NMR Spectra of Triterpenoids. I. Conformation of the Side Chain of Hopane and Isohopane, and Their Derivatives

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The ^{1}H- and ^{13}C-NMR signals of eight triterpenoids belonging to the hopane and isohopane groups were completely assigned, and the conformations of their side chains are discussed on the basis of Chem3D Plus and MM2 calculations and nuclear Overhauser effect spectroscopy spectra.

Keywords ^{1}H-NMR; ^{13}C-NMR; triterpenoid; hopane; isohopane; side chain conformation

Although the NMR spectra of hopane and isohopane triterpenoids clearly indicate that the isopropyl side chain or its equivalent has only one stable conformation in most cases, no one has yet determined the conformation and the exact assignments of the NMR signals of the side chain. Recent developments in ^{1}H- and ^{13}C-NMR measurement of organic compounds mean that this should now be possible without estimation by anomalies with those of the related compounds except for minor cases. Also the minimum-steric-energy conformations of organic compounds are readily obtainable by using the Chem3D Plus an MM2 programs.[1] These considerations prompted us to study the conformation of the side chain of several triterpenoids, hopane (**1**),[2] hop-22(29)-ene (**2**),[3] 22-hydroxyhopane (**3**),[4] 29-hydroxyhopane (neriifoliol, **4**),[5] 3-hydroxyhopane (dryocrassol, **5**),[5] isohopane (**6**),[2] isohop-22(29)-ene (**7**)[2] and 22-hydroxyisohopane (**8**),[2] and to make precise assignments of the ^{1}H- and ^{13}C-NMR signals of these compounds using appropriate NMR techniques.

Experimental

General Procedure The ^{1}H-/^{13}C-NMR spectra of compounds in $CDCl_3$ solution were run at 500/125 MHz. The ^{13}C-signals were classified by means of the distortionless enhancement by polarization transfer (DEPT) method and the signals were correlated with ^{1}H-signals by the ^{13}C–^{1}H correlated spectroscopy (C–H COSY) method. Methyl proton signals and related carbon signals were correlated by the heteronuclear multiple bond correlation (HMBC) method. Signals of methylene and methine protons attached to the same or neighboring carbons were correlated by the ^{1}H–^{1}H correlated spectroscopy (H–H COSY) method. On the other hand, the most stable conformation of the compounds with minimum steric energy was simulated by using the Chem3D Plus and MM2 programs[1] and finally the isopropyl signals (H-28, H-29 and H-30) were confirmed by obtaining nuclear Overhauser effect spectroscopy (NOESY) spectra. The program indicated only one preferred conformation for each of **1**, **3**, **4**, **5**, **6**, **7** and **8**, but two conformations for **2**.

Numbering of the Side Chain The isopropyl side chains are numbered according to the numbering system for neriifoliol (**4**) and dryocrassol (**5**).[5] In the case of hopane (**1**) and isohopane (**6**) C-29 is *pro R* and C-30 is *pro S*. The side chains of 22-hydroxyhopane (**3**) and 22-hydroxyisohopane (**8**) are numbered to be substituted at 22-H of **1** and **6** by OH.

Conditions of NMR Measurement The 1D and 2D NMR spectra were measured on a JEOL A500 spectrometer equipped with a VAX station 3200 computer, using a $CDCl_3$ solution of *ca.* 10 mg in 0.8 ml with tetramethylsilane as the internal standard, at room temperature (24 °C). The chemical shifts are reported on the δ scale. For 1D ^{1}H-NMR at 500.00 MHz, 16 kilo data points and a frequency width of 10000.0 Hz were used, giving a digital resolution of 0.6 Hz per point. For 1D ^{13}C-NMR at 125.65 MHz, 16 kilo data points and a frequency width of 33898.3 Hz were used, giving a digital resolution of 2.1 Hz per point. DEPT and 2D NMR spectra were obtained with the standard JEOL pulse sequences. The H–H COSY and NOESY spectra were obtained at 500.00 MHz. The frequency width was 4450.4 Hz and the final matrix was 1024 × 1024 complex data points after zero-filling once. The NOESY spectrum was obtained using a mixing time of 600 ms. The C–H COSY spectrum was obtained using the frequency ranges of 25773.2 and 4449.6 Hz for ^{13}C and ^{1}H, respectively. The final matrix, after zero-filling once, was 2048 × 512 complex data points, thus giving digital resolutions of 12.6 and 8.7 Hz per point in the row and column directions, respectively. A sine-bell window function was applied before Fourier transformation; 64 scans were acquired per t_1 increment. In some cases, for sensitivity reasons, the ^{1}H-detected heteronuclear single-quantum coherence (HSQC) spectrum was used with ^{13}C decoupling during acquisition. The HMBC spectrum was recorded at 500.00 MHz with 64 scans (32 dummy scans). The delay τ_1 was set to the value of $1/(2J_{CH})$, 3.6 ms, and τ_2 was set to the value of $1/(2^{2,3}J_{CH})$, 60 ms.

