Isolation of Porphyrins From Shale Oil and Oil Shale

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INTRODUCTION

Oil shale is a laminated rock of sedimentary origin that ranges from gray to dark brown to almost black. It owes its color to carbonaceous matter called "kerogen" which is derived from plant and animal remains (1). Kerogen is largely insoluble in common organic solvents, but when heated to about 900°F it yields shale oil. This shale oil resembles petroleum in that it is composed of hydrocarbons and sulfur-, nitrogen-, and oxygen-derivatives of hydrocarbons.

The discovery of porphyrins in petroleum and oil shale by Treibs (12, 13) in 1934 gave direct evidence for the organic origin of petroleum and oil shales. In 1953 Groennings (5) published a method for extracting and spectrophotometrically determining porphyrins in petroleums. Groennings' procedure stimulated the work on the analysis of porphyrins in natural products. In 1954 Moore and Dunning (8) extracted Green River oil shale with various solvents and obtained a number of extracts that contained porphyrin-metal complexes. They concluded that the majority of the porphyrin exists in the shale as an iron-porphyrin complex. Although these researchers have reported the occurrence of porphyrins in oil shale, no one has reported their presence in shale oil. The present work was undertaken to determine if porphyrins were able to survive the retorting step and if so, what changes were brought about by retorting.

It was found in this investigation that:

(1) Porphyrins are present in shale oil so they survive the retorting step.

(2) Retorting changes the porphyrins from phyllo to etio type, and their average molecular weight is lowered. This lowering of the molecular weight is partially accounted for by decarboxylation.

(3) Porphyrins present in shale oil are shown to be a complex mixture of predominantly etio type with an average of nine methylene substituents on the porphine ring. The absorption spectrum of the purest porphyrin prepared was nearly identical to the spectrum of a synthesized etio-type porphyrin.

EXPERIMENTAL WORK

Method of Extracting Porphyrins

Groennings' method (5) for the extraction of porphyrins was used with two modifications: (1) To reduce loss of porphyrins to the organic phase, a 20 percent

hydrochloric acid solution was used instead of the recommended 7 percent solution, and (2) to minimize decomposition of the porphyrin by contact with halogenated solvents (2) the final transfer of the porphyrins was made into benzene instead of into chloroform.

Source of Materials Studied

The oil shale studied was from the Mahogany Ledge of the Green River formation near Rifle, Colo. The shale contained 35 weight percent organic matter and assayed 64.3 gallons of oil per ton by the Modified Fischer assay method (10). Because the shale contained approximately 10 percent by weight of CO_2 as mineral carbonates, it was pretreated with 4 percent hydrochloric acid and air-dried prior to the porphyrin extraction step.

The crude shale oil was produced in an internally fired retort. The feed shale for this retort was also from the Mahogany Ledge of the Green River formation and averaged about 30 gallons of oil per ton. Selected properties of the oil, using the Bureau of Mines shale-oil assay method (11), were specific gravity, 0.950; weight percent nitrogen, 2.11; weight percent sulfur, 0.88; and a distillation analysis of 4.6 volume percent naphtha, 14.3 volume percent light distillate, 26.7 volume percent heavy distillate, and 54.3 volume percent residuum.

Spectral Procedures

The absorption spectra from 450 to 650 mu of all porphyrin extracts, concentrates, and reference compounds were obtained in benzene solution. The method of Dunning (2) was used for correcting for background absorption in determining the type and quantity of porphyrins. The spectral reference compounds used in this research were mesoporphyrin IX dimethylester and etioporphyrin I.

Low-ionizing-voltage and high-ionizing-voltage mass spectra were obtained on selected extracts and concentrates. When a nickel complex of a porphyrin sample was introduced into the mass spectrometer, the spectrum obtained was of the nickel complex. The introduction of uncomplexed porphyrins resulted in the spectrum of the indium chloride complex of the porphyrins.1/ In both cases the mass spectra will be discussed as the spectra of the uncomplexed porphyrins.

