the first reaction step and from formation of compounds of diarylmethane type. The final product did not contain methylethylnaphthalenes in concentrations above 10% (w/w), nevertheless these products were used to complement identification of methylethylnaphthalenes prepared by other ways. Thus in the reaction products from 2-acetylnaphthalene we identified 1-methyl-6-ethyl and 1-methyl-7-ethylnaphthalenes, whereas in the product from 1-acetylnaphthalene 1-methyl-5-ethyl- and 1-methyl-8-ethylnaphthalenes were found.

Cyclization of 2-(1-naphthyl)propionic acid by action of phosphoric acid and phosphorus pentoxide gave a mixture of perinaphthindan-1-one and benz[*e*]indan-3-one which was reduced to a mixture of 67·1% 2,3-dihydro-1*H*-phenalene and 32·9% benz[*e*]indan. Ratio of the former two ketones can obviously be affected by the choice of cyclization agent (application of liquid hydrogen fluoride according to ref.[49] gave the mixture of 93·1% perinaphthindan-1-one and 6·9% benz[*e*]indan-3-one). However, the presence of 2,3-dihydro-1*H*-phenalene in the analyzed sample is rather uncertain, because this substance is eluted at the same elution time as 9-methylfluorene, and no hydrocarbon of different molecular formula was found by GLC-MS in the peak of 9-methylfluorene.

The mixture of methylazulenes isolated from the high-boiling fraction of pyrolysis oil had the following composition: 49·7% azulene, 24·1% 2-methylazulene, 9·6% 1-methylazulene, 14·2% 4-methylazulene, and 2·4% (w/w) of an unidentified methyl-

azulene. The identification was carried out on the basis of known elution data[10]. With respect to negligible concentration in the sample of azulene itself, its methyl-homologues were not included in Table II.

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