Synthesis of Biological Markers in Fossil Fuels. 3. Degraded and Rearranged C_{27} Hopanes

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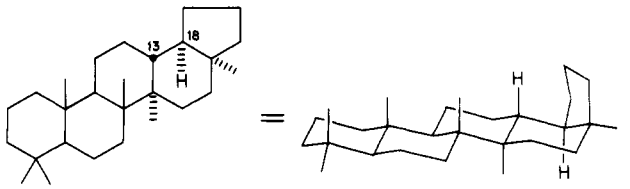
22-Hydroxyhopan-3-one was converted to various C_{27} hopane hydrocarbons: 22,29,30-trinorhopane, 22,29,30-trinor-17α-hopane, 22,29,30-trinor-28(18→17*S*)*abeo*-13α,18β-hopane, and 22,29,30-trinor-28(18→17*S*)*abeo*-13α,18α-hopane. These hydrocarbons are useful as biological markers in studies related to the source, maturation, and migration of crude oils.

Thermal maturation and biodegradation of crude oils and other bituminous substances in sediments result in the removal of normal steranes and triterpanes and enrich these materials in their rearranged and degraded counterparts.[1] These unusual hydrocarbon "biological markers"[2] provide valuable information regarding source, maturation, and migration of crude oils,[3] but the lack of authentic samples limits their utility as biomarkers. One family of rearranged triterpanes, the 28(18→17*S*)*abeo*-hopanes, appears sporadically in nature[4] and occurs widely in crude oils.[3a,5]

The direct isolation of 22,29,30-trinor-28(18→17*S*)-*abeo*-hopane (**1**) from a Nigerian crude oil[6] and the subsequent "identification" of this material in other petroleum deposits suggests that this partially degraded triterpane would make a useful "biological marker". However, the subsequent identification of **1** in petroleum samples utilizes capillary gas chromatography–mass spectrometry, and this raises the possibility that other diastereomers of **1** might exhibit identical retention times and similar fragmentation patterns. To investigate this possibility, we have investigated the stereorational synthesis of the 13α,18β- and 13α,18α-diastereomers of **1**.[7]



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Degradation of 22-hydroxyhopan-3-one[8] (**2**) furnishes 22,29,30-trinorhopan-21-one (**3**) shown in Scheme I. Epimerization of **3** to its 17α-epimer **4** and independent reduction of each ketone **3** and **4** with Barton's xanthate procedure[9] provide 22,29,30-trinorhopane (**7**) and 22,29,30-trinor-17α-hopane (**10**), respectively. Wolff–Kisher reduction[10] of the thermodynamically more stable epimer **4** also provides **10** but in reduced yield relative to the xanthate procedure as a consequence of azine formation. These degraded hopanes provide vital ^{13}C NMR data (Table I) necessary for the successful interpretation of rearranged and degraded hopanes.

The reported acid-catalyzed rearrangement[11,12] of 22-hydroxyhopan-3-one (**2**) to hopenone II (**11**) suggested a logical route to 22,29,30-trinor-28(18→17*S*)*abeo*-13(18)-hopene (**12**) from 22,29,30-trinorhopan-21ζ-ol (**5**). As

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(7) The fourth 13β,18β-diasteromer i would possess a D ring in a boat conformation in which the angular methyl groups at C-14 and C-17 are locked in an unfavorable "flagpole-bowsprit" interaction and as a consequence, was deemed an unworthy candidate for synthesis.

