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AROMATIC HYDROCARBONS FROM GEOLOGICAL SOURCES—I

NEW NATURALLY OCCURRING PHENANTHRENE AND CHRYSENE DERIVATIVES

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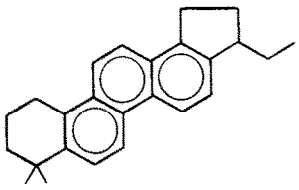
Abstract—The phenanthrene and chrysene derivatives 1 and 2 have been identified in the Messel oil shale by comparison with synthesized reference compounds. These molecules have most probably been formed by progressive geochemical aromatization of triterpene precursors of the hopane series which is widespread in the geological environment.

Aromatic compounds occur extensively in geological sources such as petroleum, coal, soils, oil shale and various other sediments.[1-7] Those which are related to steroids and triterpenoids from biological material can be particularly useful because structural comparison with their precursors is possible. This can give information on the geochemical pathways leading over disproportionation reactions to the fossil aromatic molecules, as well as on the stages of sedimentation in which such reactions occur and, in some cases, on the origin of these compounds. Pentacyclic compounds of this type containing one or more aromatic rings have been isolated from coal, brown coal and crude oil, but only a small number of these compounds has been fully characterized.[1,3]

A few years ago, we have noticed in the Messel oil shale (Eocene, 50×10^6 yr old; near Darmstadt, Germany) the presence of a series of pentacyclic compounds with various degrees of aromatization (1–4 aromatic rings).[8,9] We now wish to report the conclusive identification, by comparison with synthetic reference compounds, of two members of this series, the phenanthrene and chrysene derivatives 1 and 2.



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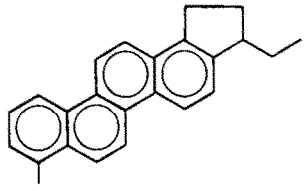

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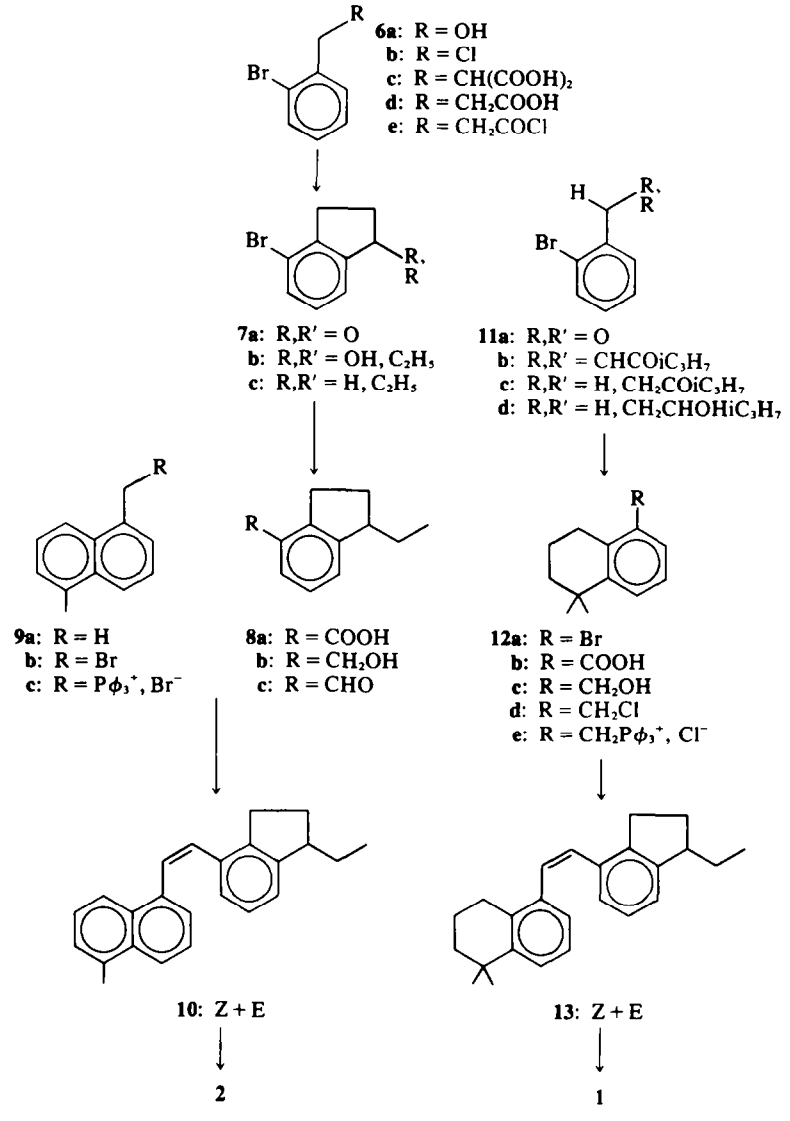
The crushed shale (500 g) has been extensively extracted with chloroform and the total extract separated into acidic and neutral compounds. The saturated, olefinic and aromatic hydrocarbons have been eluted from a silica gel column with pentane and further fractionated by thin layer chromatography on silica gel impregnated with silver nitrate and with picric acid. Small amounts of nearly pure compounds have been obtained from the various fractions by preparative gas chromatography.

