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LETTERS

# A Novel Demethylated Oxygenated Triterpenoid in Crude Oils from the Canadian Beaufort Sea and Northeast Alaska

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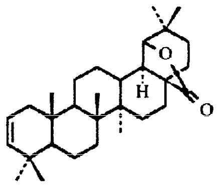
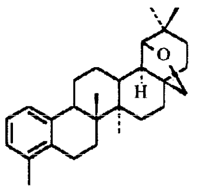
***Abstract:*** 19,28-epoxy-24-nor-18α-oleanane (**1**) has been identified in the Amauligak and Hammerhead crude oils by comparison with an authentic standard prepared from betulin. The biological origin of this novel biomarker is likely to be 23-hydroxybetulin (**10**).

Sedimentary organic matter derived from higher plants is frequently characterised by the presence of triterpenoid biomarkers with carbon skeletons indicating an origin from lupeol and α- and β-amyrin.[1-6] In contrast to this there have been fewer reports of biomarkers (e.g. **2-4**) derived from the betulin group of triterpenoid natural products[7-9] the majority of these having arisen by processes involving the well known betulin-allobetulin and betulinic acid-oxyallobetulin rearrangements.[10-11]



**(2)**



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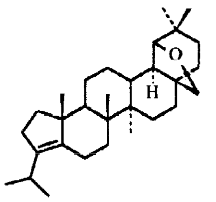
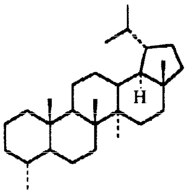


**(4)**

Recent studies of a suite of commercial oil deposits from the Canadian Beaufort Sea, in particular from the Amauligak field, in conjunction with synthetic studies have led to the identification of a number of 24-nortriterpenoid biomarkers (e.g. **5**,**6**).[2,4]



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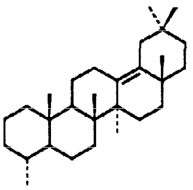

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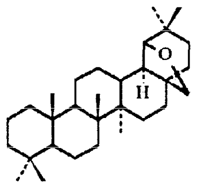

**(7)**

This oil also contains two interesting unknown triterpenoids referred to previously as compounds H and I.[2] Both compounds have also been observed in the Hammerhead crude oil from northeast Alaska[3] and compound I in deep-sea sediments from Baffin Bay.[5] The mass spectrum of H[3] has a molecular ion at m/z 412 and a base peak at m/z 177, the latter suggesting a 24-nortriterpenoid.[4,6] Other diagnostic ions in the mass spectrum are

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observed at m/z 341 (M-71), corresponding to loss of a $C_5H_{11}$ radical, which is characteristic of 19,28-epoxy-18α-oleanane derivatives[12] and m/z 381 (M-31) probably from loss of a methoxy radical. The mass spectral data suggested therefore that compound H is 19,28-epoxy-24-nor-18α-oleanane (**1**). Further evidence for this hypothesis came from synthesis[13] of the known parent homologue 19,28-epoxy-18α-oleanane (**7**),[10,12,14] whose mass spectrum is almost identical to that of (**1**) but with the key fragment ions increased by fourteen mass units.[13]

A synthesis of 19,28-epoxy-24-nor-18α-oleanane (**1**) was carried out utilising cyclopalladiation methodology[15] which has been shown to be applicable to the preparation of 24-nortriterpenoids.[4] The target compound[16] was obtained as illustrated in Fig. 1 starting from the known 19,28-epoxy-18α-oleanan-3-one oxime (**9**), which can be obtained in four steps from betulin (**8**).[10]

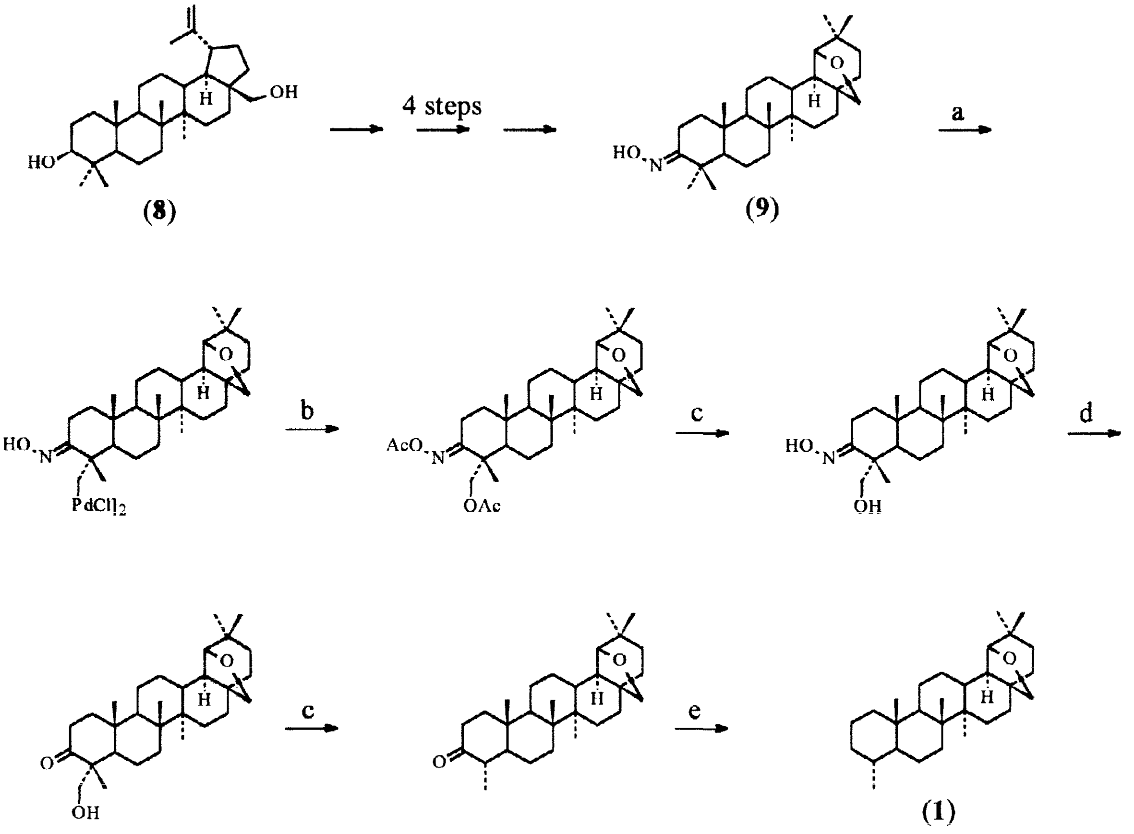
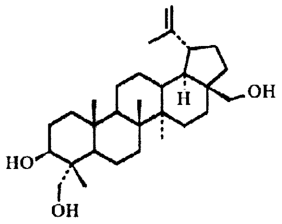


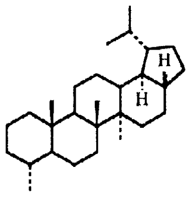
Fig. 1. Scheme showing the preparation of 19,28-epoxy-24-nor-18α-oleanane (**1**) from betulin (**8**). Key: a $Na_2PdCl_4$, NaOAc, EtOH; b (i) $Ac_2O$, DMAP, $NEt_3$, $CH_2Cl_2$ (ii) Pyridine, THF (iii) $Pb(OAc)_4$, HOAc (iv) $NaBH_4$, NaOH; c $K_2CO_3$, MeOH; d $TiCl_3$, $NH_4OAc$, THF, $H_2O$; e (i) $N_2H_4$, diethylene glycol, 1-butanol (ii) KOH.

The mass spectrum of (**1**) (Fig. 2) is almost identical to that reported for compound H[3] and furthermore co-elutes with it under high resolution capillary gas chromatographic conditions[17] indicating that H is indeed 19,28-epoxy-24-nor-18α-oleanane.

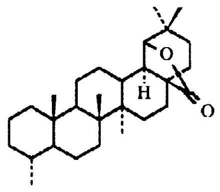
The origin of this novel biomarker can be rationalised in terms of a betulin derivative, a particularly attractive possibility being that of 23-hydroxybetulin (**10**) which has been characterised in Mountain Ash.[18] It is also tempting to speculate that this compound is the biological precursor of the 24,28-dinorlupanes (**11**) identified in sediments and crude oils[19] and which co-occur with (**1**) in both the Amauligak and Hammerhead oils.[2,3] This study points to the wider occurrence of biomarker compounds derived from triterpenoids of the betulin family. In the case of (**1**) this biomarker would appear to be specific for plants, which are capable of biosynthesising further oxygenated betulin derivatives such as 23-hydroxybetulin.