Assignments of NMR Signals and Discussion

The assignments of methyl and olefinic proton signals are listed in Table I, those of methylene and methine proton signals in Table II, and those of all carbon signals in Table III.

Hopane (1) Assignments of the methyl protons of this compound reported from our laboratory,[2,6] and ^{13}C-NMR assignments by Wilkins *et al.*[7] and also by us[8,9] do not allow discrimination between C-26 and C-27, and C-29 and

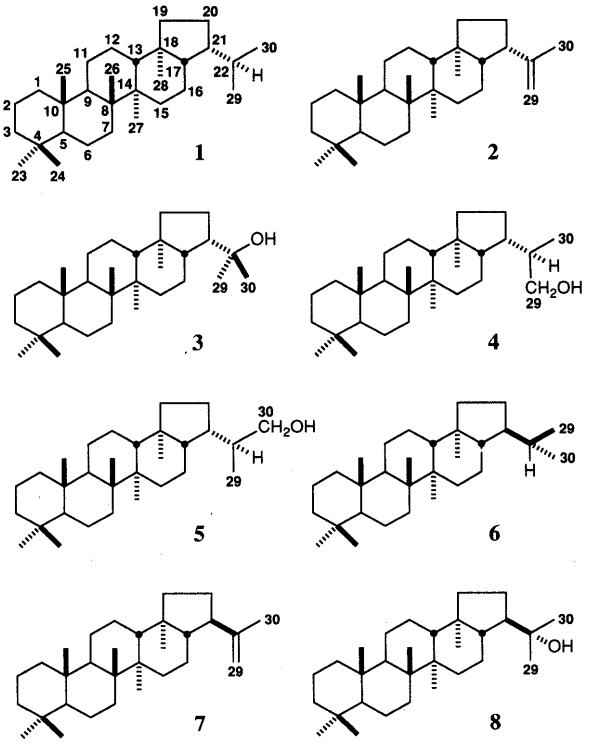

Chart 1

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TABLE I. ^{1}H-Chemical Shifts for Methyl and Olefinic Protons of Triterpenoids Belonging to Hopane and Isohopane Groups (500 MHz, $CDCl_3$, δ)

	1	2	3	4	5	6	7	8
H-23	0.845	0.844	0.848	0.846	0.847	0.847	0.848	0.848
H-24	0.792	0.791	0.790	0.791	0.791	0.794	0.793	0.793
H-25	0.814	0.814	0.812	0.815	0.815	0.816	0.821	0.820
H-26	0.951	0.960	0.954	0.951	0.954	0.970	0.976	0.977
H-27	0.951	0.943	0.954	0.951	0.954	0.942	0.946	0.948
H-28	0.703	0.721	0.759	0.712	0.722	0.648	0.681 (d, 1.2)	0.693 (d, 0.6)
H-29	0.927 (d, 6.1)	4.781 (2H, s)	1.179	3.347 (1H, dd, 10.5, 7.5) 3.747 (1H, dd, 10.5, 3.0)	1.051 (d, 6.7)	0.889 (d, 6.7)	4.671 (1H, dd, 2.4, 0.9) 4.694 (1H, dq, 2.4, 1.2)	1.190
H-30	0.806 (d, 6.1)	1.751	1.207	0.928 (d, 6.7)	3.382 (1H, dd, 10.5, 6.7) 3.632 (1H, dd, 10.5, 3.0)	0.788 (d, 6.7)	1.673	1.184

Signals, unless otherwise stated, are 3H singlet. Multiplicity and coupling constants (J) are shown in parentheses.

TABLE II. ^{1}H-Chemical Shifts for Methylene and Methine Protons of Triterpenoids Belonging to Hopane and Isohopane Groups (500 MHz, $CDCl_3$, δ)

	1	2	3	4	5	6	7	8
H-1	0.77; 1.64	0.76; 1.64	0.76; 1.64	0.76; 1.65	0.76; 1.64	0.77; 1.65	0.77; 1.67	0.77; 1.65
H-2	1.35; 1.56	1.38; 1.52	1.38; 1.56	1.38; 1.56	1.36; 1.56	1.37; 1.57	1.37; 1.57	1.37; 1.55
H-3	1.12; 1.34	1.12; 1.34	1.12; 1.34	1.13; 1.34	1.13; 1.34	1.13; 1.34	1.16; 1.32	1.13; 1.35
H-5	0.71	0.71	0.70	0.70	0.71	0.72	0.72	0.72
H-6	1.49; 1.40	1.48; 1.40	1.50; 1.35	1.50; 1.33	1.49; 1.31	1.48; 1.33	1.49; 1.34	1.47; 1.34
H-7	1.22; 1.46	1.21; 1.45	1.20; 1.45	1.22; 1.45	1.22; 1.45	1.22; 1.45	1.21; 1.45	1.21; 1.46
H-9	1.24	1.25	1.23	1.23	1.25	1.25	1.25	1.25
H-11	1.52; 1.32	1.52; 1.32	1.53; 1.32	1.52; 1.32	1.52; 1.32	1.51; 1.33	1.52; 1.34	1.51; 1.32
H-12	1.43; 1.34	1.44; 1.37	1.45; 1.37	1.43; 1.35	1.43; 1.39	1.48; 1.38	1.50; 1.42	1.45; 1.38
H-13	1.32	1.35	1.40	1.33	1.33	1.38	1.40	1.41
H-15	1.25; 1.35	1.23; 1.38	1.24; 1.38	1.25; 1.38	1.26; 1.37	1.18; 1.35	1.21; 1.39	1.18; 1.40
H-16	1.53; 1.70	1.42; 1.63	1.57; 1.93	1.53; 1.63	1.53; 1.71	1.22; 1.50	1.20; 1.39	1.38; 1.77
H-17	1.25	1.38	1.45	1.27	1.34	0.80	1.02	0.98
H-19	1.51; 0.89	1.60; 1.02	1.53; 0.93	1.53; 0.93	1.54; 0.93	1.43; 0.89	1.49; 1.01	1.45; 0.95
H-20	1.48; 1.77	1.77; 1.87	1.49; 1.74	1.59; 1.76	1.57; 1.82	1.59; 1.27	1.84; 1.43	1.74; 1.31
H-21	1.64	2.68	2.22	1.87	1.81	1.53	2.24	1.74
H-22	1.58	—	1.60[a)]	1.72	1.65	1.69	—	1.60[a)]

Methylene protons are listed as α-H; β-H in each column (confirmed by the NOESY spectra, and by the splitting patterns). *a)* –OH.

C-30. The H-26 and H-27 signals of this compound are superimposable and thus assignments of the C-26 and C-27 signals cannot be made from the HMBC spectrum. The C-8 and C-14 signals are also difficult to assign for all hopane and isohopane derivatives. In Table III, preferred values for C-26 and C-27, as well as C-8 and C-14, assigned by comparison with those of related compounds, are listed. Carbon signals for C-1, 3, 4, 6, 7, 10, 13, 15, 17, 18, 19, 21 and 22 were assigned from the HMBC spectrum with the H-23, 24, 25, 26, 27, 28, 29 and 30 signals without ambiguity. Other carbon signals (C-2, 6, 11, 12, 16 and 20) were assigned from the corresponding proton signals, confirmed by the H–H COSY spectrum with the signals of proton(s) attached to the neighboring carbon(s). All the proton signals of **1** are shown in Tables I and II. The conformation of **1** with minimum steric energy (89.497 kcal/mol) was simulated as shown in Fig. 1, and all NOEs observed in the NOESY spectrum except those between two protons attached to the same carbon are shown in the figure. The indicated conformation of the side chain was firmly supported by the cross peaks between H-22 and H-28; H-29 and H-16α (δ 1.53), H-16α and H-28, H-28 and H-27; H-29 and H-16β (δ 1.70), H-16β and H-17; H-30 and H-20α (δ 1.48), H-20α and H-28 in the NOESY spectrum. The signals for C-29 and C-30, as well as H-29 and H-30 are now clearly assigned in relation to the conformation of the side chain for the first time.

