P224-WE

BIOMARKERS INCORPORATED IN COAL ORGANIC MATTER AS REVEALED BY PYROLYSIS

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Pyrolysis of fossil materials (i.e. lignites, coals, shales, etc.) in a stream of water vapor was examined by Minkova *et al.* (1991). It was demonstrated that water influenced the yields and characteristics of liquid products in comparison with the standard pyrolysis at 520^{o}C in Fisher retort. The main advantages of pyrolysis in water vapor were higher yields of liquid products, appreciable desulphurisation effect, and solid by-products with high porosity;

In the present study Chururovo lignite, Bulgaria (R_o=0.20±0.02) preliminary extracted by chloroform was pyrolysed in a stream of water vapor. Coal sample and bitumen and biomarker assemblage were described by Stefanova *et al*. (2005).

Pyrolysis of 50g lignite (5-6 mm) was performed in laboratory scale installation at atmospheric pressure, temperature 300-550^{o} C with 10^{o}C/min and an isotherm at the final temperature for 1h. Volatiles were removed by constant flow of water vapor (120ml/min). Liquid products of pyrolysis were dispersed/dissolved in water. From the aqueous phase they were extracted by hexane (3x200ml), concentrated, dried and analyzed by GC-MS.

Aliphatic portion was composed by alkanes, *n*C_{15}-*n*C_{33} with CPI =1.01, 32.0%; alkenes, *n*$C_{15:1}$-*n*$C_{19:1}$, 12% ; isoprenoids, 4.70% (Prist-1-ene/Prist-2-ene); Diterpenoids, 12.53% with 16α(H)-Phyllocladane dominance; steroids (Stigmastan-3,5-dien, 1.25%). Two groups of triterpenoids were registered: - *Angiosperm*- and bacterially-derived triterpenoids. Hopanoids were saturated/unsaturated with biologically-inherited but thermodynamically unstable 17β(H),21β(H)-configuration (27β(H), 29$\beta\beta$(H)-31 $\beta\beta$(H)).

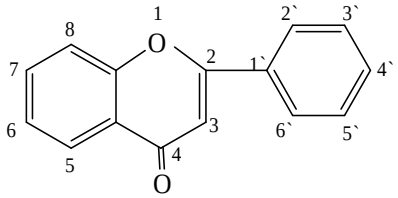
High quantity of fatty acid methyl esters (FAMe) was determined in the polar fraction: -saturated FAMe, *n*C_{16}-*n*C_{30}, 10.42% ; maximizing at *n*C_{16}, 3.38% ; unsaturated FAMe, *n*$C_{18:1}$, 18.45% ; Phenolic terpenoids were the other abundant components, 9.24% with ferruginol dominance, 3.21% ; Tocopherol (0.83%), friedelin, (0.55%), guaiacyl structures (5.54%) and, triterpenoid acids, methyl esters were the other components.

A combination of preparative scale “off-line” TMAH thermochemolysis and TEAAc treatment was applied to discriminate fatty acids present as “free” uncombined acids, methyl esters present as tightly trapped molecules within the coal organic matter matrix, or acids chemically bounded by ester groups (Grasset *et al.* 2002). In products of reactions the

following groups of compounds were registered: - high quantity of lignin-derived phenolic derivatives with guaiacyl structures (*Gymnospermae* contribution); - FAMe miximising at nC_{16}; - *n*-alkanols, nC_{14}- nC_{24}, even numbered, etc. TEAAc treatment proved the presence of tightly trapped FAMe as well as methyl ester of vanillic acid. Flavones were registered as acetylated derivatives in products of TMAH thermochemolysis.

Table 1. Flavones presented in products of TMAH thermochemolysis

Structure	Position				
	3	5	7	2`	3`
Acacetin	H	OH	OH	H	OCH_3
Kaempferol	OH	OH	OH	H	OH
Dimethoxy flavone	H	H	OH	OCH_3	OCH_3
Methoxy genistein	H	OCH_3	OH	H	OH



Our results demonstrated that coal organic matter contained preserved biomacromolecules of plant or microbial origin. These components have partly survived biodegradation and have preserved their basic natural product skeleton. Pyrolysis in a stream of water vapor could be recommended as a mild technique to isolate tightly incorporated biomarkers in fossils. Thermochemolysis with different alkylation agents unequivocally proved the presence of esters groups as linkage in lignite organic matter and discriminate “free” and “bound” acids.

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