

JOINT SYMPOSIUM ON OIL SHALE, TAR SANDS, AND RELATED MATERIAL
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ANALYSIS OF THE MINERAL ENTRAPPED FATTY ACIDS ISOLATED
FROM THE GREEN RIVER SHALE (EOCENE)

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INTRODUCTION

The Green River Shale, of Eocene age, has been the object of extensive organic geochemical studies. Most of the investigations have been concerned with the extractables and have resulted in the characterization of various classes of compounds. The hydrocarbon fraction, which has been most thoroughly investigated, includes normals, isoprenoids, iso and anteiso alkanes, steranes and triterpanes, and aromatics (1-5). Various reports have dealt with the organic acid fraction. The presence of a homologous series of normal fatty acids (6, 7), iso and anteiso acids (8), isoprenoid acids ranging from C₉ to C₂₁, with the exception of C₁₈ (9-12), dicarboxylic acids ranging from C₁₂ to C₁₈ (12), C₁₁ and C₁₄ methylketoacids (13), and several series of aromatic acids (14) have been established.

We wish to report on the analysis of the organic acids liberated after demineralization of the exhaustively extracted shale. The families of compounds found were essentially the same as those reported present in the solvent soluble fraction of the shale.

EXPERIMENTAL

A sample of Green River Shale from Parachute Creek, 8 miles NW of Grand Valley, Colorado (long. W 108°7'; lat. N 39°37'; el. 7300') was pulverized to pass 200 mesh. The powdered rock was exhaustively extracted using ultrasonication, as well as Soxhlet extraction with 3:1 benzene/methanol. This was followed by two room temperature digestions (2 days each) with 1:1 concentrated hydrofluoric acid/hydrochloric acid. To remove sulfides and free sulfur, the residue was further treated with zinc dust and 6M hydrochloric acid (Forsman and Hunt). By repetitive ultrasonic extractions with 4:1 benzene/methanol 0.17% (by weight of original rock) of solubilized organics were isolated and subsequently separated into 0.04% neutrals and 0.13% acids (the kerogen residue amounted to 48%). The acid fraction was esterified with BF₃/methanol, passed over silica gel and clathrated with urea yielding 1:3 normals/branched-cyclics (see flow-sheet Fig. 1). The total, normal and branched-cyclic fractions were chromatographed on a 5' x 1/8" column, packed with 3% SE-30 on chromosorb and programmed from 100-270°C at 10°/min. with a flow rate of 50 ml/min. The GLC components were identified by their retention times, coinjection of standards, low resolution mass spectra and then correlated to the high resolution mass spectra of the total mixtures run on a C. E. C. 21-110B mass spectrometer with direct inlet at ion source temperatures from 150-270°C. Figure 2 illustrates a GLC run on the three fractions. In the normal fraction there is an even/odd predominance as established by characterization of the peaks. The labeled peaks were checked by coinjection of authentic standards. This same distribution is also found in the summation of the high resolution mass spectra at varying ion source temperatures of each fraction. Figure 3 is an example of a summed high resolution mass spectrum of the totals fraction. The masses are plotted in methylene units (15). On the abscissa, each major division marker corresponds to the saturated ion, e.g. C_nH_{2n+1}, with the number of carbon/hydrogen atoms given below. There are 14 units between each major division, and the number of hydrogen atoms of an unsaturated or cyclic ion is obtained simply by determining the difference from the position of the next higher saturated ion. The even/odd predominance of the monocarboxylic acids is also evident in the high resolution mass spectra of the normals and totals fraction, and can be easily discerned in the C/H O and C/H O₂ plots of Figure 3.

