Comparison of Porphyrins from Shale Oil, Oil Shale, and Petroleum by Absorption and Mass Spectroscopy

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Mass and absorption spectroscopy were used to characterize porphyrins extracted by a hydrogen bromide–acetic acid solution from an oil shale, a shale oil, and a petroleum. The porphyrins in oil shale and petroleum were shown to be similar and to consist of at least two homologous series. These porphyrins were alkylsubstituted and contain from 7 to 13 methylene substituents per molecule, and most of the molecules also contained a carboalkoxy group. Their average molecular weights were 508 for the shale porphyrins and 494 for the petroleum porphyrins; their visible spectra were of the phyllo type. The porphyrins in shale oil are a complex mixture of etio-type porphyrins. They have a molecular weight range of 366 to 522. There is evidence for the lack of an isocyclic ring and for the presence of both one and two carboalkoxy groups per molecule.

THIS is the first report of the presence of porphyrins in shale oil; however, their presence in petroleum and oil shale has been known for three decades (*11, 15, 16*). This is also the first report of the use of mass spectroscopy to characterize naturally occurring porphyrins. The present work was undertaken to isolate porphyrins from shale oil and to compare them with porphyrins from oil shale and petroleum.

EXPERIMENTAL

Materials Studied. The oil shale studied was from the Mahogany Ledge of the Green River formation near Rifle, Colo. (*2*). This shale contained 35 wt. % organic matter and assayed 64.3 gallons of oil per ton by the modified Fischer assay method (*13*).

The crude shale oil investigated was produced from Green River oil shale in an internally fired retort. Selected properties of the oil, using the Bureau of Mines shale-oil analysis method (*14*), were: specific gravity, 0.950; wt. % of nitrogen, 2.11; wt. % of sulfur, 0.88; and a distillation analysis of 4.6 volume % napthha, 14.3 volume % light distillate, 26.7 volume % heavy distillate, and 54.3 volume % residuum.

The petroleum studied was a Wilmington (Calif.) crude oil which was produced from a relatively recent formation (Tertiary). This Wilmington crude oil was an asphaltic oil which contained relatively large amounts of nonhydrocarbons (*1*).

Extraction and Purfication of Porphyrins. A method similar to Groennings' (*8*) was used to extract the porphyrins. Before this procedure could be applied to the oil shale, it was necessary to treat the shale with hydrochloric acid to remove mineral carbonates. Samples of carbonate-free shale, shale oil, and Wilmington petroleum were each extracted with the hydrogen bromide–acetic acid reagent, and impurities were removed from the extract by repeated transfers between ether and 20 % hydrochloric acid solution. In Groennings' procedure, the last transfer is made from hydrochloric acid solution into chloroform; however, to minimize the decomposition (*5*) of the porphyrins in this work, benzene was used as the final solvent.

In the oil-shale and petroleum work, this extraction procedure resulted in porphyrin extracts that could be characterized without further purification. However, it was necessary to purify further the shale-oil extracts before characterization. This was accomplished by two different procedures. The first procedure continued the transference of the porphyrins between acid and ether as in Groennings' procedure until a total of 10 transfers had been made. In the second procedure, the shale-oil extract was chromatographed on alumina. Two independent chromatographic separations on alumina were made. In the first separation, a small-scale sample of the shale-oil extract was chromatographed, and the porphyrin band was recovered as one fraction. In the second, a large-scale sample was chromatographed, and the porphyrin band was cut into a number of fractions. Selected fractions from the large-scale separation were further purified by countercurrent extraction with $0.25N$ hydrochloric acid and cyclohexane as the immiscible solvents.

Spectral Procedures. The absorption spectra from 450 to 650mμ of all porphyrin extracts, concentrates, and reference compounds were obtained in benzene solution. The method of Dunning (*5*) was used to correct for background absorption in determining the type and quantity of porphyrins. The reference compounds used in this research were mesoporphyrin IX dimethylester and etioporphyrin I. Extinction coefficients were used to compare the purity of the extracts and concentrates.

A mass spectrometer fitted with a heated inlet system (*3*) was used to obtain high- and low-ionizing voltage mass spectra. In the initial phase of this work, the valve between the holding volume and the exhaust pump of the mass spectrometer was an indium valve which had been exposed previously to chlorinated solvents yielding indium chloride. This compound reacted with the porphyrins, while they were in the holding volume, to form the indium monochloride-porphyrin complex. The spectra of the resulting complexes were calculated in some cases to the metal-free porphyrins and will be discussed as such. In the latter phases of this work, the indium valve was replaced by an all-glass system, and the resulting spectra were of the uncomplexed porphyrins.

The reasons for discussing the mass spectra of both the indium monochloride-porphyrin complexes and the uncomplexed porphyrin aggregates will be brought forth explicitly in the following sections of this paper.

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 the porphine ring (*12*). This conjugated ring system is heat stable and can be halogenated, nitrated, or sublimed without destroying the macrocyclic structure (*7*). Porphyrins dissolved in organic solvents have a typical, four-banded absorption spectrum in the region between 450 and 650 mμ. Their spectra have been classified into etio, phyllo, and rhodo types according to the intensities of the absorption bands relative to one another (*6*).

