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Characterisation of 24-*nor*-Triterpenoids Occurring in Sediments and Crude Oils by Comparison with Synthesized Standards

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Abstract: *A series of 24-nor-triterpenoids; 24-nor-urs-12-ene, 24-nor-olean-12-ene and 24-nor-lupane have been identified in sediments and crude oils by comparison with standards obtained by synthesis. A further suite of 24-nor-oleanenes has also been identified by comparison with the acid-catalysed rearrangement products of 24-nor-olean-12-ene. The presence of these components in sedimentary organic matter points to an important new pathway of terrigenous triterpenoid diagenesis.*

INTRODUCTION

Pentacyclic triterpenoids of higher plant origin, especially those belonging to the oleanane, ursane, friedelane and lupane families, have been identified in sedimentary organic matter[1-7] although their occurrence is limited compared with that of the almost ubiquitous presence of bacterial hopanoids.[8] This restricted occurrence of higher plant triterpenoids has proved useful in solving problems of a geochemical nature, such as correlation of crude oils and source rocks, and in the assessment of the palaeoenvironment of deposition.[3] During early diagenesis various processes have been observed which affect the structure of these higher plant triterpenoids. These processes, which appear to be mediated by micro-organisms, the catalytic effect of minerals and the effect of heat, as a consequence of increasing thermal gradient with increasing depth of burial, include ring A degradation,[1,4] aromatisation,[5] demethylation[1,6] and rearrangement.[7a]

We have now characterised a series of 24-*nor*-triterpenoids[9] occurring in several crude oils and sediment samples by comparison with standards obtained by synthesis and acid-catalysed rearrangement. The presence of these components in sedimentary organic matter, often in high relative abundance, would appear to point to an important new pathway of terrigenous triterpenoid diagenesis.

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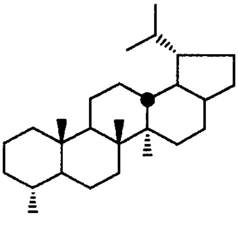
RESULTS AND DISCUSSION

Occurrence and identification of 24-nor-triterpenoids in sediments and crude oils

Recent GC-MS studies of bitumen fractions from Baffin Bay sediments,[7] recovered at Site 645 during Leg 105 of the Ocean Drilling Program, and crude oils from the Mackenzie Delta and offshore Canadian Beaufort[10] have indicated the presence of high concentrations of triterpenoids derived from higher plants. Mass spectral interpretations have also pointed to the occurrence of various oleanane, ursane and lupane components with a methylene unit missing from the A/B ring part of the molecule. Examination of the organic geochemical literature suggests that sediments from the Japan Trench[2] and rock samples from the Maoming oil shale in China,[11] also contain some of these degraded compounds. In view of the earlier identification of 24,28-*dinor*-lupanes (**1**) in immature sediments from Greenland[6a] we speculated that these components could be 24-*nor*-triterpenoids.



(**1**)

This hypothesis has now been confirmed by comparison of these naturally occurring triterpenoids with standards obtained by synthesis and acid-catalysed rearrangement.[12] Thus, we have confirmed the presence of 24-*nor*-urs-12-ene (**2i**), 24-*nor*-olean-12-ene (**3i**), 24-*nor*-olean-13(18)-ene (**5**), 24-*nor*-olean-18-ene (**6**), 24-*nor*-18α-olean-12-ene (**7**) and 24-*nor*-lupane (**4i**)[13] in both the sediments from Baffin Bay and crude oils from offshore Canada. An example of the distribution of these 24-*nor*-triterpenoids in the Amauligak crude oil from offshore Canada is shown in Figure 1.

