

## Perylene in basin sediments off southern California

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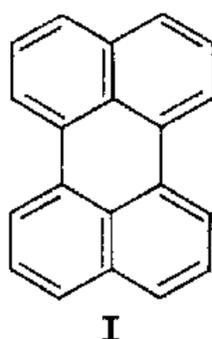
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**Abstract**—The distribution of perylene in basin sediments off southern California is reported and discussed in terms of the depositional environments. It is suggested that this hydrocarbon is formed by reduction of peri-hydroxyperylenequinone pigments of biological origin. The reduction to perylene takes place in anaerobic sediments after burial. The precursor quinones may be destroyed in oxidizing environments before burial in which case perylene may not be formed by later development of anaerobic conditions in the sediment.

### INTRODUCTION

DURING the course of work on hydrocarbon content of marine sediments off southern California (ORR and EMERY, 1956), the presence of polycyclic hydrocarbon perylene (I) was noted in some aromatic hydrocarbon fractions. This hydrocarbon is easily detected because of distinctive ultraviolet-visible absorption maxima which are at longer wavelengths than those of accompanying components. Perylene has been noted in Recent sediments also by other investigators (BLUMER, 1957; MEINSCHEN, 1959) but quantitative data have not been reported.



We have examined a few sediments from selected depositional environments and made semi-quantitative estimates of the perylene content. These results are discussed in terms of possible sources and the relationship of abundance to depositional environment. It is suggested that this hydrocarbon is formed by reduction of perihydroxy perylenequinone pigments of biological origin.

### EXPERIMENTAL

Extraction and chromatographic techniques were similar to those described previously (ORR and EMERY, 1956). Separations were made on activated alumina, eluting saturated hydrocarbons with n-heptane and aromatic hydrocarbons with

benzene. Minor amounts of O, N and S compounds were also eluted with benzene but the major portion of these "asphaltic" components were in subsequent fractions eluted by methanol. In the separations reported here, the volume of benzene was increased over that previously described and the aromatic eluant was collected in 60-90 small fractions. The perylene content of appropriate fractions was evaluated from the absorbance maximum at 440  $m\mu$  (in benzene) using the absorptivity reported by SCHNURMANN, MADDAMS and BARLOW (1953). The perylene content of the chromatographic fractions was quite low (*ca.* 2-10%), and the presence of other materials required an absorbance correction.

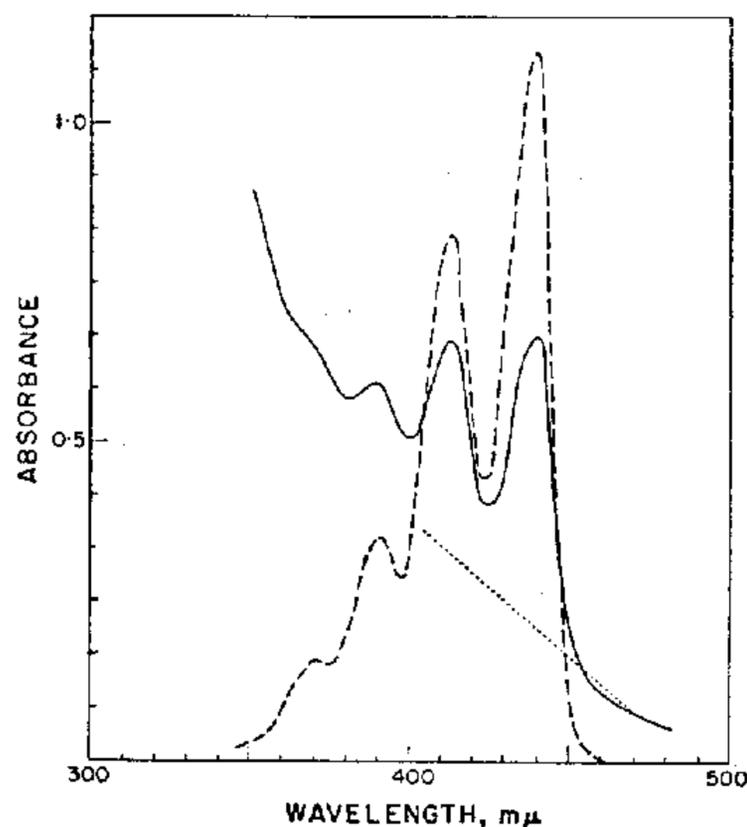


Fig. 1. Absorption spectra. Solid line: sediment fraction containing perylene. Dashed line: perylene. Dotted line: background correction for sediment fraction (see text).