Table 1

Organic Acids from the Demineralized, Exhaustively Extracted
Green River Shale

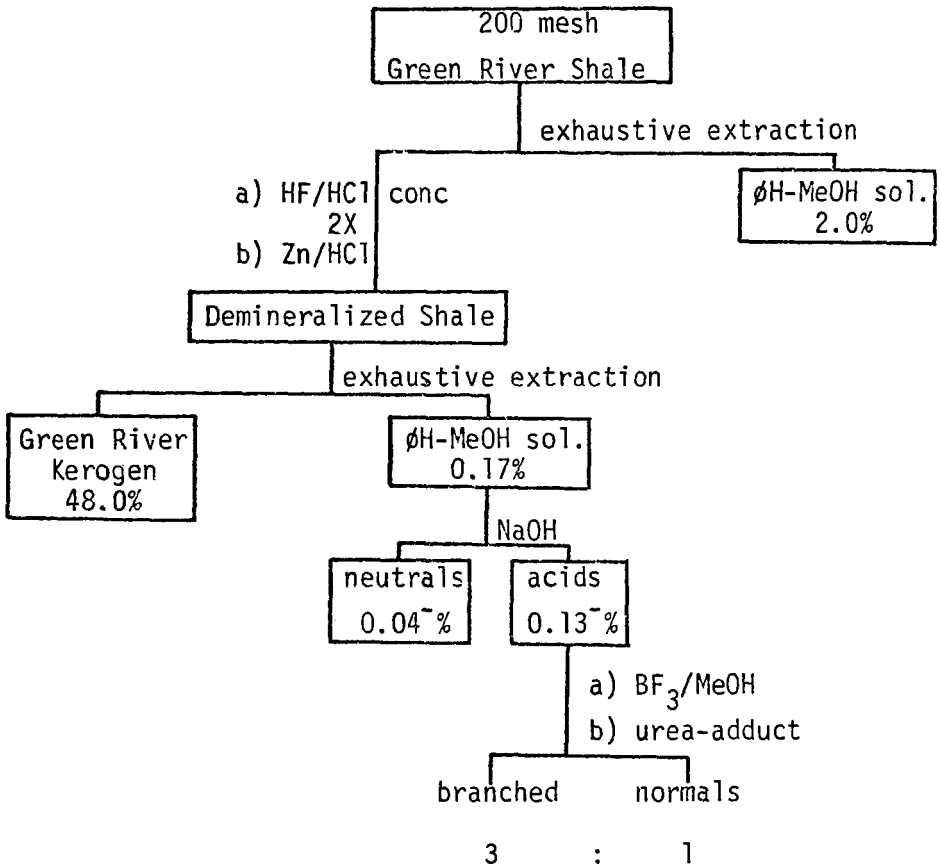
	<u>Range</u>	<u>Max. Conc.</u>
Normal Acids	C ₁ -C ₃₂ [*] C ₈ -C ₃₀ [≠]	C ₁₆ and C ₂₄
Branched Acids	C ₈ -C ₂₂ [*] C ₈ -C ₁₅ [≠]	C ₂₀
Dicarboxylic Acids	C ₃ -C ₁₈ ^{*≠}	C ₆
Methylketoacids	C ₄ -C ₁₆ [*]	C ₁₁
Aromatic Acids (phenyl)	C ₇ -C ₁₅ [*]	C ₉
Aromatic Acids (naphthyl)	C ₁₀ -C ₁₄ [*]	C ₁₁
Triterpenoid Acids	C ₂₈ -C ₃₄ [*]	C ₃₀

