

THERMAL ALTERATION OF ORGANIC MATTER IN RECENT MARINE SEDIMENTS

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ABSTRACT

Sediment from Tanner Basin, the outer continental shelf off southern California, was analyzed for photosynthetic pigments and their derivatives, namely carotenenes and chlorins. Samples of the sediment were also exposed to raised temperatures (65°, 100°, 150°C) for various periods of time (1 week, 1 month, 2 months). Analysis of the heat-treated sediment revealed the presence of α -ionene and 2,6-dimethylnaphthalene, thermal-degradation products of β -carotene. Chlorins were converted to nickel porphyrins of both DPEP and etio series. Possible mechanisms of these transformations are presented.

INTRODUCTION

The work reported here forms part of a series of investigations regarding the fate of naturally-occurring lipids and pigments in marine sediments exposed to elevated temperatures.

We have chosen two environments for our study. One is a very young sediment collected from shallow water 400 m directly off the mouth of Rio Ameca, Bandaras Bay in the Eastern Gulf of Mexico (Drever 1971), which contains 1.65% organic carbon and is known to have a large terrigenous component in the organic matter. The other is from Tanner Basin, 200 km from shore in the outer continental shelf off southern California at 1,500 m water depth (Emery 1960). The organic carbon content is relatively high (11.7% dry weight) and it is mainly marine in origin (Aizenshtat 1973).

These sediments provide useful models for thermal alteration studies, as the compounds identifiable in the natural sediment can be compared with those present in the same sediment after laboratory thermal treatment, and may yield useful information on degradative pathways occurring during diagenesis and metamorphism. This approach might also reveal the biological, chemical, and physical history of ancient sediment.

The aim of the present report is to establish the pattern of change undergone by certain photoreactive pigments (carotenoids and chlorophylls) in sediments, when exposed to raised temperatures.

Few such studies have been made on heat-treated unlithified sediments. Day and Erdman (1963) subjected a marine sediment to

elevated temperature and identified α -ionene as a product of carotenoid breakdown. Hoering (1967) analyzed a recent marine sediment (San Nicholas Basin) which had been extracted with benzene-methanol, dried and heat-treated in a sealed bomb. Of particular interest to the present study, was the production of two homologous series of porphyrins in these experiments.

Carotenoids are ubiquitous in nature. They occur in plants and algae, in photosynthetic and in some non-photosynthetic bacteria, in fungi and in ahermatypic corals (Jensen 1962; Fox 1972). Carotenoids were first reported in marine sediments by Trask and Wu (1930). Comprehensive reviews on the fate of carotenoids have been given by Vallentyne (1960) and Erdman (1961). A number of fresh water and marine sediment cores have been analyzed for carotenoids as a function of depth (Fox et al. 1944; Vallentyne 1956). The data so obtained suggest that carotenoids are relatively stable in wet sediments. The oldest unaltered carotenoid-containing sediments yet discovered are estimated to be between 20,000 and 100,000 years old (Anderson and Gundersen 1955; Vallentyne, 1957). One notable fact about sedimentary carotenoids is the apparent lack of cis-isomers, an observation first made by Vallentyne (1956). Fox et al. (1944) and others have pointed out that factors which tend to favor the preservation of carotenoids and also hdroporphyrins in wet sediments are: lack of oxygen and light, low temperature and the water-insolubility of the components. The identification of the saturated hydrocarbon, perhydro- β -carotene in the Eocene Green River Shale illustrates the stability of β -carotene in a reducing environment

(Murphy et al. 1967). Day and Erdman (1963) have speculated on the role sediment carotenoids may play as progenitors of petroleum. These speculations were based on the fact that thermal treatment of β -carotene in organic-rich sediment yielded small amounts of aromatic hydrocarbons of low molecular weight, namely, toluene, m-xylene, 2,6-dimethylnaphthalene and α -ionene.

The green pheophytin pigments (chlorins) in recent sediments, are believed to have originated from chlorophylls. The change of chlorophylls into porphyrins involves a number of steps, including loss of magnesium, loss of the phytyl chain (pheophorbide), dehydrogenation and re-complexing with other metals. The first two stages take place in sediments during early diagenesis (Corcoran 1957).

The alteration of the metallic constituent of chlorophyll could take place either by direct replacement of magnesium by another metal, or formation of a free chlorin pigment which is later re-complexed with other metals such as nickel or vanadium. The conversion of chlorin to a porphyrin can be accomplished by a reduction of both, the vinyl group at position 2 of the basic structure, and the carbonyl group at position 9 in the isocyclic ring, and subsequent spontaneous dehydrogenation at positions 7 and 8 (Figure 1).

EXPERIMENTAL

Sample Handling

The sediments were frozen after collection until analyzed. The entire sediment was homogenized then divided into aliquots for exposure to different temperatures. Fifty-gram samples

(wet weight) were transferred to thick-walled glass tubes, the tubes frozen, flushed with nitrogen and sealed. The sealed bombs were heated at 65°, 100° and 150°C for 7, 30 and 64 days, respectively. One sample was freeze-dried prior to heating.

Analytical Procedures

In each sample, the following procedures were developed to determine hydrocarbons, fatty acids and esters, alcohols, sterols, chlorins and porphyrins. In some cases, other compounds were also identified, such as: triterpenes, steranes, resin acids and ketones.

Extractable organic material was removed from the sediment with benzene-methanol (70:30) using a Virtis homogenizer. A detailed description of the extraction procedure is given by Aizenshtat et al. (1973). A crude separation of the extract was achieved by silicic acid chromatography (Figure 2). Reported here are methods used for identification of carotenes, chlorins, porphyrins and related compounds.

The visible absorption spectrum of the hydrocarbon fraction, containing β -carotene was determined using a Cary 14 Spectrophotometer equipped with a 0.1 cc microcell, and major absorption bands were observed at 438, 452, 485 nm. The amount present was calculated using the absorbance at 452 nm and the extinction coefficient of 13.8×10^4 1/mole/cm (Karrer and Jucker 1950). The purity of β -carotene isolated from the sediment was examined by TLC on silica gel G plates (0.25 mm) using pure β -carotene as a reference and developing with petrol ether-benzene (50:50), $R_f = 0.96$. Mass spectrum of β -carotene was determined on an

AEI MS-9 spectrometer at 70 and 20 ev and 225°C.

