

**IDENTIFICATION OF AN EARLY-ELUTING REARRANGED HOPANE SERIES.
SYNTHESIS FROM HOP-17(21)-ENES AND DETECTION OF INTERMEDIATES IN
SEDIMENTS**

Hans Peter NYTOFT¹, Kate LUND¹, Toni Kennet CORLEONÉ JØRGENSEN¹, Jens
Valdemar THOMSEN¹, Steen WENDEL SØRENSEN¹, Bjart Frode LUTNÆS², Geir
KILDAHL-ANDERSEN² and Jon Eigill JOHANSEN³

1. Geological Survey of Denmark and Greenland (GEUS), Øster Voldgade 10, DK-1350K. Copenhagen
Denmark.

2. Department of Chemistry, Norwegian University of Science and Technology (NTNU), NO-7491, Trondheim,
Norway.

3. CHIRON AS, Stiklestadvn. 1, NO-7041 Trondheim, Norway.

In addition to regular hopanes, three series of rearranged hopanes (18 α -neohopanes, 17 α -diahopanes and an unidentified, early-eluting series) have been known for many years (Moldowan et al., 1991; Farrimond and Telnæs, 1996). Recently, a new series – 28-norspergulananes or 21-methyl-28-norhopanes was identified (Nytoft et al., 2006).

Compounds with the diahopane structure have not been identified in bacteria or plants and are believed to derive from diagenetic rearrangement of the regular hopane skeleton. We have prepared the diahopane structure by oxidation of hop-17(21)-ene **1** to 17,21-epoxyhopane **2** which was dehydrated to hopa-15,17(21)-diene **3** followed by acid-catalyzed rearrangement to a complex mixture of rearranged hopadienes. Only two of these dienes **4** and **5** (10-15 % of the products) were isolated and characterized by NMR. Mild hydrogenation gave 17 α -15 α -methyl-27-norhop-13-ene (or "17 α -diahop-13-ene") **6** in almost quantitative yield. Hydrogenation using more severe conditions gave 17 α -diahopane **7**. Hydrogenation of unidentified isomers of **4** and **5** produced a novel spirotriterpane coeluting with 17 α -diahopane **7**. 17 α -Diahop-13-ene was also formed in low yield (max. 5%) directly by acid-catalyzed isomerization of hop-17(21)-ene. Major products were neohop-13(18)-ene **8**, fernenes, spiro-triterpenes and several unidentified compounds. Acid catalyzed isomerization of diahop-13-ene yielded one major product, which was identified as 9,15-dimethyl-25,27-bisnorhop-5(10)-ene **9** by NMR. Hydrogenation gave 9,15-dimethyl-25,27-bisnorhopane **10** in high yield. The latter coeluted with the early-eluting rearranged hopane in oils and had an identical mass spectrum. The shift of a methyl group from C-5 to C-9 and from C-14 to C-15 results in a shorter molecule with a large cross-section explaining the very short GC-retention times of 9,15-dimethyl-25,27-bisnorhopanes.

The synthetic route to 17 α -diahopane **7** and 9,15-dimethyl-25,27-bisnorhopane **10** is probably identical or very similar to the way these compounds are formed in geological

samples. The intermediates **3**, **6** and **9** have been identified in geological samples. Hopa-15,17(21)-dienes are abundant in immature samples with huminite reflectances from 0.2 to 0.3 % R_o . 17 α -Diahop-13-enes and 9,15-dimethyl-25,27-bisnorhop-5(10)-enes occur at higher maturities (0.35 – 0.5 % R_o).