Oil Shale. The porphyrins in the extract from oil shale were characterized by mass- and visible-absorption spectra. The absorption spectrum of this oil-shale extract is shown in Figure 1. This spectrum is characteristic of phyllo-type porphyrins and indicates the presence of an isocyclic ring or a substituent group on one of the bridge-carbon atoms.

Table I is the high-voltage mass spectrum of the shale extract. This spectrum was obtained in the all-glass system, and only that portion of the spectrum in the molecular-weight region of the porphyrins is shown. In this spectrum the two homologous series beginning at the mass-to-charge ratios (*m/e*) of 420 and 422 account for more than 60% of the even-numbered ions in the molecular-weight region of the porphyrins.

A comparison of Table I with the spectrum of etioporphyrin I, shown in Table II, demonstrates the multiplicity of porphyrins present in the shale extract. In the etioporphyrin I spectrum, by far the largest peak is at *m/e* 478 which is the parent-ion peak. The size of the peaks in the same homologous series as the parent ion and in the homologous series two mass units less, are all smaller than 15% of the parent-ion peak, but in the spectrum of the shale extract, the peaks in both the alkylporphyrin series and series two mass units less are as large as 86% of the largest peak in the spectrum. This demonstrates that the shale porphrins are composed of several porphyrins in each of the two homologous series. The series two mass units less than the alkylporphyrin series can be accounted for by an isocyclic ring which can also account for the phyllo-type spectrum of this extract.

The peaks occurring up to *m/e* 480 (Table II), can be reasonably explained as being derived from electron impact upon the etioporphyrin I. The small peak at *m/e* 492 is probably due to an additional CH_2 group. The larger peaks at *m/e* 539 to 542 are not easily explained and are most probably impurities introduced in synthesizing the porphyrin and not due to condensation products resulting from thermal degradation.

A much different spectrum is obtained when the shale extract is introduced into the mass spectrometer equipped with an indium valve, and this spectrum is shown in Table III. By

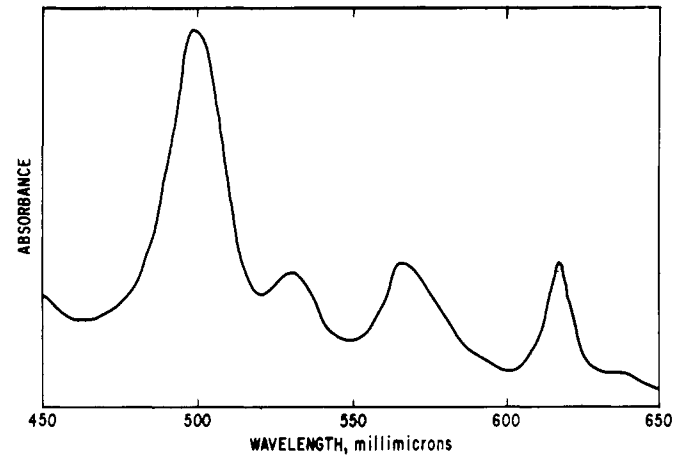

Figure 1. Spectrum of an oil-shale extract

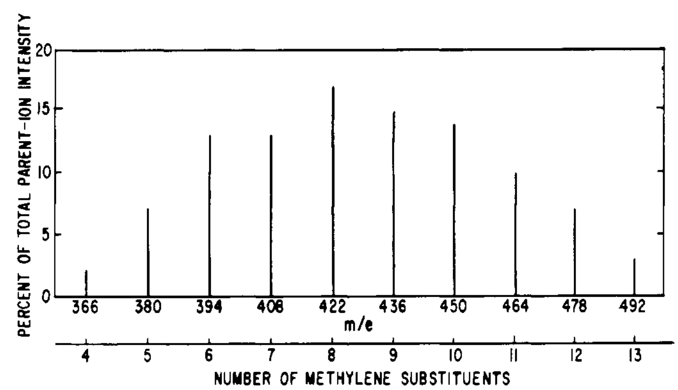

Figure 2. Distribution of ion intensities of shale-oil porphyrins

Table I. Partial Mass Spectrum of Oil-Shale Porphyrins Obtained in All-Glass System

m/e	Relative[a] Intensity	*m/e*	Relative[a] Intensity	*m/e*	Relative[a] Intensity	*m/e*	Relative[a] Intensity	*m/e*	Relative[a] Intensity
400	3.9	424	3.9	448	49.4	472	5.8	496	1.0
401	6.1	425	2.5	449	38.1	473	5.1	497	1.0
402	6.4	426	2.3	450	78.4	474	9.2	498	3.4
403	10.0	427	2.7	451	28.3	475	14.5	499	1.8
404	7.5	428	3.7	452	7.5	476	92.3	500	2.3
405	9.0	429	5.8	453	2.2	477	40.1	501	1.7
406	6.8	430	6.8	454	1.5	478	68.4	502	2.9
407	6.8	431	11.1	455	1.7	479	24.7	503	1.8
408	8.2	432	10.7	456	2.5	480	5.8	504	2.5
409	4.2	433	17.4	457	2.7	481	1.3	505	1.5
410	2.9	434	24.6	458	4.6	482	0.5	506	1.8
411	2.9	435	24.2	459	6.1	483	0.6	507	0.8
412	2.9	436	40.0	460	9.2	484	3.4	508	0.5
413	3.7	437	14.5	461	24.6	485	1.5	509	1.0
414	4.1	438	6.4	462	86.8	486	2.9	510	1.1
415	7.1	439	2.3	463	48.2	487	2.3	511	1.3
416	8.0	440	2.0	464	100.0[a]	488	5.1	512	1.8
417	12.6	441	2.0	465	36.7	489	3.4	513	1.0
418	11.4	442	2.3	466	8.7	490	20.8	514	1.0
419	14.1	443	3.7	467	2.7	491	9.4	515	0.6
420	12.4	444	4.7	468	1.3	492	6.8	516	1.5
421	12.8	445	8.2	469	1.3	493	3.0	517	1.0
422	18.1	446	10.6	470	3.0	494	1.3	518	2.2
423	7.8	447	22.2	471	2.7	495	0.8	519	0.6
								520	0.8

