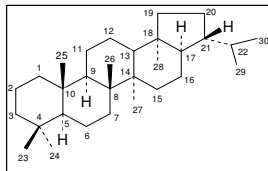




Rearranged Hopanes

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:

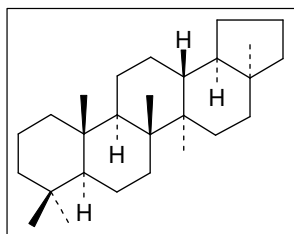
- Neohopanes
- 17 α (H)-Diahopanes
- 28-nor-Spergulanes



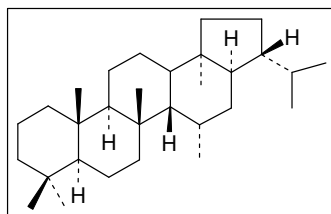
Cat.No.
0132.30
17 α (H),21 β (H)-
Hopane
(30 $\alpha\beta$)



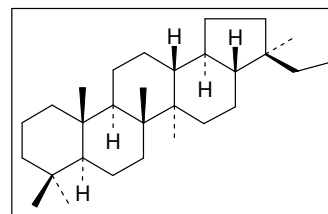
In the case of the neohopanes, C₂₇Ts (**2635.27**) is the most prominent representative, in the case of 17 α (H)-diahopanes, the C₃₀ (30Dia or C₃₀, **2886.30**) dominate, while the C₂₉ Nsp, *i.e.* 29Nsp (**2882.29**) is the dominant 28-nor-spergulane.¹



Cat. No. 2635.27
18 α (H)-22,29,30-
Trisnorneohopane
(Ts or 27Ts)



Cat. No. 2886.30
17 α (H)-30-Diahopane
(30Dia)



Cat. No. 2883.29
17 β (H),18 α (H)-28-Nor-spergulane
(29Nsp)

Standards available from Chiron

- μg quantities are supplied in convenient 300 μL GC-vials for dilution (for qualitative use)
- Quantities are measured relative to the intensity (TIC) of the 30 α 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

Neohopanes:

2635.27-1UG 18 α (H)-22,29,30-Trisnorneohopane Ts (27Ts) ca. 1 μg

Diahopanes:

2886.30-5UG 17 α (H)-Diahopane 30Dia (C₃₀) ca. 5 μg

2887.30-5UG 17 α (H)-30-Diahop-13(14)-ene ca. 5 μg

28-Nor-spergulanes:

2883.29-5UG 17 β (H),18 α (H)-28-Nor-spergulane 29Nsp ca. 5 μg

2884.30-5UG 17 β (H),18 α (H)-22-Methyl-28-nor-spergulane 30Nsp ca. 5 μg

Other hopanes described in this Biomarker Focus:

0615.27-100-IO 17 α (H)-22,29,30-Trisnorhopane Tm 100 $\mu\text{g/mL}^x$

2639.27-5UG 17 β (H)-22,29,30-Trisnorhopane, purity 55% β Tm ca. 5 μg^*

1321.29-50-IO 17 α (H),21 β (H)-30-Norhopane 29 $\alpha\beta$ 50 $\mu\text{g/mL}^x$

^x: 1x1mL in isoctane

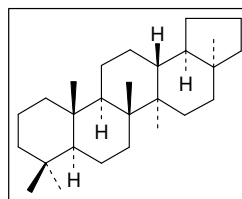


NEOHOPANES

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

Source and Maturity parameters:²

Ts/(Ts+Tm). 27Ts is more stable than the non-rearranged (C₂₇) Tm (17 α (H)-22,29,30-Trisnorhopane, Cat No. **0615.27**), and thus the ratio Ts/(Ts+Tm) (or sometimes reported as Ts/Tm) is an 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.



Cat. No. 2635.27
18 α (H)-22,29,30-Trisnorneohopane
(Ts or 27Ts)

The 17 β (H)-22,29,30-Trisnorhopane (β Tm, Cat No. **2639.27**) is relatively more stable than hopane (30 $\beta\beta$ or 17 β (H),21 β (H)-hopane, Cat. No. **0613.30**), but less stable than moretane (30 $\beta\alpha$ or 17 β (H), 21 α (H)-hopane, Cat No. **0612.30**).