Synthesis of the 24-nor-triterpenoids

The preparation of 24-*nor*-triterpenoids (Fig. 2) followed that developed for the 4α-demethylation of lanost-8-en-3-one.[14] This method involves cyclopalladiation of the hindered C-4 equatorial methyl group starting from a 3-one oxime functionality; a reaction which has also been shown to be applicable to triterpenoids.[15] Thus, we successfully converted urs-12-en-3-one oxime (**2a**), olean-12-en-3-one oxime (**3a**) and, as previously reported,[15] lupan-3-one oxime (**4a**) (prepared from α-amyrin, β-amyrin and lup-20(29)-en-3-one, respectively) into their corresponding dimeric cyclopalladiates (**2b-4b**) in yields of typically 85%. The O-oxime acetates of the cyclopalladiates were transformed into their pyridine monomer complexes and oxidised *in situ* with lead tetra-acetate. Reductive work-up, with sodium borohydride, afforded the 23-acetoxy O-oxime acetates (**2c-4c**) which, after base catalysed de-acetylation and regeneration of the ketone group with buffered titanium trichloride, afforded the 23-ol-3-ones (**2e-4e**). Loss of formaldehyde, through a base-catalysed retro-aldol reaction, afforded the 24-*nor*-3-ones (**2f-4f**). The overall yield of the 24-*nor*-3-ones from the cyclopalladiates was typically 25%. With a view to obtaining possible geochemical precursors and/or intermediates of the 24-*nor*-triterpenoids we elected to reduce the ketone group with sodium borohydride in ethanol to give a mixture of the corresponding alcohols, which were readily separated by chromatography. Tosylation of the major 3β-alcohols (**2g-4g**) followed by reduction with lithium aluminium hydride afforded the corresponding hydrocarbons (**2i-4i**). The mass spectra of the final products were in accordance with their structures and, as expected, showed striking similarities in their fragmentation patterns to those of their undegraded homologues.[16] The

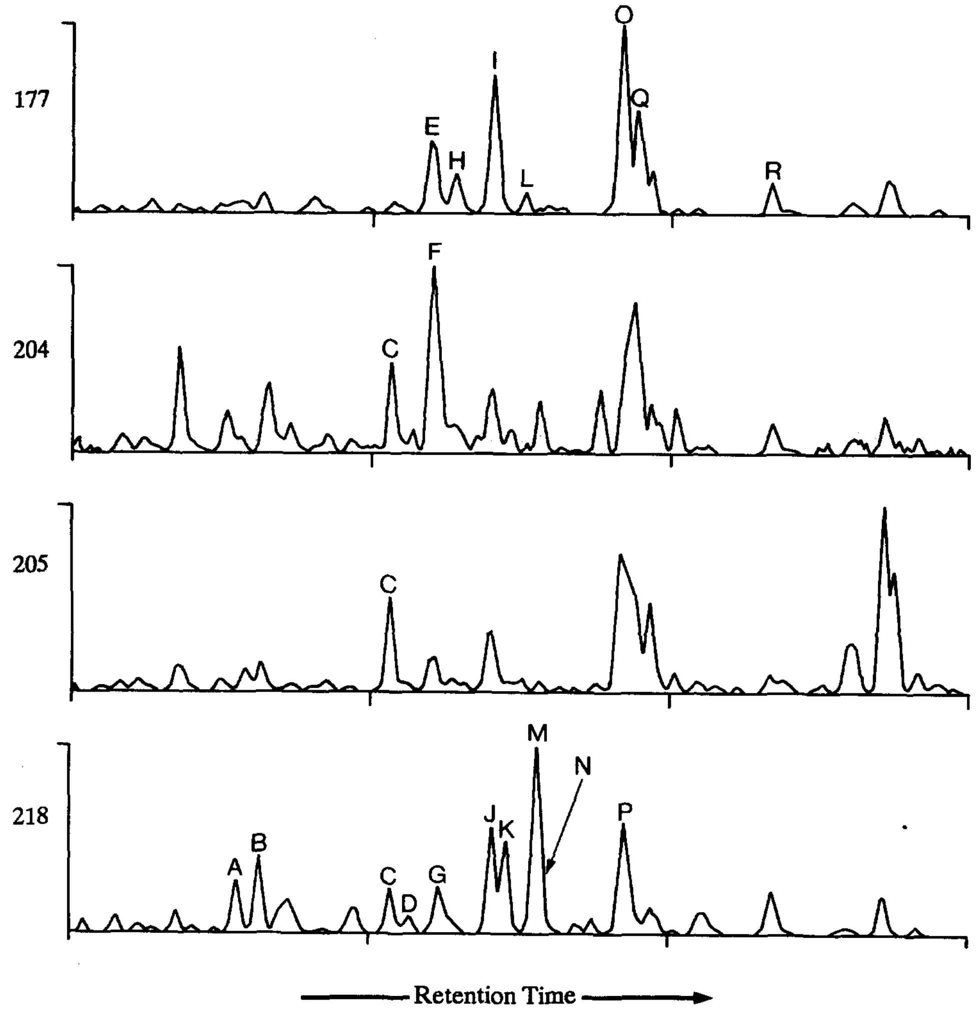
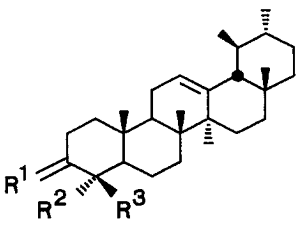
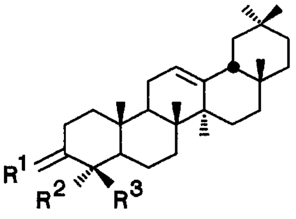