[a] Relative to the largest peak in the spectrum, *m/e* 464.

Table II. Partial Mass Spectrum of Etioporphyrin I Obtained in All-Glass System

m/e	Relative[a] Intensity	m/e	Relative[a] Intensity	m/e	Relative[a] Intensity	m/e	Relative[a] Intensity	m/e	Relative[a] Intensity
400	0.3	436	0.9	472	0.3	499	0.3	529	0.9
401	0.5	437	0.4	473	0.3	500	0.3	530	0.8
402	0.6	438	0.2	474	1.0	501	0.5	532	2.7
403	1.0	443	0.1	475	1.4	502	0.3	533	1.0
404	0.8	444	0.3	476	14.3	503	0.1	534	0.6
405	0.7	445	1.0	477	10.8	504	0.2	535	0.1
406	0.3	446	1.6	478	100.0[a]	506	0.2	536	0.1
407	0.2	447	4.1	479	38.3	507	0.3	537	0.7
413[b]	0.1	448	4.8	480	8.2	508	0.7	538	0.9
414	0.3	449	3.7	481	1.7	509	1.3	539	11.1
415	0.7	450	5.2	482	0.6	510	1.3	540	14.3
416	0.8	451	2.5	483	0.4	511	1.5	541	9.0
417	1.6	452	1.1	484	0.4	512	1.3	542	8.0
418	1.3	453	0.7	485	0.3	513	0.9	543	3.3
419	1.7	454	0.4	486	0.5	514	0.8	544	4.2
420	0.8	455	0.2	487	0.2	515	0.4	545	1.8
421	0.4	456	0.1	488	0.1	516	0.3	546	0.8
422	0.3	459	0.3	489	0.1	517	0.4	547	0.5
423	0.1	460	0.5	490	1.1	518	0.5	548	0.3
428	0.1	461	2.7	491	0.6	519	0.2	550	0.1
429	0.5	462	3.0	492	1.5	522	0.2	551	0.2
430	0.6	463	15.4	493	1.1	523	0.3	552	0.3
431	1.6	464	13.6	494	1.0	524	1.8	553	0.4
432	1.8	465	3.9	495	0.9	525	3.1	554	0.2
433	2.7	466	0.8	496	0.7	526	2.8	555	0.2
434	1.5	467	0.1	497	0.6	527	2.0	556	0.1
435	1.3	471	0.1	498	0.4	528	1.3	557	0.1

[a] Relative to the molecular-ion peak of etioporphyrin I, *m/e* 478.

[b] Missing *m/e* value indicates zero galvanometer response.

Table III. Partial Mass Spectrum of Oil-Shale Porphyrins Obtained with Indium Valve in Holding Volume

m/e	Relative[a] Intensity	m/e	Relative[a] Intensity	m/e	Relative[a] Intensity	m/e	Relative[a] Intensity	m/e	Relative[a] Intensity
500	6	531	32	562	x	595	5	641	x
501	9	532	27	563	85	596	10	642	66
502	10	533	26	564	30	597	x	643	x
503	12	534	19	565	7	598	27	644	52
504	13	535	24	566	2	600	13	645	x
505	9	536	10	567	1	601	7	653	x
506	8	537	13	568	2	602	7	654	36
507	7	538	10	569	4	603	10	655	x
508	6	539	15	570	4	604	4	656	100[a]
509	7	540	14	571	5	605	3	657	x
510	8	541	16	572	9	609	x	658	75
511	11	542	21	573	16	610	17	659	x
512	11	543	24	574	x	611	x	667	x
513	10	544	28	575	54	612	38	668	45
514	12	545	31	576	x	613	x	669	x
515	15	546	30	577	97	614	25	670	95
516	17	547	35	578	35	615	12	671	x
517	20	548	31	579	6	616	12	672	60
518	19	549	42	581[c]	2	623	x	673	x
519	18	550	16	582	3	624	20	681	x
520	12	551	5	583	x	625	x	682	6
521	13	552	2	584	16	626	37	683	x
522	8	553	2	585	x	627	x	684	12
523	12	554	3	586	8	628	80	685	x
524	12	555	3	587	10	629	x	686	13
525	18	556	7	588	x	630	26	687	x
526	17	557	11	589	53	631	x	698	3
527	19	558	16	590	x	637	x	699	x
528	23	559	22	591	92	638	9	700	3
529	26	560	x[b]	592	22	639	x	701	x
530	29	561	50	593	3	640	25		

[a] Relative to the largest peak in the spectrum, *m/e* 656.