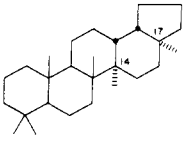

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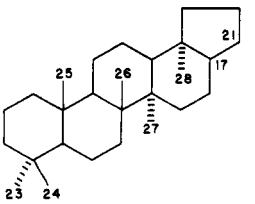
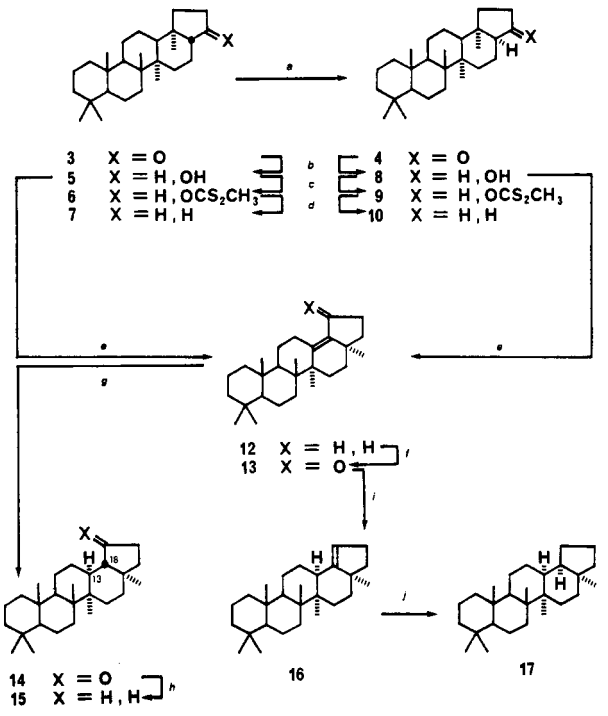
Table I. ^{13}C NMR Data



C	7	10	17	15	12	13	14	4	5	8
1	40.36	40.31	40.31	40.76	40.56	40.49	40.30[a]	40.30	40.30	40.34[c]
2	18.75[a]	18.70[a]	18.56[c]	18.29[a]	18.75[c]	18.64[c]	18.50[c]	18.61[c]	18.69[a]	18.60[a]
3	42.15	42.13	42.03	42.16	42.04	41.96	41.90	42.05	42.07	42.11
4	33.32	33.26	33.11	33.39	33.32	33.27[a]	33.10	33.24	33.65	33.26
5	56.15	56.30	56.70	56.83	56.75	56.58[a]	56.58	56.25[c]	56.58	56.42[c]
6	18.75[a]	18.70[a]	18.66[c]	18.77[a]	18.84[c]	18.97[a,c]	18.57[c]	18.67[a]	18.69[a]	18.72[a]
7	33.26	33.09	34.22	35.65	34.52	34.43	33.68	32.96	33.26[a]	33.17
8	41.96	42.08	41.61	41.19	42.04	43.40	41.09	41.93	41.97	42.19
9	51.04[b]	50.85	47.97	47.25	52.19	51.66	47.24	50.77	50.33	51.11
10	37.42	37.45	37.87	37.69	37.79	37.74	38.36	37.43	37.38	37.49
11	20.98	21.58[a]	22.32[b]	20.39[b]	21.52[a,b]	21.70[b]	22.78[b]	21.30[b]	20.82[b]	21.58[b]
12	24.16	23.48	28.02[b]	26.98[b]	27.09[b]	35.87[b]	35.63[b]	23.50[b]	23.67[b]	24.15[b]
13	48.27	37.87	45.54	44.96	131.74	157.34	42.95	38.13	49.01	43.29
14	42.23	41.45	40.79	40.98	40.46	44.77	38.36	40.86	43.48	40.67
15	27.61	28.96	28.58	31.36	29.36	28.86	35.60	26.87	32.80	29.66
16	22.66	25.34	23.12	27.08	36.92	36.63	37.74	17.50	18.77	19.47
17	50.41[b]	46.20	39.64	42.52	42.41	40.12	38.92	57.44	56.07	49.83
18	43.62	43.15	43.37	54.73	139.45	136.99	57.12	41.56	42.30	42.34
19	40.76	42.67	35.61	39.26	28.00	209.21	225.65	34.58	41.35	41.35
20	32.69	d	21.18	17.57	21.56	24.02	28.18	35.62	33.65[a]	33.43
21	20.24	21.84	40.40	41.49	42.58	37.43	37.76	221.36	74.95	78.01
23	33.43	33.39	33.52	33.27	33.33	33.27[a]	33.49	33.36	33.40	33.39
24	21.60	21.58[a]	21.88	21.52	21.52[a]	21.52	21.93	21.51	21.58	21.58
25	16.73[a]	16.26	16.07	17.03[c]	16.72	16.62	16.04	16.16	16.34[c]	16.31
26	16.73[a]	16.11[b]	26.89	17.23[c]	18.67	18.97[a]	29.20	15.27	16.72[c]	17.36
27	15.86	15.92[b]	20.65	21.50	23.57	24.30	20.59	15.97	15.84	16.15
28	14.02	23.77	29.33	29.99	26.74	27.27	26.23	24.39	16.72	26.10

