were necessary as the products obtained at 20°C were of constant composition (nonanoic, oleic, 10-nonadecenoic and 11-eicosenoic acids). At 40°C nonanoic acid was the dominant product. When the residue from extraction was treated with tetra-butyl ammonium hydroxide (TBAH) as a swelling agent, the esters present hydrolysed, and the resulting acids capped with methyl iodide (Liotta *et al.*, 1981), only a small amount of product was obtained. The product consisted essentially of the same acid esters as were obtained by extraction. Model compound experiments showed that osmium tetroxide/periodate specifically oxidises unsaturated compounds with little or no side reaction. Using this reagent, approximately half the hydrolysis residue was solubilized. The principal products were nonanal, pentadecanal and eicosanal. A new method of using ruthenium tetroxide to oxidise ethers to esters without cleavage of aromatics was developed. TBAH and methyl iodide was subsequently used to hydrolyse and cap the esters formed. The products obtained from the osmium tetroxide residue are almost exclusively diacids with C_{21}, C_{16} and C_{19} di-acids being the dominant products. These products are consistent with those obtained by a modified approach to the BBr_3 method of Albrecht *et al.*, (Chappe *et al.*, 1979). A final residue of not greater than 2% of the initial coorongite was obtained.

Using the results from this degradation scheme a model for the complete coorongite macromolecule can be constructed. The structure is polyunsaturated and linear (the sample clearly belonged to the A race of coorongite) with the bulk of the unsaturations occurring internally. Crosslinking in the structure occurs predominately via ether linkages, with an average molecular weight between these crosslinks of approximately 2000. This crosslinking is responsible for the characteristic rubbery texture of coorongite.

The reaction scheme as described has been shown to be equally effective on a range of immature sediments.

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7.15) Structural features of geolipids and kerogen isolated from a Spanish oil shale

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Oil shales have a special geochemical interest both as source rocks and as an energy resource in themselves. In fact, many outstanding works on the application of biomarkers for source rocks-oil correlations have been carried out in these sedimentary rocks.

The most important oil shale deposit in the Iberian Peninsula is located in the Puertollano Basin (Ciudad Real, Spain) from the upper Stephanian age, whose stratigraphy and palaeontology has recently been described (Wagner, 1985). However, there is not an integral study of this oil shale from the organic geochemical point of view. There are only a few comparative studies on specific characteristics of its kerogen (Robinson and Dinneen, 1965). In order to fill that gap, the aim of this study is to analyze the nature of the geolipids in the shale extracts and the structural features of the kerogen.

Our approach includes the comparison between conventional extraction technique and extraction with liquid CO_2. In addition, in order to investigate the influence of the separation protocols on some common biomarker parameters, the total extracts have been fractionated by various procedures, such as TLC, column chromatography on different solid phases and Bond Elut cartridges. The kerogen has also been characterized by conventional geochemical methods (EA, vitrinite reflectance, Rock-Eval), as well as by destructive (thermal and chemical degradations) and non-destructive (FT-IR and solid state NMR spectroscopy) techniques. A study has also been made of the bitumens trapped in the kerogen matrix by steric hindrance. This material can be recovered after acid treatment by sequential extraction with organic solvents.

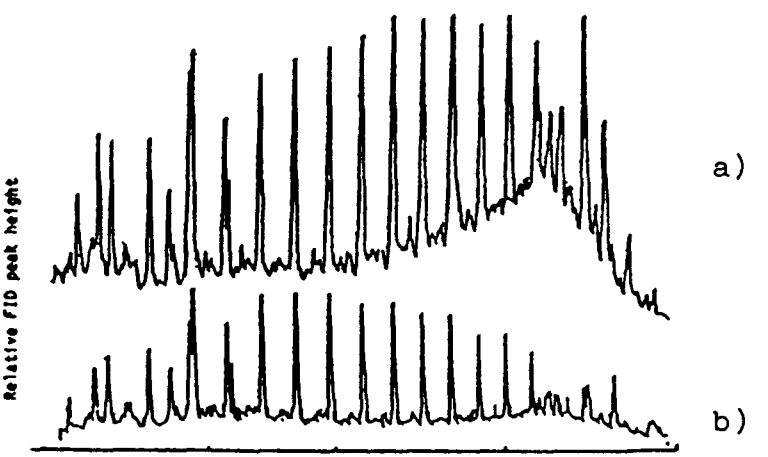

Fig. 1. Hydrocarbon patterns after fractionation by columns of silica gel: alumina (a) and florisil (b)