[b] An x indicates that the peak height was uncertain because of incomplete resolution.

[c] Missing *m/e* value indicates zero galvanometer response.

making two assumptions, the origin of the major peaks in this spectrum can be explained. The first assumption is that the spectrum obtained in the all-glass system (Table I) is the spectrum of the shale porphyrins which have undergone decarboxylation while in the heated (250° C.) inlet system of the mass spectrometer. This assumption is substantiated by the presence of a large peak at *m/e* 44. The second assumption is that with indium chloride present, the porphyrins form an indium monochloride complex. This complex is less easily decarboxylated than is the original uncomplexed porphyrin and, therefore, its mass spectrum can be observed.

The composition of the peaks at *m/e* 658, 656, and 654; 614, 612, and 610; and 577 and 575 can be explained as follows: two porphyrins are present in the extract. One has a molecular weight of 508 and is made up of one carboxy group and 11 methylene substituents. The other has a molecular weight of 506 and is made up of *one carboxy group, one isocyclic ring,* and enough methylene substituents to give the 506 molecular weight. When these two porphyrins complex with the indium chloride, the complexes will have molecular weights of 654, 656, and 658. Part of the 656 complex and all of the 658 complex will be due to the formation of the complex containing Cl^{37} isotope. Decarboxylation may occur at any time before or after the complex is formed. This decarboxylation reaction results in molecules having as their molecular weights 610, 612, and 614, which are the indium monochloride complexes of the decarboxylated porphyrins having molecular weights of 462 and 464 (Table I). Electron-impact fragmentation of these de-

Table IV. Partial Mass Spectrum of Mesoporphyrin IX Dimethylester with Inlet System at 250° C.

m/e	Relative[a] Intensity	*m/e*	Relative[a] Intensity	*m/e*	Relative[a] Intensity	*m/e*	Relative[a] Intensity	*m/e*	Relative[a] Intensity
380	0.4	436	7.8	491	1.4	546	1.1	601	0.4
381	0.3	437	2.7	492	1.5	547	1.1	602	0.4
382	0.4	438	0.5	493	1.8	548	2.0	606	0.3
383	0.4	439	0.3	494	2.3	549	1.4	607	0.8
385[b]	0.7	440	0.3	495	1.4	550	1.9	608	1.5
386	0.9	441	0.4	496	1.5	551	0.9	609	0.9
387	1.3	442	0.4	497	0.8	552	0.5	610	0.9
388	1.4	443	0.9	498	1.3	553	0.3	611	0.5
389	1.7	444	1.6	499	0.9	554	0.3	612	0.3
390	1.4	445	2.8	500	2.2	555	0.2	613	0.1
391	1.4	446	4.5	501	0.8	556	0.2	614	0.1
392	0.9	447	8.0	502	0.8	557	0.3	623	0.2
393	0.8	448	10.6	503	0.5	558	0.6	624	0.3
394	0.9	449	15.2	504	1.1	559	0.7	625	0.3
395	0.4	450	16.6	505	2.3	560	1.0	626	0.5
396	0.2	451	5.1	506	3.3	561	1.4	627	0.6
397	0.2	452	0.9	507	7.5	562	2.6	628	0.6
398	0.3	453	0.3	508	11.7	563	3.6	629	0.5
399	0.7	454	0.3	509	4.7	564	2.3	630	0.5
400	1.0	455	0.6	510	1.9	565	1.3	631	0.3
401	1.7	456	0.7	511	1.3	566	1.8	632	0.2
402	2.0	457	1.1	512	1.2	567	1.0	633	0.2
403	3.1	458	1.6	513	0.5	568	0.8	634	0.1
404	2.6	459	2.2	514	0.5	569	0.9	635	0.2
405	2.9	460	3.8	515	0.4	570	0.8	636	0.3
406	1.7	461	6.1	516	0.7	571	0.4	637	0.4
407	1.5	462	8.5	517	0.6	572	0.3	638	0.4
408	1.7	463	11.9	518	1.4	573	0.3	639	0.1
409	0.7	464	15.5	519	3.0	574	0.9	644	0.3
410	0.2	465	5.2	520	20.3	575	2.2	645	0.8
411	0.2	466	1.1	521	38.4	576	3.7	646	1.1
412	0.3	467	0.4	522	55.6	577	1.3	647	1.0
413	0.6	468	0.3	523	20.0	578	2.5	648	0.9
414	1.2	469	0.7	524	4.2	579	3.9	649	0.9
415	2.3	470	0.8	525	1.1	580	3.8	650	1.3
416	3.0	471	1.2	526	0.7	581	1.9	651	4.4
417	4.7	472	1.7	527	0.3	582	3.0	652	11.5
418	4.4	473	1.2	528	0.3	583	5.1	653	5.5
419	5.3	474	1.6	529	0.3	584	4.7	654	2.1
420	3.6	475	2.7	530	0.6	585	3.1	655	1.0
421	3.3	476	5.2	531	0.5	586	1.9	656	0.8
422	3.7	477	5.2	532	1.1	587	1.0	657	0.8
423	1.3	478	7.7	533	3.8	588	0.8	658	1.0
424	0.4	479	3.1	534	8.1	589	0.6	659	3.3
425	0.3	480	1.2	535	16.9	590	1.4	660	10.3
426	0.3	481	0.7	536	35.0	591	1.6	661	17.8
427	0.6	482	0.6	537	14.4	592	5.0	662	12.7
428	1.0	483	1.6	538	3.4	593	44.7	663	10.5
429	1.8	484	3.4	539	0.8	594	100.0[a]	664	6.3
430	2.7	485	1.9	540	0.4	595	45.0	665	5.6
431	4.6	486	2.2	541	0.2	596	12.2	666	1.6
432	5.9	487	1.2	542	0.2	597	3.6	667	0.6
433	8.4	488	0.9	543	0.9	598	2.3		
434	7.0	489	0.6	544	1.8	599	1.3		
435	7.4	490	1.2	545	1.1	600	0.9		

