STRUCTURAL ELUCIDATION OF A NOVEL TRITERPANE FROM THE NEOPROTEROZOIC ERA USING MICROCRYOPROBE NMR

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Precambrian biomarkers can provide valuable information on early life on Earth. However, the unambiguous identification of such biomarkers can be a challenging task. Due to the fact that most samples have a complex matrix and contain only low concentrations of individual compounds, characterization and identification is usually accomplished by GC-MS and multiple-reaction-monitoring mass spectrometry in comparison to reference compounds. But these data are usually not sufficient for the unambiguous structural elucidation of previously unknown molecules. In a recent case study, it was shown that exceptionally sensitive microcryoprobe NMR spectroscopy can be successfully applied to the structure determination of fossil compounds (Wolkenstein et al., 2015). We therefore chose this methodology to elucidate the structure of a previously unidentified biomarker from the Neoproterozoic Era.

We found a previously unidentified triterpenoid in a bitumen from the Neoproterozoic (about 630 Ma) Mirassol d'Oeste Formation (Araras Platform, Brazil) (van Maldegem et al., 2017). Using GC-MS and high-resolution time-of-flight mass spectrometry, the compound was preliminarily characterized as a pentacyclic triterpenoid, and its molecular formula was determined as $C_{28}H_{48}$. However, it was not possible to determine the structure among several possible structural isomers. By multiple steps of molecular sieving, liquid chromatography, and preparative gas chromatography (van Maldegem et al., 2017), about 20 µg of the compound could be isolated in high purity (> 95%). The structure of the fossil compound was analyzed in detail using ^{1}H NMR, correlated spectroscopy (COSY) (Fig. 1), ^{1}H-^{13}C heteronuclear single quantum coherence (HSQC), and ^{1}H-^{13}C heteronuclear multiple-bond correlation (HMBC) spectroscopy. Finally, it was unambiguously identified as 25,28-bisnorgammacerane. Even the relative configuration could be determined using nuclear Overhauser effect spectroscopy (NOESY), suggesting that the primary configuration is still preserved. In conclusion, our study shows that microcryoprobe NMR allows structure determination of tiny amounts of fossil biomarkers and thus is a powerful tool to unravel the structural composition of traces of early life.

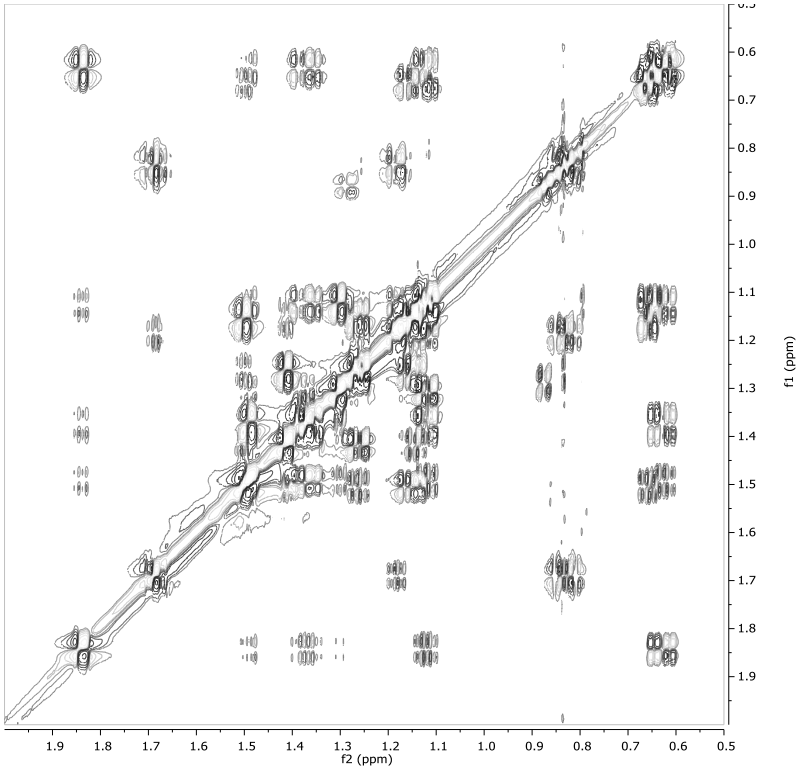

Figure 1 *COSY spectrum of novel Neoproterozoic triterpane.*

References

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