[a] Signals overlap. [b,c] Signals may be interchanged. [d] Unable to identify and presumably overlapped with another methylene signal.

Scheme I[a]



[a] a, NaOEt, EtOH; b, $NaBH_4$; c, *n*-BuLi; CS_2; CH_3I; d, $(n\text{-}Bu)_3SnH$; e, PPA; f, $CrO_3 \cdot 2Py$; g, Li, NH_3; h, H_2NNH_2, Na, DEG; i, Zn(Hg), HCl; j, H_2, PtO_2.

shown in Scheme I, the rearrangement of either **5** or **8** with polyphosphoric acid furnished the olefin **12** in high yield. All efforts to reduce this olefin using catalytic hydrogenation (900 psi H_2, PtO_2, 110 °C, 5 days) or dissolving metal reductions (Na, HMPA)[13] were unsuccessful. Consequently, we employed an allylic oxidation procedure to transform the olefin **12** to an enone **13** which we could reduce more readily than **12**. As shown in Scheme I, the chromium trioxide–pyridine oxidation[14] of **12** and the lithium in ammonia reduction of **13** secure the saturated ketone **14** possessing the 13α,18β-stereochemistry. Preferential protonation of the intermediate radical anion or dianion at C-13 from the α-face via a chair-like transition state for ring D leads to the observed 13α,18β-diastereomer. Further reduction of **14** secures the hydrocarbon **15** whose structure was confirmed by X-ray crystallography (Figure 1). This hydrocarbon coelutes with the previously reported 13β,18α-diastereomer **1** under all gas chromatographic conditions investigated to date, but differs from **1** in that **15** displays a 1:1 ratio of ions m/e 370:355 whereas **1** displays ca. a 2:1 ratio of these ions.

To synthesize the 13α,18α-diastereomer, we employed an olefin transposition reaction which permits the controlled introduction of stereochemistry at C-13 and C-18. The Clemmensen reduction[15] of the enone **13** derived from the olefin **12** furnished the transposed olefin **16** in which the 13α-stereochemistry again reflects the preference for protonation at C-13 on the α-face. Catalytic reduction of **16** from the convex face then secures the hydrocarbon **17** possessing the 13α,18α-stereochemistry. Hydrocarbon **17** produces a mass spectrum showing a 1:2 ratio of ions of

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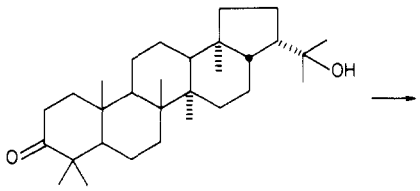

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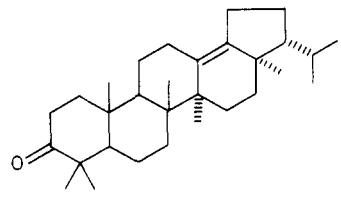

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m/e 370:355, differing from the other two isomers. It fails to coelute by GC with any significant peak in the saturated fraction of several petroleums and rock extracts.