α -Ionene (1,1,6-trimethyl-1,2,3,4-tetrahydronaphthalene) was synthesized from α -ionone by the method of Bogert and Fourman (1933) and checked for purity of GLC. Co-injection of α -ionene and 2,6-dimethylnaphthalene with the hydrocarbon fractions confirmed their presence in the heat-treated samples. Furthermore, the mass spectrum of α -ionene in the hydrocarbon fraction was obtained using a Varian model 1200 gas chromatograph coupled with a 21-491 CEC mass spectrometer. The 5'X1/8" stainless steel chromatographic column was packed with 3% OV-101 on 100-120 mesh Gas Chrom Q and programmed from 50° to 300° at 4°/min.

The chlorins, which were in the methanol fraction of the silicic acid column (Figure 2), were quantitatively determined using the visible absorption band at 665 nm, and $E = 3 \times 10^4$ l/mole/cm (Goedheer 1966). Separation of pheophytins and pheophorbides was achieved by TLC. The chlorin mixture in acetone was spotted on silica gel G (0.25 mm) plates and developed with chloroform-benzene-acetone (100:40:20). Observation under ultraviolet light revealed the presence of three red zones. The upper ($R_f = 0.95$) corresponds to dihydro-pheophytin a, a middle zone ($R_f = 0.81$), to dihydro-pheophytin b and the lower one to ($R_f = 0.54$) pheophorbides.

The concentration of porphyrins was calculated from visible spectra using the Soret peak at 390-408 nm and the extinction coefficient of 3.3×10^5 l/mole/cm (Hodgson et al. 1968).

A portion of the benzene fraction from the silicic acid column containing porphyrins was purified on a micro column (0.5X7 cm) packed with activated silica gel. Elution with

benzene removed the major portion of porphyrins. The elution was made in a dark room to minimize decomposition and could be followed by the bluish-pink fluorescence of porphyrins under ultraviolet light. The R_f value of 0.9 - 1.00 for porphyrins (silica gel G: developing with chloroform-benzene [2:1]) indicate that these porphyrins contain no polar groups. Porphyrins isolated from crude oil had similar chromatographic characteristics.

Mass spectra of chlorins and porphyrins isolated from sediment and purified by micro-column and thin-layer chromatography were obtained on a AEI MS-9 spectrometer. The temperature of the source for a typical run was 210-230°C using beam energies of 70 and 15 ev.

RESULTS

Carotenoids

Quantitative data of β -carotene from Tanner Basin are given in Table 1. The trans- β -carotene originally present in the sediment appeared to increase after being kept at room temperature for two months. It could also withstand heating to 65°C, however, heating to 100°C or higher caused complete degradation (see Figure 3), and resulted in formation of α -ionene as an end product. Heating of the freeze-dried sample produced 2,6-dimethylnaphthalene as well as α -ionene. These compounds most likely were formed by cyclization of the polyene chain of β -carotene (see Figure 4). α -Ionene could not be identified (by GLC) in samples treated at 65°C and 100°C, but was found in all three samples heated to 150°C. The amount increased from 16 μ g/100 g

for 7 days' heat treatment to $140\mu\text{g}/100\text{ g}$ for 2 months' treatment.

β -Carotene was also identified in the Bandaras Bay original sediment in the amount of $36.8\ \mu\text{g}/100\text{ g}$. As in the Tanner sediment, complete degradation occurred by heating to 100°C .

Mass spectra of β -carotene from a pure sample (from J.T. Baker Chemical Co., Phillipsburg, N.J.), or from the sediment, displayed a strong molecular ion of mass 536 and two main fragments at $m/e\ 444$ (loss of toluene 92) and at 378 (loss of dimethylnaphthalene, 158). These results are in accordance with the recent mass spectrometric studies of deuterated carotenoids by Kj \ddot{o} sen and Liaaen-Jensen (1971), and thus support the elimination reactions mentioned above.

The molecular ion of α -ionene appeared at $m/e\ 174$ in the mass spectrum (Figure 5); it loses methyl groups to first form 1,6-dimethyl-1,2,3,4-tetrahydronaphthalene and later after further loss of methyl groups forms a carbonium ion, stabilized by the aromatic ring, which rearranges to the tetrahydroazulenium ion (Figure 6).

Chlorins and Porphyrins

Data for chlorins and porphyrins identified in the Tanner sediment are given in Table II and Figures 7 and 8. Chromatographic and spectroscopic studies of the tetrapyrrole-type pigments of Tanner Basin reveal that pheophytins ($\text{H}_2\text{P}_\text{C}\ \text{COOR}$) (P_C refers to "pigment chlorin") and pheophorbides ($\text{H}_2\text{P}_\text{C}\ \text{COOH}$) are the predominant pigments of the natural sediment (Fig. 1) which is in accordance with the results of Orr and Grady (1957), Corcoran (1957), Vallentyne (1960) and Baker and Hodgson (1968).

Both pheophytins a and b were isolated by TLC and identified by MS. The mass spectrum of pheophytin a (upper TLC band) had a molecular ion of 872, indicating it is probably dihydropheophytin. A 594 peak (loss of 278, phytadiene) is presumed to arise via a mechanism proposed for the formation of pheophorbide (Budzikiewicz et al. 1964). Furthermore, a peak at 884 (middle TLC band) indicates the presence of dihydropheophytin b (Baker 1970). The lower TLC band had peaks at 577 and 579, which correspond to pheophorbide a (M-15) and its dihydro analogue.

No chlorophyll could be detected in the Tanner Basin or Bandaras Bay. Chlorophyll is not usually preserved in sediments, however, its presence has been reported in areas of rapid deposition by Corcoran (1957) and by Koyama et al. (1968). Nissenbaum et al. (1972) detected chlorophyll a in sediments from the Dead Sea, which they attributed to slow degradation of organic matter and to high concentrations of magnesium in the water. It has generally been assumed that saponification of the phytol ester linkage occurs very early in the diagenetic process. Our study presents evidence for the preservation of ester linkage under mild thermal treatment, to 100°C for short periods of time.