[a] Relative to the molecular-ion peak of mesoporphyrin IX dimethylester, *m/e* 594.

[b] Missing *m/e* value indicates zero galvanometer response.

carboxylated, indium monochloride complexes account for the peaks occurring at m/e 577 and 575 by the loss of chlorine. Similar treatment of the other groups of peaks at 8, 9, 10, 12, and 13 methylene substituents account for the major peaks shown in Table III.

Table V. Temperature Dependence of Thermal Decarbomethoxylation of Mesoporphyrin IX Dimethylester

Selected Peak	Unit or Units Lost	Ratio of Selected Peaks to the m/e 594 Peak	
		250° C.[a]	300° C.[a]
594	parent (no loss)	1.00	1.00
536	$(\text{—COOCH}_2\text{—})$	0.35	2.45
522	$(\text{—CH}_2\text{COOCH}_2\text{—})$	0.56	1.90
508	$(\text{—CH}_2\text{CH}_2\text{COOCH}_2\text{—})$	0.12	0.46
478	$2(\text{—COOCH}_2\text{—})$	0.18	1.15
464	$(\text{—COOCH}_2\text{—}) + (\text{—CH}_2\text{COOCH}_2\text{—})$	0.15	1.45
450	$2(\text{—CH}_2\text{COOCH}_2\text{—})$	0.16	0.93
436	$(\text{—CH}_2\text{COOCH}_2\text{—}) + (\text{—CH}_2\text{CH}_2\text{COOCH}_2\text{—})$	0.08	0.33

[a] Approximate holding-volume temperature.

The major part of the shale porphyrins contain a carboxy group and 8 to 13 methylene substituents on the porphine ring. There is evidence from both the absorption and mass spectra that some of the porphyrin molecules contain an isocyclic ring. The above discussion does not preclude some carboalkoxy substitution because the treatment is only qualitative and the thermal loss of a carboalkoxy group would also fit the data.

Table IV shows the mass spectrum of mesoporphyrin IX dimethylester in the parent-ion region. The parent-ion peak is the largest peak in this spectrum, but there are also other major peaks present that can be explained by thermal decarbomethoxylation. The larger peaks beyond the parent-ion peaks are likely impurities in the sample. The peak at m/e 608 may be due to an additional $\text{—CH}_2\text{—}$, the peak at 652 may be due to an extra $\text{—COOCH}_2\text{—}$, and the one at 661 may possibly be the gallium complex of mesoporphyrin IX dimethylester because gallium is used in the inlet system of the mass spectrometer.

Ion-impact fragmentation explains the small peaks at m/e 579 (loss of —CH_3), 563 (loss of —OCH_3), 550 (loss of CO_2), 548 (loss of —CH_3 and —OCH_3), 535 (loss of —COOCH_3), and 520 (loss of —CH_3 and —COOCH_3). The occurrence of thermal

Table VI. Partial Mass Spectrum of Ten-Stage Solvent Extraction Sample of Shale-Oil Porphyrins[a]

