Rearranged Hopanes

Triterpenoids in general, and specifically the hopanoids, easily undergo skeletal rearrangements where the methyl groups shifts positions, particular upon acid treatment. Several rearranged hopane-series have been identified:

- Neohopanes
- 17α(H)-Diahopanes
- 28-nor-Spergulanes

In the case of the neohopanes, C27Ts (2635.27) is the most prominent representative, in the case of 17α(H)-diahopanes, the C30 (30Dia or C30*, 2886.30) dominate, while the C29 Nsp, i.e. 29Nsp (2882.29) is the dominant 28-nor-spergulane.1

Standards available from Chiron

- 5 µg quantities are supplied in convenient 300µL GC-vials for dilution to e.g. 50-100µg/mL.
- Quantities are measured relative to the intensity (TIC) of the 30α hopane (Cat.No. 0132.30) or by gravimetry
- The purity is generally 95%+, but in some instances (*) it is a mixture with other hopane biomarkers

<table>
<thead>
<tr>
<th>Neohopanes:</th>
<th>Diahopanes:</th>
<th>28-Nor-spergulanes:</th>
<th>Other hopanes described in this Biomarker Focus:</th>
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<tr>
<td>2635.27-5UG</td>
<td>2886.30-5UG</td>
<td>2883.29-5UG</td>
<td>0615.27-100-IO</td>
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<tr>
<td>18α(H)-22,29,30-Trisnorhopane (Ts or 27Ts)</td>
<td>17α(H)-Diahopane</td>
<td>17β(H),18α(H)-28-Nor-spergulane</td>
<td>17α(H)-22,29,30-Trisnorhopane Tm</td>
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<tr>
<td>2635.27-5UG</td>
<td>2887.30-5UG</td>
<td>2884.30-5UG</td>
<td>2639.27-5UG</td>
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<td></td>
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<td>17β(H),18α(H)-22-Methyl-28-nor-spergulane</td>
<td>2639.27-5UG</td>
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<td>2885.29-5UG</td>
<td>1321.29-50-IO</td>
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<td></td>
<td></td>
<td>28-Nor-spergula-12(13),17(18)-diene</td>
<td>1321.29-50-IO</td>
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<td>17α(H),21 β(H)-30-Norhopane 29αβ</td>
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</table>

1:100ug/mL, 1x1mL in isooctane

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The dominant member of the neohopane series is Ts (or 27Ts, 18α(H)-22,29,30-Trisnorhopane, Cat. No. 2635.27), but 29Ts and 30Ts are also present in petroleum.

**Source and Maturity parameters:**

Ts/(Ts+Tm). 27Ts is more stable than the non-rearranged (C27) Tm (17α(H)-22,29,30-Trisnorhopane, Cat No. 0615.27), and thus the ratio Ts/(Ts+Tm) (or sometimes reported as Ts/Tm) is a extensively used maturity parameter. The ratio may also relate to the source as it is not clear whether the conversion from Tm to Ts actually occurs. The ratio should be used with caution, and reference standards are required as Tm and Ts commonly co-elute with tricyclic or tetracyclic terpanes on the m/z 191 mass chromatogram.

The 17β(H)-22,29,30-Trisnorhopane (βTm, Cat No. 2639.27) is relatively more stable than hopane (30ββ or 17β(H),21β(H)-hopane, Cat. No. 0613.30), but less stable than moretane (30βα or 17β(H), 21α(H)-hopane, Cat No. 0612.30).

29Ts/(29αβ+29Ts). It is suggested that the abundance of 29Ts relative to 29αβ (17α(H),21β(H)-30-Norhopane, Cat No. 1321.29) is related to thermal maturity as 29Ts is more stable than 29αβ.

30Dia/29Ts. It appears that the relative amounts of 30Dia and 29Ts depends on the environment of deposition, i.e. oxic or anoxic conditions. Also it seems that the compounds of the diahopane series are more stable than the normal 17α(H)-series hopanes and the 18α(H)-neohopane (Ts) series. Thus the 30Dia/αβ ratio has a similar application.