Extraction and Concentration of Porphyrins From Shale Oil

Small-Scale Extraction

A 100-gram sample of the crude shale oil was extracted using the modified Groennings' method. This extract was purified by chromatographing it on a column containing 100 grams of activated alumina. Benzene was used to prewet the alumina and as the initial eluent. Benzene elution was continued until the solvent was almost colorless. Spectral examination of the benzene showed that no prophyrins were

1/ The indium chloride in the instrument resulted from the reaction of indium used for the valves in the sample introduction system and chlorine from chlorinated solvents used in other mass spectral projects.

removed. The porphyrin band was removed from the column using 1,2-dichloroethane, and elution with this solvent was continued until no porphyrins were discernible in the eluent. Visible absorption spectra were obtained on the extract before and after the chromatographic step. Low- and high-voltage mass spectra were obtained on the chromatographically purified extract.

Large-Scale Extraction

To obtain enough porphyrin extract for a characterization study, 2,300 grams of crude shale oil was extracted by the modified Groennings' method. The extract was chromatographed on 1,000 grams of activated alumina. Benzene was used to prewet the column and to elute the colored impurities, as was done on the small-scale experiment. The porphyrins were slowly eluted, using first recycled benzene and then mixtures of benzene and 1,2-dichloroethane. Twenty fractions were collected using benzene and 11 using benzene containing increasing quantities of 1,2-dichloroethane. Visible absorption spectra were obtained on all fractions, and mass spectra were obtained on selected fractions.

Countercurrent extraction was used as an additional separation on several of the fractions from the large-scale chromatographic separation. In each case, cyclohexane and 0.25 N hydrochloric acid were used as the immiscible solvents and 100 transfers were made. Absorption data were used to determine the distribution of porphyrins in the 100 tubes. Each time the separation was into four areas with concentration maxima occurring near tubes 33, 55, 75, and 95. The porphyrins in the tubes in each of the concentration areas were combined, and mass and absorption spectra were obtained on the recovered porphyrins.

Extraction of Porphyrins From Oil Shale

A sample of the hydrochloric acid leached shale, containing 105 grams of organic matter, was placed in a glass bomb, and 300 ml of benzene was added as a dispersant. The modified Groennings' extraction procedure was used to extract the porphyrins, except that the bomb was shaken continuously during the extraction. Visible absorption and mass spectra were obtained on the resulting extract.

RESULTS AND DISCUSSION

Porphyrin is the term applied to a class of compounds in which four pyrrole rings are united by bridge carbons to form a conjugated, macrocyclic structure, known as porphine. Figure 1 shows the numbering system that will be used in this paper for the porphine ring (9). This conjugated ring system is heat stable and can be halogenated, nitrated, or sublimed without destroying the macrocyclic structure (4).

Porphyrins, dissolved in organic solvents, have a typical, four-banded absorption spectrum in the visible region between 450 and 650 mu. They have been classified into etio, phyllo, and rhodo types according to the height of the individual peaks relative to one another (3). Representative spectra of each of these three types are shown in figure 2. The four bands or peaks are numbered I, II, III, and IV starting from the long-wavelength end of the spectrum. In general, the height of the peaks increases toward the shorter wavelengths.

Porphyrins that have methyl, ethyl, vinyl, propionic acid, or hydrogen in positions 2, 3, 7, 8, 12, 13, 17, and 18 (see figure 1) around the porphine ring

give the etio-type spectrum. This etio-type spectrum, which is characteristic of blood-pigment porphyrins, has four peaks, which become progressively higher proceeding from the longer to the shorter wavelengths. The shale-oil extracts and concentrates gave etio-type spectra.

The phyllo-type spectrum, which is typical of the chlorophyll porphyrins, has peak II larger than III. This type of spectrum has been attributed either to the presence of an isocyclic ring between one of the pyrrole rings and the adjacent bridge carbon atom or to an alkyl group on one of the bridge carbon atoms. The oil-shale extracts gave phyllo-type spectra.

The rhodo-type spectrum has been observed in compounds having a carbonyl group attached to one of the pyrrole rings and has the number III peak as the strongest of the four main peaks. The rhodo-type spectrum was not observed for any of the oil-shale or shale-oil extracts.

The porphyrins in the extract from oil shale were characterized by the use of absorption and mass spectra. The absorption spectrum of this oil-shale extract is shown in figure 3. This spectrum is characteristic of phyllo-type porphyrin, which has peak II higher than peak III.