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

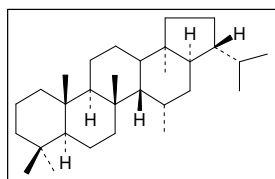
30Dia/29Ts. It appears that the relative amounts of 30Dia and 29Ts depends on the environment of deposition, *i.e.* oxic or anoxic conditions. Also it seems that the compounds of the diahopane series are more stable than the normal 17 α (H)-series hopanes and the 18 α (H)-neohopane (Ts) series. Thus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

Elution order:

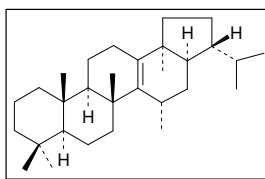
27Ts (Cat. No. **2635.27**) elutes in front of most C₂₇ hopanes, *e.g.* TNH (two isomers of 25,28,30-trisnorhopane, Cat. No. **2632.27** and **2634.27**) and much earlier than Tm (Cat. No. **0615.27**). The 29Ts elutes immediately after 29 $\alpha\beta$ (Cat No. **1321.29**), and may partly be co-eluting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

DIAHOPANES

The rearranged series of diahopanes ranges from C₂₉ to C₃₄. C₃₀ 17 α (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 29Ts.² Diahopanes are likely to originate from bacterial input to sediments containing clays deposited under oxic or anoxic conditions.⁵ The stable olefin, 17 α (H)-30-diahop-13(14)-ene (Cat. No. **2887.30**) is found in immature source rocks (*R*₀ = 0.35-0.50).



Cat. No. 2886.30
17 α (H)-Diahopane (30Dia or C₃₀)



Cat. No. 2887.30
17 α (H)-30-Diahop-13(14)-ene

The 30Dia/29Ts and 30Dia/30 $\alpha\beta$ parameters:²

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 17 α -series hopanes and the 18 α -neohopane (Ts) series. Thus the 30Dia/30 $\alpha\beta$ ratio has a similar application.

**Elution order and mass spectra:**

17 α (H)-Diahopane (**2886.30**) elutes slightly after 29Ts and in front of another rearranged hopane, 17 β (H),18 α (H)-28-*nor*-spiegulane⁶ (29Nsp, **2883.29**) and 29 $\beta\alpha$ (**0614.29**). However the elution order may vary from column to column and a reference standard is required for safe identification.

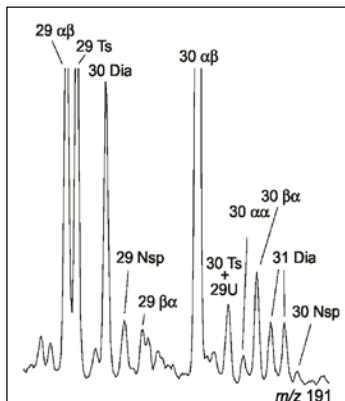
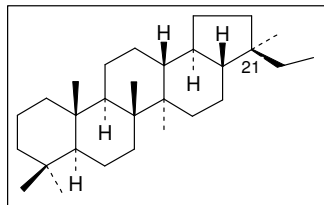


Fig 1.: 398→191 and 398→69 transitions showing C₂₉ triterpanes in a coal extract from Danish North Sea (Courtesy of Peter Nytoft, GEUS, Denmark)

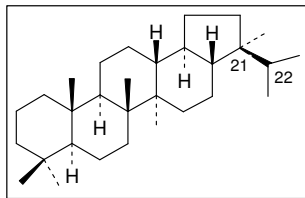
28-*nor*-SPERGULANES

A new series of **rearranged hopanes** ranging from C₂₉ to C₃₄ has recently been identified as 28-*nor*-spergulanes (or 21-methyl-28-*nor*-hopanes). The C₂₉ member of the series was unambiguously identified as 17 β (H),18 α (H)-28-*nor*-spergulane (29Nsp) by NMR-spectroscopy.⁵

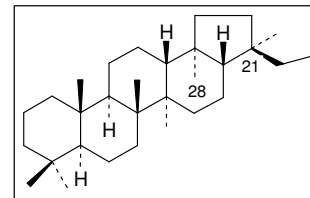
Chiron now offers the two first of this series, 29Nsp and 30Nsp.



Cat. No. 2883.29
17 β (H),18 α (H)-28-*nor*-spergulane
(29Nsp)



Cat. No. 2884.30
17 β (H),18 α (H)-22-Methyl-28-*nor*-
-spergulane
(30Nsp)



Spergulane

Present in petroleum:

The C₂₉ 28-*nor*-spergulane (29Nsp) elutes midway between C₃₀ 17 α (H)-diahopane (30Dia or C₃₀, **2886.30**) and 17 β (H),21 α (H)-30-norhopane (29 $\alpha\beta$, **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.

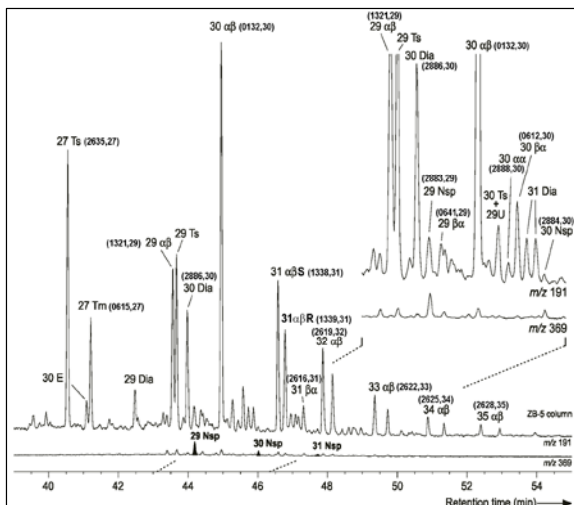


Fig. 2.: GC-MS of a coal extract from Danish North Sea (Courtesy of Peter Nytoft, GEUS, Denmark)

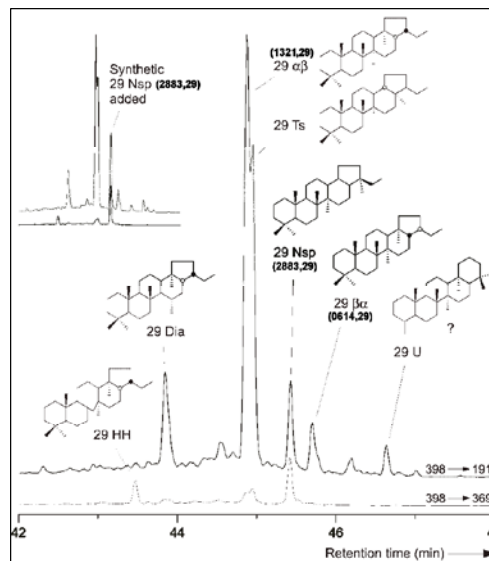


Fig. 3: 398→191 and 398→369 transitions showing C₂₉ triterpanes in a lacustrine oil from Vietnam (Courtesy of Peter Nytoft, GEUS, Denmark)

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-spegulanes most likely arise from bacterial hopanoids, which undergo rearrangement during diagenesis. Laboratory experiments indicate that precursors of 28-nor-spegulanes could be 28-nor-spegula-12(13),17(18)-dienes, which easily are formed from hop-17(21)-enes.

References:

1. P. Farrimond and N. Tælnes, *Organic Geochemistry*, **25**(1996)165-177 and references therein.
2. K. E. Peters, C. C. Walters and J. M. Moldowan, *The Biomarker Guide*, 2. ed. Vol. 1 and 2, Cambridge University Press, Cambridge 2005.
3. J.M. Moldowan, F.J. Fago, and R.M.J. Carlsson, *Geocosmica et Geochimica Acta*, **55** (1991), 3333-3335
4. J.M. Moldowan, F.J. Fago, B.J. Huizinga and S.J. Jacobsen in *Organic Geochemistry. Advances and applications in the natural environment* (D.A.C. Manning, ed.) Manchester University Press, Manchester, UK, 1991, pp 195-197
5. H. P. Nytoft, B. F. Lutnæs, J. E. Johansen, *Organic Geochemistry*, **37**(2006)772-786.
6. P. Farmond and N. Tælnes, *Organic Geochemistry*, **25**, (1996), 165-177