Experimental Section

Infrared spectra were determined on a Beckman Microlab 600 spectrometer. The abbreviation TF deontes thin film. NMR spectra were determined on a JEOL 270-MHz NMR spectrometer. Mass spectra were determined on either a Varian MAT CH5 or a VG ZAB-1F mass spectrometer. Gas chromatography–mass spectroscopy of hydrocarbons was performed on a VG ZAB-1F spectrometer or on a Finnigan 4000 quadrupole system with 60 m DB-1CB fused silica capillary GC columns from J and W Scientific. The 60 m DB-1CB column was used in a Hewlett-Packard 5880A ıs chromatograph for analysis of the hydrocarbons. Mel' ıoints were determined by using a Thomas-Hoover meltiı t apparatus and are uncorrected. Elemental analyses wer: :med by Atlantic Microlabs, Atlanta, GA.

22,29,30-T opan-21β-ol (5). To 17 mg (0.45 mmol) of lithium alum ydride in 1 mL of anhydrous ether at 0 °C was added 20' 538 mmol) of ketone **3**[8] in 2 mL of anhydrous THF. The m was stirred for 2 h at 0 °C, and the reaction was quenchec ı ice. The product was diluted with ether, washed success / with 2 M hydrochloric acid solution, saturated sodium bicarbonate solution, and brine, and dried over anhydrous magnesium sulfate. The product was chromatographed on two Macherey-Nagel silica gel F254 preparative-layer plates in 1:5 ethyl acetate–hexane to afford 146 mg (70%) of 22,29,30-trinorhopan-21β-ol (**5**): mp 210.5–211.5 °C (lit.[16] mp 215–218 °C, 208–211 °C); IR (KBr) 3412 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.79, 0.81, 0.85, 0.88, 0.96, 0.98 (6 s, 18, quaternary CH_3), 4.20–4.24 (m, 1, C-21 H); mass spectrum (70 eV), m/e (relative intensity) 386 (25), 371 (14), 191 (100), 165 (75); exact mass spectrum calcd for $C_{27}H_{46}O$ 386.3549, found 386.3567. The stereochemical assignment at C-21 is only tentative.

S-Methyl (21ζ)-22,29,30-Trinorhopan-21β-yl Dithiocarbonate (6). The procedure of Barton[9] as modified by us[8] was repeated with 79 mg (0.205 mmol) of alcohol **5** to afford, after chromatography on one Macherey-Nagel silica gel F254 preparative-layer plate in 1:20 ethyl acetate–hexane, 70.8 mg (72%) of xanthate **6**: mp 207–208 °C; IR (KBr) 1240, 1215, 1077 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.79, 0.82, 0.85, 0.87, 0.97, 0.99 (6 s, 18, quaternary CH_3), 2.51 (s, 3, CS_2CH_3), 5.84–5.92 (m, 1, $CHOCS_2CH_3$); mass spectrum (70 eV), m/e (relative intensity) 369 ($M^+ - OCS_2CH_3$, 79), 191 (67), 107 (23), 95 (100). The stereochemical assignment at C-21 is only tentative.

Anal. Calcd for $C_{29}H_{48}OS_2$: C, 73.05; H, 10.15. Found: C, 73.12; H, 10.15.

22,29,30-Trinorhopane (7). The procedure of Barton[9] as modified by us[8] was repeated with 80 mg (0.168 mmol) of xanthate **6** to afford 31.5 mg (50%) of **7**: mp 160–161 °C (from ethanol–dichloromethane); IR (KBr) 2940, 2859, 1454 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.60, 0.79, 0.81, 0.84, 0.95, 0.96 (6 s, 18, quaternary CH_3); mass spectrum (70 eV), m/e (relative intensity) 370 (26), 355 (15), 191 (52), 149 (100).

Anal. Calcd for $C_{27}H_{46}$: C, 87.49; H, 12.51. Found: C, 87.31; H, 12.57.