After heat treatment of the sediment, comparison of the newly-formed pigments with those extracted from the original sediment (standard sample) indicated a severe destruction of the components (chlorins) responsible for the 667 nm absorption maxima (Fig. 8) at 397, 407 (soret peaks) and 518, 555 and 580 nm (non-soret peaks). In some cases, an intermediate stage

was also observed, with the chlorin band at 655-658 nm (Figure 7; curve 4) which is characteristic of the nickel complex of pheophytin (Hodgson et al. 1960).

The absorption spectra of the newly-formed pigments after heating are very similar to nickel porphyrin complexes extracted from crude oils. The presence of nickel porphyrins in our heat-treated samples was confirmed by comparing mass spectra with those published by Baker et al. (1967). The mass spectral data of the metallo-porphyrin fraction isolated from heat-treated sediment had the following peaks: 476, 490, 504, 518, 532, 546, 560, 574, 588, 602 (at low ev), which corresponds to M-2 (DPEP) series of nickel alkyl porphyrins, and 478, 392, 506, etc.....590, 604 correspond to the M(etio) series.

Two series of odd-numbered peaks observed in the mass spectrum in the range 429-625 and 431-627 m/e may be due to vanadyl alkyl porphyrins (Yen et al. 1969; Blumer and Rudrum 1970), however, identification at this time is tentative.

Examination of Table II shows a gradual increase in porphyrins, as the temperature is raised and time of heating is increased. The amount of porphyrins formed in the sediment (667 $\mu\text{g}/100\text{ g}$) at 150°C for 2 months) was significantly lower than the amount of chlorin in the starting material (2070 $\mu\text{g}/100\text{ g}$). The loss of chlorins is probably due to the several reactions they undergo during heating, such as oligomerization and bonding with high molecular weight humic acids, kerogens, etc. present in the sediment. Blumer and Snyder (1967) have presented evidence for dimeric porphyrin structures in some oil shales. More recently, Blumer and Rudrum (1970) identified porphyrins having 43-44 carbon atoms substituted upon the tetrapyrrole ring. Hoering (1969)

recently stated that chlorophyll residues may be bonded into the marine humic acid and are liberated as free porphyrins on reduction. In the present study, mass spectral data indicate larger molecules might also be present, however, no convincing characterization was achieved.

DISCUSSION

The objective to the present study was to determine the fate of carotenes and tetrapyrroles in sediments which have been exposed to raised temperatures for different periods of time.

In samples heated to 100°C or higher, β -carotene could not be detected. Two transformation products of β -carotene, α -ionene and 2,6-dimethylnaphthalene, were detected in the heat-treated samples. The quantity of α -ionene increased with time and temperature. These same hydrocarbons have been shown to form in cigarette smoke by Edmunds and Johnstone (1965) during combustion of tobacco.

Using thin-layer chromatography, absorption spectroscopy and mass spectroscopy, we separated and identified dihydro-pheophytins a and b, and pheophorbide a from Tanner Basin sediment. The major chlorophylls are unstable and are incorporated into the sediment primarily as pheophytins. In this study, we were unable to determine the rate at which this conversion occurs. Pheophytin is generally hydrolyzed to pheophorbide during early diagenesis, although in rapidly-sedimenting and reducing environments, pheophytin can be preserved (Baker 1970; Aizenshtat et al. 1973). The loss of chlorin pigments during diagenesis is a function of several environmental factors such as pH, redox,

temperature and biological activity. The relatively small conversion (20-30%) of chlorins to prophyryns, may be due to their thermochemical grafting onto relatively polar humic and fulvic acids, which may then cause them to become insoluble, and hence non-extractable.

Conversion of free chlorins to metal complexes appears to occur quite rapidly in sediment at temperatures of $\sim 65^{\circ}\text{C}$ without the addition of Ni or lowering of pH as performed by Hodgson et al. (1960). It is noteworthy that Hodgson et al. (1960) first pointed out the apparent ease with which the nickel complex of pheophytin can form, and suggested that at 10°C , only a few decades would be required for the formation of significant amounts of the complex.

We assume that the overall reaction path in our laboratory simulation experiments is the entry of nickel (and possibly V) into free chlorins (which are abundant in the sediment) followed by reduction and dehydrogenation to metallo-porphyrins. However, as suggested by Hodgson et al. (1960), prior formation of free porphyrin, which then forms a complex with other metals, especially with vanadium, cannot be excluded.

As the porphyrin ring system is remarkably stable due to its aromaticity, it is interesting that increase in molecular weight occurs due to addition of alkyl to the tetrapyrrole nucleus. Baker et al. (1967) and Eglinton et al. (1971) have considered trans-alkylation by ionic or free radicals as the mechanism for adding alkyl groups to the porphyrin. This could account for the higher molecular weight porphyrins suspected to form in the heat-treated sediment. Casagrande and Hodgson (1971) showed that a homologous series of porphyrins could be generated by heating a single porphyrin to 250°C .

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TABLE I: Tanner Basin β -carotene*, produced or degraded during heating.

Time of Incubation (days)	Temperature ($^{\circ}$ C)			
	25 $^{\circ}$	65 $^{\circ}$	100 $^{\circ}$	150 $^{\circ}$
Standard	8			
7	--	128	n.d.	n.d.
30	--	155	n.d.	n.d.
64	214	296	n.d.	n.d.