Table 1. Biomarkers identified in the oil shale extract

	range	major hom.	‰
n-alkanes	C13-C39	C23	350
iso/anteiso-alkanes	C16-C32		40
methyl-alkanes (middle)	C16-C32		40
acyclic isoprenoids	C15-C20	C19	80
n-alkyl-cyclohexanes	C13-C28		80
methyl-*n*-alkyl-cyclohexanes	C18-C28		80
bicyclic terpanes	C14-C16	C16	40
tricyclic terpanes (extended)	C19-C28	C23	40
diterpanes	C19		5
tetracyclic terpanes	C24		5
tetracyclic 17,21-secohopanes	C24		5
tetracyclic 8,14-secohopanes	C27-C30		1-3
steranes	C27-C29		5
diasteranes	C27-C29		5
pentacyclic hopanes	C27-C35	C30	200
gammacerane	C30		1-3
8,14-secohopanes aromatized (D)	C27-C31	C29	15
benzohopanes	C32-C35	C32	10

RESULTS

The main results obtained can be summarized as follows:

—extraction with liquid CO_2 does not improve either the yields of the extracts obtained by other methods or the variety of the extracted compounds.

—by comparing the different fractionation procedures it is apparent that the more relevant parameters of source and maturity calculated from the saturate fractions, such as the ratios pristane/phytane (2.2), pristane/nC_{17} (1.1) and phytane/nC_{18} (0.5) do not change significantly. However, some differences in the different hydrocarbon patterns were observed, particularly in the chromatogram zone where the polycyclic hydrocarbons are eluted, as Fig. 1 illustrates for two particular cases.

—the high maturity level of the sediment has been inferred from well known parameters calculated from the distribution of tricyclic and pentacyclic terpanes and steranes. Some other significant biomarker series were also identified, which are shown in Table 1 with indication of the predominant homologues and relative concentrations.

—as revealed by extraction with *n*-hexane and chloroform it seems that several kinds of compounds, probably arising from insoluble highly aliphatic biopolymers, are physically entrapped in the kerogen structure, as also found previously in similar samples (Behar and Vandenbroucke, 1988).

—multiple ion detection (MID) of the kerogen pyrolysates allows the identification of different biomarkers series, including *n*-alkanes, *n*-alkenes,

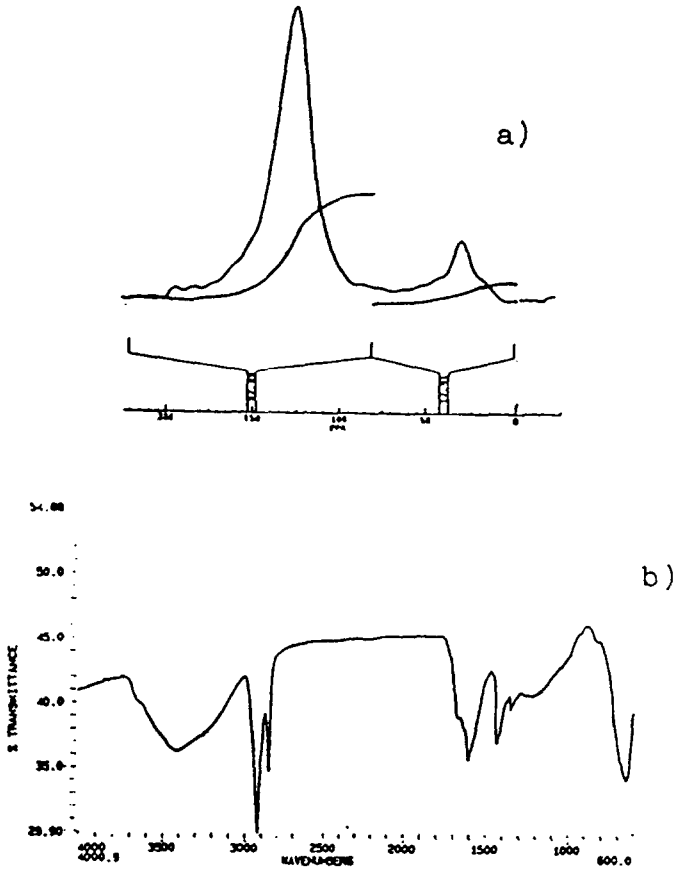

Fig. 2. ^{13}C-NMR (a) and FT-IR (b) spectra of the oil shale kerogen

terpanes and steranes, among the pyrolysis products. Possible input of different biopolymers can be suggested from analysis of the different pyrolysis products.

—analysis of the kerogen by FT-IR and solid state NMR reveals its predominantly aromatic character, although marked contribution of aliphatic structures is also evident (Fig. 2).

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