**Elution order:**

27Ts (Cat. No. 2635.27) elutes in front of most C27 hopanes, *e.g.* TNH (two isomers of 25,28,30-trisnorhopane, Cat. No. 2632.27 and 2634.27) and much earlier than Tm (Cat. No. 0615.27). The 29Ts elutes immediately after 29αβ (Cat No. 1321.29), and may partly be co-eluting on some columns. The 30Ts co-elutes with U29 (possibly norgammacerane)2, after 30αβ (Cat. No. 0132.30) and in front of 30αα (Cat. No. 2882.30).

**DIAHOPANES**

The rearranged series of diahopanes ranges from C29 to C34. C30 17α(H)-Diahopane (30Dia or C30*, 2886.30) was first identified in a Prudhoe Bay oil and characterized by X-ray crystallography.3,4 These rearranged hopanes have even a more stable carbon skeleton than the neohopanes. 27Ts and 29Ts5 Diahopenes are likely to originate from bacterial input to sediments containing clays deposited under oxic or anoxic conditions.5 The stable olefin, 17α(H)-30-diahop-13(14)-ene (Cat. No. 2887.30) is found in immature source rocks (R0 = 0.35-0.50).

**The 30Dia/29Ts and 30Dia/30αβ parameters:**

It appears that the relative amounts of 30Dia and 29Ts depends on the environment of deposition, i.e. oxic or anoxic conditions. Also it seems that the compounds of the diahopane series are more stable than the normal 17a-series hopanes and the 18a-neohopane (Ts) series. Thus the 30Dia/30αβ ratio has a similar application.
Elution order and mass spectra:

17α(H)-Diahopane (2886.30) elutes slightly after 29Ts and in front of another rearranged hopane, 17β(H),18α(H)-28-nor-spegulane* (29Nsp, 2883.29) and 29βα(0614.29). However the elution order may vary from column to column and a reference standard is required for safe identification.

Fig 1.: 398→191 and 398→69 transitions showing C29 triterpanes in a coal extract from Danish North Sea
(Courtesy of Peter Nytoft, GEUS, Denmark)

28-nor-SPERGULANES

A new series of rearranged hopanes ranging from C29 to C34 has recently been identified as 28-nor-spegulanes (or 21-methyl-28-nor-hopanes). The C29 member of the series was unambiguously identified as 17β(H),18α(H)-28-nor-spegulane (29Nsp) by NMR-spectroscopy.3

Chiron now offers the two first of this series, 29Nsp and 30Nsp.

Present in petroleum:
The C29 28-nor-spegulane (29Nsp) elutes midway between C30 17α(H)-diahopane (30Dia or C30*, 2886.30) and 17β(H),21α(H)-30-norhopane (29β, 1321.29). 29Nsp is always the dominant member of the series and can be detected in most crude oils or mature sediments using GC-MS. Their content is generally high in samples having high amounts of rearranged hopanes (diahopanes and neohopanes). 29Nsp seems to be particularly abundant in some oils from lacustrine source rocks in South East Asia. The elution order may vary from column to column, and a reference standard is required for safe identification.
Fig 2.: GC-MS of a coal extract from Danish North Sea (Courtesy of Peter Nytoft, GEUS, Denmark)

Fig. 3: 398→191 and 398→369 transitions showing C₂₉ triterpanes in a lacustrine oil from Vietnam (Courtesy of Peter Nytoft, GEUS, Denmark)

Mass spectra with an intense m/z 369:
All members of the series have typical hopane mass spectra with an m/z 191 base peak, but the m/z 369 fragment is unusually intense (70-90%).

Possible precursors:
Like the case of the other rearranged hopane series, 28-nor-spergulanes most likely arise from bacterial hopanoids, which undergo rearrangement during diagenesis. Laboratory experiments indicate that precursors of 28-nor-spergulanes could be 28-nor-spergula-12(13),17(18)-dienes, which easily are formed from hop-17(21)-enes.

References: