

**POSSIBLE NEW INDICATOR FOR BIODEGRADATION INTENSITY: CASE STUDY OF BRAZILIAN OILS**

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In the present work, we report a comparative analysis of representative saline lacustrine oils with distinct degrees of biodegradation (“A”, “B” and “C”) from the Campos Basin, Brazil, in order to verify modifications of the relative composition of biomarkers in both neutral and acidic fractions that could be related to biodegradation.

The studied oil samples were collected in reservoirs with different depths and temperatures: “A” (Lower Cretaceous sandstones); “B” (Albian/Cenomanian carbonates) and “C” (Tertiary sandstones) and GC/MS and GC/MS/MS analyses was carried out.

The biomarker data for the neutral fractions showed a high degree of similarity for maturity and thermal evolution. The geochemical data from both neutral and acid fraction revealed that oil “A” (2812-2821m), oil “B” (2600-2610m) and oil “C” (2088-2100m) are light, moderate and heavily biodegraded, respectively, according to the Peters K.E. *et al.*, 2005 biodegradation scale. In a previous communication (Lima, S.G. *et al.*, 2006) we reported the identification of  $3\beta(n\text{-propyl})\text{-}5\alpha(\text{H})\text{-}24\text{-norcholestan-}23\text{-oic acid}$  **5**;  $3\beta(n\text{-propyl})\text{-}5\alpha(\text{H})\text{-}26,26\text{-dinorergostan-}25\text{-oic acid}$  **9**;  $3\beta(n\text{-propyl})\text{-}5\alpha(\text{H})\text{-ergostanoic acid}$  **14** from these oils.

Analyses of acidic fraction revealed the presence of C<sub>32</sub> (m/z 263) due to hopanic methyl esters which showed an increasing relative abundance of the less stable configuration 17 $\beta$ (H), 21 $\beta$ (H) 22 R with the increasing biodegradation (see Figure 1). Since all geochemical parameters, including the ratio of the homohopane compounds 17 $\alpha$ (H), 21 $\beta$ (H) 22 R and S and 17 $\beta$ (H), 21 $\alpha$ (H) 22 R e S, in all three oils samples indicated similar sources and thermal maturity levels, the direct correlation between the relative abundance of the biologic isomer 17 $\beta$ (H), 21 $\beta$ (H) 22 R and biodegradation intensity strongly supports the conclusion that these products were synthesized by bacteria during biodegradation.

Quantitative analyses of these the hydrocarbon derivatives of acidic fraction using 5 $\beta$ -cholane as internal standard allowed us to detect other 3-propyl-steranes compounds (1 to 4; 6 to 8 and 13) with MW range from 330 to 428 which corresponds to C<sub>24</sub> to C<sub>31</sub>. One can observe an interesting variation of their relative composition with modification of the biodegradation level as shown in Figure 1.

Since a careful re-analysis of neutral fraction confirms the presence of the already reported stigmastane and 3-methyl-stigmastane and none higher homologue of 3-alkylsteranes (Lima, S.G. *et al.*, 2006), one can infer that 3-propyl-steranoic compounds are biodegradation products of 3-propyl ergostanes.

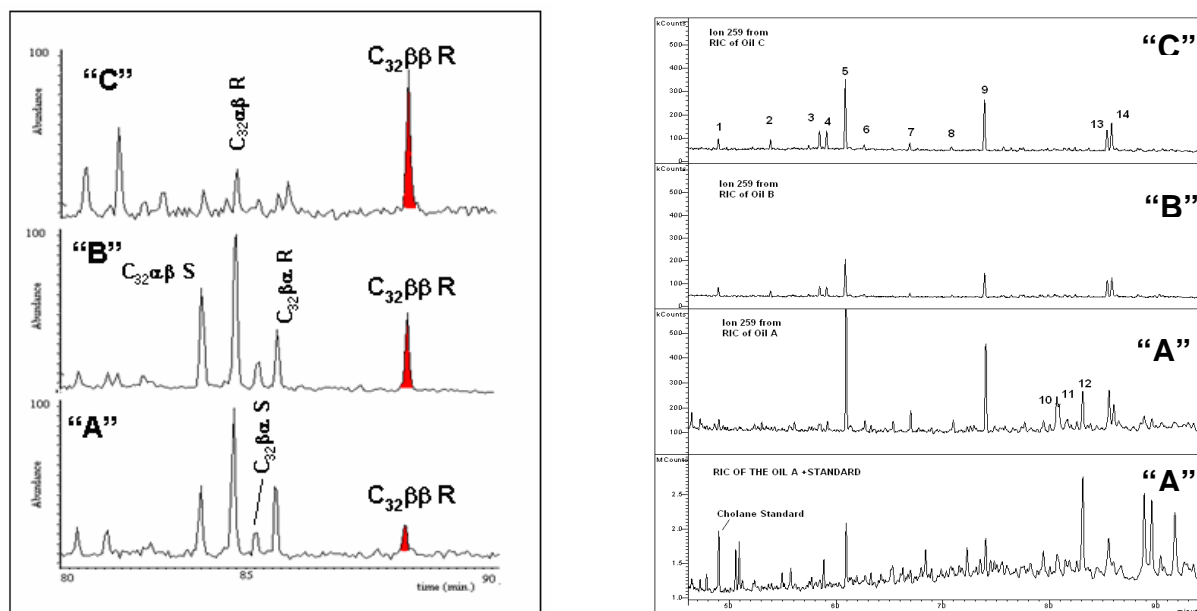


Figure 1. On the left RIC  $m/z$  263 ( $C_{32}$ ) homologues of the hopanic methyl esters, showing the progressive increase of  $C_{32}\beta\beta R$  biologic isomer in oils "A" to "C". On the right, a comparative injection of hydrocarbon derivatives of acid fractions, oils "A" to "C", with variation of the relative composition of the new biomarkers 3-propyl-steranoic acids biomarkers.

## REFERENCES

- Lima S.G., Reis F de A.M., Koike L., Santos Neto E.V., Lopes J.A.D. (2006) Identification of 3-propyl-carboxyalkyl-steranes, novel biomarkers in Brazilian oils, 10<sup>th</sup> ALAGO Congress of Organic Geochemistry, Salvador, Brazil, p. 405-407.
- Peters, K. E.; Walters, C. C.; Moldowan, J. M., 2005, *The biomarkers Guide*, Cambridge University Press.