m/e	Relative[b] Intensity	m/e	Relative[b] Intensity	m/e	Relative[b] Intensity	m/e	Relative[b] Intensity	m/e	Relative[b] Intensity
431	144	474	162	517	77	560	48	601	x
432	284	475	126	518	89	561	45	602	79
433	247	476	193	519	107	562	30	603	33
434	308	477	164	520	112	563	56	604	14
435	267	478	203	521	206	564	36	605	11
436	290	479	214	522	99	565	16	606	7
437	247	480	170	523	48	566	16	607	7
438	315	481	123	524	49	567	16	608	7
439	260	482	153	525	41	568	27	609	10
440	349	483	152	526	51	569	27	610	16
441	315	484	153	527	37	570	51	611	x
442	326	485	108	528	60	571	x[c]	612	33
443	260	486	129	529	36	572	84	613	x
444	307	487	85	530	55	573	x	614	95
445	206	488	140	531	45	574	69	615	47
446	247	489	123	532	52	575	41	616	75
447	212	490	164	533	85	576	23	617	25
448	253	491	158	534	71	577	30	618	7
449	211	492	171	535	158	578	15	626	26
450	263	493	234	536	71	579	10	627	x
451	203	494	140	537	41	580	10	628	73
452	256	495	93	538	44	581	12	629	36
453	201	496	112	539	33	582	16	630	58
454	270	497	118	540	40	583	x	631	23
455	267	498	122	541	34	584	37	632	10
456	269	499	75	542	66	585	x	640	21
457	204	500	103	543	48	586	92	641	x
458	241	501	75	544	66	587	x	642	52
459	162	502	110	545	51	588	84	643	25
460	193	503	103	546	58	589	38	644	36
461	164	504	130	547	70	590	15	645	14
462	222	505	144	548	58	591	14	654	12
463	185	506	137	549	110	592	10	655	x
464	222	507	215	550	52	593	7	656	27
465	178	508	121	551	27	594	7	657	14
466	219	509	66	552	27	595	11	658	16
467	164	510	73	553	19	596	16	659	5
468	208	511	63	554	27	597	x	668	7
469	210	512	69	555	26	598	38	669	x
470	204	513	45	556	55	599	x	670	11
471	158	514	78	557	52	600	100[b]	671	4
472	184	515	55	558	60				
473	123	516	82	559	40				

[a] Spectrum obtained with an indium valve in the holding volume.
[b] Relative to the molecular-ion peak of the largest porphyrin molecular ion in the spectrum, m/e 600.
[c] An x indicates that the peak height was uncertain because of incomplete resolution.

decarbomethoxylation in the holding volume can account for the substantial peaks at *m/e* 536, 522, 508, 478, 464, 450, and 436.

To demonstrate the thermal instability of carboalkoxylated porphyrins, the spectrum of mesoporphyrin IX dimethylester was obtained at a higher temperature than was the spectrum shown in Table IV. Comparisons of selected peaks in each of these two spectra are shown in Table V. The increase with temperature in the ratios of the decarbomethoxylated porphyrins to the original parent is credited to the additional thermal decarbomethoxylation.

The occurrence of the thermal decarbomethoxylation of mesoporphyrin IX dimethylester in the mass spectrometer, along with the different spectra obtained with the shale porphyrins in the all-glass system and with the indium valve present, leads to the conclusion that carboxylated porphyrins predominate in the shale porphyrins.

Shale Oil. Table VI is a high-voltage mass spectrum of a ten-stage, solvent-extraction sample of shale-oil porphyrins. This spectrum was obtained when indium chloride was present in the mass spectrometer. Unlike the shale porphyrins, these shale-oil porphyrins did not give a characterizable spectrum when there was no chance to form the indium chloride complex. This is because the molecular weights of the nonporphyrin impurities in the shale-oil extracts are in the same range as the molecular weights of the shale-oil porphyrins. Because the amount of impurity is large, the peaks due to the porphyrins are lost in the noncharacterizable spectrum of the impurity which has a large peak at each *m/e*. The interference from the nonporphyrin impurity can be seen in that part of the spectrum shown in Table VI from *m/e* 431 to *m/e* 500. Formation of the indium monochloride complex of the shale-oil porphyrins increased the molecular weights of the porphyrins by 148 mass units. This separated the porphyrins from the nonporphyrin impurity and made possible characterization of the porphyrins. Thus, it was only with the indium chloride complex that any mass-spectral data were obtained on the shale-oil porphyrins from the ten-stage extraction.

The spectrum shown in Table VI is quite different from the spectrum of the indium chloride complex of the shale extract, shown in Table III. The most singular difference is the size of the peaks in the series four mass units greater than the alkylporphine series—i.e., at *m/e* 530, 544, etc. The sizes of the peaks in this series in Table VI are too large to be accounted for by Cl^{37} isotope of the peaks in the series *m/e* 528, 542, etc. The structure of the porphyrins in this series can best be accounted for by the presence of two carboxy or carboalkoxy groups. Why these were not evident in the oil-shale porphyrins before retorting is not apparent.

Another difference is the absence of any concentration of ions in the series two mass units less than the alkylporphine series. This could explain the absorption spectra of the shale-oil porphyrins which were of the etio type indicating no isocyclic ring present.

The only ion-impact fragments which are discernible in this shale-oil porphyrin spectrum are those ions resulting from the loss of chlorine from the alkylporphine series. These ions appear at *m/e* 479, 493, ... 577.

The molecular-weight range of the indium monochloride-free porphyrins in this shale-oil extract is 366 to 522. The molecular-weight range of the porphyrin in the shale extract is 436 to 536. Thus, the molecular weights of the porphyrins were lowered during retorting.

Further purification of the shale-oil porphyrins by alumina chromatography removed much of the impurity left by the repeated-transfer technique. The recovery of the porphyrins from the alumina column in the small-scale purification was about 95% as measured by the amount of absorption in the visible region. The mass spectra, however, were very different from the spectrum shown in Table VI, with no indication of carboxy or carboalkoxy groups. Because the recovery was nearly complete, decarboxylation or decarboalkoxylation of the porphyrins must have occurred on the alumina.

