The software package Statistica 8 (Statsoft Inc.) was used in the statistical calculations. A $X(11 \times 15)$ matrix for saturated and aromatic biomarker ratios was created and a Principal component analysis (PCA) was carried out based on the covariance matrix. All variables were mean centered and scaled by the sample standard deviation.

Results and Discussion

The geochemical parameters were calculated for biomarkers in B/C and in aromatic fractions. The main focus of this study was the characterization of thermal maturity using biomarkers (Table 1). Since the origin and the degree of biodegradation can affect the abundance of most of the biomarkers used in the maturation parameters, these aspects are briefly discussed for the analyzed samples.

Table 1. Selected biomarker ratios in B/C fractions of the crude oils measured using GC×GC-TOFMS.

Regarding the origin, some selected source-dependent parameters (Table 1) St27-St29/H29-H33, Tr26/Tr25, $3\beta$-MH31/H30 % indicates a lacustrine source for oils S01, S02, S08 and S09, a marine source for oils S10, S04, S05, S6, S07 and S11, and a mixture of sources for oil S03 (Peters et al., 2005).

The biodegradation process was monitored with the 25-norhopane to C30 hopane ($25\text{NH}/H30$) ratio (Table 1). According to this parameter, only samples S02 and S07 are significantly altered. Biodegradation can affect other parameters. The hopanes, for example, are preferentially removed compared to the tricyclic terpanes. Tr19-Tr30 (S+R)/H28-H34 (S+R) ratio (Table 1), corroborates that oils S02 and S07 are biodegraded. Interestingly, the oil S09 although could be considered biodegraded according to this ratio, but do not show nor-hopanes ($25\text{NH}/H30 = 0.01$).

Regarding maturity (Table 1), the routinely used steranes and terpanes ratios indicate that most of the oils have reached a moderate to high degree of maturity (between the beginning of the oil window and the peak of oil generation). Practically all the oils have reached the equilibrium for the $22S/(22S+22R) H32$ ratio. Oil samples S05 and S06 show the highest values for the $[20S/(20S+20R) St29]$ and $[\beta\beta(S+R)/\beta\beta(S+R)+aa(S+R) St29]$ steranes ratios, being considered the most mature, whereas oils S02, S03 and S09 show lower values for these ratios and therefore are
Less routinely used saturated biomarker maturity ratios, however, lead to somewhat conflicting results. According to the C29 trisnorhopane/C29 hopane \((H29Ts/H29)\) ratio, which increases with increasing maturation, S05, S07 and S09 should be the most mature oil samples. On the other hand, according to the moretane/hopane \((M30/H30)\) ratio, which decreases with increasing maturation, oils S05 and S07 are the most mature while the oils S02 and S09 are the less mature. Finally, Ts/(Ts+Tm) ratios indicate that S01, S02 and S09 oil samples has the lowest degree of thermal maturity whereas S05 and S07 are the most mature samples.

Aromatic biomarker maturity ratios were also analyzed. Methyl- and dimethyl-dibenzothiophenes \((MDBDT \text{ and DMBDT})\) ratios, which can be used for highly mature oils, show the highest values in the S06 and S07 oil samples. The percentage of mono- and triaromatic steroid ratio of MA C21 / (MA C21 + C28)\% and TA C20/(TA C20 + C27)\%, which increase with increasing maturation show the highest values in the S05 oil sample.

**Principle component analysis**

With the aim of integrating the results from the diverse parameters, a PCA analysis was carried out with all ratios presented in Table 1. The analysis allowed the separation of distinct groups of oils (Fig. 1A). PC1 analysis clearly separated oils S05, S06 and S07 from the others, being the aromatic maturation parameters the principal components (Fig. 1B). PC2 separated S02 and S09, being the \(3\beta\)-methylhopane index one driving force to this. In addition, sample S02 is also influenced by biodegradation processes \((25NH/H30)\). Thus, maturation parameters separated samples S05, S06 and S07 as the most mature within this set of samples, and S02 as the most biodegraded.