



How to Get the Hump



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Summary

Petroleum is complex mixture of components, a large part of which is not resolvable by conventional chromatographic techniques. This material is known as the unresolved complex mixture (UCM) or, more prosaically, the hump. Chemical, chromatographic and spectroscopic investigations of both the aliphatic and the aromatic UCM isolated from petroleum have shown that many of the components are isomeric. Consequently, we wondered whether it would be possible to create a UCM from structurally similar components. We report the synthesis and chromatographic and mass spectrometric properties of a subset of all the possible alkanes having a molecular formula of C₁₉H₄₀.

Introduction

The total number of isomers theoretically possible for any particular molecular formula increases rapidly as the number of atoms increases. For example, there are *only* 75 constitutional isomers of C₁₀H₂₂, while there are 148,284 and 366,319 constitutional isomers of C₁₉H₄₀ and C₂₀H₄₂, respectively^[1]. Inclusion of stereoisomers increases these numbers still further.

The synthesis and purification of even 75 compounds would be challenging; addressing hundreds of thousands of compounds is out of the question. Since the UCM typically elutes within the GC retention time of C₁₅-C₃₀ *n*-alkanes, we wanted the synthetic targets to fall within this range.

To make the synthetic challenge more manageable we focused on a subset of the total number of isomers of a single carbon-number and we decided that structures possessing a T-branch topology would be synthetically straightforward. An acyclic alkane with 19 carbon atoms has a total of 27 T-branch isomers comprising: **eight methyloctadecanes**, **seven ethylheptadecanes**, **five propylhexadecanes**, **four butylpentadecanes**, **two pentyltetradecanes** and **a single hexyltridecane** (Fig. 1).

