Chemical structural investigation of asphaltenes and kerogens by pyrolysis–methylation

J. C. DEL RÍO, F. MARTÍN, F. J. GONZÁLEZ-VILA and T. VERDEJO
Instituto de Recursos Naturales y Agrobiología de Sevilla, C.S.I.C., P.O. Box 1052, 41080 Seville, Spain

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Abstract—Molecular characterization of kerogen and asphaltene fractions isolated from three oil shales taken from the Puertollano deposit has been carried out by pyrolysis–methylation. Long-chain n-alkanes, n-alk-1-enes, long-chain carboxylic acid methyl esters and aromatic compounds were the major thermal degradation products obtained for both kerogen and asphaltene fractions. Different monomeric and dimeric lignin-derived compounds were also released. The use of pyrolysis–methylation provides additional information about the chemical structural composition of the macromolecular organic matter comprising kerogens and asphaltenes at a molecular level, to that gained from conventional pyrolysis. The chemical structures of the released products indicate that considerable amounts of functionalized compounds are bound to the macromolecular structure of asphaltenes and kerogens via ester and ether linkages. Copyright © 1996 Elsevier Science Ltd

Key words—asphaltenes, kerogen pyrolysis, pyrolysis–methylation of kerogen, fatty acids in kerogen pyrolysates, polar compounds

INTRODUCTION

The molecular characterization of asphaltene and kerogen fractions, isolated from different fossil fuels, has been the subject of numerous investigations (Béhar and Pelet, 1985; Mycke and Michaelis, 1986; Goth et al., 1988; Barakat and Yen, 1990; Stout, 1991; Strausz et al., 1992; Barakat, 1993). Asphaltenes are generally considered to be composed of small solubilized, less-condensed kerogen moieties (Tissot and Welte, 1984). Knowledge of the chemical nature of these geopolymers may help to provide a better understanding of the source of precursor materials, the environmental conditions of deposition, and the type of diagenetic, catagenic and maturation processes involved. The great complexity of both fractions has hindered the formulation of individual molecular structures, although a number of different models have been proposed for kerogen (Oberlin et al., 1980; Béhar and Vandenbroucke, 1987).

A wide variety of methods has been applied to the study of asphaltenes and kerogens. Bulk methods, such as elemental analysis, FT-IR and solid-state NMR spectroscopy give useful overall information, while chemical and thermal degradative techniques provide more detailed molecular information. Since the early 1980s, pyrolysis gas chromatography mass spectrometry (Py–GC–MS) has been widely used in the structural investigation of asphaltenes and kerogen (van de Meent et al., 1980; Larter and Douglas, 1982; Béhar and Pelet, 1983; Tannenbaum et al., 1986; Hartgers et al., 1992; de del Río et al., 1993a). The results of Py–GC–MS have improved our knowledge considerably of the chemical macromolecular structure of kerogens and asphaltenes. However, one should realize that only a part of the organic matter can be analyzed and that some moieties can be drastically altered due to the nature of the technique. Pyrolysis seems to underestimate the presence of carboxyl-bearing units among the structural building blocks. In fact, flash pyrolysis of polymers containing benzenecarboxylic acid moieties (such as fulvic and humic acids) leads to biased structural interpretations since it has been shown that these units undergo decarboxylation in this process (Martin et al., 1994). Consequently, our view of the molecular composition of kerogens and asphaltenes may be very limited, and possibly highly biased, when based on conventional pyrolysis data.

Recently, pyrolysis in the presence of tetramethylammonium hydroxide (TMAH) has been introduced for the detection of benzenecarboxylic acids by pyrolytic methods (Martin et al., 1994; Saiz-Jimenez, 1994). This technique, also called “simultaneous pyrolysis methylation”, produces methyl esters of carboxylic acids and methyl ethers of phenols; aliphatic hydroxy compounds become partially methylated (Challinor, 1989). It has been demonstrated that the reaction that takes place involves thermally assisted chemolysis rather than the methylation of released pyrolysis products (de Leeuw and Baas, 1993; Martin et al., 1994). This technique has already been successfully applied in structural elucidation studies of different natural and artificial...
polymers such as cutins, natural resinites, alkyd resins, polyester fibres, lignins and humic substances (Challinor, 1989, 1991a, b; Anderson and Winans, 1991; de Leeuw and Baas, 1993; Saiz-Jimenez et al., 1993, 1994; Martin et al., 1994, 1995a; b; del Rio et al., 1994b; Hatcher et al., 1994; Hatcher and Clifford, 1994; Chiavari et al., 1994).