Extraneous components cause a sharp increase in absorbance with decreasing wavelength in the region of 450-350  $m\mu$ . This can be seen in Fig. 1 by comparing the spectrum of a typical perylene containing fraction (solid curve) with the spectrum of pure perylene (dashed curve). The absorbance of extraneous components was approximated by the dotted line (Fig. 1) and was determined as described below. Absorbance at 470  $m\mu$  was assumed to be due entirely to extraneous components. Background absorbance was assumed to be linear from 470 to below 413  $m\mu$  and the slope of the line was drawn so that the ratio of the absorbance at 413  $m\mu$  to the absorbance of 440  $m\mu$  above the line corresponds to the ratio of pure perylene (0.74). The perylene content of each fraction was then calculated from the absorbance at 440  $m\mu$  above the correction line. Extraneous absorbance may not be linear and this approximation probably leads to a slight underestimation of the perylene content. However, failure to correct for the extraneous absorbance would lead to a greatly overestimated perylene content.

Confirmation that the spectrum is actually due to perylene rather than alkyl substituted perylenes was obtained by mass spectra. Figure 2(A) shows the mass spectrum of pure perylene. There is a strong molecular-ion peak at mass 252 and

also strong peaks corresponding to  $M + 1$  and  $M - 2$  (masses 253 and 250). Figure 2(B) shows the mass spectrum of a typical perylene containing fraction. The corresponding strong peaks at masses 252, 250 and 253 are evident and establish that unsubstituted perylene is the major polycyclic aromatic hydrocarbon in the fraction. The high background at other masses indicates a large number of other components, each present in small amounts relative to perylene.

### RESULTS AND DISCUSSION

EMERY (1960) has discussed the basins off southern California in detail and pointed out the environmental factors bearing on the accumulation and preservation of organic matter in their sediments.