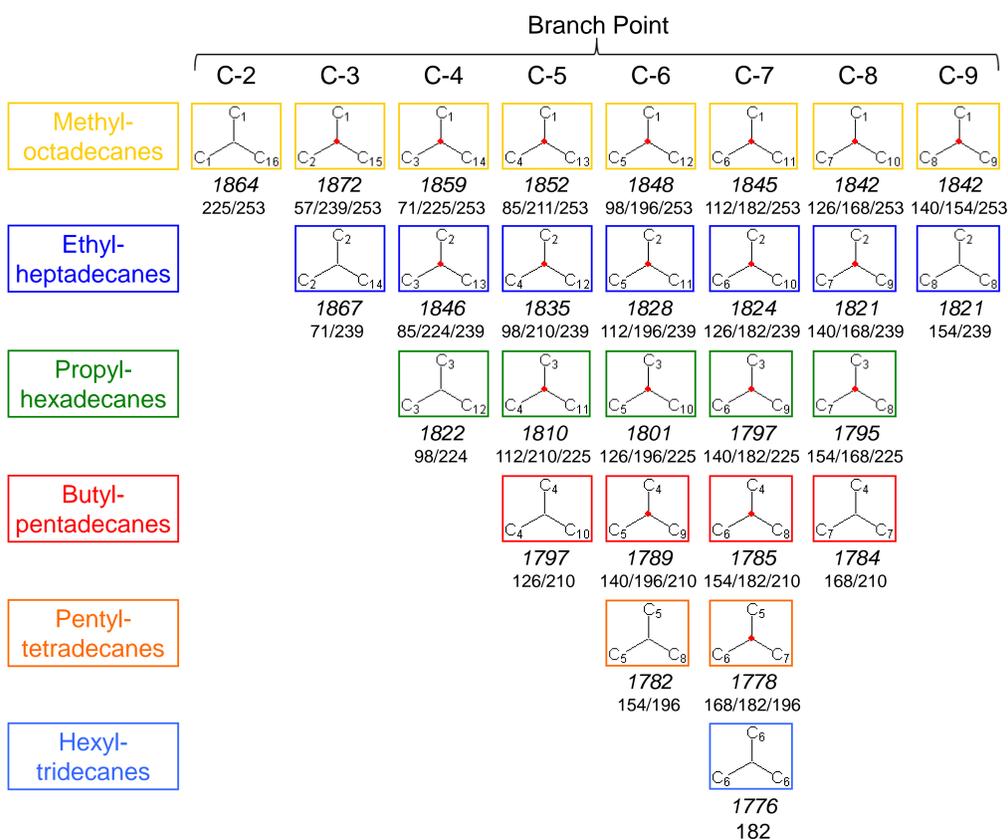


Figure 1: Abbreviated structures of the 27 C₁₉H₄₀ T-branch alkanes. Subscripted numbers indicate the length of each alkyl chain (or “leg”) and red dots indicate a stereocentre. Below the structures are first the *RRI* and second the characteristic mass spectral ions.

Methods

Synthesis of T-branch alkanes is possible using straightforward reactions, involving the creation of a new C–C bond with concomitant formation of a tertiary carbon centre.

A Grignard reaction between a ketone and an alkyl bromide yielded a tertiary alcohol (Fig. 2a). The alcohol was then dehydrated to an isomeric mixture of alkenes (Fig. 2b). Finally, the mixture of alkenes was hydrogenated to yield the target alkane (Fig. 2c). The synthesis is not stereospecific and a racemic mixture is formed for isomers where the tertiary carbon is also a stereocentre (19 of the 27; Fig. 1).

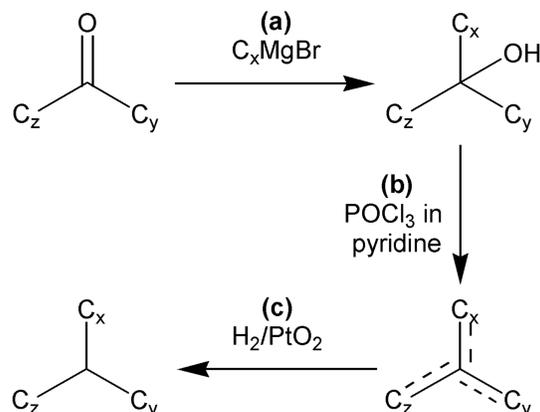


Figure 2: Generalised synthetic scheme for the synthesis of all 27 C₁₉H₄₀ T-branch alkanes. (a) Grignard reaction between a ketone and an alkyl magnesium bromide to form a tertiary alcohol; (b), phosphorus(V) oxychloride dehydration of the alcohol to a mixture of alkenes; (c), H₂/platinum(IV) oxide (Adam’s catalyst) hydrogenation of the alkenes to the alkane.

Results

We have synthesised all 27 C₁₉H₄₀ T-branch alkanes and they have all been analysed using a range of chromatographic and spectroscopic techniques.

NMR proved to be relatively uninformative for structure elucidation. On the other hand, the mass spectra are characteristic, with significant ions being produced by cleavage at the tertiary carbon atom and in most cases each “leg” of the T-branch alkane can be identified unambiguously (Fig. 1).

The T-branch alkanes elute between *n*-C₁₇ and *n*-C₁₉ and some of the isomers co-elute to a greater or lesser extent producing a mini UCM (Fig. 3a & b). The full chromatogram of an analysis of the mix of 27 T-branch alkanes and an aromatic “mini-UCM” isolated by preparative-GC (Fig. 3b) are strikingly similar in their chromatographic profile. While the latter is undoubtedly more complex and the former more resolved, inclusion of additional isomers of C₁₉H₄₀ will lead to further co-elution and therefore greater prominence of the UCM in the mixture of alkanes. For example, 5,5-diethylpentadecane (an isomer having a quaternary carbon centre) elutes between *n*-C₁₈ and phytane^[2,3]. The 3,3-diethyl-isomer elutes more closely to *n*-C₁₉^[2]. The *RRI* of isomeric branched C₁₉H₄₀ alkanes currently ranges from pristane (1707) to 3-methyloctadecane (1872) and although it is probable that more highly branched isomers elute before pristane the addition of many of thousands of additional components will rapidly fill the available chromatographic space.