Characterization of the chromatographed porphyrins, even though they had been decarboxylated, was made in order to emphasize the complexity of the porphyrins occurring in shale

Table VII. Partial Mass Spectrum of Chromatographed Sample of Shale-Oil Porphyrins[a]

m/e	Relative[b] Intensity	*m/e*	Relative[b] Intensity	*m/e*	Relative[b] Intensity	*m/e*	Relative[b] Intensity	*m/e*	Relative[b] Intensity
330	1.2	356	1.8	390	1.7	428	0.5	471	0.2
331	1.1	357	0.9	391	6.5	429	0.3	472	0.4
332	1.2	358	1.9	392	3.3	430	0.4	474	0.4
333	1.3	359	0.4	393	21.2	431	0.4	475	0.2
334	3.7	360	1.6	394	17.6	432	0.6	476	2.0
335	2.0	361	2.8	399	0.7	433	0.6	477	0.4
336	2.2	362	3.4	400	1.0	434	4.6	478	0.8
337	2.0	363	5.1	401	0.9	435	0.6	482	0.3
338	2.9	364	3.1	402	0.6	436	41.3	484	0.5
339	1.4	365	11.9	403	2.0	442	0.2	486	0.6
340	1.9	366	41.2	404	1.2	443	0.5	488	1.0
341	1.4	370	1.2[c]	405	4.4	444	0.3	490	0.3
342	1.7	371	1.0	406	3.4	445	0.4	492	0.4
343	1.2	372	1.5	407	1.5	446	0.2	494	0.1
344	2.0	373	1.2	408	82.6	447	0.4	496	0.1
345	1.1	374	1.8	414	0.2	448	2.0	498	0.4
346	1.6	375	3.1	415	1.1	449	1.8	502	0.3
347	2.9	376	3.0	416	0.7	450	4.2	504	0.6
348	3.9	377	8.7	417	0.9	455	0.2	508	0.9
349	2.8	378	4.5	418	0.7	456	0.7	510	0.9
350	3.3	379	8.9	419	2.6	458	0.4	512	0.2
351	4.6	380	100.0[b]	420	2.1	460	0.5	514	0.1
352	9.6	386	1.3	421	5.2	462	2.9	516	0.1
353	3.3	387	2.0	422	17.3	463	1.1	518	0.1
354	0.8	388	1.0	426	0.2	464	18.8	520	0.1
355	0.1	389	2.8	427	0.3	470	0.5		

[a] Spectrum obtained on nickel-porphyrin complex and calculated to the nickel-free monoisotopic value.
[b] Relative to the highest peak in the spectrum, *m/e* 380.
[c] Missing *m/e* value indicates zero peak height.

Table VIII. Partial Low-Voltage Mass Spectrum of Chromatographed Sample of Shale-Oil Porphyrins[a]

m/e	Relative[b] Intensity	Number of —CH_2— Substituents	m/e	Relative[b] Intensity	Number of —CH_2— Substituents
346	1		420	5	
348	1[c]		421	5	
350	2		422	4	
351	1		423	4	
352	10	3	424	8	8
354	1		425	1	
358	1		426	1	
360	1		430	2	
362	1		433	1	
364	1		434	5	
365	5		435	6	
366	38	4	436	46	9
368	1		440	2	
370	1		441	1	
372	1		444	1	
376	1		446	1	
378	2		448	4	
379	16		449	1	
380	100[b]	5	450	7	10
374	1		454	1	
386	2		458	1	
390	1		461	1	
392	2		462	4	
393	6		463	4	
394	28	6	464	21	11
398	1		472	1	
400	1		474	1	
406	4		476	1	
407	15		478	2	12
408	92	7	486	1	
415	1		488	1	
416	1		490	1	
418	1				

[a] Spectrum obtained on nickel-porphyrin complex and calculated to the nickel-free monoisotopic value.

[b] Relative to the highest peak in the spectrum, m/e 380.

[c] Missing m/e value indicates zero peak height.

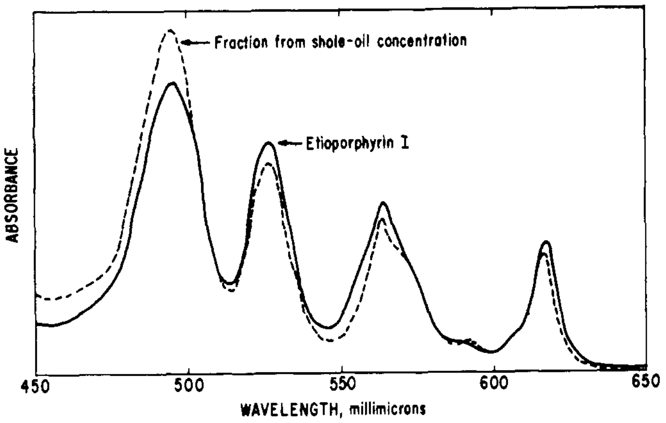

Figure 3. Comparison of spectra of shale-oil porphyrins and etioporphyrin I.