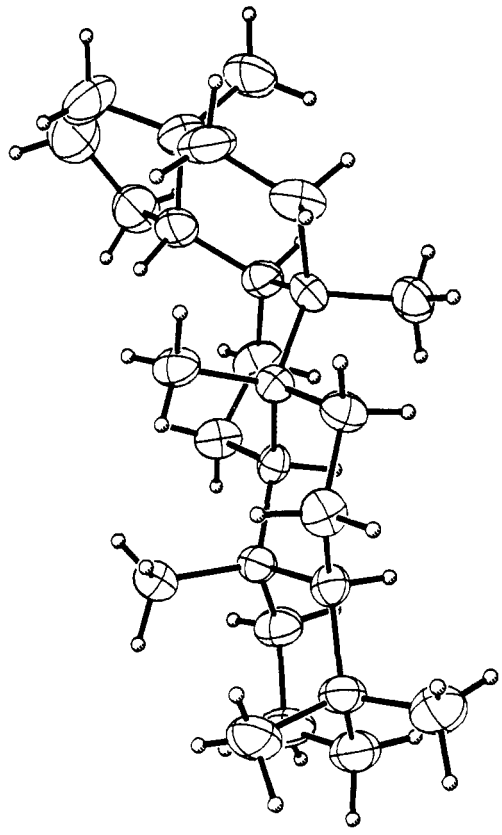

Figure 1. 22,29,30-Trinor-28(18→17*S*)*abeo*-13α,18β-hopane (**15**).

22,29,30-Trinor-17α-hopan-21β-ol (8). The procedure described for the preparation of alcohol **5** was repeated with 80 mg (0.21 mmol) of ketone **4**[8] to afford, after chromatography on a Macherey-Nagel silica gel F254 preparative-layer plate in 1:5 ethyl acetate–hexane, 46 mg (58%) of the 21β-isomer of **8**: mp 224–225 °C; IR (KBr) 3433 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.79, 0.82, 0.85, 0.960, 0.963, 1.00 (six s, 18, quaternary CH_3), 4.28–4.34 (m, 1, $CHOH$); mass spectrum (70 eV), m/e (relative intensity) 386 (51), 371 (8), 368 (9), 191 (100); exact mass spectrum calcd for $C_{27}H_{46}O$ 386.3524, found 386.3562.

S-Methyl (21β)-22,29,30-Trinor-17α-hopan-21-yl Dithiocarbonate (9). The procedure of Barton[9] as modified by us[8] was repeated with 152 mg (0.39 mmol) of alcohol **8** to afford, after chromatography on a Macherey–Nagel silica gel F254 preparative-layer plate in 1:5 ethyl acetate–hexane, 153 mg (82%) of **9**: IR (KBr) 1052, 1197, 1223 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.79, 0.84, 0.85, 1.00, 1.01, 1.05 (6 s, 18, quaternary CH_3), 2.58 (s, 3, CS_2CH_3), 5.99–6.11 (m, 1, $CHOCS_2CH_3$).

Anal. Calcd for $C_{29}H_{48}OS_2$: C, 73.05; H, 10.15. Found: C, 73.14; H, 10.16.

22,29,30-Trinor-17α-hopane (10). The procedure of Barton[9] as modified by us[8] was repeated with 143 mg (0.30 mmol) of xanthate **9** to afford, after chromatography on two Macherey-Nagel silica gel F254 preparative-layer plates in hexane and crystallization from ethanol–dichloromethane, 75 mg (67%) of **10**: mp 220–221 °C; ^1H NMR ($CDCl_3$) δ 0.79, 0.82, 0.84, 0.93, 0.96, 0.99 (6 s, 18, quaternary CH_3).

Anal. Calcd for $C_{27}H_{46}$: C, 87.49; H, 12.51. Found: C, 87.42; H, 12.51.