In this paper, we present data for the analysis by pyrolysis-methylation of a set of kerogens and asphaltenes isolated from oil shales. The aim is to study the feasibility of using pyrolysis-methylation for the structural characterization of kerogen and asphaltenes. The study will provide information on the polar moieties bonded to the macromolecular structure of asphaltenes and kerogens through ester linkages. Kralert et al. (1991) and Challinor (1991b) have already presented some preliminary data for the use of pyrolysis-methylation in the characterization of aliphatic ester moieties in kerogens and coals.

MATERIALS AND METHODS

The oil shale samples were taken from the Puertollano (Ciudad Real, Spain) deposit. The geological setting of this oil shale, from the Stephanian B, has already been described (Wallis, 1983; Wagner, 1985). The organic geochemical characterization of the bituminous fractions has also been published (del Rio et al., 1993, 1994a). Two samples were collected from the Emma mine, at two different strata of increasing depth (Emma I and Emma 2). The other sample was taken from the B seam at the Calvo Sotelo mine (PB).

Raw oil shale samples were milled and extracted exhaustively with methylene chloride:methanol (2:1). Minerals were removed by successive treatments with 20% HCl (12 h, 60 °C) and HCl:HF (1:1) (24 h, 60 °C, twice). The kerogens were thoroughly rinsed with water until the washings were free of chloride ions and then dried. Aliquots of the oil shale extracts were dissolved in a minimum amount of chloroform and the asphaltenes precipitated by adding a 30-fold excess of n-pentane. Asphaltenes were separated by centrifugation, and subsequently recovered by decantation. The precipitation process was repeated twice in order to purify the asphaltenes.

The pine and beech milled wood lignins (MWL) used in this study were prepared from extracted pine (Pinus pinea) and beech (Fagus silvatica) by ball milling and extracting with dioxane/water as described by Björkman (1956).

The elemental analysis and atomic ratios of the kerogen and asphaltene fractions are shown in Table 1.

Pyrolysis–gas chromatography–mass spectrometry

The samples (1–2 mg) were first moistened with 10–20 µl of TMAH (25% aqueous solution) and dried in a desiccator overnight. Kerogens were prepared as suspensions in TMAH. The syrups were placed on the ribbon foil of the CDS pyroprobe and heated to 500 °C for 10 s. Separation of the pyrolysis products was achieved on a 25 m × 0.2 mm i.d. fused silica capillary column (SE-52, J and W Scientific). The gas chromatograph (Hewlett Packard HP-5890) was programmed from 40 °C to 300 °C at a rate of 6 °C/min. Helium (1 ml/min flow rate) was used as carrier gas. The mass spectrometer (HP 598X A) was set at 70 eV. Identifications were achieved by mass fragmentography, library search and comparison with literature data. When possible, identifications were accomplished by comparison with authentic standards. The substitution patterns of the different positional isomers were established by comparison of relative retention times with literature data and, when possible, confirmed by co-injection with authentic standards.

Nuclear magnetic resonance

High resolution solid-state 13C-NMR spectra of the kerogen and asphaltene samples were collected at 25.2 MHz under cross polarization–magic angle spinning conditions (CP/MAS) using the quantitation conditions described elsewhere (Fründ and Lüdemann, 1991).

RESULTS AND DISCUSSION

Figure 1 shows the 13C-NMR spectra of the kerogen and asphaltene samples isolated from the selected oil shales. The quantitation of the different spectral regions is shown in Table 2. The spectra show two broad signals in the “aliphatic” (5–46 ppm) and “aromatic” (110–160 ppm) regions and indicate a structural similarity between the kerogen and asphaltene samples. A higher aliphaticity was observed in the kerogens than in their associated asphaltenes. The band in the aliphatic region may reflect the contribution to the organic matter of these materials of highly aliphatic, non-hydrolyzable biopolymers similar to those recently described in different organisms (Larueau et al., 1984, 1986; Nip et al., 1986; Kadouri et al., 1988; de Leeuw et al., 1991). In fact, the alga Botryococcus braunii, whose presence has been described in the Puertollano oil shales (Gómez-Borrego, 1992), possesses a highly

Table 1. Elemental analysis and atomic ratios of the kerogen and asphaltene samples (on a dry, ash-free basis)