* μ g/100 g dry weight sediment
n.d. = not detected

Table II: Tanner Basin Chlorins and Porphyrins*

Time of Incubation (days)	Temperature (°C)							
	25°		65°		100°		150°	
	C	P	C	P	C	P	C	P
<u>Standard</u>	2070							
7			2600	77	166	--	--	104
30			1790	89	163	150	--	199
64	3400		2340	92	108	149	--	667
64								326 ^{xx}

* $\mu\text{g}/100 \text{ g}$ of dry weight sediment

C = chlorins

P = porphyrins

xx = freeze-dried sample

FIGURE DESCRIPTIONS

- Figure 1: Structures of pheophytin a and pheophorbide a
- Figure 2: Flow chart of isolation and separation of organic matter of sediments.
- Figure 3: Absorption spectra of carotenes (in benzene).
1. Neat β -carotene; 2. Tanner Basin sediment (T. B.s.); 3. T. B.s. 2 months at room temperature; 4. T.B.s. 1 month at 65°C; 5. T.B.s. 1 month at 100°C.
- Figure 4: Proposed pathway of formation of 2,6-dimethyl-naphthalene and α -ionene from β -carotene.
- Figure 5: Mass spectra of α -ionene. A - of T.B.s.; B - of synthetic.
- Figure 6: Breakdown pattern of α -ionene in mass spectrometer.
- Figure 7: Absorption spectra of Tanner Basin sediment chlorins (in benzene). 1. standard; 2. two months at room temperature; 3. two months at 65°C; 4. two months at 100°C; 5. one week at 150°C.
- Figure 8: Absorption spectra of Tanner Basin sediment porphyrins (in benzene). 1. standard; 2. two months at 65°C; 3. two months at 100°C; 4. and 4'. one week at 150°C; 5 and 5'. two months at 150°C.

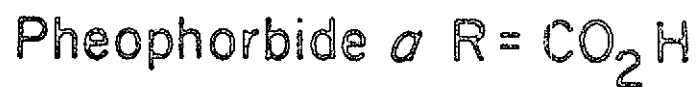
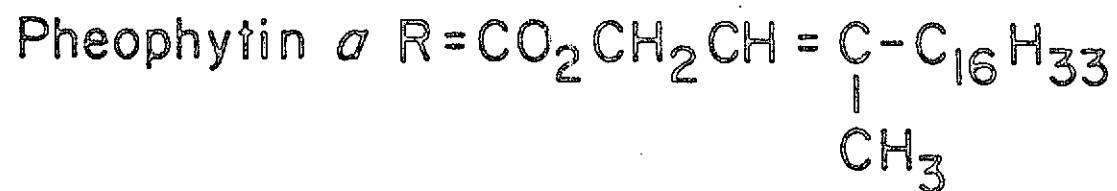
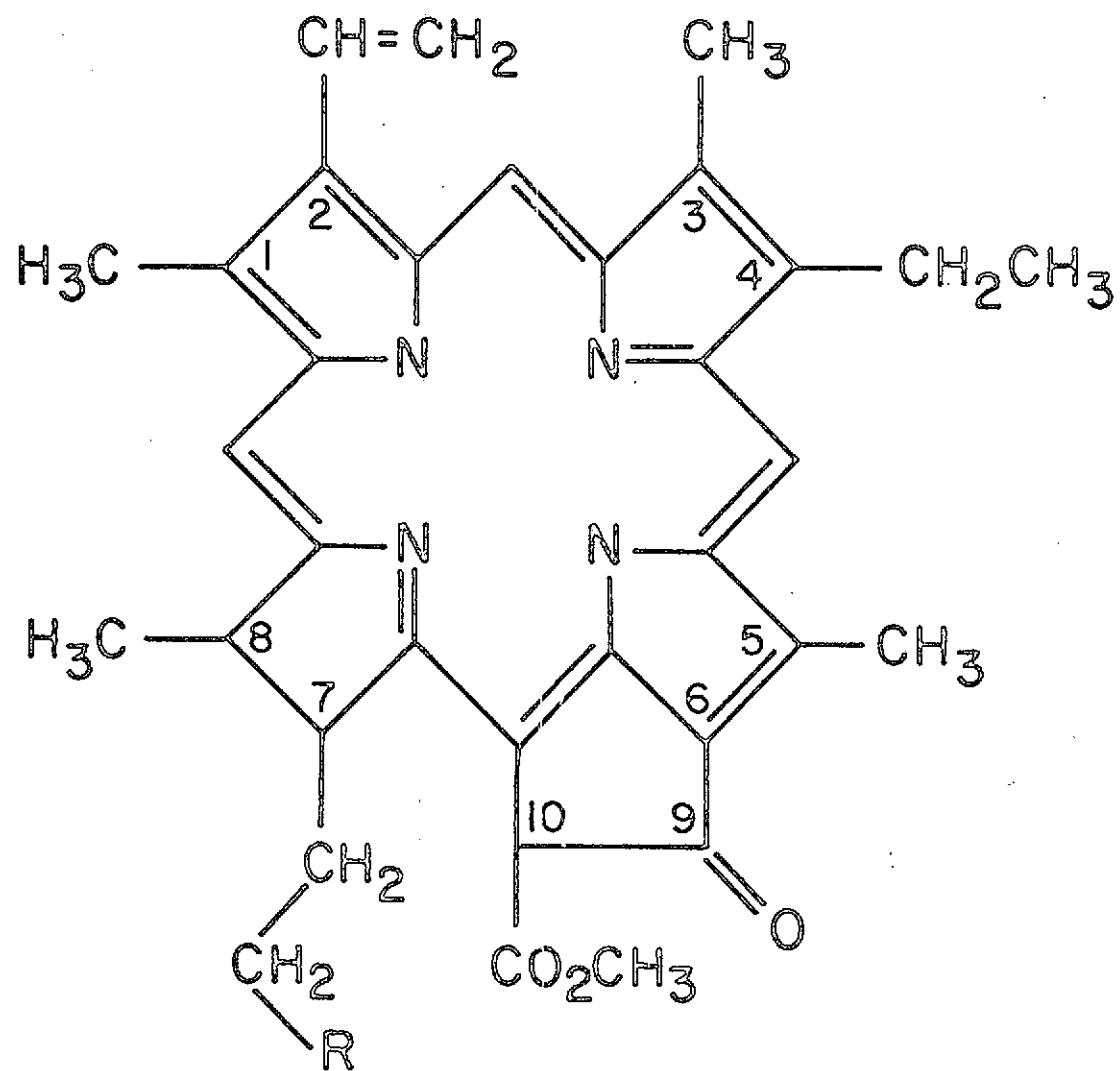
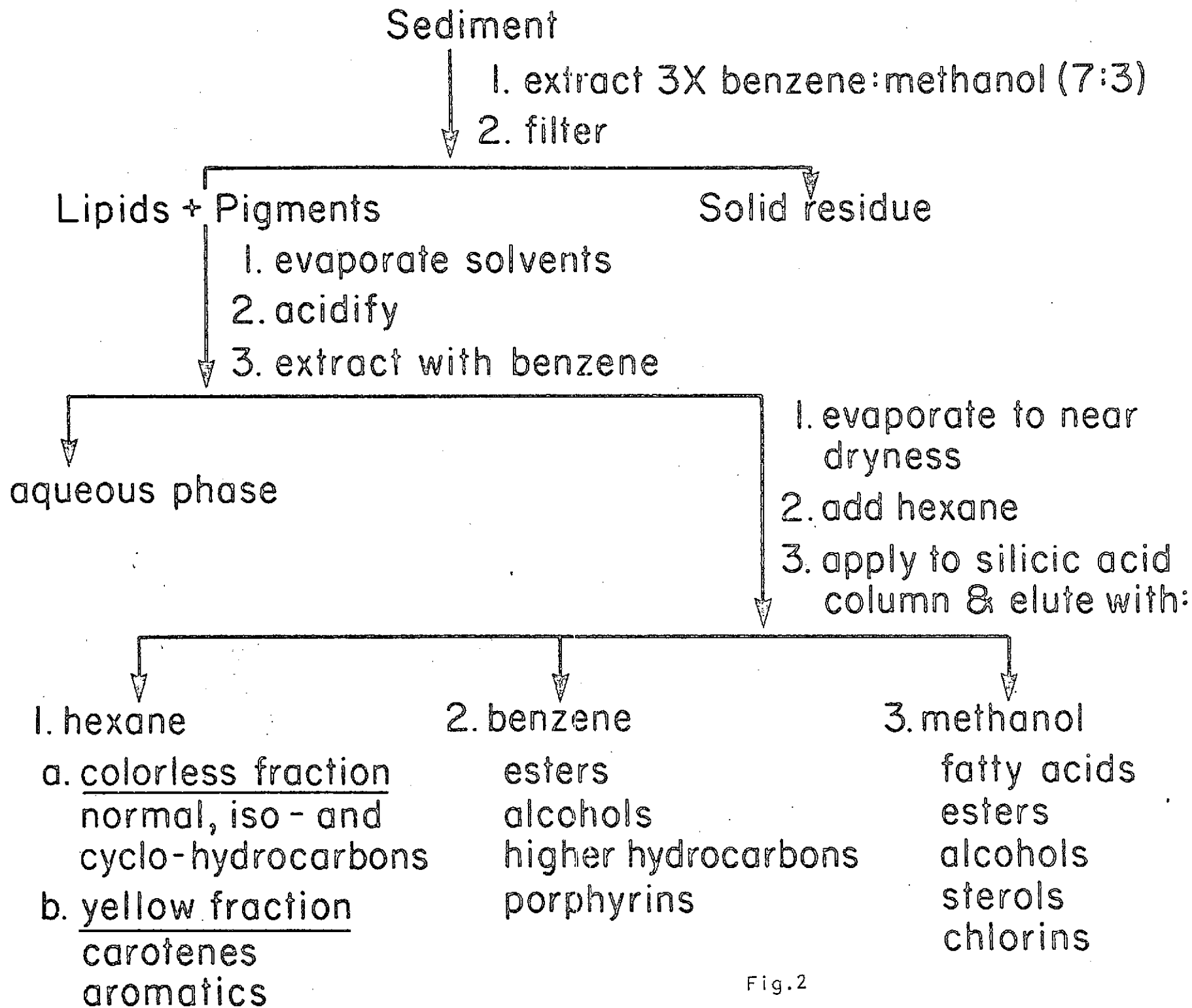