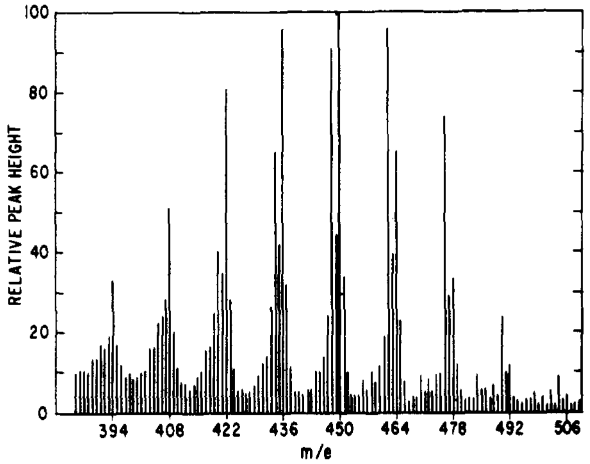

Figure 4. Partial mass spectrum of Wilmington crude-oil porphyrins

oil. The low-voltage spectrum of the small-scale chromatographic concentrate was obtained using the indium valve. This spectrum was corrected for the indium chloride and the calculated low-voltage spectrum had major ions in only two homologous series. About 90% were in the alkylporphyrin series, and the rest were in the series two mass units less. Figure 2 shows the distribution of the ions in the alkylporphyrin series.

The low-voltage spectrum of this concentrate, obtained in an all-glass system, was nearly identical to the indium chloride-free spectrum from which Figure 2 was derived. The fact that the two spectra—with and without the indium chloride complex—were the same was evidence for the absence of carboxy groups in the chromatographed shale-oil porphyrins. Additional evidence for the absence of carboxy groups in the chromatographed extract was obtained from the high-voltage spectrum of the indium chloride complex. In this spectrum, there was no series of peaks corresponding to the thermal loss of a carboxy group either before or after complexing. Thus the chromatographed shale-oil porphyrins were concluded to be primarily alkylporphyrins with a range of 4 to 13 methylene substituents. Their average molecular weight was 436 which is equivalent to the porphine ring with nine methylene substituents.

Table VII shows the monoisotopic, high-ionizing voltage mass spectrum of one of the fractions from the large-scale chromatographic purification. Table VIII is the monoisotopic, low-ionizing voltage mass spectrum of the same fraction. In the high-ionizing voltage spectrum, the distribution of peaks was similar to that reported by Hood (*9*) and Meade (*10*) for the metal complexes of etioporphyrin. In the low-ionizing voltage spectrum, peaks occurred very predominately in the alkylporphyrin series indicating that these peaks were due to parent ions. The reason for the greater abundance of odd-numbered methylene substituents over even-numbered ones is unexplained; this distribution is not evident in the low-voltage spectrum of the total, chromatographed concentrate shown in Figure 2.

The purest porphyrin concentrate studied was prepared by countercurrent extraction of a chromatographed fraction of shale-oil porphyrins. In Figure 3, the visible absorption spectrum of this concentrate is compared with the visible spectrum of etioporphyrin I. The close agreement confirms the conclusions from the mass-spectral data that the chromatographed, shale-oil porphyrins are mainly alkylsubstituted porphyrins.

Wilmington Petroleum. The porphyrins in the extract from Wilmington petroleum had a phyllo-type absorption spectrum. Figure 4 shows the high-voltage mass spectrum of the extract in the molecular-weight region of the porphyrins. This spectrum was obtained in the all-glass system and is the spectrum of decarboxylated, metal-free porphyrins. It is similar to the spectrum in Table I which is the high-voltage spectrum of the oil-shale extract using the all-glass system. The low-voltage spectra, using the all-glass system, were also very similar as were the spectra obtained using the indium valve.

These similarities suggest that, like the oil-shale porphyrins, the Wilmington porphyrins are mostly alkylsubstituted, carboxylated porphyrins. The molecular-weight range of the Wilmington crude-oil porphyrins was 438 to 550. The average molecular weight was 494 which is equivalent to the porphine ring with one carboxy and 10 methylene substituents.

Dunning (*4*), working with a heavy crude oil of the North Belridge field in Kern County, Calif., concluded that the porphyrins present in this crude were largely decarboxylated types. This conclusion was based on R_f data obtained from paper chromatographic separations of alumina-chromatographed porphyrins. The present data concerning the absence of carboxy units in alumina-chromatographed porphyrins could explain the absence of carboxylated porphyrins in the North Belridge crude.

CONCLUSIONS

The porphyrins in oil shale and Wilmington petroleum were shown to be similar and to contain at least two homologous series. The porphyrins are alkylsubstituted and contain from 7 to 13 methylene substituents per molecule. Most of the porphyrin molecules also contain a carboxyl group. A part of the alkyl substitution in some of the porphyrin molecules may exist as an isocyclic ring.

The porphyrins in shale oil are a complex mixture of etio-type porphyrins. They have a molecular-weight range of 366 to 522. There is evidence for the lack of an isocyclic ring and for the presence of both one and two carboalkoxy groups.

This work demonstrated that the skeleton of the porphyrin molecules in oil shale can survive retorting temperatures. However, the substituent groups on the skeleton are changed, with the resulting porphyrins having a lower molecular weight. The phyllo-type character of the shale porphyrins is changed to an etio-type character by the retorting process. The reaction necessary to bring about this change in spectral classification is the removal of a substituent group from one of the bridge-carbon atoms.

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