<table>
<thead>
<tr>
<th></th>
<th>Kerogen asphaltene</th>
<th>Kerogen asphaltene</th>
<th>Kerogen asphaltene</th>
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<tbody>
<tr>
<td>PB</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>74.0</td>
<td>74.0</td>
<td>74.0</td>
</tr>
<tr>
<td>H</td>
<td>10.4</td>
<td>8.7</td>
<td>8.8</td>
</tr>
<tr>
<td>N</td>
<td>2.5</td>
<td>3.0</td>
<td>2.5</td>
</tr>
<tr>
<td>(O + S)n*</td>
<td>13.5</td>
<td>13.5</td>
<td>21.0</td>
</tr>
<tr>
<td>H/C</td>
<td>1.55</td>
<td>1.34</td>
<td>1.35</td>
</tr>
<tr>
<td>O/C</td>
<td>0.14</td>
<td>0.14</td>
<td>0.22</td>
</tr>
</tbody>
</table>

* by difference.
aliphatic biopolymer called algaenan, which shows a $^{13}$C-NMR spectrum dominated by a broad band with a sharp maximum at 29 ppm, corresponding to polymethylenic chains (Largeau et al., 1984; Kadouri et al., 1988).

Unfortunately, the NMR data obtained cannot provide further information at the molecular level. Pyrolytic techniques have been shown to be excellent complementary techniques for providing additional insights at the molecular level. Because of the known limitations of conventional pyrolysis (Martin et al., 1994; Saiz-Jimenez, 1994) in elucidating the chemical structure of macromolecular organic matter, we have used pyrolysis–methylation or pyrolysis in the presence of tetramethylammonium hydroxide, which provides additional information.

Figure 2 shows the chromatograms (FID) of the thermal degradation products released after pyrolysis–methylation of the kerogens and asphaltenes respectively. The main compounds identified were a series of alkanes/alkenes, long-chain carboxylic acid methyl esters and benzenecarboxylic acid methyl esters. Some triterpenoid compounds with hopanoid skeletons, as well as compounds arising from lignin moieties, were also released after pyrolysis–methylation.

**Hydrocarbons**

Aliphatic compounds were identified in the pyrograms as series of $n$-alkanes and $n$-alkenes, with chain lengths up to $C_{10}$. Distributions of alkane/alkene pairs were similar to those obtained after conventional pyrolysis (del Rio et al., 1993a) and indicate the presence of significant amounts of polyalkyl components in the structures of the kerogens and asphaltenes, in accordance with $^{13}$C-NMR observations. As previously suggested for similar materials, the major contributors to the alkyl components might be non-saponifiable, highly aliphatic biopolymers such as those recently identified in present-day and fossil plant cuticles and in the cell walls of some algae species (Nip et al., 1986; Largeau et al., 1984, 1986; Kadouri et al., 1988). As stated above, one of these biopolymers, referred to as algaenan, occurs in the outer cell walls of the common green algae Botryococcus braunii. Remains of B. braunii have recently been reported in these oil shales (Gómez-Borrego, 1992). Such biopolymers yield, on conventional pyrolysis, a series of $n$-alkanes/$n$-alkenes with a distribution similar to that found in our pyrolyzates (Largeau et al., 1986). Although these biopolymers are minor constituents of the original biomass, they are more refractory than other major organic components and may be subsequently enriched in the sediment during diagenesis (Tegelaar et al., 1989; de Leeuw et al., 1991).

Table 2. Integration values (% area) for the different regions of the $^{13}$C-NMR spectra of the kerogen and asphaltene samples

<table>
<thead>
<tr>
<th></th>
<th>Kerogen asphaltenene</th>
<th>Kerogen asphaltenene</th>
<th>Kerogen asphaltenene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PB</td>
<td>Emma 1</td>
<td>Emma 2</td>
</tr>
<tr>
<td>110–160 ppm</td>
<td>22</td>
<td>33</td>
<td>19</td>
</tr>
<tr>
<td>5–46 ppm</td>
<td>78</td>
<td>67</td>
<td>80</td>
</tr>
</tbody>
</table>