The low-voltage mass spectrum showed porphyrins with molecular weights from 462 to 536. The ions in this spectrum were in the three following homologous series: (1) The alkyl-substituted porphine series, (2) the series two mass units greater than the porphine series, and (3) the series two mass units less than the porphine series. Figure 4 shows the distribution of intensities of the ions for the series occurring at two mass units greater than the porphine series. The average molecular weight of the porphyrins in this series (as calculated from this distribution) is 508. More than half of the total ions in the low-voltage spectrum were in this series, and the data presented in figure 4 represent the three series.

In the high-voltage spectrum of the oil-shale extract there was a series of ions 44 mass units less than the parent ions. This series of ions was shown to be a fragment ion series corresponding to the loss of CO_2 from the porphyrins.

These characterization data show the following facts about the oil-shale porphyrins:

(1) Oil-shale porphyrins are composed of at least three homologous series of compounds with no fewer than six different compounds in each series.

(2) The majority of these compounds have a phyllo-type spectrum.

(3) Some of these porphyrins have carboxyl substituents.

(4) The average molecular weight of 508 for the oil-shale porphyrins can be accounted for by 1 carboxyl and 11 methylene substituents on the porphine ring.

Before the porphyrins from the small-scale extraction of shale oil could be characterized, it was necessary to remove some of the impurities carried along by Groennings' extraction. This was done by chromatographing on alumina, and the absorption spectra of the porphyrin extract before and after chromatography are shown in figure 5. Improvement in the purity of the porphyrins by the chromatographic step is shown by the smaller background absorption in the chromatographed concentrate. The shale-oil extract both before and after chromatographing gave an etio-type spectrum, whereas the oil-shale extract showed a phyllo-type spectrum.

In the low-voltage mass spectrum of the shale-oil extract, more than 90 percent of the parent ions were in the alkyl-substituted porphine series. Figure 6 shows the distribution of the ions in this series with molecular weight range from 366 to 492. The abscissa scale shows both m/e of the ions (molecular weights) and the number of methylene substituents necessary on the porphine ring to have this molecular weight. The average molecular weight of the porphyrins in shale oil (as calculated from this distribution) is 436, or the equivalent of nine methylene substituents on the porphine ring.

In the high-voltage spectrum of the shale-oil extract, there was no evidence of a fragment ion series 44 mass units less than the parent ions. This indicates that there are no carboxyl groups present in shale-oil porphyrins.

These characterization data show that shale-oil porphyrins are predominantly alkyl-substituted porphines with 4 to 13 methylene groups per molecule. Because the absorption spectrum of this extract is of the etio type, these alkyl substituents are on the eight pyrrole carbons in the porphine ring.

Comparison of the character of the porphyrins from oil shale with the character of the porphyrins from shale oil indicates the changes that porphyrins undergo during retorting. These changes are as follows:

(1) The molecular weight is lowered an average of 72 mass units. In part, this is explained by decarboxylation. The decrease in average molecular weight is equivalent to the loss of one carboxyl and two methylene groups per molecule.

(2) The phyllo-type character is changed to an etio-type character. The reaction necessary to bring about this change in spectral type is the removal of substituents from the bridge carbons on the porphine ring. This could also contribute to the lowering of the molecular weight of the porphyrins.

Further characterization of the porphyrins in shale oil was accomplished by examining the fractions from the chromatographic separation of the large-scale shale-oil extraction. The absorption spectra of the first 25 fractions from this chromatographic separation were of the etio type, and these fractions contained 70 percent of the total porphyrins recovered. Beginning with the 26th fraction, the height of peak II relative to peak III became increasingly greater. This indicated that some phyllo-type porphyrins were being eluted with the 1,2-dichloroethane. This presence of a phyllo-type porphyrin in the shale-oil extract is an indication that a part of the porphyrins is relatively unchanged during retorting.

A benzene-eluted fraction was used to demonstrate further the character of the etio-type porphyrins in shale oil. A nickel complex of the 15th fraction was prepared, and low- and high-voltage mass spectra of this complex were obtained. The peak heights in these spectra were corrected for isotope contribution. Figure 7a is the resulting low-voltage spectrum, and figure 7b is the resulting high-voltage spectrum. Each of the figures shows the corrected peaks only in the molecular weight region of the porphyrins.