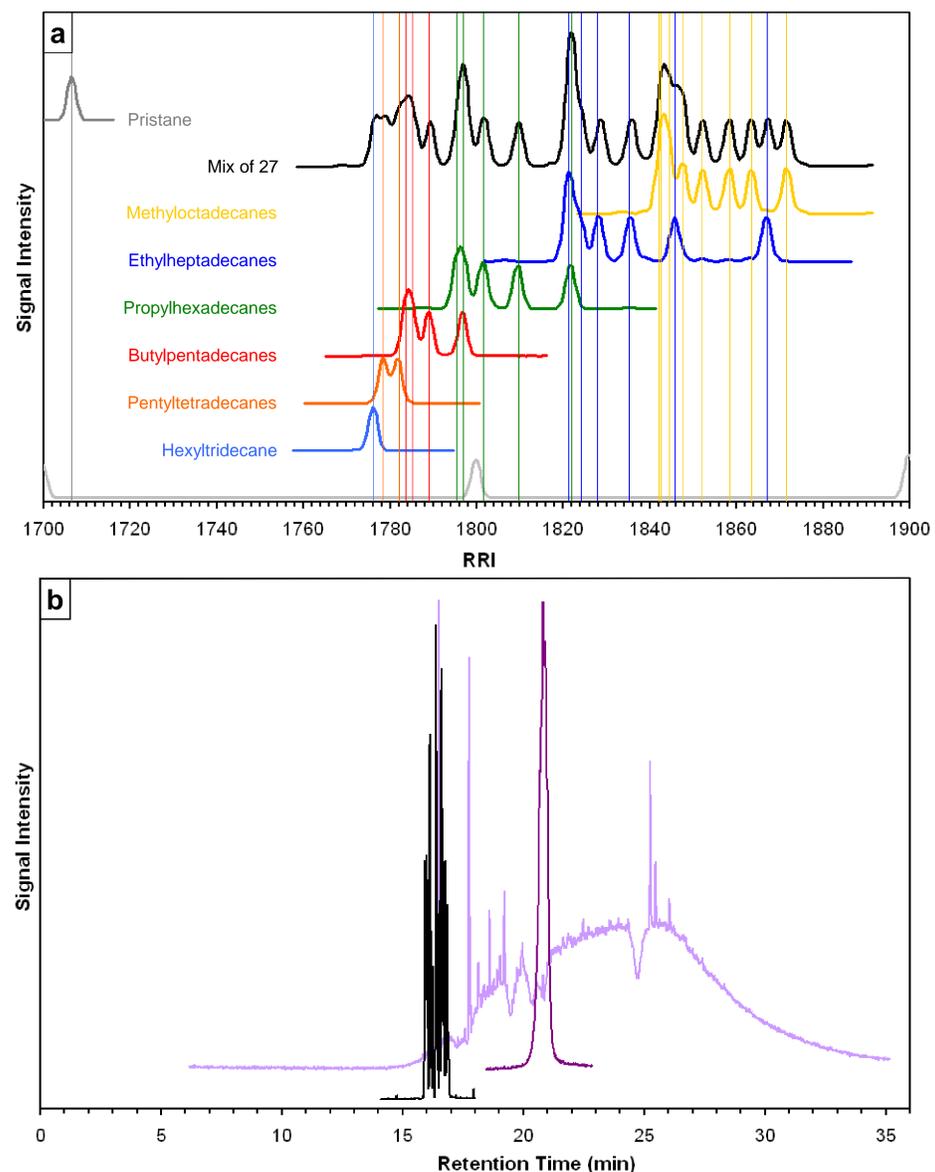


Figure 3: (a) Reconstructed partial chromatogram showing *n*-alkane *RRI* markers, pristane, the methyloctadecanes, ethylheptadecanes, propylhexadecanes, butylpentadecanes, pentyltetradecanes and hexyltridecane T-branch isomers synthesised and the mixture of all 27 isomers; (b) reconstructed chromatogram of the mix of 27 C₁₉H₄₀ T-branch isomers, an aromatic UCM and a “mini-UCM” isolated from it by preparative-GC.

References

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