The Wolff–Kishner reduction[10] of 160 mg of ketone **4**[8] afforded, after chromatography on a Merck silica gel F254 preparative-layer plate in hexane, 31 mg (20%) of **10** and 160 mg of the azine derived from **4**.

22,29,30-Trinor-28(18→17*S*)*abeo*-hop-13(18)-ene (12). A mixture of 82 mg (0.21 mmol) of alcohol **5** and 20 mL of polyphosphoric acid was stirred at 100 °C for 1 h, cooled, and diluted

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with 30 mL of water. The mixture was extracted with 4:1 ether–dichloromethane, washed successively with water, aqueous sodium bicarbonate, and brine, and dried over anhydrous magnesium sulfate. The product was chromatographed on a Macherey-Nagel silica gel F254 preparative-layer plate in 1:10 ethyl acetate–hexane to afford 71 mg (91%) of **12**: mp 189–190 °C; IR (KBr) 2939, 1461 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.79, 0.83, 0.86, 0.87 and 1.11 (6 s, signal at 0.86 consists of two superimposed s, 18, quaternary CH_3); mass spectrum (70 eV), *m/e* (relative intensity) 368 (30), 353 (18), 191 (100), 176 (98), 163 (89); exact mass spectrum calcd $C_{27}H_{44}$ 368.3442, found 368.3442. The rearrangement of the isomeric alcohol **8** proceeded with equal facility to give **12**.

Anal. Calcd for $C_{27}H_{44}$: C, 87.97; H, 12.03. Found: C, 88.03; H, 12.04.

22,29,30-Trinor-28(18→17*S*)*abeo*-hop-13(18)-en-19-one (13). The procedure of Dauben[3] was repeated with 582 mg (1.6 mmol) of olefin **12** and 7.34 g (28.5 mmol) of chromium trioxide–dipyridine complex in 50 mL of anhydrous dichloromethane to afford, after chromatography on four preparative-layer Macherey-Nagel silica gel plates in 1:5 ethyl acetate–hexane, 242 mg (40%) of enone **13**: R_f 0.45; mp 207–309 °C (from hexane); IR (KBr) 1699, 1611 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.79, 0.83, 0.86, 0.89, 1.01, and 1.19 (6 s, 18, quaternary CH_3) 4.05–4.13 (m, 2 H, C-12 CH_2); mass spectrum (70 eV), *m/e* (relative intensity) 382 (100), 2246 (23), 191 (78), 178 (40); exact mass spectrum calcd for $C_{27}H_{42}O$ 382.3226, found 382.3206.

Anal. Calcd for $C_{27}H_{42}O$: C, 84.76; H, 11.06. Found: C, 84.85; H, 11.15.

22,29,30-Trinor-28(18→17*S*)*abeo*-hopan-19-one (14). To 100 mL of anhydrous ammonia under a slow stream of nitrogen in a 500-mL three-necked flask equipped with a dry ice–acetone condenser was added 49 mg (7 mmol) of lithium followed by 242 mg (0.63 mmol) of enone **13** in 16 mL of anhydrous THF. The blue solution was stirred for 1 h, quenched with ammonium chloride, and diluted with ether. The ammonia was allowed to evaporate. An ether solution of the crude product was then washed successively with 1 M hydrochloric acid solution, water, and brine and dried over anhydrous magnesium sulfate. The product was chromatographed on three Macherey-Nagel silica gel F254 preparative-layer plates in dichloromethane to afford 122 mg (50%) of **14**: mp 186–187.5 °C (from hexane); IR (KBr) 1731 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.81, 0.85, 0.89, 0.91, 1.01, and 1.03 (6 s, 18, quaternary CH_3); mass spectrum (70 eV), *m/e* (relative intensity) 384 (10), 369 (12), 191 (100), exact mass spectrum calcd for $C_{27}H_{44}O$ 384.3393, found 384.3400.

Anal. Calcd for $C_{27}H_{44}O$: C, 84.31; H, 11.53. Found: C, 84.15; H, 11.55.