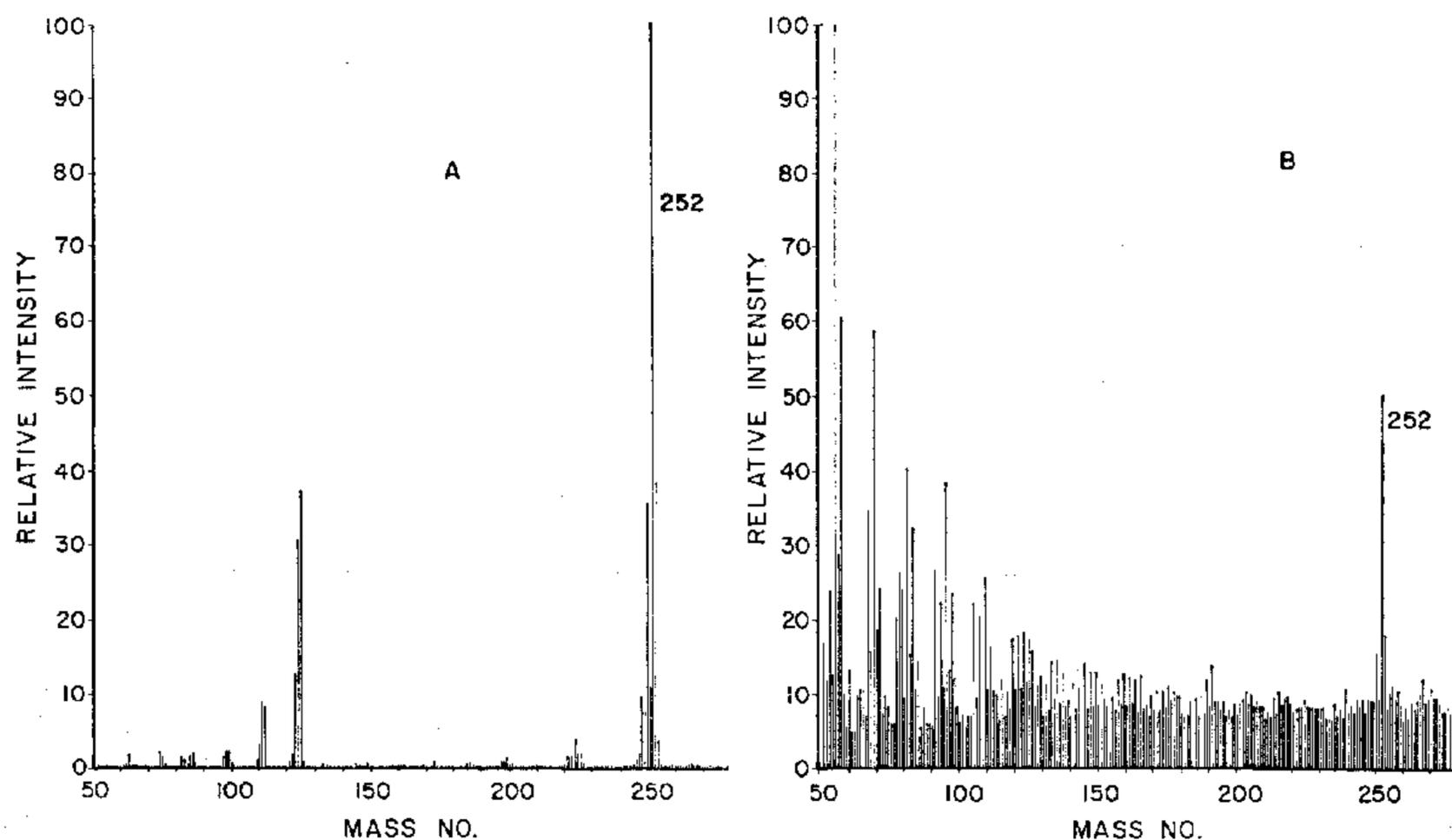


Fig. 2. A. Mass spectrum of perylene.  
B. Mass spectrum of sediment fraction containing perylene.

A great deal of study has been given to the distribution of various organic components in these sediments. Hydrocarbon distribution was first reported by ORR and EMERY (1956). A more detailed study of saturated hydrocarbons was made by BRAY and EVANS (1962). Pigments related to chlorophyll were studied by ORR, EMERY and GRADY (1958). KAPLAN, EMERY and RITTENBERG (1963) measured the distribution of sulfur isotopes in sulfur compounds and made some observations on organic sulfur compounds. DEGENS, REUTER and SHAW (1964) measured the distribution of various biochemical compounds (amino acids, sugars, phenols and indoles in the sea water and sediments. SCHWENDINGER and ERDMAN (1963, 1964) included some southern California basin sediments in their study of the distribution of carotenoid pigments and sterols in Recent sediments. Sediments from the San Nicolas and Tanner basins were included in a study of fatty acids and n-paraffins in some Recent and ancient sediments (KVENVOLDEN, 1966).

The Santa Barbara, Tanner, and San Clemente basins chosen for this study

represent a wide range of conditions of water depth, sedimentation rate, and oxidation potential ( $Eh$ ) in the sediment. Sediment grain size is similar in all three basins. Organic content is high in these sediments; the Tanner Basin being higher than the other two. Some of the average properties of the basin floor sediments are collected in Table 1

Nine Recent sediment samples from these three offshore basins have been examined for their perylene content. Results are given in Table 2. All sediment samples

Table 1. Some characteristics of basin floor sediments\*

	Santa Barbara Basin	Tanner Basin	San Clemente Basin
Water depth (m)			
Basin floor	627	1551	2107
Sill	475	1165	1816
Average sedimentation rate (mg/cm <sup>2</sup> per yr)	90	11.2	23.6
Median dia. ( $\mu$ )	4.5	4.8	4.0
Calcium carbonate (wt. % of dry sediment)	11.6	34.4	14.4
Organic matter (wt. % of dry sediment)	5.8	11.7	5.7
Hydrocarbons ( $\mu$ g/g of dry sediment)	240	98	43
Green pigments ( $\mu$ g/g of dry sediment)	103	39	5
Depth to $Eh = 0$ in sediment cm	0	0-10	>300

\* Data from EMERY (1960), Tables 7, 14 and 20.

except one were from basin floors, near maximum depth in each basin. Core 3504 was the exception. It was from the slope of the Santa Barbara Basin near sill depth.