Fig. 1. Solid-state $^{13}$C-NMR of the asphaltene and kerogen fractions isolated from the selected oil shale samples. The integration values for the different spectral regions are given in Table 2.
Long-chain carboxylic acids methyl esters
A series of long-chain carboxylic acid methyl esters from C₈ up to C₇₆ was also produced, indicating that these moieties are present in the structure of the kerogen and asphaltene. The m/z 74 mass chromatograms presented in Fig. 3 shows distributions of the series of long-chain carboxylic acids (as methyl esters) released from the kerogen and asphaltene samples after pyrolysis–methylation. In general, the distributions of fatty acids show a slight even-over-odd predominance and maxima at C₁₈ and C₂₅. Kralert et al. (1991) also observed the release of long-chain carboxylic acid methyl esters with an even-to-odd predominance after pyrolysis–methylation of kerogens. Likewise, Barakat (1993) obtained different series of fatty acids with an even carbon
number predominance from Monterey kerogen by alkaline hydrolysis. Series of 2-methoxy fatty acid methyl esters, $\omega$-methoxy fatty acid methyl esters and $\omega,\omega$-dicarboxylic acid dimethyl esters were also identified in all of the samples: they had a strong even-over-odd predominance. At this point it is not known whether the methoxyl groups are originally present as such or
derive from the TMAH. In the latter case, the hydroxyl groups could be present either in the free form, or linked to the macromolecular network via ether bonds. All of these series were more predominant in the asphaltenes than in the respective kerogens. Minor amounts of 2-methyl fatty acid methyl esters ranging from C_{26} to C_{14} with a maximum at C_{30} were detected only in the kerogens from Emma 1 and Emma 2. Fatty acids characteristic of a bacterial input, such as the iso- and anteiso-C_{15} and C_{17} compounds, could not be detected in the samples. A striking feature, however, was the release of unsaturated C_{18:1} and C_{18}, fatty acid methyl esters after pyrolysis-methylation, present in comparatively low concentrations. These unsaturated moieties may have been incorporated and preserved within the kerogen and asphaltene macromolecular network, and not previously detected, possibly due to the fact that the methods used have been very drastic or not appropriate. Unsaturated fatty acids have been

![Retention time (min)](image-url)
released from these kerogens by room temperature alkaline permanganate oxidation (del Rio et al., 1993c) and also from Monterey kerogen by alkaline hydrolysis (Barakat, 1993).

The fact that the series of \( n \)-alkanes/\( n \)-alkenes, and long-chain carboxylic acid methyl esters, are released upon pyrolysis–methylation seems to suggest that the long-chain carboxylic acids arise from different aliphatic moieties than the \( n \)-alkanes/\( n \)-alkenes. This is supported by the fact that there is no parallel between the chain-length distribution of \( n \)-carboxylic acids and their equivalent hydrocarbons in the asphaltene or kerogen pyrolyzates.

The above series may be collectively derived from ester-bound long-chain carboxylic acids protected in the most refractory part of the macromolecular

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Fig. 3. (a) m/z 74 Mass chromatograms showing the distribution of fatty acids (as methyl esters) released from the kerogen samples. (b) m/z 74 Mass chromatograms showing the distribution of fatty acids (as methyl esters) released from the asphaltene samples.
network. Kawamura and Ishiwatari (1985) defined the tightly bound carboxylic acids as those only released on pyrolysis. Tightly bound carboxylic acids are generally considered to originate from the incorporation of partly altered lipids, directly inherited from living organisms, into kerogens at an early stage of sedimentation (Harrison, 1978; Peters et al., 1981; Taylor et al., 1984; Kawamura and Ishiwatari, 1985; Kawamura et al., 1986; Largeau et al., 1986; Jaffé and Gardinali, 1991; Derenne et al., 1991). However, for torbanites, tightly bound carboxylic acids were shown to be directly inherited from the source organism, the colonial microalga Botryococcus braunii (Largeau et al., 1986). In fact, pyrolysis-methylation of the biopolymer algæan released fatty acid methyl esters from C14 to C18 as the dominant products (McKinney et al., 1995).

The long-chain carboxylic acids released on pyrolysis were linked to the macromolecular network via sterically protected, and hence, non-hydrolyzable, ester bonds. Subsequently, such acids would be protected from diagenetic degradation and would be released only during laboratory heating experiments or during natural catagenic evolution (Kawamura et al., 1986; Jaffé and Gardinali, 1991).

The apparent similarity of the distributions of bound carboxylic acids in the asphaltene and respective kerogens indicates a close compositional relationship between the two geopolymers. However, some minor differences can also be observed between the kerogens and the respective asphaltenes. The fatty acids released from the asphaltenes show a predominance of the higher homologues and a stronger even-over-odd predominance in this region with respect to their corresponding kerogens. The asphaltenes also release larger amounts of methylated hydroxyacids, particularly for the PB sample.