The low-voltage mass spectrum has only ions in the porphine series. The number of substituents on the porphine ring is from 3 to 12 methylene groups with an average of 7 methylene substituents per molecule. The greater abundance of odd-numbered substituents over even-numbered is unexplained; this distribution is not evident in the low-voltage spectrum of the total shale-oil concentrate (see figure 5).

Hood (6) and Mead (7) have reported the mass spectral cracking pattern for metal complexes of etioporphyrin, and they concluded that the main fragmentation process is the loss of methyl groups. The peaks shown in figure 7b at one mass unit less than the porphine series could be due to the loss of methyl groups and indicate the presence of methyl or ethyl substituents on the porphine ring of shale-oil porphyrins.

The high-voltage spectrum of this fraction shows the presence of singly charged ions at every m/e from the molecular weight of the porphyrins to the doubly charged parent ions.[2/] Both Hood and Mead have shown that in the mass spectrum of etioporphyrin I the porphyrin skeleton remains intact because no singly charged ions occur between the molecular weight of the porphyrin skeleton and the doubly charged parent ions. The conclusion, therefore, is that the fraction shows the presence of impurities. Because the low-voltage spectrum of this fraction showed no molecular ions other than porphyrins, the impurity is probably nonaromatic.

Countercurrent extraction was used to further purify the porphyrin concentrates. Fraction 14 from the large-scale chromatographic separation was countercurrent extracted and separated into four concentrates. Judging by the comparison of specific extinction coefficients, one of these concentrates was the purest porphyrin concentrate prepared in this work. That the impurity was still present can be seen by comparing the molar extinction coefficient (2) for this fraction which was 1.8×10^3 in benzene, with that for etioporphyrin I, which was 6.2×10^3 in benzene. This impurity, however, has low absorption in the visible region. This is illustrated by the good agreement of the visible spectrum of this concentrate with the spectrum of a synthesized etio-type porphyrin as shown in figure 8.

The low-voltage mass spectrum of the porphyrin concentrates from countercurrent extraction showed a series of molecular ions in the porphine series. One of the concentrates had parent ions occurring at molecular weights corresponding to four to eight methylene substituents on the porphine ring. Of the total parent ions present in the mass spectrum of this concentrate, 25 percent showed the presence of four methylene substituents, and 65 percent showed the presence of five methylene substituents.

CONCLUSION

This work has demonstrated that the skeleton of the porphyrin molecules in oil shale is capable of surviving retorting temperatures. However, the substituent groups on the skeleton are changed. As expected, reduction in average molecular weight is the most obvious change. Partial explanation of this reduction was demonstrated to be decarboxylation. Another change that can be inferred to take place is the removal of substituents responsible for the phyllo character of the oil-shale porphyrins. This could result either from the destruction of an isocyclic ring or from the removal of substituents from a bridge-carbon atom.

The porphyrins present in shale oil were shown to be a complex mixture of predominantly etio type. The absorption spectrum of the purest porphyrin prepared was nearly identical to the spectrum of a synthesized etio-type porphyrin. The porphyrins in shale oil have an average molecular weight equivalent to the porphine ring with nine carbon atoms of methylene substituents. The total number of carbon substituents ranged from 4 to 13.

2/ This was true for all extracts and concentrates prepared in this work.

ACKNOWLEDGMENTS

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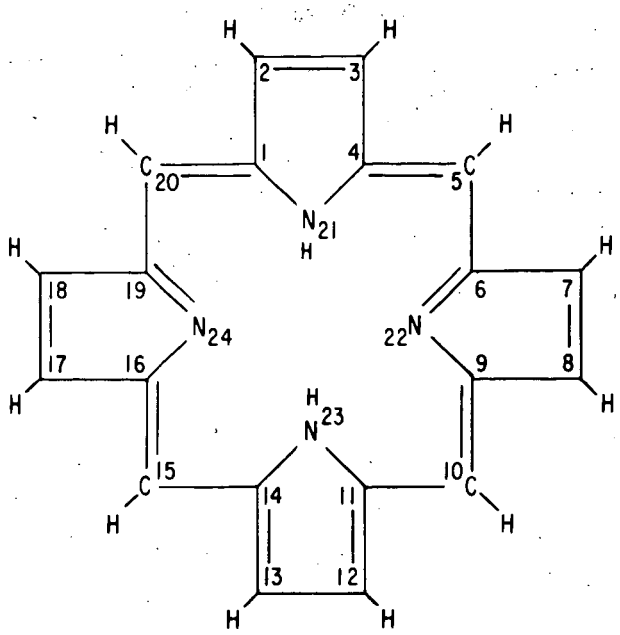