The sample listed as "tar seep" in Table 2 was from an active submarine tar seep producing tar mounds off Point Conception. These seeps were described by VERNON and SLATER (1963). The sample was a portion of a shallow core taken near a tar mound. The tar seeps through fractures in gently dipping beds of upper Miocene-lower Pliocene clay shale and is probably typical of other submarine tar seeps in the area. The negligible perylene content of the tar suggests that perylene found in the sediments does not have its source in the tar and oil seeps.

Perylene is quite abundant for an individual hydrocarbon in the Santa Barbara Basin floor samples. It makes up from about 0.04 to 0.20% of the total hydrocarbons. Only traces of perylene were found in the Tanner Basin sediment and the hydrocarbon could not be detected in the San Clemente Basin sediment. This abundance trend is similar to that for chlorophyll derivatives (ORR, EMERY and GRADY, 1958; cf. green pigments in Table 1) and other sensitive biochemical components.

The Santa Barbara Basin has the highest sedimentation rate, the shortest water column (depth), and the lowest oxygen content in the bottom water. Benthonic organisms are scarce or absent and hence their activity does not consume organic matter or stir the sediment. Thin laminations, probably annual or seasonal layers, are preserved in this sediment (EMERY, 1960). The net result of these factors is to

Table 2. Perylene content of basin sediments off southern California

Core No.	Location (lat. N. long. W.)	Basin and depth in core (cm)	Water depth (m)	Total hydrocar- bons‡ based on dry sediment (µg/g)	Perylene (µg/g) based on		
					Dry sediment†	Extracted org. matter	Total hydro- carbons
Santa Barbara							
AHF 2622	34°13.5' 120°01.9'	0-50	600	208	0.078	31	370
AHF 3503	34°13.5' 120°02.2'	51-81	600	212	0.086	—	410
FRL 163G	34°11.0' 120°03.0'	76-150	580	144	0.244	169	1690
AHF 2622	34°13.5' 120°01.9'	124-137	600	133	0.260	150	1950
AHF 3504	34°08.9' 120°01.6'	0-50	493	—	<0.0002	—	—
Tanner Basin							
AHF 4696	32°57.4' 119°44.5'	3-38	1510	166	<0.001	—	—
AHF 4696	32°57.4' 119°44.5'	64-152	1510	89	<0.001	—	—
AHF 4696	32°57.4' 119°44.5'	305-331	1510	39	<0.001	—	—
San Clemente							
AHF 3669	32°37.7' 118°07.5'	0-5	2060	43	<0.0002	—	—
Tar seep	34°26' 120°23.7'	Near Point Conception*	27	—	—	<0.0002	—

\* Tar seeps described by VERNON and SLATER (1963). Sample furnished by J. W. VERNON.

† Detection limit was about 0.0002 µg/g for the sample size used.

‡ Total hydrocarbons refers to higher molecular weight saturated and aromatic hydrocarbons determined as described by ORR and EMERY (1956).

create an anaerobic environment ( $-Eh$ ) extending to the sediment-water interface. Rapid sedimentation, low oxygen content in the water, and an anaerobic sediment result in the preservation of a larger proportion of materials which are easily oxidized.

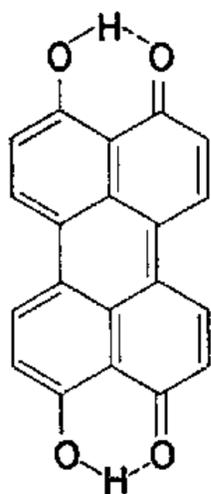
It is also interesting to note that the perylene content increases sharply with depth in the Santa Barbara Basin sediment. This trend is opposed to that observed for chlorophyll derivatives and other biochemical components which usually decrease in abundance with depth of burial (EMERY, 1960). This contrast suggests that perylene is being formed after burial by a relatively slow process.

The low perylene content of the sample from the Santa Barbara Basin slope at about sill depth (AHF 3504) is of special interest. This sediment has about the same grain size (medium dia.  $4.5 \mu$ ) and organic content as the basin floor sediment. The source of organic and inorganic detrital materials is expected to be similar. Major differences must be attributed to the slightly higher oxygen content of the bottom water and the presence of burrowing organisms which consume detrital organic matter as food and mix the sediment with oxygen containing water. This core differs from the basin floor cores in having a positive  $Eh$  to a depth of about 30 cm in the sediment.