Fig. 1



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Fig.2

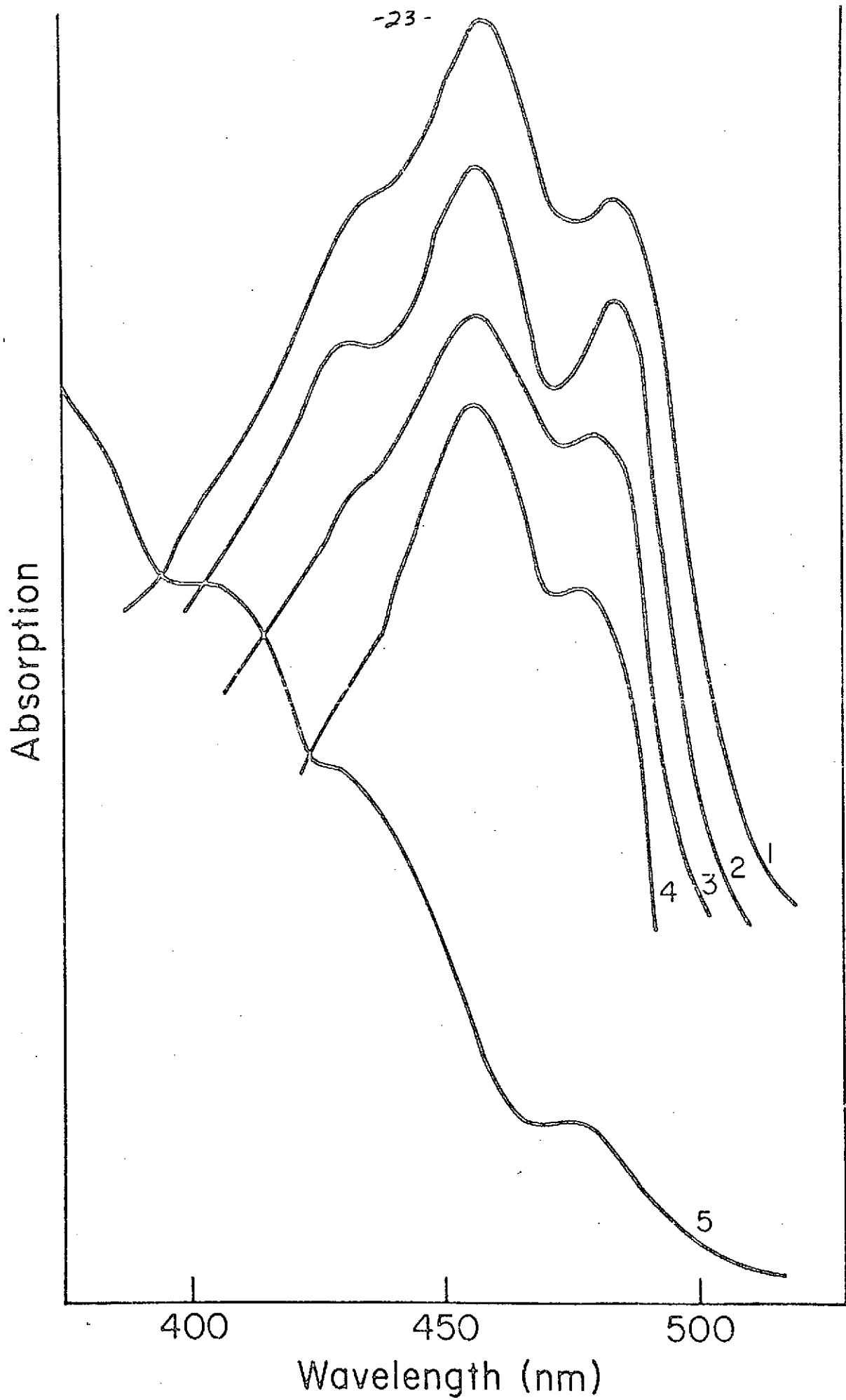
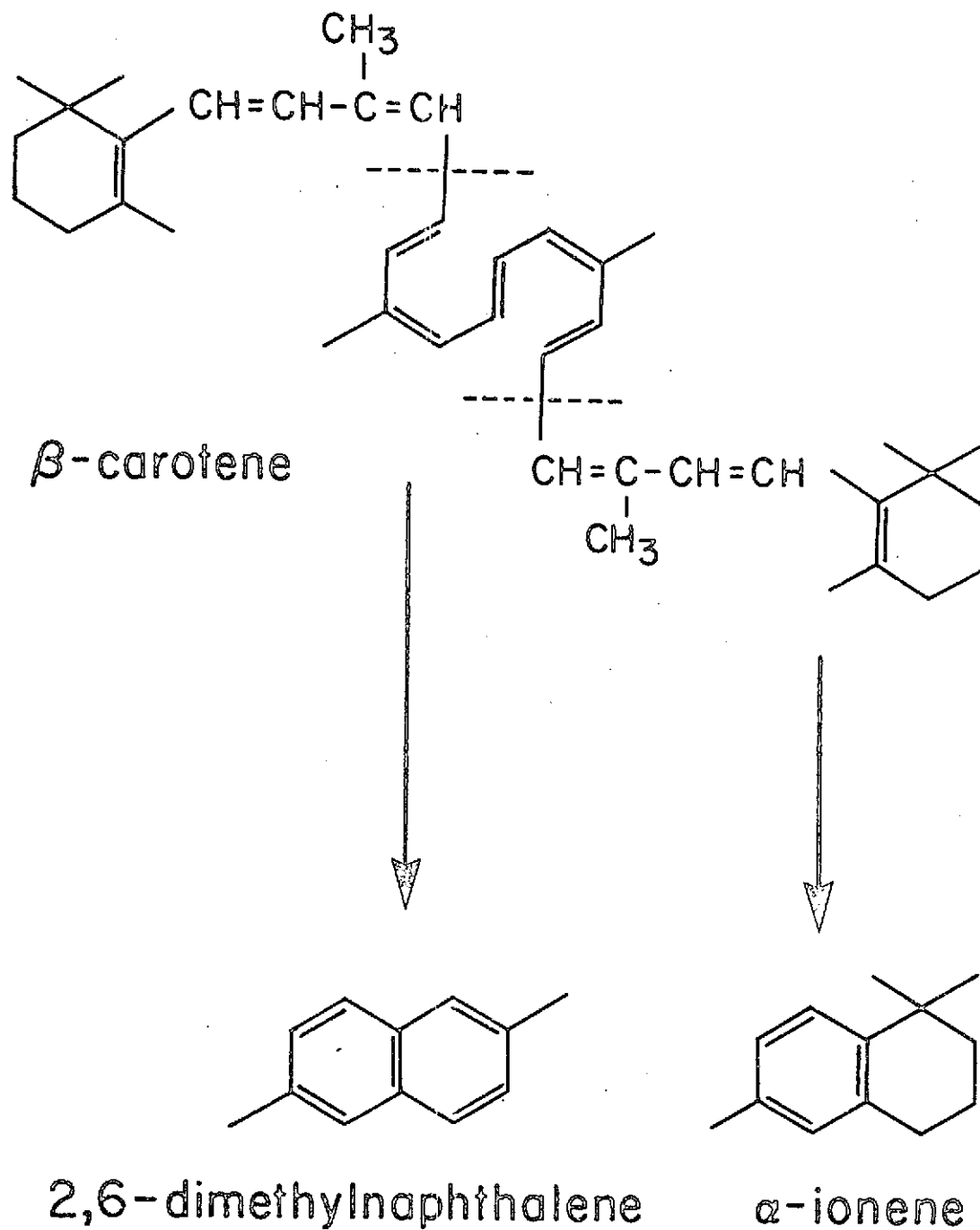