**(10)**



**(11)**



**(12)**

The mass spectrum of compound I[3] is characterised by a base peak at m/z 177 indicating a 24-nortriterpenoid. The molecular ion is observed at m/z 426. Assuming that this compound is also a $C_{29}$ triterpenoid then two oxygen atoms are required to account for the molecular weight, which can be accommodated by the related 24-nor-18α-oleano-28,19-lactone (**12**).

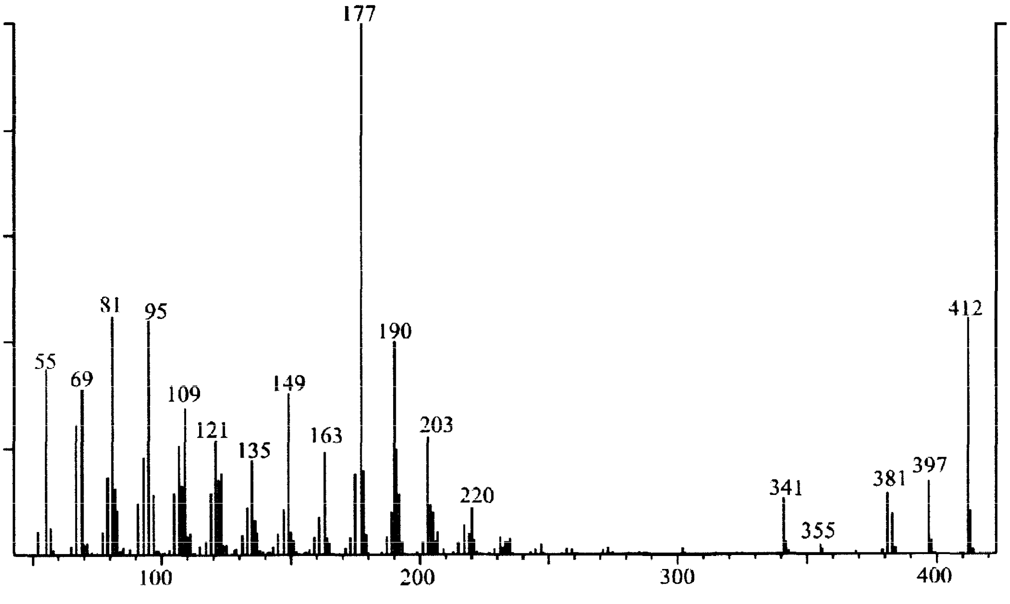


Fig. 2. Mass spectrum of authentic 19,28-epoxy-24-nor-18α-oleanane (**1**)

## REFERENCES AND NOTES

1. e.g. (a) Trendel, J.M.; Lohmann, F.; Kintzinger, J.P.; Albrecht, P.; Chiaroni, A.; Riche, C.; Cesario, M.; Guilhem, J.; Pascard C. *Tetrahedron* **1989**, *45*, 4457-4470 (b) Wolff, G.A.; Trendel, J.M.; Albrecht P. *Tetrahedron* **1989**, *45*, 6721-6728 (c) Woolhouse, A.D.; Oung, J.N.; Philp, R.P.; Weston R.J. *Org.*

*Geochem.* **1992**, *18*, 23-31 (d) Rullkötter, J.; Peakman, T.M.; ten Haven, H.L. *Org.Geochem.* **1994**, *21*, 215-233 (e) Moldowan, J.M.; Dahl, J.; Huizinga, B.J.; Fago, F.J.; Hickey, L.J.; Peakman, T.M.; Taylor, D.W. *Science* **1994**, *265*, 768-771.