FIGURE 1.-Numbering system for the Porphine Ring

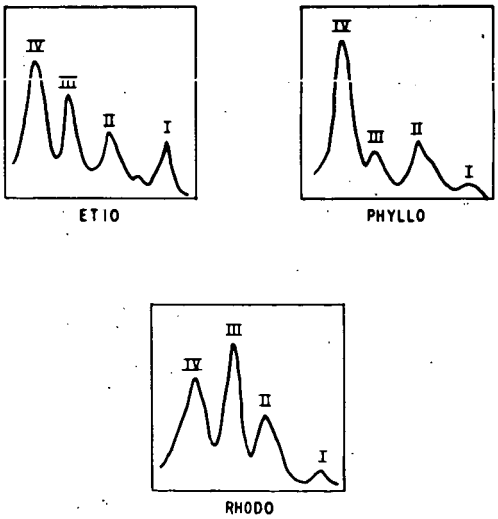

FIGURE 2.-Types of Porphyrin Spectra.

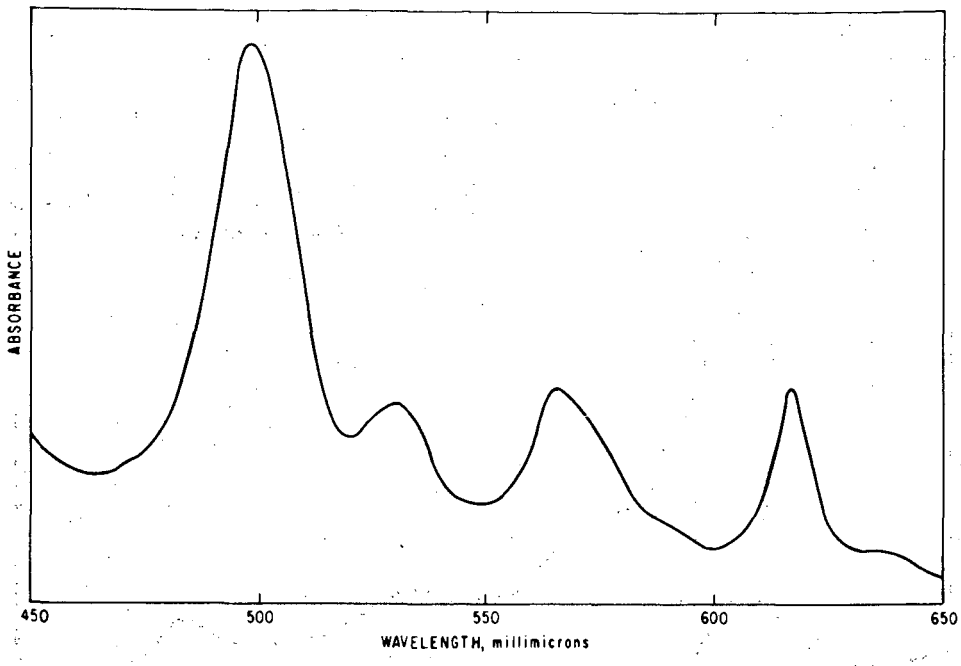

FIGURE 3.-Spectrum of oil-shale extract