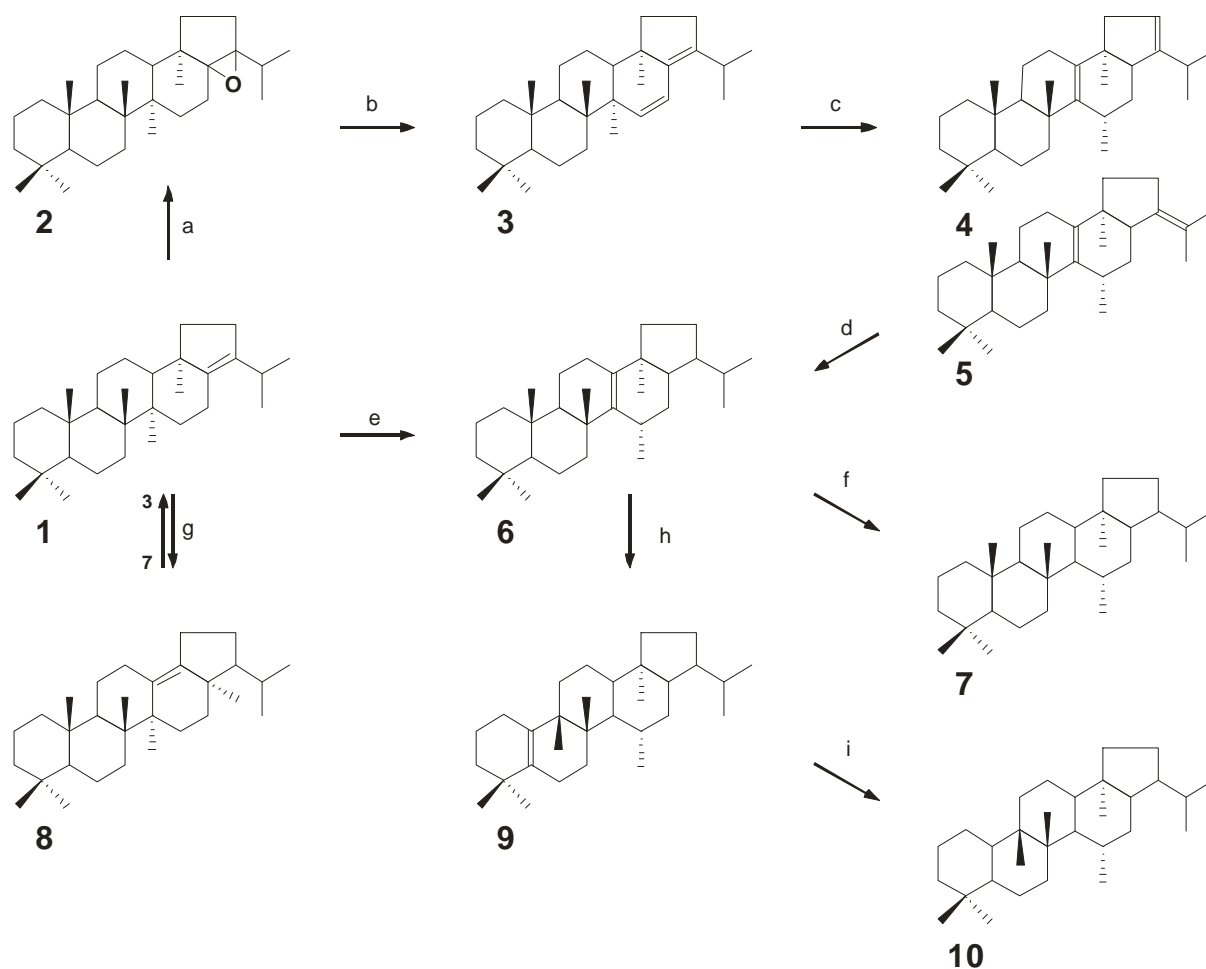


Figure 1. Synthesis of 9,15-dimethyl-25,27-dinor-hopane **10**. Reagents and conditions: (a) $\text{Cl}_6\text{H}_4\text{CO}_3\text{H}$ (1.1 equiv), 2 °C, 10 min, 90%; (b) $\text{C}_2\text{H}_5\text{OH}$: 37% HCl (10:1), reflux, 2h, 70%; (c) EtOAc :0.1N HClO_4 in CH_3COOH (1:2) under N_2 , 11h, 40 °C, 10-15%; (d) PtO_2 , hexane, rt, 1h, >90%; (e) 0.1N HClO_4 in CH_3COOH , 24h, 50 °C, 4%; (f) PtO_2 , 0.1N HClO_4 in CH_3COOH , rt, 1h, >90%; (g) 0.1N HClO_4 in CH_3COOH , 50 °C, (h) 0.1N HClO_4 in CH_3COOH , 120h, 75 °C, ~50%; (i) PtO_2 , 0.1N HClO_4 in CH_3COOH , 75 °C, 1h, ~50%.

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