The two reference compounds have been synthesized using the following Scheme 1.

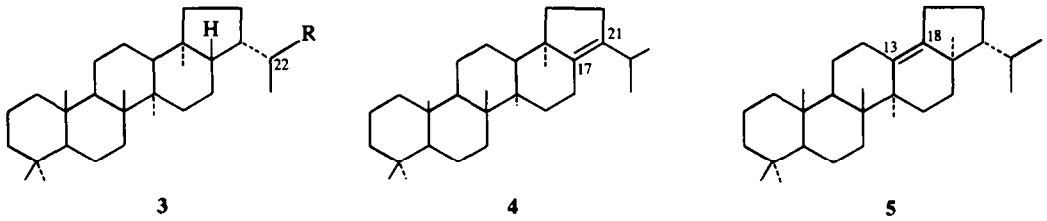
Full identification of the geological compounds with the synthetic samples is based on the following criteria: identical UV, NMR and mass spectra; co-elution on two packed glass columns (SE 30, OV 17) and two capillary columns (Apiezon L, OV 101).

Compound 2 has meanwhile also been identified in various other ancient sediments and one crude oil.[10] However the absence of compounds 1 and 2 in two recent sediments seems to indicate that these geochemical aromatization sequences probably do not occur in the very first stages of sediment formation.[10] The most reasonable hypothesis which can be put forward at this stage is that structures 1 and 2 arise from progressive aromatization of hopane derivatives 3 (hopane: R=CH_3), the ubiquitous occurrence of which in the geological environment can be explained on the basis of their microbiological origin.[11,12] This hypothesis is strongly favored by the presence in the Messel oil shale of significant amounts of olefins of the hopane series (mainly hop-17(21)-ene 4[13] and smaller amounts of "hopene-II" ($\Delta^{13(18)}$) 5[14] probably formed in the geological environment from 3-desoxyhopane precursors such as diplopterol (22-hydroxyhopane) or diploptene 3 (R=CH_2) which are widespread in living organisms, especially in microorganisms.[15-17] The position 13 (18) in ring D is also the ultimate, most stable, position of the double bond when olefins of the hopane series are treated in strong acidic conditions.[18] This would explain aromatization starting in ring D and progressively spreading over to ring A in contrast to other examples where aromatization is obviously induced by the loss of the usual functional group at position 3 on ring A of pentacyclic triterpenes.

The presence of an ethyl side chain in compounds 1 and 2 is intriguing, since it points towards a C_{29} precursor. However adiantone 3 (R=O), a C_{29} compound of the hopane series, has been identified previously in biological material.[18] This compound could either have entered the sediment as such or have been produced *in situ* in the sedimentary environment by microbial oxidation of



Scheme 1.



3 4 5

diploptene 3 (R=CH_2) which has been identified in various recent sediments.[19] Adiantone could then by well recognized geochemical reactions, such as reduction, dehydration and isomerization,[9] lead to a suitable C_{29} olefinic intermediate.

Further work aiming at the isolation of intermediates as well as the full identification of the mono- and di-aromatic compounds of the series present in the Messel oil shale is underway and should help to clarify some of our hypotheses.