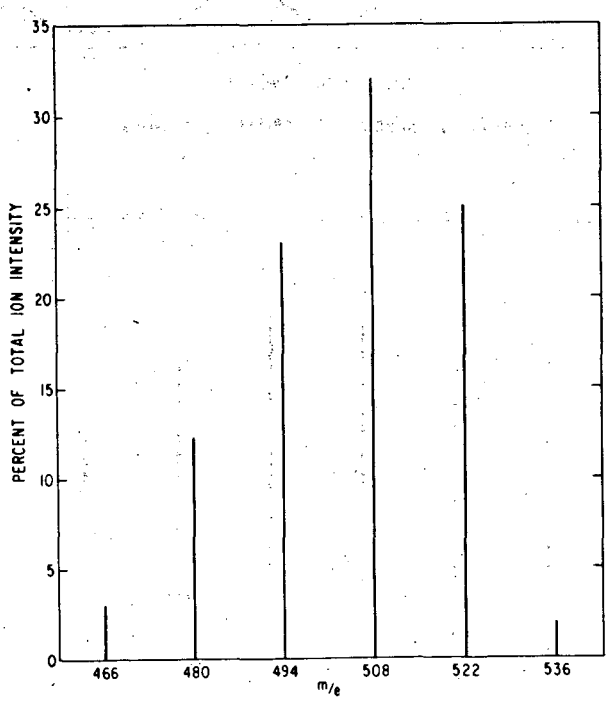

FIGURE 4-Distributions of ion intensities for oil-shale porphyrins

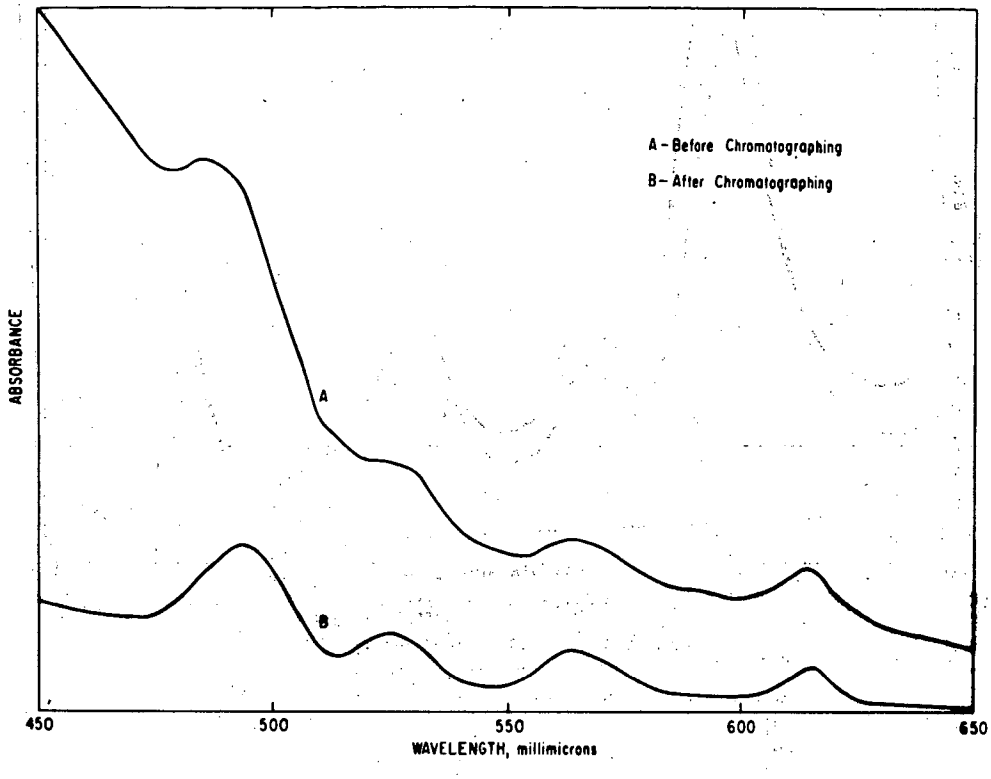

FIGURE 5.- Spectra of shale-oil porphyrins

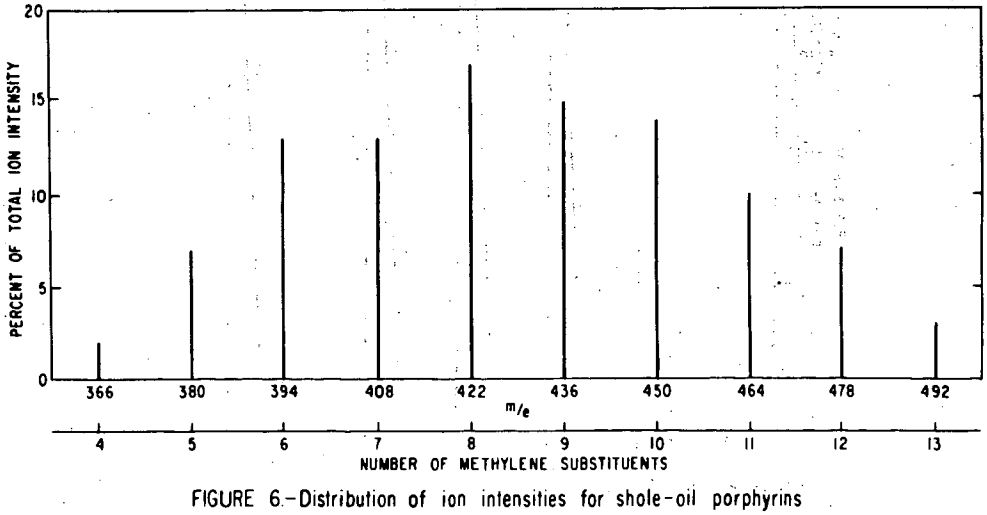