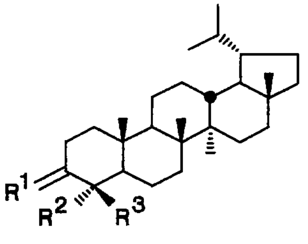
Figure 1. Selected partial mass chromatograms from GC-MS analysis (MID mode) of the branched/cyclic hydrocarbon fraction from the Amauligak crude oil showing the distributions of 24-*nor*-triterpenoids. Key: A = (20*R*)-24-methyl-5α,14β,17β(H)-cholestane, B = (20*S*)-24-methyl-5α,14β,17β(H)-cholestane, C = 24-*nor*-olean-13(18)-ene (**5**), D = 24-*nor*-olean-12-ene (**3i**), E = isomer of 24,28-*dinor*-lupane, F = 24-*nor*-olean-18-ene (**6**), G = (20*S*)-24-ethyl-5α(H)-cholestane, H = 24,28-*dinor*-17α-lupane (**1**), I = 24,28-*dinor*-17β-lupane (**1**), J = (20*R*)-24-ethyl-5α,14β,17β(H)-cholestane, K = (20*S*)-24-ethyl-5α,14β,17β(H)-cholestane, L = isomer of 24,28-*dinor*-lupane, M = 24-*nor*-urs-12-ene (**2i**), N = 24-*nor*-18α-olean-12-ene (**7**); O = 24-*nor*-lupane (**4i**), P = (20*R*)-24-ethyl-5α-cholestane, Q = 30-*nor*-17α, 21β(H)-hopane, R = 30-*nor*-17β, 21α(H)-hopane.



(2)



(3)



(4)

a	R^1 = N-OH(*E*)	$R^2 = CH_3$	$R^3 = CH_3$
b	R^1 = N-OH(*E*)	$R^2 = CH_2PdCl]_2$	$R^3 = CH_3$
c	R^1 = N-OAc(*E*)	$R^2 = CH_2OAc$	$R^3 = CH_3$
d	R^1 = N-OH(*E*)	$R^2 = CH_2OH$	$R^3 = CH_3$
e	R^1 = O	$R^2 = CH_2OH$	$R^3 = CH_3$
f	R^1 = O	$R^2 = CH_3$	R^3 = H
g	R^1 = HO(β) H(α)	$R^2 = CH_3$	R^3 = H
h	R^1 = HO(α) H(β)	$R^2 = CH_3$	R^3 = H
i	$R^1 = H_2$	$R^2 = CH_3$	R^3 = H

Figure 2. Synthesized triterpenoids

structures, and in particular the site of demethylation, were confirmed by high field ^{1}H NMR spectroscopy.

Acid-catalysed rearrangement of 24-nor-olean-12-ene

In order to obtain various double bond isomers of 24-*nor*-olean-12-ene we turned to the known acid-catalysed rearrangement of olean-12-ene.[17] Treatment of 24-*nor*-olean-12-ene (**3i**) with trifluoroacetic acid in toluene afforded a mixture of four alkenes (Fig. 3) which were separated by column chromatography on silica gel impregnated with silver nitrate. The products of acid treatment, in addition to starting material, were identified as 24-*nor*-olean-13(18)-ene (**5**), 24-*nor*-olean-18-ene (**6**) and 24-*nor*-18α-olean-12-ene (**7**) on the basis of comparison of their mass spectra with those of the corresponding oleanenes[16] and by interpretation of their ^{1}H NMR spectra.

Origin of 24-nor-triterpenoids in sedimentary organic matter

These studies point to another general pathway of triterpenoid diagenesis in immature sediments, in addition to those previously identified,[1,4-6] whereby a substituent is lost from C-4. The nature of this loss is at present speculative, although a facile loss of carbon dioxide from a 3-on-23- or -24-oic acid (*i.e.* a β-keto acid) precursor may be a possibility. However, we cannot at present exclude a direct contribution of 24-*nor*-triterpenoids to sedimentary organic matter, since naturally occurring examples have been reported.[18] Studies aimed at elucidating the origin of the 24-*nor*-triterpenoids in sedimentary organic matter, utilising some of the oxygenated intermediates described herein, are in progress.

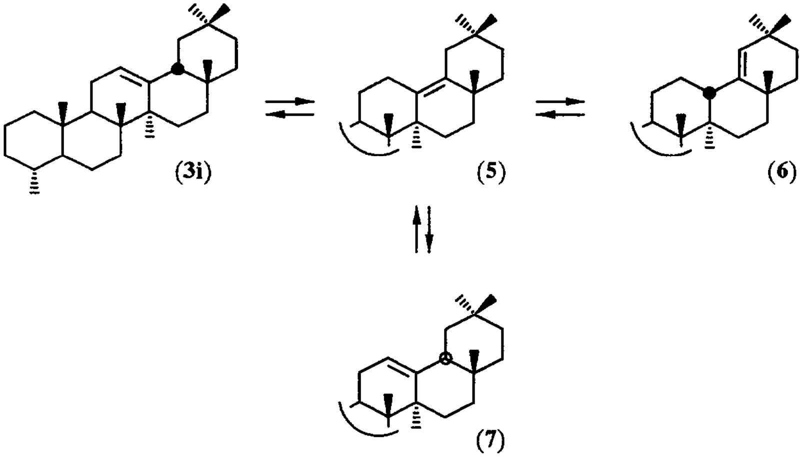


Figure 3. Acid-catalysed rearrangement of 24-*nor*-olean-12-ene.

EXPERIMENTAL

General

Gas Chromatography was performed on either a Varian 3700 gas chromatograph fitted with an Ultra-1 capillary column (25 m x 0.32 mm, d_f=0.52 μm) or a Carlo Erba 6000 gas chromatograph fitted with an SE-54 capillary column (25m x 0.32 mm, d_f=0.25 μm) *Gas Chromatography-Mass Spectrometry (GC-MS)* was performed with either a Carlo Erba 4160 gas chromatograph coupled to a VG 7070E mass spectrometer or a Finnigan 5100SP GC-MS system. The gas chromatographs were equipped with a 50 m x 0.32 mm capillary column coated with CPSil-5 (d_f=0,4 μm) *High Resolution Mass Spectrometry (HRMS)* was performed with the VG 7070E mass spectrometer. *^1H Nuclear Magnetic Resonance Spectroscopy (^1H NMR)* was carried on either a Varian EM-390 (90 MHz), a Bruker CXP200 (200 MHz) or a Bruker AC-300 (300 MHz) spectrometer. Spectra were recorded in deuterochloroform. 90 MHz and 200 MHz Spectra were calibrated against tetramethylsilane and 300 MHz spectra against residual chloroform (δ 7.26 ppm). *Infra-red Spectra (IR)* were recorded using potassium bromide discs on a Perkin Elmer 783 spectrophotometer. *R_f values* refer to relative mobilities on thin layer chromatography plates.

Preparation of the 24-nor-triterpenoids

Dimeric triterpen-3-one oxime cyclopalladiates (**2b, 3b, 4b**): A solution of the triterpen-3-one oxime (1 mmol), sodium acetate (1.05 mmol) and sodium tetrachloropalladate (1.1 mmol) in glacial acetic acid (30 ml) was stirred for 3 days in a dry atmosphere. The precipitated material was removed by filtration and washed with water. After drying over phosphorous pentoxide the metal complexes were obtained as pale yellow powders with yields of 82-89%.