Aromatic compounds

The main aromatic compounds released after pyrolysis-methylation were the benzenecarboxylic acids (as methyl esters) and their methoxylated counterparts. The major compounds were the benzenedicarboxylic acid methyl esters in all samples. Benzetenetri- and benzenetetracarboxylic acids (as methyl esters) were also released, although in lesser amounts. Different methoxylated benzenecarboxylic acid moieties, such as 3,4-dimethoxybenzenecarboxylic acid and 3,4,5-trimethoxybenzenecarboxylic acid were other important aromatic components released from these samples. Figure 4 shows a partial summed mass chromatogram of the distribution of benzenecarboxylic acids and their methoxylated counterparts obtained for kerogen PB, which is typical of those obtained for the kerogens and asphaltenes investigated. The presence of carboxylic acids and their methoxylated counterparts is of interest as they represent the final steps in the oxidation of the side chains in the lignin macromolecule. These benzenecarboxylic acids represent structural constituents of the asphaltene and kerogen macromolecules, not previously identified by conventional pyrolytic techniques, and are probably present in the macromolecular matrix either free or linked by ester bonds.

Dimeric thermal degradation products of lignins were also generated on pyrolysis–methylation. The mass spectrum and the structure of a lignin dimeric compound is shown in Fig. 5. It was identified as a syringoresinol-type (A) by comparison with a mass
Chemical structural investigation of asphaltenes and kerogens

spectrum available in a commercial library (Wiley) and is shown in Fig. 5. It was identified in all the asphaltene samples and in minor amounts in the kerogen of Emma 2. The identity of this compound was also confirmed by comparison with the compounds released after pyrolysis–methylation of pure lignins. Figure 6 shows a comparison of the m/z 181 mass chromatograms of the thermal degradation products obtained after pyrolysis–methylation of asphaltenes PB and beech lignin. It can be seen that compound A is present in both pyrolyzates, suggesting that it is a characteristic lignin pyrolysis

![Figure 5](image)

**Fig. 5.** Mass spectra of some compounds identified as lignin dimers. A: pinoresinol-structure. B and C: unknowns.
product. The mass spectra of two other related compounds (B and C) observed in the m/z 181 mass chromatogram of Fig. 6, and not yet identified, are also shown in Fig. 5. Several other dimeric compounds were also detected in the kerogen and asphaltene pyrolyzates by comparison with the products released after pyrolysis–methylation of different lignins. This is the case for a cluster of compounds observed in the m/z 410 mass chromatogram of beech and pine lignin and also released from the asphaltenes and kerogen samples. Figure 7 shows a comparison of the m/z 410 mass chromatogram of the compounds released after pyrolysis–methylation of asphaltenes PB and beech lignin and a representative mass spectrum of one of these compounds. In general, all of these aromatic components detected in the kerogen and asphaltene pyrolyzates might derive from higher plant lignins and possibly also from tannins and would therefore be indicators of a terrestrial origin. Since the original lignin from which these compounds are derived is not soluble, the occurrence of lignin-derived materials in the asphaltene fractions seems to suggest that these compounds represent low molecular weight degradation products. On the other hand, the presence of lignin-derived moieties has already been shown in the Messel oil shale kerogen using mild hydrogenation (Mycke and Michaels, 1986).

**Hopanoid compounds**

Pyrolysis–methylation also released hopanoid compounds from the asphaltenes and kerogens. Hopanoid compounds have previously been released from other kerogens and asphaltenes by conventional pyrolysis and chemical degradation methods (Tannenbaum et al., 1986; Barakat and Yen, 1990; Barakat, 1993). The main compounds released from our samples were hopanoic acid methyl esters, hopanes and hopenones. A representative m/z 191 mass chromatogram showing the distribution of hopanoid compounds is presented in Fig. 8. The identities of the different compounds, assessed by mass fragmentation and relative retention times published in the literature, are listed in Table 3. The distribution of the hopanoid compounds released was similar in all of the samples, with 17α(H),21β(H) and 17β(H),21α(H) hopanes and hopanoic acid methyl esters being
predominant. All identified triterpenoids belong to the hopane family, and no triterpenoids characteristic of terrestrial higher plants, such as oleananes and ursanes, were found. The abundance of hopanes indicates a contribution from bacteria to the oil shale organic matter. The fact that hopanoic acids are released from the kerogen matrix by pyrolysis–methylation indicates that they are bonded at their side chain to the complex network of the kerogen and asphaltene, presumably through an ester linkage. Hopanoid compounds bound through ether bonds are released as hopenes since the aliphatic alcohols do not become methylated. The identification of hopenes substantiates previous suggestions that significant amounts of triterpanols are linked via ether bonds to the geopolymeric matrix. However, the possibility that hopenes may derive from hopanoid carboxylic acids via decarboxylation due to inefficiencies in the methylation procedure, should not be ruled out.