EXPERIMENTAL

General. M.ps and b.ps are uncorrected. IR spectra were recorded on a Perkin-Elmer 257, UV spectra on a Cary 14 spectrophotometer. NMR spectra were obtained on a Varian A-60, a Perkin Elmer R 12B or a Brucker WA 90 instrument and chemical shifts are expressed in ppm from TMS as internal standard. Mass spectra were taken on a LKB 9000 S instrument. Gas chromatographic studies were made on a Varian 1700 or a Perkin-Elmer 990 using packed (1% OV 17, 1·5 m × 0·3 mm; 2% SE 30, 2 m × 0·3 mm) and capillary columns (OV 101, 30 m × 0·5 mm i.d.; Apiezon L, 30 m × 0·5 mm). All compounds gave satisfactory results on microanalysis and mass spectrometry.

Extraction and separation of the geological compounds. A sample of 500 g of powdered Messel oil shale was extracted with chloroform at 40° using ultrasonics. The extract (5·60 g) was separated into neutral and acidic compounds using silicagel impregnated with KOH.[20] The neutral fraction (4·35 g) was eluted over silicagel with increasing concentrations of EtOAc in

petroleum ether. Fractions containing hydrocarbons were re-chromatographed on silicagel (petroleum ether·benzene 4:1). Further purification and separation of the crude aromatic fraction (80 mg) was realized on silicagel impregnated with 10% $AgNO_3$ or with 10% picric acid. Finally preparative gas chromatography eluted the fractions with same R_f in thin layer chromatography as phenanthrene and chrysene (2% OV 1, 3 m × 0·6 mm) and yielded small amounts (~0·5 mg) of nearly pure **1** and **2**.

o-Bromobenzylchloride **6b**. Alcohol **6a** (22·8 g) and triphenylphosphine (33·4 g) were heated for 6 hr in CCl_4 under reflux. After removal of excess CCl_4, triphenylphosphine oxide cristallised out. Filtering and washing with petroleum ether gave **6b** (23·3 g). NMR ($CDCl_3$): 4·75 (2H, s), 7·3 (4H, m).

o-Bromobenzylmalonic acid **6c**. Compound **6b** (10·0 g) was added to a soln of NaOMe (from 2 g Na) in MeOH (75 ml) and dimethyl malonate (17·5 ml) and the mixture was refluxed for 2 hr. After cooling to room temp 75 ml of a 20% KOHaq was added and refluxing continued for 1 more hr. Neutral impurities were extracted with ether. The remaining soln was acidified with conc HCl and extracted with ether to yield acid **6c** (12·5 g), m.p. 143–144° from benzene/petroleum ether; IR (KBr): ν CO 1715 cm^{-1}; NMR ($CDCl_3$): 3·25 (2H, m), 3·70 (1H, m), 7·25 (3H, m), 10·9 (2H, broad).

3-(*o-Bromophenyl*) *propionic acid* **6d**. Diacid **6c** (12·5 g) was refluxed in dist. H_2O (100 ml) for 12 hr. Subsequent extraction with ether gave the crystalline acid **6d** (9·5 g), m.p.: 99–100° from chloroform/petroleum ether; IR (KBr): νOH 3300–2200 cm^{-1} (broad) νCO 1700 cm^{-1}; NMR ($CECl_3$): 2·9 (4H, m), 7·2 (4H, m), 11·6 (1H, s).

4-*Bromo-indan*-1-*one* **7a**. Acid **6d** (26·0 g) and $SOCl_2$ (25 ml) were heated at 40° with stirring for 0·5 hr. The excess of reagent was removed and anhyd methylene chloride was added to the acid **6e**. Anhyd $AlCl_3$ (30 g) was added over 1 hr with cooling in an ice bath. Stirring was continued for another hr and the mixture was poured on crushed ice. Extraction with benzene gave **7a** (20·3 g), m.p.: 97° (lit. 97°) from benzene/petroleum ether, IR (KBr): νCO 1710 cm^{-1}; NMR ($CDCl_3$): 2·9 (4H, m), 7·5 (3H, m).