* determined by mass spectrometry

≠ determined from gas chromatograms

Figure 1

Experimental Flowsheet



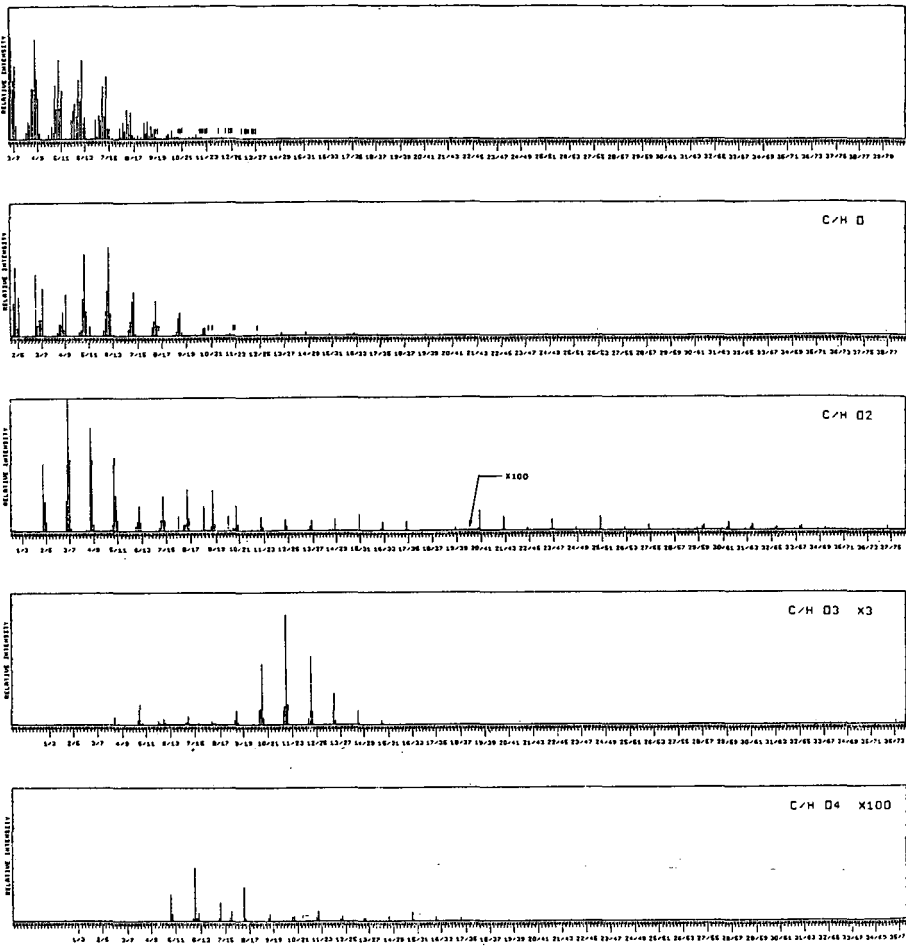
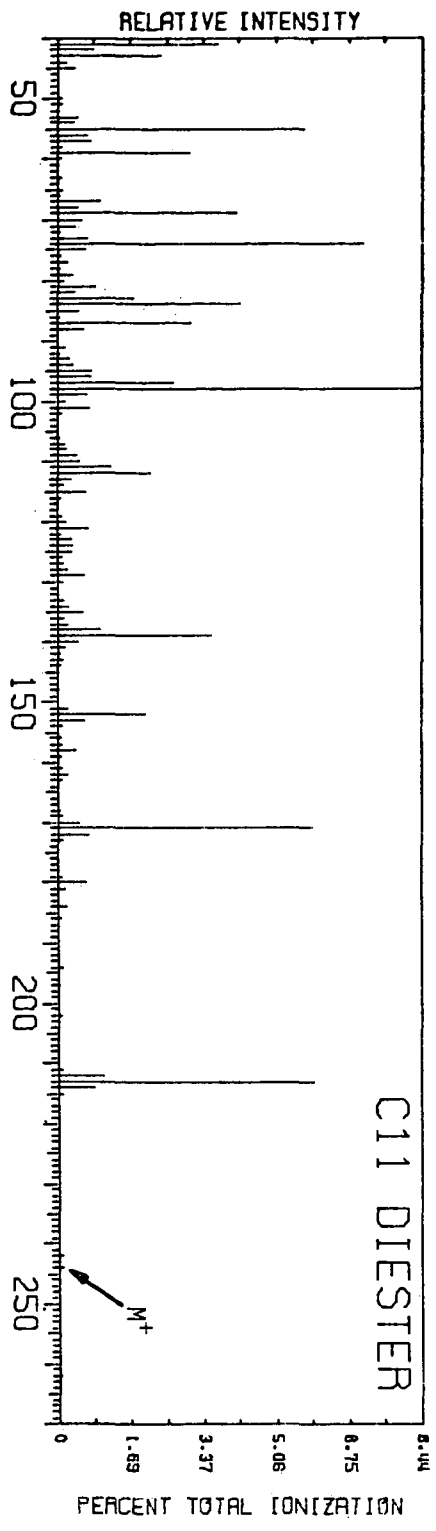


FIGURE 3 HIGH RESOLUTION MASS SPECTRUM OF THE TOTAL FRACTION OF ACID ESTERS ISOLATED AFTER DEMINERALIZATION OF THE GREEN RIVER SHALE (ION SOURCE TEMP. 150-170° C).

Figure 4 Low resolution mass spectrum of Dimethyl undecane-1,11-dioate isolated from Green River Shale.