2. Curiale J.A. *Chem.Geol.* **1991**, *93*, 21-45.
3. Curiale J.A. *Org.Geochem.* **1995**, *23*, 177-182.
4. Peakman, T.M.; ten Haven, H.L.; Rullkötter, J.; Curiale J.A. *Tetrahedron* **1991**, *47*, 3779-3786.
5. ten Haven, H.L.; Peakman, T.M.; Rullkötter J. *Geochim.Cosmochim:Acta* **1992**, *56*, 2001-2024.
6. Trendel, J.M.; Graff, R.; Albrecht, P.; Riva A. *Tetrahedron Lett.* **1991**, *32*, 2959-2962.
7. Ruhemann, S.; Raud H. *Brennstoff-Chem.* **1932**, *13*, 341-345.
8. Barton, D.H.R.; Carruthers, W.; Overton K.H. *J.Chem.Soc.*, **1956**, 163.
9. Jarolim, V.; Hejno, K.; Sorm F. *Coll.Czech.Chem.Commun.* **1963**, *28*, 2443-2454.
10. Schulze, H.; Pieroh, K. *Ber.* **1922**, *55*, 2332-2346.
11. (a) Davy, G.S.; Halsall, T.G.; Jones, E.R.H. *J.Chem.Soc.* **1951**, 2696-2702 (b) Davy, G.S.; Halsall, T.G.; Jones, E.R.H.; Meakins G.D. *J.Chem.Soc.* **1951**, 2702-2705.
12. Errington, S.G.; Ghisalberti, E.L.; Jefferies, P.R. *Aust.J.Chem.* **1976**, *29*, 1809-1814.
13. 19,28-epoxy-18$\alpha$-oleanane (7) was prepared by Wolff-Kishner reduction of the known[10] 19,28-epoxy-18$\alpha$-olean-3-one and has: $^1$H NMR (400 MHz, $CDCl_3$) 0.79 (6H, s, 24-$H_3$ and 29-$H_3$), 0.84 (3H, s, 25-$H_3$), 0.85 (3H, s, 23-$H_3$), 0.92 (3H, s, 27-$H_3$), 0.93 (3H, s, 30-$H_3$), 0.97 (3H, s, 26-$H_3$), 3.43 (1H, d, J=7.8 Hz, 28 pro *R* H), 3.53 (1H, s, 19$\alpha$-H), 3.78 (1H, d, J=7.8 Hz, 28 pro *S* H); MS 426 ($M^+$ 42), 411 (12), 395 (20), 369 (4), 355 (11), 203 (25), 191 (100), 177 (27), 163 (17), 149 (26), 136 (22), 123 (23), 109 (28), 95 (40), 81 (31), 69 (34), 55 (12).
14. Ruzicka, L.; Heineman S.D. *Helv.Chim.Acta* **1940**, *23*, 1512-1518.
15. (a) Constable, A.G.; McDonald, W.S.; Sawkins, L.C.; Shaw, B.L. *J.Chem.Soc., Dalton* **1980**, 1992-2000 (b) Baldwin, J.E.; Jones, R.H.; Najera, C.; Yus, M. *Tetrahedron* **1985**, *41*, 699-711 (c) Carr, K.; Saxton, J H.M.; Sutherland, K. *J.Chem.Soc., Perkin Trans. 1* **1988**, 1599-1601.
16. 19,28-epoxy-24-nor-18$\alpha$-oleanane (1) has: $^1$H NMR (400 MHz, $CDCl_3$) 0.57 (1H, ddd, J=2.7, 10.2, 12.2 Hz, 5$\alpha$-H); 0.77 (3H, s, 25-$H_3$); 0.80 (3H, s, 29-$H_3$); 0.80 (3H, d, J=6.6 Hz, 23-$H_3$); 0.92 (3H, s, 27-$H_3$); 0.93 (3H, s, 30-$H_3$); 0.98 (3H, s, 26-$H_3$); 3.44 (1H, d, J=7.8 Hz, 27 pro *R* H); 3.53 (1H, s, 19$\alpha$-H); 3.78 (1H, dd, J=1.5, 7.8 Hz, 27 pro *S* H).
17. GC co-injection experiments were carried out on a 50m x 0.32mm CPSil5 CB ($d_f$=0.12$\mu$m) capillary column (Chrompack) using hydrogen as carrier gas.
18. Lawrie, W.; McLean, J.; Taylor, G.R. *J.Chem.Soc.* **1960**, 4303-4308.
19. Rullkötter, J.; Leythaeuser, D.; Wendisch, D. *Geochim.Cosmochim.Acta*, **1982**, *46*, 2501-2510.