4-*Bromo*-1-*ethyl-indan*-1-*ol* **7b**. Indanone **7a** (19 g) in anhyd diethyl ether (200 ml) was added to a soln of EtMgI prepared from diethyl ether (100 ml), EtI (11·8 ml) and Mg (3·6 g) under argon. After stirring for 2 hr the mixture was treated with a sat NH_4Cl aq and the usual work-up gave crude **7b** as a yellow oil (21·5 g). An analytical sample obtained by chromatography over silicagel with petroleum ether/EtOAc (95:5) melted at 59° (from petroleum ether at −20°). IR (KBr): νOH 3300 cm^{-1}; NMR ($CDCl_3$): 0·9 (3H, t), 2·0 (5H, m), 2·85 (2H, t), 7·25 (3H, m).

4-*Bromo*-1-*ethyl-indane* **7c**. Crude **7b** (21 g) in EtOAc (40 ml) was hydrogenolysed with PtO_2 as a catalyst (500 mg). After absorption of the theoretical volume of H_2, the catalyst was filtered off. Distillation gave **7c** (14·5 g), $b.p._{23\ mmHg}$: 123°; NMR ($CDCl_3$): 0·95 (3H, t), 1·3–2·5 (4H, m), 2·9 (3H, t and m), 7·1 (3H, m).

1-*Ethyl-indane*-4-*carboxylic acid* **8a**. To a mixture of Mg (0·5 g), anhyd ether (40 ml) and **7c** (2·30 g) under argon ethylene bromide (0·2 ml) was added to initiate the reaction. After 1 hr a stream of CO_2 dried over $CaCl_2$ was bubbled through the soln. Dil HCl was added and the ether layer was extracted with dil alkali. Acidification and usual work up gave acid **8a** (1·65 g), m.p.: 125·5–126·5° from ether/petroleum ether; IR (KBr): νOH 3400–2100 cm^{-1} (broad), νCO 1670 cm^{-1}, νC=C aromatic 1590 cm^{-1}; NMR ($CDCl_3$): 1·0 (3H, t), 1·3–2·5 (4H, m), 3·2 (3H, m), 7·3 (2H, m), 7·9 (1H), 12·0 (1H).

1-*Ethyl-indane*-4-*carbinol* **8b**. Acid **8a** (440 mg) in anhyd ether was reduced with LAH (200 mg) under reflux for 1 hr. After cooling a few drops of a saturated potassium and sodium tartrate soln were added. The white voluminous ppt was filtered off and washed successively with ether and chloroform. Evaporation of the solvents gave **8b** (370 mg) as an oil; IR (neat): νOH 3310 cm^{-1}; NMR ($CDCl_3$): 1·0 (3H, t), 1·2–2·5 (4H, m), 2·75 (4H, m), 4·5 (2H, s), 7·1 (3H, s).

1-*Ethyl-indane*-4-*carboxyaldehyde* **8c**. Carbinol **8b** (120 mg) and active MnO_2 (Merck; 200 mg) were stirred in pentane (20 ml) for 20 hr under argon. The mixture was filtered and gave the aldehyde **8c** in quantitative yield; IR (neat): νC–H ald. 2720 cm^{-1}, νCO 1690 cm^{-1}, νC=C arom. 1590 cm^{-1}, NMR ($CDCl_3$): 0·95 (3H, t), 1·2–2·7 (4H), 3·2 (3H) 7·4 (3H), 10·1 (1H, s).

Triphenylphosphonium salt of 1-*bromomethyl*-5-*methylnaphtalene* **9c**. This compound was prepared as described in the literature.[21]

(5 - *Methyl* - 1 - *naphtyl*)3 - *ethyl* 2-*cyclopenteno styrene* **10** (Z + E). To a soln of Na (50 mg) in MeOH (8 ml) were added successively the phosphonium salt **9c** (500 mg) and the aldehyde **8c** (200 mg in 2 ml of methanol). After stirring for 2 days under argon the MeOH was removed from the mixture which was chromatographed over silicagel with petroleum ether/benzene (75:25) to give a mixture of *cis* and *trans* isomers **10** (355 mg) as an oil; IR (neat): νC=C arom. 1590 cm^{-1}, νC–H arom. 785 cm^{-1}; NMR ($CDCl_3$): 0·85–2·2 (7H, m), 2·6–3·2 (6H), 6·6–8·0 (11H); UV cyclohexane: λ_{max} 265, 275, 320 nm.