FIGURE 6.-Distribution of ion intensities for shale-oil porphyrins

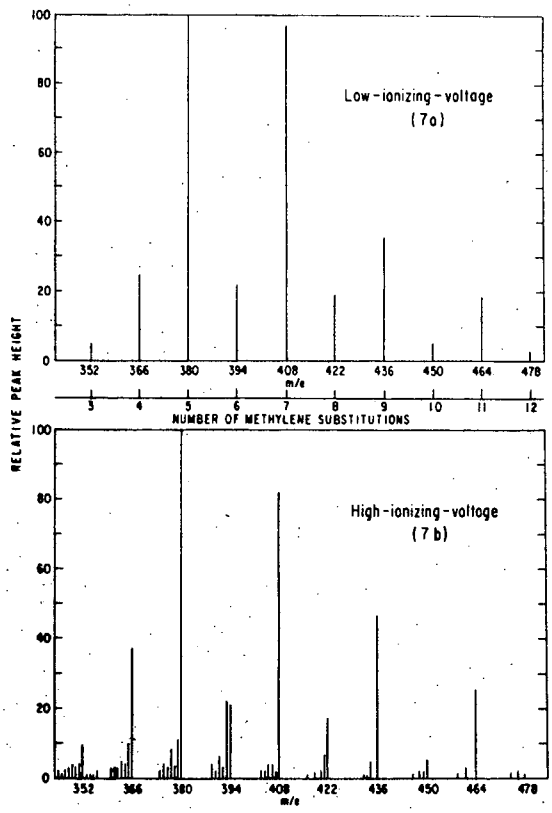

FIGURE 7.-Mass Spectra of Fraction 15.

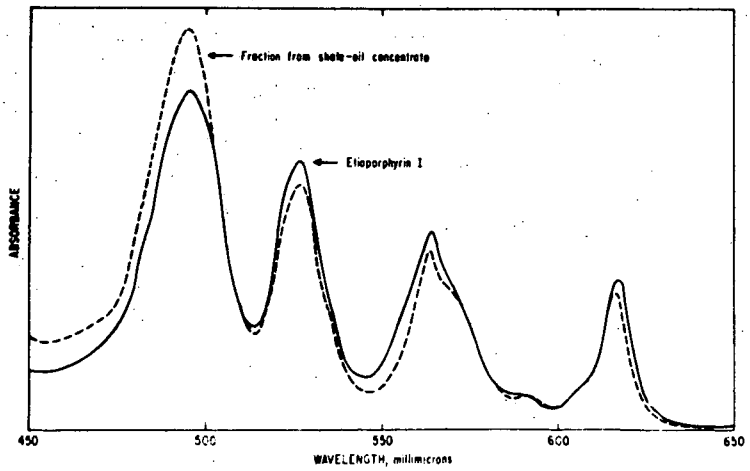

FIGURE 8.-Comparison of spectra