Fig.3



-HC-

Fig.4

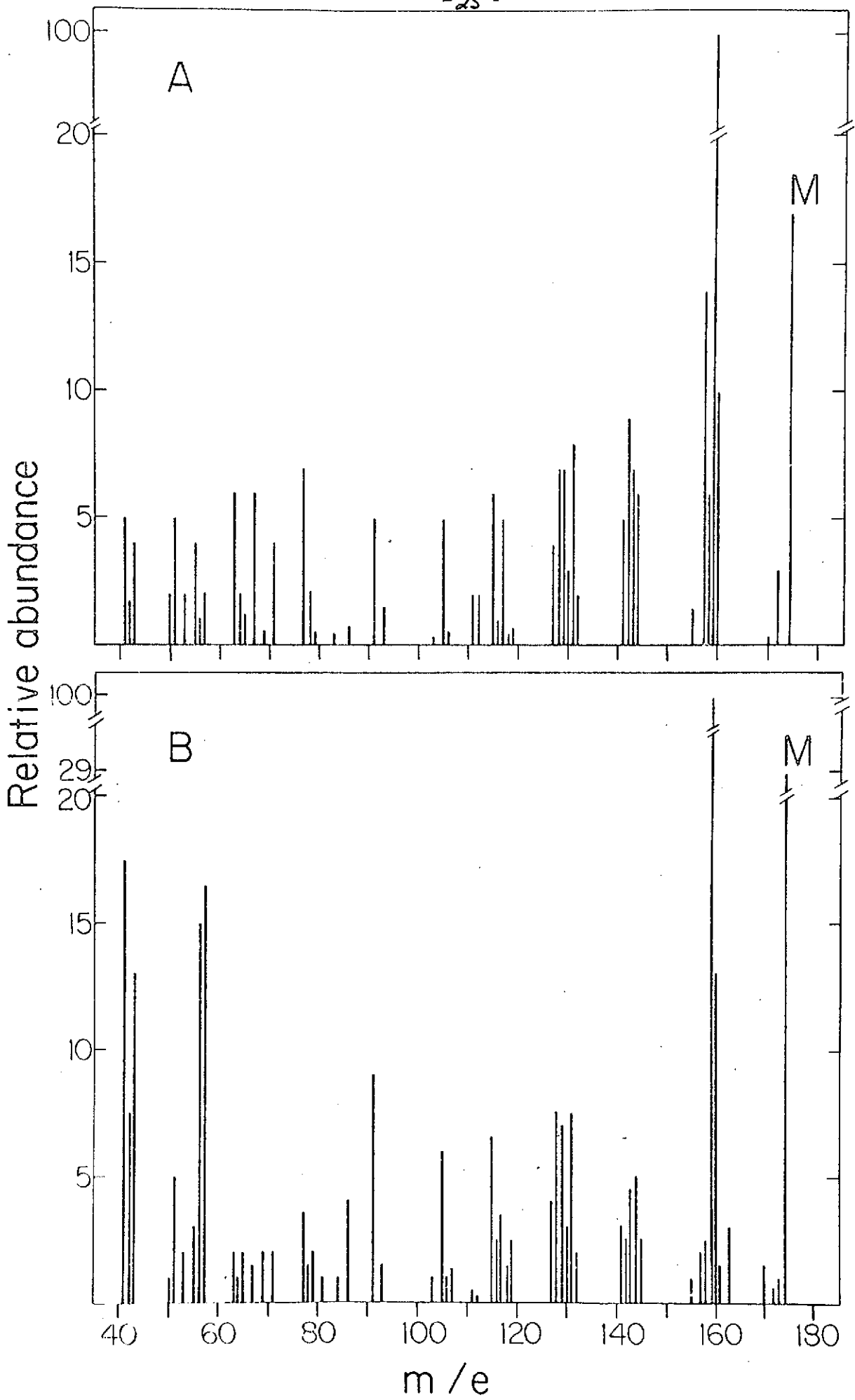


Fig. 5

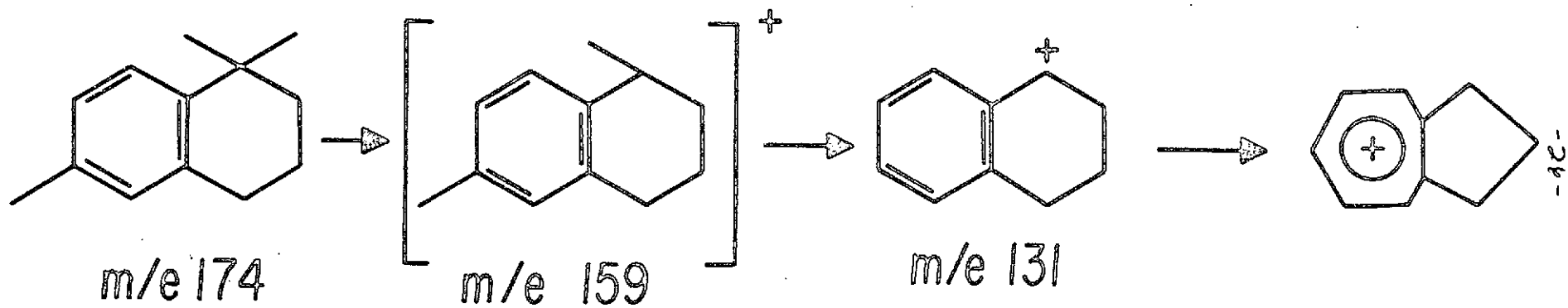


Fig. 6