Triterpen-3-on-23-acetoxy O-oxime acetates (**2c, 3c, 4c**): The dimeric triterpen-3-one oxime cyclopalladiates (0.35 mmol) were acetylated by stirring in dry dichloromethane (15 ml) with acetic anhydride (1 mmol), triethylamine (1 mmol) and N,N-dimethylaminopyridine (5 mg) under nitrogen at room temperature for 45 min. The solution was washed with water (x2) and dried with magnesium sulphate. After filtration and removal of the solvent under reduced pressure the resulting triterpen-3-one O-oxime acetates were immediately taken up in dry THF (25 ml). Pyridine (0.7 mmol) was added at room temperature with stirring under nitrogen to form the pyridine monomer complexes (15 min) which were then oxidised with lead tetraacetate (0.7 mmol) in acetic acid (10 ml) at -30°C (1 h) warming to room temperature (20 h). Sodium borohydride (0.8 mmol) in 1N sodium hydroxide solution (10 ml) was added and the reaction mixture was stirred (15 min). The product was isolated by filtration through Celite, diluting with water and extracting with ether. The combined ether extracts were neutralised with sodium bicarbonate, washed with brine and dried with sodium sulphate. After filtration the solvent was removed under reduced pressure to afford a yellow oil which was purified by flash chromatography using hexane-ether (4:1) as eluant. The purified products (R_f=0.2, 2:1 hexane-ether) were obtained as colourless oils in yields of 58-70%. ^{1}H NMR spectra (90 MHz) were characterised by the presence of two singlet acetate methyl resonances (typically δ2.05 and 2.17 ppm) and a second order pair of doublets for the two inequivalent C-23 hydrogens (typically δ4.07 and 4.24, J=12 Hz).

Triterpen-3-on-23-ol oximes (**2d, 3d, 4d**): The triterpen-3-on-23-acetoxy O-oxime acetates (0.3 mmol) were de-acetylated by stirring with sodium carbonate (150 mg) in methanol (25 ml) at room temperature in a dry atmosphere for 16 h. The methanol was removed under reduced pressure and the residue taken up in ether and washed with 2N hydrochloric acid and brine. After drying with sodium sulphate, filtration and removal of the solvent a white solid was obtained which was considered sufficiently pure to use in the next step.

Triterpen-3-on-23-ols (**2e, 3e, 4e**): The oxime derivate of the triterpen-3-on-23-ols was removed by adding a 30% solution of titanium trichloride in water (460 μl) to a mixture of the oxime (0.2 mmol) in THF (15 ml) and ammonium acetate (7 7 mmol) in water (16 ml) After stirring for 20 h the initial deep blue colour had disappeared and the product was obtained by diluting with water and extracting with ether. The combined ether extracts were neutralised with sodium bicarbonate, washed with brine and dried with sodium sulphate. After filtration and removal of the solvent under reduced pressure a white solid was obtained which was purified by flash chromatography eluting with hexane through to hexane-ether (1:1). The purified product had R_f=0.2 (3:1 hexane-ether). The yield of triterpen-3-on-23-ols from the triterpen-3-on-23-acetoxy O-oxime acetates was 59-68%. ^{1}H NMR spectra (90 MHz) showed the typical presence of the two inequivalent C-23 hydrogens (typically δ3.42 and 3.67, both *d*, J=11 Hz).

24-nor-triterpen-3-ones (**2f, 3f, 4f**)· The triterpen-3-on-23-ols (0.15 mmol) were stirred with sodium carbonate (200 mg) in methanol (40 ml) at room temperature in a dry atmosphere (40 h). The methanol was removed under reduced pressure and the residue taken up in ether and washed with 2N hydrochloric acid and brine. After drying with sodium sulphate and filtration the solvent was removed to afford a white solid. This was purified by flash chromatography using hexane-ether (10·1) as eluant. The purified product had R_f=0.7 (1:1 hexane-ether). The yield of 24-*nor*-triterpen-3-ones was 60-68%. 24-*nor*-Urs-12-en-3-one (**2f**) had: IR ν_{max} 1710 cm^{-1}; LRMS 410 (M^+ 5), 395 (3), 218 (100), 203 (20), 191 (7), 189 (14), 177 (7); HRMS 410.3538 (calculated for $C_{29}H_{46}O$ 410.3548); ^{1}H NMR (300 MHz) 0.79, 3H, *d*, J=5.4 Hz (C-29 or C-30), 0.80, 3H, *d*, J=6 1 Hz (C-29 or C-30), 0 91, 3H, *s* (C-28), 1 01, 3H, *d*, J=6 5 Hz (C-23), 1 06, 3H, *d*, J=0 5 Hz (C-26), 1.09, 3H, *s* (C-27), 1.17, 3H, *d*, J=0.6 Hz (C-25), 5.14, 1H, *dd*, J's=3.6 Hz (C-12). 24-*nor*-Olean-12-en-3-one (**3f**) had· IR ν_{max} 1707 cm^{-1}; LRMS 410 (M^+ 11), 395 (6), 218 (100), 203 (33), 191 (4), 189 (13), 177 (3); HRMS 410.3535 (calculated for $C_{29}H_{46}O$ 410.3548); ^{1}H NMR (300 MHz) 0 85, 3H, *s* (C-28), 0.87, 6H, *s* (C-29 and C-30), 1.01, 3H, *d*, J=6.5 Hz (C-23), 1.05, 3H, *s* (C-26), 1.13, 3H, *s* (C-25), 1.15, 3H, *s* (C-27) 24-*nor*-Lupan-3-one (**4f**) had IR ν_{max} 1711 cm^{-1}; LRMS 412 (M^+ 20), 397 (12), 369 (22), 231 (9), 219 (13), 205 (28), 191 (100), 177 (38), 163 (98); HRMS 412 3705 (calculated for $C_{29}H_{48}O$ 412.3705); ^{1}H NMR (300 MHz) 0.76, 3H, *d*, J=6 8 Hz (C-29 or C-30), 0.77, 3H, *s* (C-28), 0.84, 3H, *d*, J=6.9 Hz (C-29 or C-30), 0 92, 3H, *d*, J=0.7 Hz (C-27), 0.98, 3H, *d*, J=0.7 Hz (C-27), 0.98, 3H, *d*, J=6.6 Hz (C-23), 1.04, 3H, *d*, J=0.6 Hz (C-26), 1 10, 3H, *s* (C-25).