In spite of the high organic content of the Tanner Basin sediment and the development of a negative  $Eh$  near the sediment surface, the perylene content was found to be low. An increase in perylene with depth of burial, as observed in the Santa Barbara sediment, was not detected in this sediment. This may suggest that the perylene precursors do not survive initial burial because of the longer water column, higher oxygen content of the bottom water, and the slower sedimentation rate.

These observations are consistent with the hypothesis that perylene is formed in anaerobic sediments by reduction of non-hydrocarbon precursors of biological origin which are sensitive toward oxidative destruction during sedimentation.

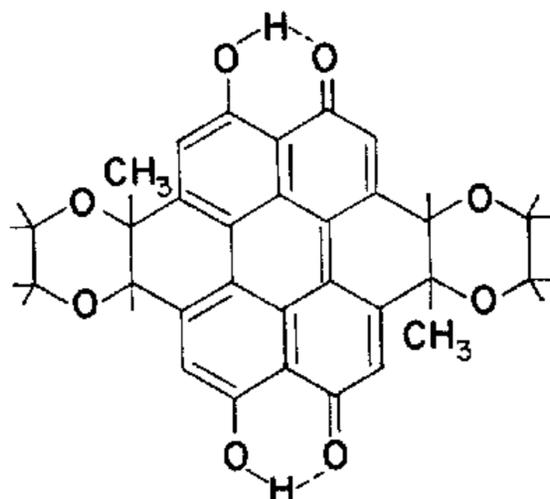
Reasonable biological precursors are found in the extended quinones related to 4,9-dihydroxyperylene-3,10-quinone (II). This hydroxyquinone (II) was isolated from the fungus *Daldinia concentrica* (ANDERSON and MURRAY, 1956; ALLPORT and BU'LOCK, 1960). A closely related pigment was isolated from another fungus by READ *et al.* (1959) but the structure was not completely established. Chemical reduction of both of these pigments gives the hydrocarbon perylene.



II

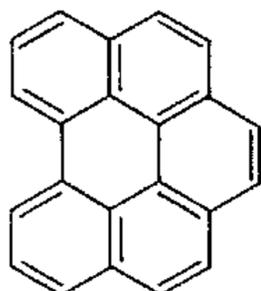
Other related perylene-quinone pigments are the erythroaphin pigments isolated from insects of the *Aphididae* family. These pigments have been extensively studied

by Todd and coworkers (THOMPSON, 1957). Erythroaphins are a group of closely related pigments which have the general structure III. Except for the exact positions and steric arrangement (cis-trans relationships) of the methyl groups in the various isomers, the structures are firmly established.

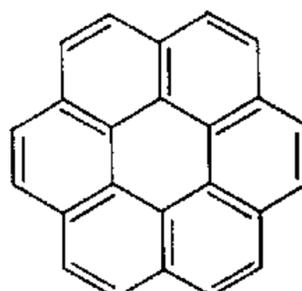


III

Chemical reduction of erythroaphin pigments gives perylene (I) as well as small amounts of 1,12-benzperylene (IV) and coronene (V). The latter two hydrocarbons have been observed also in Recent sediments (MEINSCHEIN, 1959). The reductive elimination of substituents such as those in positions 1, 6, 7 and 12 of III is a general property of perihydroxyquinones so that the reductive formation of unsubstituted perylene from III is not surprising (THOMPSON, 1955).