7-*Methyl*-3'-*ethyl*-1,2 *cyclopentenochrysene* **2**. The mixture of isomers **10** (148 mg) in cyclohexane (120 ml) containing a little I_2 was photocyclised for 1 hr in a quartz apparatus using a high pressure mercury vapor lamp (Phillips HPK 125). On evaporation of the solvent compound **2** (141 mg) was isolated, m.p.: 236–238° from benzene; IR (KBr): νC=C arom. 1590 cm^{-1}, νC–H arom. 825, 790, 765 cm^{-1}; NMR (CCl_4): 1·05 (3H, m), 1·5–2·6 (4H, m), 2·8 (3H), 3·3 (3H), 7·2–8·8 (9H, m). UV EtOH: λ_{max} (log ϵ_{max}) 224 (4·55), 229 (4·52), 263 (4·91), 273 (5·14), 286 (4·14), 300 (4·14), 313 (4·18), 326 (4·16), 347 (3·23). Ms (70 eV): *m/e* = 310 (M, 52%); 281 (100%); 266 (24%); 265 (24%); 155 (4%); 140·5 (19%); 133 (15%).

1 - o - *Bromophenyl* - 4 - *methyl* - 1 - *penten* - 3 - *one* **11b**. A mixture of *o*-bromobenzaldehyde (4·1 g), methylisopropylketone (2 g), EtOH (4 ml) and a 25% NaOH aq (0·9 ml) was stirred for 1 day at room temp. After dilution with water extraction with benzene gave **11b** as a pale yellow oil in nearly quantitative yield, $b.p._{0.25\ mm\ Hg}$ = 172°. An analytical sample was obtained by chromatography over silicagel and microdistillation. IR (neat): νCO 1690 cm^{-1}, 1665 cm^{-1}, νC=C 1610 cm^{-1}, NMR ($CDCl_3$): 1·18 (6H, d, J = 7 Hz), 3·0 (1H, m), 6·5–8·1 (4H).

1 - o - *Bromophenyl* - 4 - *methyl* - *pentan* - 3 - *one* **11c**. The ketone **11b** (6 g) in EtOAc (20 ml) was hydrogenated over PtO_2 (200 mg). After the theoretical amount of H_2 was absorbed the catalyst was filtered off and evaporation of the solvent gave crude **11c** (5·9 g). An analytical sample was obtained as a colourless oil by chromatography over silicagel and distillation, $b.p._{0.28\ mm\ Hg}$: 150°. IR (neat): νCO 1710 cm^{-1}; NMR ($CDCl_3$): 1·05 (6H, d, J = 8 Hz), 2·4–3·2 (5H), 6·9–7·6 (4H, m).

1 - o - *Bromophenyl* - 4 - *methyl* - *pentan* - 3 - *ol* **11d**. The crude **11c** (2g) was dissolved in MeOH (50 ml) and treated at 0° with an excess of $NaBH_4$ (0·6 g). Work-up with ether gave crude **11d** which was purified over silicagel to yield 1·8 g of pure alcohol as a colourless oil, $b.p._{0.20\ mm\ Hg}$: 161°; IR (neat): νOH 3600 and 3390 cm^{-1} (broad); NMR ($CDCl_3$): 0·95 (6H, d, J = 7 Hz), 1·5–2·1 ppm (H, m), 2·9 ppm (H, m), 3·4 (1H, m), 6·8–7·6 (4H, m).

1,1 - *Dimethyl* - 5 - *bromo* - *tetrahydro* - 1,2,3,4 - *naphtalene* **12a**. The alcohol **11d** (400 mg) was added to polyphosphoric acid (5 g) and the mixture was heated to 150° for 15 min. After cooling, water was added and work-up with ether gave **12a** as a colourless oil (350 mg) which was purified by distillation, $b.p._{0.14\ mm\ Hg}$ = 160°; IR (neat): νC–H arom. 715, 735, 780 cm^{-1}; NMR ($CDCl_3$): 1·22 (6H, s), 1·4–2·0 (4H, m), 2·75 (t, J = 6 Hz), 6·7–7·5 (3H, m).