CONCLUSIONS

The structural characterization of the kerogen and asphaltene fractions isolated from the Puertollano oil shale has been approached by the use of pyrolysis in the presence of tetramethylammonium hydroxide (TMAH), the so-called pyrolysis–methylation. In contrast to conventional pyrolysis, pyrolysis–methylation releases considerable amounts of functionalized compounds bound to the macromolecular structure of kerogens and asphaltenes. The main compounds released were series of alkanes/alkenes, long-chain carboxylic acid methyl esters, methylated benzenecarboxylic acids, lignin-derived aromatic units and hopanoid compounds (hydrocarbons and carboxylic acids), indicating that polar compounds are also part of the macromolecular structure of these materials. The release of polar compounds from the macromolecular networks of geopolymeric materials has usually been approached by tedious, time consuming
Hopanoid hydrocarbons

Fig. 8. m/z 191 Mass chromatogram showing the hopanoid distribution in a representative sample. The assignments of the different chromatographic peaks are listed in Table 3.

methods, such as chemical degradations. The use of pyrolysis–methylation is a fast, sensitive, one-step procedure for the analysis of geomacromolecules containing polar functionalities, and requires very minor amounts of sample. Finally, the results further support previous suggestions of a broad similarity between the structure of asphaltenes and kerogens derived from a given source rock, although some minor differences could be appreciated between them.

### Table 3. Hopanoid compounds identified in the pyrolyzates

<table>
<thead>
<tr>
<th>Hopanoid hydrocarbons</th>
<th>Retention time (min)</th>
<th>Relative abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 trisnorhopene C27:1</td>
<td>22.29,30-trisnorhop-17,21-ene</td>
<td>3</td>
</tr>
<tr>
<td>2 17(\beta)(H)-22,29,30-trisnorhopane</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>3 norhopene C29:1</td>
<td>5 norhopene C29:1</td>
<td>6 17(\beta)(H),21(\alpha)(H)-30-norhopane</td>
</tr>
<tr>
<td>7 norhopene C29:1</td>
<td>8 17(\beta)(H),21(\alpha)(H)-30-norhopane</td>
<td>9 hopene C30:1</td>
</tr>
<tr>
<td>10 hopene C30:1</td>
<td>11 homohopene C31:1</td>
<td></td>
</tr>
</tbody>
</table>

### Hopanoic acids

| 12 17\(\beta\)(H),21\(\alpha\)(H)-hopanoic acid ME (22S) |
| 13 17\(\beta\)(H),21\(\alpha\)(H)-hopanoic acid ME (22R) |
| 14 17\(\beta\)(H),21\(\alpha\)(H)-moretanoic acid ME (22S) |
| 15 17\(\beta\)(H),21\(\alpha\)(H)-moretanoic acid ME (22R) |
| 16 17\(\beta\)(H),21\(\alpha\)(H)-moretanoic acid ME (22R) |
| 17 17\(\beta\)(H),21\(\alpha\)(H)-moretanoic acid ME (22S) |
| 18 17\(\beta\)(H),21\(\alpha\)(H)-moretanoic acid ME (22R) |
| 19 17\(\beta\)(H),21\(\alpha\)(H)-moretanoic acid ME (22R) |
| 20 17\(\beta\)(H),21\(\alpha\)(H)-moretanoic acid ME (22S) |
| 21 17\(\beta\)(H),21\(\alpha\)(H)-moretanoic acid ME (22R) |
| 22 17\(\beta\)(H),21\(\alpha\)(H)-moretanoic acid ME (22S) |
| 23 17\(\beta\)(H),21\(\alpha\)(H)-moretanoic acid ME (22R) |
| 24 17\(\beta\)(H),21\(\alpha\)(H)-moretanoic acid ME (22R) |

ME: methyl ester.
pyrolytic techniques and other conventional chromatographic methods. *Analyst* 119, 1141–1150.


del Río J.C., García-Mollá J., González-Vila F.J. and