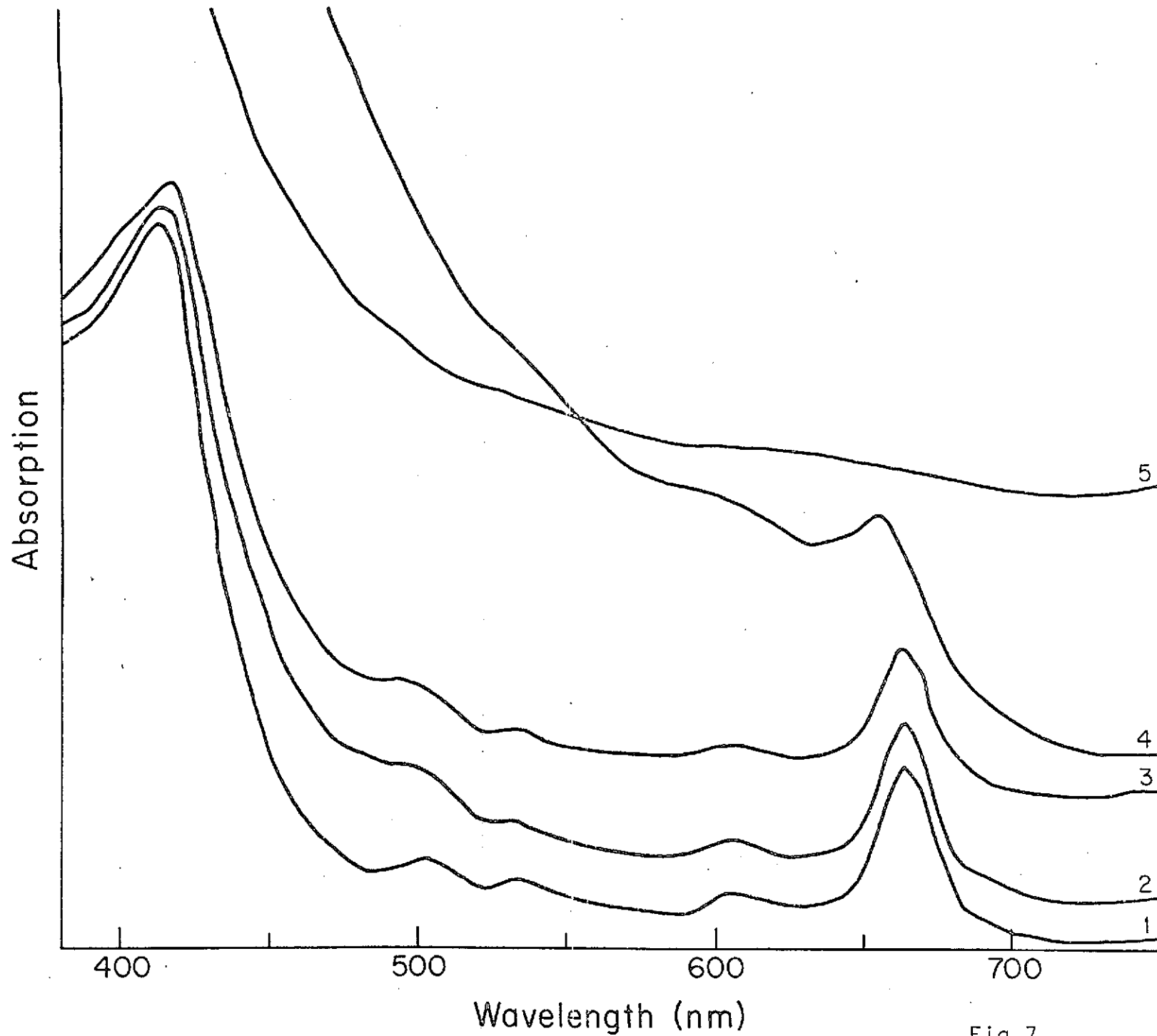


Fig.7

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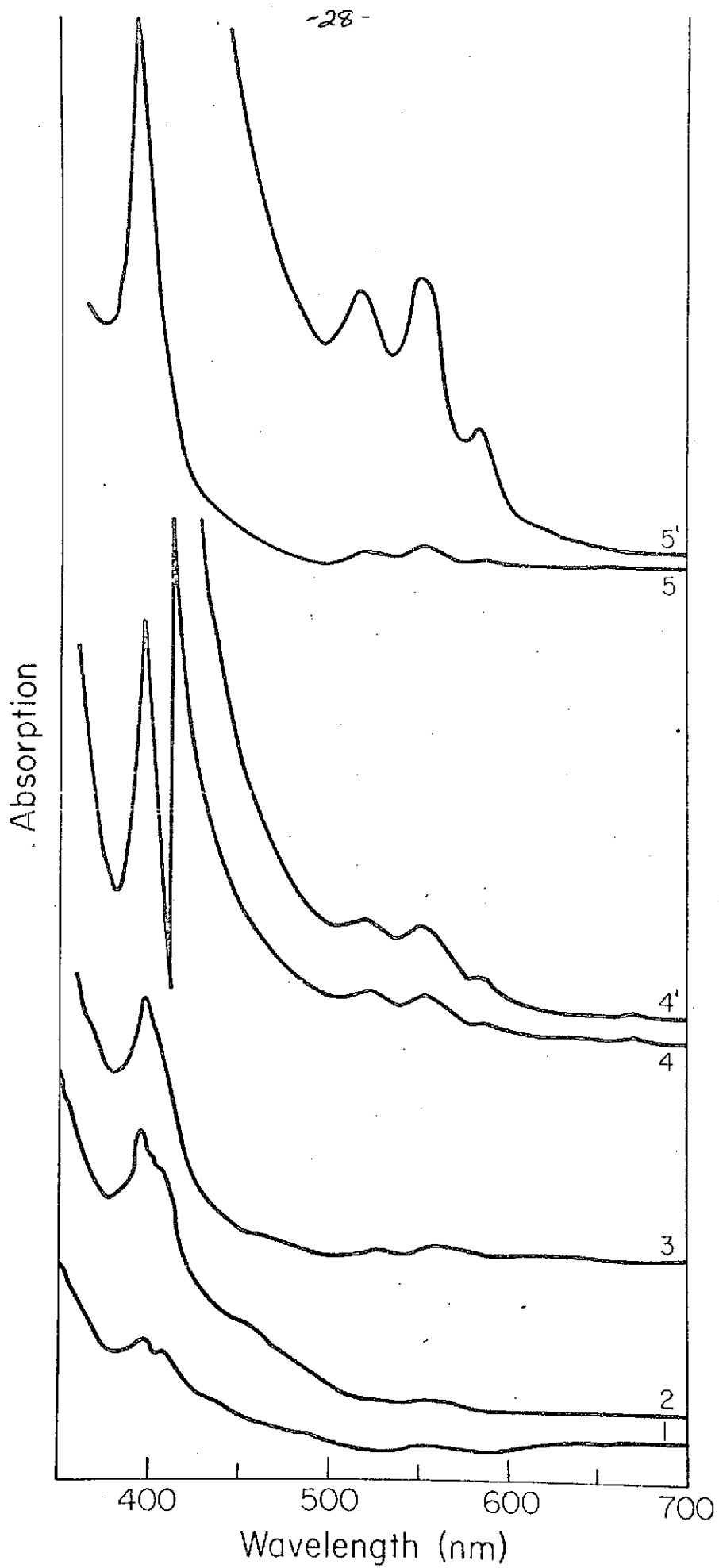


Fig. 8