24-nor-Triterpen-3-ols (**2g, 2h, 3g, 3h, 4g, 4h**): The 24-*nor*-triterpen-3-ones (0 1 mmol) were reduced by stirring with sodium borohydride (0.05 mmol) in absolute ethanol (10 ml) at room temperature under nitrogen (16 h). The reaction mixture was worked up by diluting with water and extracting with ether. After drying with sodium sulphate and filtering the solvent was removed under reduced pressure The resulting white solid was purified by flash chromatography using hexane-ethyl acetate (95:5) as eluant to obtain the corresponding axial and equatorial alcohols. The axial alcohols (**2h, 3h, 4h**; R_f=0.6, 3 1 hexane-ethyl acetate) were obtained in yields of 22-28% and the equatorial alcohols (**2g, 3g, 4g**; R_f=0 3, 3:1 hexane-ethyl acetate) in yields of 72-78% 24-*nor*-Urs-12-en-3β-ol (**2g**) had: LRMS (as trimethylsilyl ether derivative) 484 (M^+ <1), 469 (<1), 394 (<1), 379 (<1), 266 (2), 265 (2), 218 (100), 203 (22), 189 (22), 176 (29), 175 (23), 161 (25) ; ^{1}H NMR (300 MHz) 0.79, 6H, *d*, J=6.1 Hz (C-29 and C-30), 0.91, 3H, *s* (C-28), 0.93, 3H, *s* (C-25), 0.98, 3H, *d*, J=6.4 Hz (C-23), 1.04, 3H, *s* (C-26), 1.07, 3H, *s* (C-27), 3.08, 1H, *m* (C-3), 5 14, 1H, *dd*, J's=3.7 Hz (C-12). 24-*nor*-Olean-12-en-3β-ol (**3g**) had: LRMS (as trimethylsilyl ether derivative) 484 (M^+ <1), 469 (<1), 394 (<1), 379 (<1), 266 (2), 265 (1), 218 (100), 203 (44), 189 (14), 176 (21), 175 (13), 161 (11); ^{1}H NMR (300 MHz) 0 84, 3H, *s* (C-28), 0.87, 6H, *s* (C-29 and C-30), 0 91, 3H, *s* (C-25), 0.98, 3H, *d*, J=6 4 Hz (C-23), 1.00, 3H, *s* (C-26), 1 13, 3H, *s* (C-27), 3.09, 1H, *ddd*, J's=13.0, 10.4 and 5.2 Hz (C-3), 5.20, 1H, *dd*, J's=3.6 Hz (C-12) 24-*nor*-Lupan-3β-ol (**4g**) had LRMS (as trimethylsilyl ether derivative) 486 (M^+ 7), 471 (3), 443 (3), 396 (10), 381 (12), 353 (12), 266 (15), 265 (39), 231 (10), 206 (29), 205 (25), 191 (54), 189 (53), 177 (66), 176 (56), 163 (59), 161 (56), ^{1}H

