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CONTINUED STRUCTURAL INVESTIGATION OF NATURES MOST HIGHLY BRANCHED ALKANES – INTERPRETATION OF RECENT GC AND MS DATA

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Given the extensive branching and unique C-3 elongation of two previously unreported series of branched alkanes detected in a range of Neoproterozoic aged sediments (Arouri et al., 2000, Greenwood et al., 2004) there is high interest in characterising the structure of these compounds. Whereas C_{2n} and C_{5n} series of branched alkanes are well known and attributed to microbially processed acetate and isoprene addition, respectively, it is likely that the newly detected C_{3n} sequence of branched alkanes reflects a previously unknown mechanism of biosynthesis.

The mass spectra of the C_{3n} compounds show a small molecular ion allowing carbon number identification and the classical [C_nH_{2n+1}]⁺ fragmentation pattern of a saturate hydrocarbon. But a general lack of other mass spectral features precludes further structural interpretation. The C_{3n} compounds do elute at very early retention times compared to *n*-alkanes of the same carbon number - indicating an occurrence of alkyl branching. This GC characteristic of the C_{3n} compounds equates to very negative relative retention factors (RRF). The RRF values become more negative with increasing molecular weight indicating that the degree of branching must also increase with each C₃ addition. The RRF values of the C_{3n} alkanes are slightly more negative than those reported previously for highly branched isoprenoids (HBIs). Until the detection of the C_{3n} compounds the HBIs were the most branched naturally occurring hydrocarbon compounds known. A very high degree of branching is consistent with the lack of diagnostic mass spectral fragments.

Strategies to help determine the structure of the C_{3n} series include 1.) the isolation of individual compounds by prep GC; and 2.) correlation of data from authentic standards having possibly related structures.

Prep-GC isolation, followed by characterisation by MS, NMR, etc., requires the target compound(s) to be completely resolved from co-occurring compounds and ample quantities of source sample. The low concentrations of C_{3n} alkanes in the Neoproterozoic sediments together with the very limited quantities of remaining sample precludes the use of these sediments in an isolation-characterisation strategy.

However, the C_{3n} alkanes have recently been detected in water extracts (Durkay, 2002) which represents an ample supply of these compounds. Furthermore, the hydrocarbon distributions detected in the water samples (Durkay, 2002) were typically much less complex than the bitumen of the

Neoproterozoic sediments. This is an advantage for isolation/separation of components of complex mixtures using chromatographic methods.

An alternative approach to structural determination involves the correlation of data from authentic standards which may involve the synthesis of likely structural candidates. To help identify the best candidates for synthesis the GC characteristics (e.g., RRFs) of various branched alkanes compounds and series have been scrutinised.

This presentation will include an interpretation of the most recent data and discuss the relative merits of possible C_{3n} branched alkane structures being proposed.

References:

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