1,1 - *Dimethyl* - *tetrahydro* - 1,2,3,4 - *naphtalene* - 5 - *carboxylic acid* **12b**. The bromide **12a** (1·59 g) in anhyd ether (50 ml) was metalated by BuLi/halogen exchange (1 eq) at room temp. After 5 min a stream of dry CO_2 (from dry ice) was bubbled through the mixture for 30 min. The usual work-up gave **12b** (985 mg) contaminated with a little valeric acid, m.p. = 148–149° after one recrystallisation in hexane at −20°; IR (KBr): νOH 3400–2200 cm^{-1} (broad), νCO 1670 cm^{-1}, νC=C 1580 cm; NMR ($CDCl_3$): 1·3 (3H, s), 1·75 (4H, m), 3·2 (2H, m), 7·0–8·0 (3H, m).

1,1 - *Dimethyl* - *tetrahydro* - 1,2,3,4 - *naphtalene* - 5 - *carbinol* **12c**. The purified acid **12b** (1·13 g) was dissolved in anhyd ether (20 ml) and reduced with excess LAH (300 mg) at room temp. After 2 hr a few drops of a saturated soln of sodium and potassium tartrate were added. The white ppt was filtered and washed with ether and chloroform. Evaporation of the solvent gave pure **12c** (1·04 g); IR (neat: νOH 3600 and 3410 cm^{-1} (broad); NMR ($CDCl_3$): 1·3 (6H, s), 1·5–1·9 (5H, m), 2·75 (2H, m), 4·70 (2H, s), 7·2 (3H, m).

5 - (1,1 - *Dimethyltetrahydro* - 1,2,3,4 - *naphtyl)methylene* - *triphenyl phosphonium chloride* **12c**. The alcohol **12c** (1·04 g) in CCl_4 (60 ml) and excess triphenylphosphine (2 g) were refluxed for 2 days. The white ppt of phosphonium salt was filtered off and the CCl_4 evaporated. Again triphenylphosphine (1·5 g) and anhyd benzene were added to the residue, the mixture was refluxed for 2 days and the white ppt removed by filtration. In this way, 1·7 g of the phosphonium salt were obtained; NMR ($CDCl_3$): 1·25 (6H, s) 1·4 (2H, m) 2·0 (4H, m), 5·4 (2H, d, J = 13 Hz), 7·0–8·0 (18H, m).

5 - (1,1 - *Dimethyl* - *tetrahydro* - 1,2,3,4 - *naphtalene*) - 4(1 - *ethyl* - *indane*) - *ethylene* $Z + E$ **13**. The salt **12e** (562 mg) and the aldehyde **8c** (208 mg) were added to a soln of Na (50 mg) in MeOH (10 ml). The mixture was stirred for 1 day under argon. Extraction with benzene and chromatography over silicagel gave a mixture of stilbenes **13**; NMR (CCl_4): 1·0 (3H, t, J = 12 Hz), 1·3 (6H, s), 1·7 (8H, m), 2·85 (5H, m), 6·5–7·8 (8H, m).

(3' - *Ethylcyclopenteno* - 7,8)1,1 - *dimethyl*-*tetrahydro*(1,2,3,4)*chrysene* **1**. The mixture of stilbenes **13** (190 mg) in cyclohexane (100 ml) containing a little iodine were irradiated for 2 hr. Compound **1** (160 mg) was obtained after evaporation of the solvent, m.p. = 126·5–127·5° after two recrystillisations in hexane; IR (KBr): νC–H arom. 710 cm^{-1}; NMR ($CDCl_3$): 1·0 (3H, t, J = 12 Hz), 1·4 (6H, t), 1·8 (8H), 3·2 (5H, m), 7·3–8·5 (6H, m); UV (cyclohexane): λ_{max} (log ϵ_{max}), 257 (4·63), 265 (4·72), 285 (4·10), 296 (4·00), 308 (4·10). Ms (70 eV): m/e = 328 (M, 73%); 313 (70%), 299 (100%); 257 (23%); 255 (14%), 253 (12%); 229 (34%); 142 (31%); 128 (15%).

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