NMR (300 MHz) 0.75, 3H, *s* (C-28), 0.75, 3H, *d*, *J*=6.8 Hz (C-29 or C-30), 0.80, 3H, *s* (C-25), 0.82, 3H, *d*, *J*=6.9 Hz (C-29 or C-30), 0.92, 3H, *d*, *J*=0.6 Hz (C-27), 0.95, 3H, *d*, *J*=6.4 Hz (C-23), 1.04, 3H, *s* (C-26), 3.07, 1H, *m* (C-3). 24-*nor*-Urs-12-en-3α-ol (**2h**) had: LRMS (as trimethylsilyl ether derivative) 484 (M$^+$ 1), 469 (<1), 394 (<1), 379 (<1), 265 (2), 218 (100), 203 (17), 189 (14), 176 (31), 175 (13), 161 (17); ^{1}H NMR (300 MHz) 0.79, 6H, *d*, *J*=6.3 Hz (C-29 and C-30), 0.91, 6H, *s* (C-25 and C-28), 0.95, 3H, *d*, *J*=6.9 Hz (C-23), 1.04, 3H, *d*, *J*=0.3 Hz (C-26), 1.08, 3H, *d*, *J*=0.5 Hz (C-27), 3.75, 1H, broad *s* (C-3), 5.14, 1H, *dd*, *J's*=3.7 Hz (C-12). 24-*nor*-Olean-12-en-3α-ol (**3h**) had: LRMS (as trimethylsilyl ether derivative) 484 (M$^+$ 1), 469 (<1), 394 (<1), 379 (1), 265 (1), 218 (100), 203 (53), 189 (18), 176 (43), 175 (14), 161 (19); ^{1}H NMR (300 MHz) 0.83, 3H, *s* (C-28), 0.87, 6H, *s* (C-29 and C-30), 0.89, 3H, *d*, *J*=0.5 Hz (C-25), 0.95, 3H, *d*, *J*=6.9 Hz (C-23), 1.00, 3H, *s* (C-26), 1.15, 3H, *d*, *J*=0.5 Hz (C-27), 3.75, 1H, *d*, *J*=2.6 Hz (C-3), 5.19, 1H, *dd*, *J's*=3.6 Hz (C-12). 24-*nor*-Lupan-3α-ol (**4h**) had: LRMS (as trimethylsilyl ether derivative) 486 (M$^+$ 3), 471 (1), 443 (<1), 396 (6), 381 (11), 353 (5), 266 (4), 265 (5), 231 (5), 206 (8), 205 (6), 191 (26), 189 (26), 175 (100), 163 (27), 161 (25); ^{1}H NMR (300 MHz) 0.75, 3H, *s* (C-28), 0.76, 3H, *d*, *J*=6.7 Hz (C-29 or C-30), 0.78, 3H, *s* (C-25), 0.83, 3H, *d*, *J*=6.9 Hz (C-29 or C-30), 0.92, 3H, *d*, *J*=6.4 Hz (C-23), 0.93, 3H, s (C-27), 1.05, 3H, *s* (C-26).