RESULTS

The findings of this study are listed in Table 1 and described below in the same order as in the introduction. The homologous series of normal fatty acids found in the GLC ranged from C₈-C₃₀ with maxima at C₁₆ and C₂₄; the same was found in the high resolution mass spectra, only the range was C₁-C₃₂ due to greater sensitivity. The branched acids detected ranged from C₈-C₂₂; the cutoff on the GLC was C₁₅ and the major constituents were phytanic and norphytanic acids. These two aforementioned series were the major portion of the acid extract. The following series are described in order of decreasing concentration. Dicarboxylic acids ranging from C₃-C₁₈ with a maximum at C₆ (adipic acid) were found both in the GLC collection and high resolution mass spectra. Even though the molecular ions of this series are small, they were detectable and further substantiated by the presence of the strong peaks due to losses of CH₃O· and CH₂=C=O (Figure 4) (16). As, for example, in Figure 3 the C₁₁ diester of Figure 4 has its molecular ion C₁₃H₂₄O₄ in the C/H O₄ plot; the loss of CH₃O· results in the peak at C₁₂H₂₁O₃ in the C/H O₃ plot and the following loss of ketene yields the peak at C₁₀H₁₉O₂ in the C/H O₂ plot. Methylketoacids were found with compositions of C₄-C₁₆ with the distribution maximum at C₁₁ in the high resolution mass spectra. In the GLC they were buried among the major constituents. Their molecular ions were of reasonable intensity and the compound identities were further substantiated by the strong losses of CH₃O· and C₃H₅O (13,17). To illustrate with an example, again referring to Figure 3, the molecular ion C₁₁H₂₀O₃ is in the C/H O₃ plot, loss of CH₃O· results in the peak at C₁₀H₁₇O₂ in the C/H O₂ plot and M-C₃H₅O in the peak C₈H₁₅O₂ also in the C/H O₂ plot. The keto-acids exhibit a further characteristic strong peak due to M-CH₃O· - C₃H₅O, which corresponds to C₇H₁₂O for this example and is found in the C/H O plot.

The two major series of aromatic acids, namely methyl substituted benzoic and methyl substituted naphthoic acids (14) were also found. The identification of these compounds is based on the elemental compositions of the molecular ions and their respective strong M-CH₃O· peaks in the high resolution mass spectra of the total and branched-cyclic fractions. The major peaks due to the aromatic acids present in the C/H O₂ and C/H O plots of Figure 3 were deleted, since the compositions of the ions fall at the same nominal mass as the molecular ions of the saturated acids and the aromatic tic mark over the peak would be misleading (there are some aromatic ions in the C/H plot of Figure 3). The aromatic acids consisting of a substituted phenyl ranged from C₇ (benzoic acid) to C₁₅ with the distribution maximum at C₉; the bicyclic aromatic acids ranged from C₁₀ (indanoic acid) to C₁₄, the major constituent being C₁₁ (naphthoic acid). At higher ion source temperatures in the mass spectrometer, a group of triterpenoid acid esters volatilized and the following molecular ions were observed in the high resolution mass spectra of the totals and branched-cyclic fraction: 428 (C₂₈H₄₆O₂), 442 (C₃₀H₅₀O₂), 456 (C₃₁H₅₂O₂), 470 (C₃₂H₅₄O₂), 484 (C₃₃H₅₆O₂), 498 (C₃₄H₅₈O₂), 512 (C₃₅H₆₀O₂) and 458 (C₃₁H₅₄O₂). The distribution maximum was at C₃₁H₅₂O₂ and the M-CH₃O· peaks were also observed. Referring to Figure 3, the molecular ion C₃₁H₅₂O₂ is found in the C/H O₂ plot and its corresponding M-CH₃O· peak at C₃₀H₄₉O₂ in the same plot.

CONCLUSIONS

From these findings it can be concluded that these acids were indigenous to the shale and occur either trapped in the mineral-kerogen matrix, as metal salts, bound to the kerogen by easily hydrolyzed links, or possibly a combination of all three. It was shown by Eglinton *et al.* (11) that hydrofluoric acid digestion of Green River Shale does not interconvert normal acids to branched acids, lending further support to the fact that these acids did not migrate into the shale after deposition and compaction. Furthermore, these authors have found in subsequent experiments of chromic acid oxidation of kerogen residue after demineralization and exhaustive extraction (18) the same types or organic acids with a few minor differences. This leads to the conclusion that these organic acid groupings are bonded to the kerogen matrix *via* easily oxidized functionalities, or may be occluded in the polymer interstices in the form of alkanes, ketones or some other oxidizable structure, yielding the acids when liberated by the digestion and subsequent oxidation. For example, the triterpenoid acids found may have been trapped as triterpanes rather than being bonded to the kerogen.

This method of high resolution mass spectral runs using increasing ion source temperatures on whole extracts is extremely useful, especially in experiments where the fraction is too small to run on a GLC-mass spectrometer combination. Further selective experiments to determine absolutely what happens during the kerogen oxidation are in progress at this laboratory.

ACKNOWLEDGMENT

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