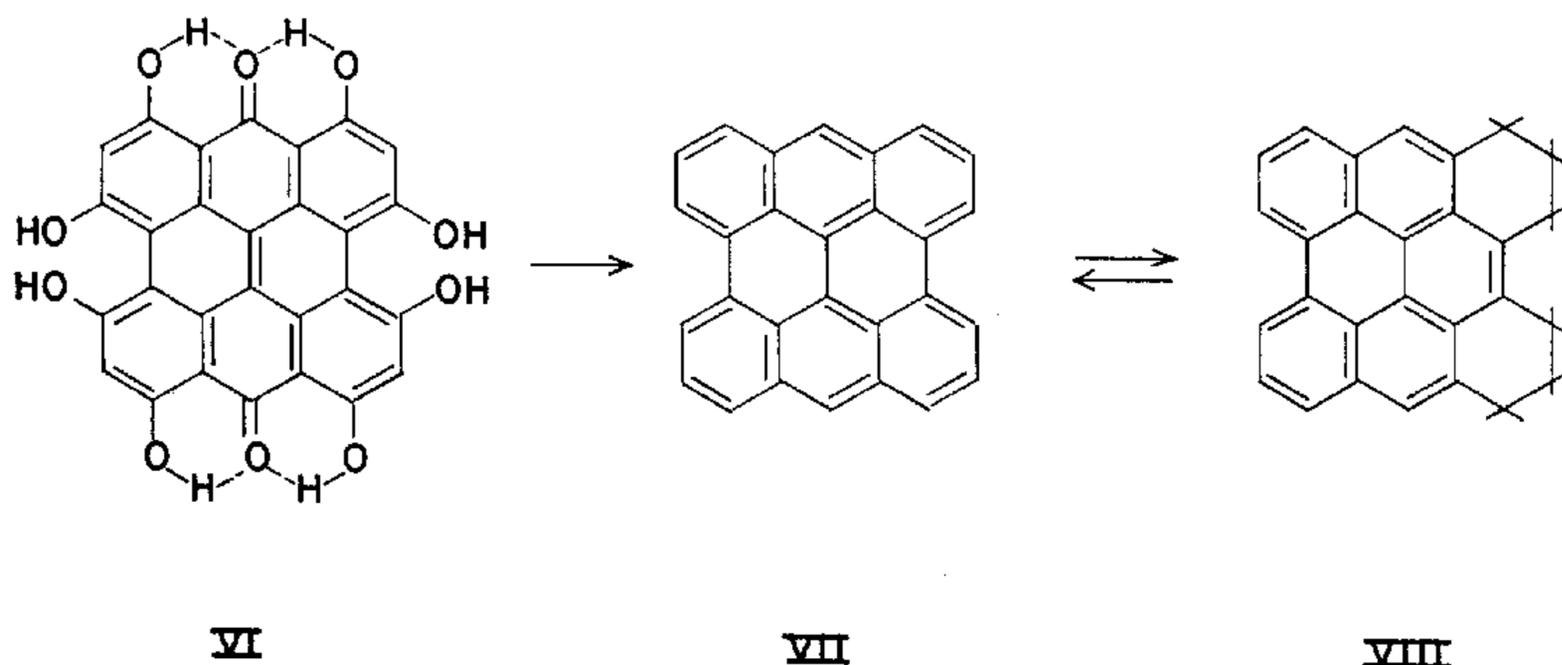
IV



V

The proposed reduction of peri-dihydroperylenequinone pigments to perylene is analogous to the reactions proposed by BLUMER (1965) to account for the hydrocarbon-pigment assemblage in a Jurassic crinoid fossil. The pigment VI (fringelite D) was proposed to be reduced through a series of peri-hydroxyquinones to VII and further to VIII (hexahydromesonaphthodianthrene). The oxygen containing pigments were still present in larger amounts than the hydrocarbons in the fossil crinoid. This indicates a very slow reduction in these macrofossils. Since we have not attempted the isolation of corresponding perylene precursors from the Recent sediments, comparison on this point cannot be made. However, the rate of reduction in the Santa Barbara Basin sediment is certainly much faster than would be expected from the behavior of the fringelite pigments in the fossil crinoid. This difference could reflect an earlier and more facile exposure to effective reducing agents such as the hydrogen sulfide-polysulfide system in the finely divided sediment.

Although the proposed biological source of perylene precursors is reasonable and attractive, other sources cannot be dismissed. So little is known about organic



chemical reactions which occur in sediments that other possible sources cannot be eliminated (e.g. condensation reactions).

Perylene and other polycyclic aromatic hydrocarbons are common pyrolytic products of organic matter and are common atmospheric contaminants. The transfer of combustion products from the atmosphere to the basin sediments is not likely to be quantitatively important and the perylene distribution observed could not be explained easily on this basis.

It is not considered likely that the perylene in the Santa Barbara Basin sediment is derived from submarine tar or oil seeps. Analysis of the tar from one of these seeps (Table 2) failed to show a detectable amount of perylene. Perylene has been reported present in some petroleums (SCHNURMANN, MADDAMS and BARLOW, 1953; CARRUTHERS and COOK, 1954) but the amounts are so small that enough petroleum to supply the perylene found in this sediment would also lead to a hydrocarbon distribution greatly different from that which is present (BRAY and EVANS, 1962).

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