24-nor-triterpenes (**2i, 3i, 4i**): The 24-*nor*-triterpen-3β-ols (0.05 mmol) were tosylated with tosyl chloride (0.1 mmol) in pyridine (5 ml) in a dry atmosphere at room temperature (2 days). The tosylate esters were obtained by dilution with ice-cold water and extracting with ether. The combined ether extracts were washed with cold 2N hydrochloric acid, copper (II) sulphate solution and brine. After drying and filtration the solvent was removed under reduced pressure to afford the crude tosylate esters. These were taken up in dry ether and reduced with lithium aluminium hydride (0.05 mmol) in refluxing ether (4 h). After allowing to cool the excess reagent was destroyed with ethyl acetate. Solid residue was dissolved by addition of 1N sodium hydroxide and the products obtained by extraction with ether. The combined ether extracts were washed with brine and dried with sodium sulphate. After filtration and removal of the solvent under reduced pressure the product hydrocarbons were purified by flash chromatography using hexane as eluant. The yield of 24-*nor*-triterpenes was 62-68%. 24-*nor*-Urs-12-ene (**2i**) had: LRMS 396 (M$^+$ 9), 381 (2), 218 (100), 203 (12), 191 (7), 189 (9), 177 (11); HRMS 396.3754 (calculated for $C_{29}H_{48}$ 396.3756); ^{1}H NMR (300 MHz) 0.80, 6H, *d*, *J*=5.3 Hz (C-29 and C-30), 0.82, 3H, *d*, *J*=6.5 Hz (C-23), 0.89, 3H, *s* (C-25), 0.91, 3H, *s* (C-28), 1.04, 3H, *s* (C-26), 1.08, 3H, *s* (C-27), 5.15, 1H, *dd*, *J's*=3.7 Hz (C-12) 24-*nor*-Olean-12-ene (**3i**) had: LRMS 396 (M$^+$ 5), 381 (2), 218 (100), 203 (47), 191 (4), 189 (14), 177 (10); HRMS 396.3754 (calculated for $C_{29}H_{48}$ 396.3756); ^{1}H NMR (300 MHz) 0.82, 3H, *d*, *J*=6.5 Hz (C-23), 0.84, 3H, *s* (C-28), 0.87, 9H, *s* (C-25, C-29 and C-30), 1.00, 3H, *d*, *J*=0.4 Hz (C-26), 1.15, 3H, *d*, *J*=0.6 Hz (C-27), 5.20, 1H, *dd*, *J's*=3.6 Hz (C-12). 24-*nor*-Lupane (**4i**) had: LRMS 398 (M$^+$ 33), 383 (8), 355 (7), 206 (8), 205 (9), 191 (28), 177 (100); HRMS 398.3906 (calculated for $C_{29}H_{50}$ 398.3912); ^{1}H NMR (300 MHz), 0.75, 3H, *s* (C-28), 0.76, 3H, *d*, *J*=6.8 Hz (C-29 or C-30), 0.77, 3H, *s* (C-25), 0.80, 3H, *d*, *J*=6.4 Hz (C-23), 0.83 , 3H, *d*, *J*=6.9 Hz (C-29 or C-30), 0.93, 3H, *d*, *J*=0.8 Hz (C-27), 1.04, 3H, *s* (C-26).

Acid-catalysed rearrangement of 24-nor-olean-12-ene (**3i**)

To 24-*nor*-olean-12-ene (15 mg) in toluene (3 ml) was added trifluoroacetic acid (1 ml) and the reaction mixture allowed to stand (42 h). After dilution with water the products were extracted with dichloromethane. After neutralisation with sodium bicarbonate solution, drying with sodium sulphate and filtering the solvent was removed under reduced pressure. Chromatography on silver nitrate-impregnated silica with hexane as eluant afforded the corresponding double bond isomers. Spectral characteristics for the 24-nor-oleanenes, in order of elution from the silver nitrate-impregnated silica column, are: 24-*nor*-olean-13(18)-ene (**5**)· LRMS 396 (M$^+$ 5), 381 (2), 218 (25), 205 (31), 191 (27), 189 (29), 177 (20); ^{1}H NMR (200 MHz) 0.70, 3H, *s* (C-29), 0.78, 3H, *s* (C-25), 0.84, 3H, *d*, *J*=6.4 Hz (C-23), 0.86, 3H, *s* (C-26), 0.93, 3H, *s* (C-30), 1.01, 3H, *s* (C-28), 1.16, 3H, *s* (C-27), 24-*nor*-olean-12-ene (**3i**, as above); 24-*nor*-18α-olean-12-ene (**7**): LRMS 396 (M$^+$ 4), 381 (5), 218 (80), 203 (58), 191 (12), 189 (21), 177 (11), 175 (17), ^{1}H NMR (200 MHz) 0.62, 3H, *s* (C-28), 0.81, 3H, *d*, *J*=6.4 Hz (C-23), 0.89, 6H, *s* (C-25 and C-30), 0.94, 3H, *s* (C-29), 1.01, 3H, *s* (C-26), 1.15, 3H, *s* (C-27), 5.17, 1H, *dd*, *J's*=1.7 Hz; 24-*nor*-olean-18-ene (**6**) had. LRMS 396 (M$^+$ 5), 381 (6), 219 (14), 204 (69), 191 (17), 189 (59), 177 (58), 175 (41), ^{1}H NMR (200 MHz) 0.74, 3H, *s* (C-27), 0.79, 3H, *d*, *J*=6.4 Hz (C-23), 0.80, 3H, *s* (C-25), 0.94, 6H, *s* (C-29 and C-30), 1.02, 3H, *s* (C-28), 1.08, 3H, *s* (C-26), 4.86, 1H, *s* (C-19).

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