22,29,30-Trinor-28(18→17*S*)*abeo*-13α,18β-hopane (15). To 5 mL of anhydrous diethylene glycol at 80 °C was added 86 mg (3.75 mmol) of sodium. To this solution at 40 °C was added 1 mL of anhydrous hydrazine followed by 96 mg (0.25 mmol) of the ketone **14**. The mixture was stirred at 200 °C for 19 h, cooled, diluted with water, acidified to pH 3, and extracted with 4:1 ether–dichloromethane. The organic layer was washed with water and brine and dried over anhydrous magnesium sulfate to afford, after chromatography on a preparative-layer Macherey-Nagel silica gel F254 plate in hexane, 55 mg (59%) of **15**: mp 175–176 °C; ^1H NMR ($CDCl_3$) δ 0.70, 0.79, 0.84, 1.06, and 1.14 (6 s, signal at 0.84 consists of two superimposed s, 18, quaternary CH_3); mass spectrum (70 eV), *m/e* (relative intensity) 370 (21), 355 (22), 191 (100), 163 (21), 149 (31), exact mass spectrum calcd for $C_{27}H_{46}$ 370.3599, found 370.3574.

X-ray Structure Determination for 22,29,30-Trinor-28-(18→17*S*)*abeo*-13α,18β-hopane (15). Details of the crystallographic work may be found in Table VI in the supplementary material. The structure was solved by direct methods (program SOLV in the SHELXTL program library, written by Prof. G. M. Sheldrick). Refinement was carried to convergence, employing a model which included anisotropic thermal parameters for all carbon atoms and placement of hydrogen atoms in calculated idealized special positions. Methyl groups were treated as rigid rotors.

22,29,30-Trinor-28(18→17*S*)*abeo*-hop-18-ene (16). To 83 mg (0.22 mmol) of **13** in 14 mL of 5 M hydrochloric acid solution and 4.4 mL of toluene was added 530 mg of zinc amalgam. The solution was refluxed for 1.5 h, cooled, and diluted with 4:1 ether–dichloromethane. The product was washed successively with water, aqueous sodium bicarbonate solution, and brine, and dried over anhydrous magnesium sulfate. The product was chromatographed on a Macherey-Nagel silica gel F254 preparative-layer plate in hexane to afford 59 mg (74%) of an inseparable mixture of olefins **16** and **12** in ca. a 1:1 ratio: ^1H NMR ($CDCl_3$) δ 5.22 (broad s, C-19 H of **16**); ^{13}C NMR ($CDCl_3$) δ 116.3 and 153.9 (vinyl C of **16**), 139.4 and 131.7 (vinyl C of **12**).

22,29,30-Trinor-28(18→17*S*)*abeo*-13α,18α-hopane (17). To 49 mg (0.133 mmol) of a mixture of olefins **16** and **12** in 4.3 mL of hexane was added 43 mg (0.19 mmol) of platinum oxide. The mixture was hydrogenated at 44 psi for 129 h and then filtered through Celite. The product was chromatographed on a siliver nitrate impregnated Macherey-Nagel silica gel F254 preparative layer plate in hexane to afford 18 mg (37%) of **17**: mp 132–133 °C; ^1H NMR ($CDCl_3$) δ 0.81, 0.85, 0.89, 0.90, 0.92, 1.03 (6 s, 18, quaternary CH_3); mass spectrum (70 eV), *m/e* (relative intensity) 370 (5), 355 (10), 191 (100); exact mass spectrum calcd for $C_{27}H_{46}$ 370.3600, found 370.3612.

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Supplementary Material Available: Table I, atomic coordinates for the non-hydrogen atoms; Table II, bond lengths; Table III, bond angles; Table IV, anisotropic thermal parameters; Table V, hydrogen atom coordinates; Figure 1 showing the atom labelling scheme used in the crystallographic work (7 pages). Ordering information is given on any current masthead page.