Hop-22(29)-ene (2) Assignments of the ^{1}H-NMR signals of this compound were published by us.[2,6,10] Wilkins *et al.*[7] presented the ^{13}C-NMR data but no discrimination was reported between the signals of C-26 and C-27. The H-26 and H-27 protons gave independent signals, H-26 and H-27, and so C-26 and C-27 are readily assigned from the HMBC spectrum as shown in Tables I and III. It is very characteristic that the endomethylene protons (H-29) of this compound appear as a sharp singlet. Simulation indicated the existence of two conformations with low steric energies (**2A**, 88.462 kcal/mol and **2B**, 89.311 kcal/mol), as partially shown in Fig. 2. These results suggested that the side chain of this compound can interchange rather freely between conformations **2A** and **2B**. The existence of two preferred conformations in solution is clearly demonstrated by the NOESY spectrum of **2**. Cross peaks were observed between the H-30 protons and most of the protons attached to both

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TABLE III. ^{13}C-Chemical Shifts for Triterpenoids of Hopane and Isohopane Groups (125 MHz, $CDCl_3$, δ)

	1	2	3	4	5	6	7	8
C-1	40.36	40.31	40.29	40.33	40.34	40.31	40.30	40.31
C-2	18.73	18.70	18.69	18.70	18.71	18.70	18.68	18.69
C-3	42.15	42.10	42.10	42.12	42.12	42.11	42.07	42.10
C-4	33.27	33.25	33.25	33.26	33.26	33.26	33.24	33.25
C-5	56.17	56.10	56.08	56.13	56.15	56.11	56.07	56.11
C-6	18.73	18.70	18.69	18.70	18.71	18.73	18.68	18.69
C-7	33.32	33.25	33.21	33.30	33.30	33.29	33.29	33.25
C-8	41.85[a]	41.90[a]	41.90[a]	41.87[a]	41.83[a]	41.89[a]	41.89[a]	41.87[a]
C-9	50.48	50.37	50.34	50.42	50.43	50.45	50.43	50.42
C-10	37.42	37.39	37.38	37.40	37.41	37.40	37.39	37.39
C-11	20.99	20.91	20.89	20.93	20.95	20.93	20.92	20.91
C-12	24.00	23.99	24.13	23.97	23.99	23.86	23.94	23.80
C-13	49.34	49.42	49.83	49.22	49.27	48.56	48.64	48.56
C-14	41.76[a]	42.07[a]	41.84[a]	41.79[a]	41.73[a]	42.29[a]	42.22[a]	41.72[a]
C-15	33.71	33.61	34.37	33.54	33.64	32.70	32.58	32.67
C-16	22.62	21.67	21.95	21.94	22.65	21.56	20.87	23.21
C-17	54.65	54.88	53.91	54.15	54.27	53.21	53.84	52.07
C-18	44.35	44.80	44.09	44.45	44.40	44.51	44.21	44.90
C-19	41.67	41.90	41.23	41.52	41.67	39.84	40.15	39.50
C-20	27.64	27.39	26.60	26.30	27.19	22.66	27.35	24.82
C-21	47.90	46.47	51.11	40.91	42.58	45.46	47.90	51.05
C-22	32.04	148.78	73.96	38.62	39.61	28.77	148.23	73.62
C-23	33.42	33.41	33.41	33.41	33.41	33.40	33.39	33.41
C-24	21.60	21.60	21.60	21.59	21.60	21.59	21.58	21.60
C-25	15.90	15.84	15.83	15.88	15.91	15.85	15.85	15.88
C-26	16.63[b]	16.70	16.71[b]	16.63	16.61[b]	16.76	16.74	16.73
C-27	16.56[b]	16.75	17.03[b]	16.63	16.53[b]	16.71	16.64	16.70
C-28	15.84	16.07	16.14	15.74	15.77	15.18	15.09	15.37
C-29	23.86	110.06	28.72	68.08	18.15	22.14	109.43	29.45
C-30	22.83	25.02	30.85	16.17	67.78	17.46	19.63	26.49

a, b) Assignments of the signals might be reversed.

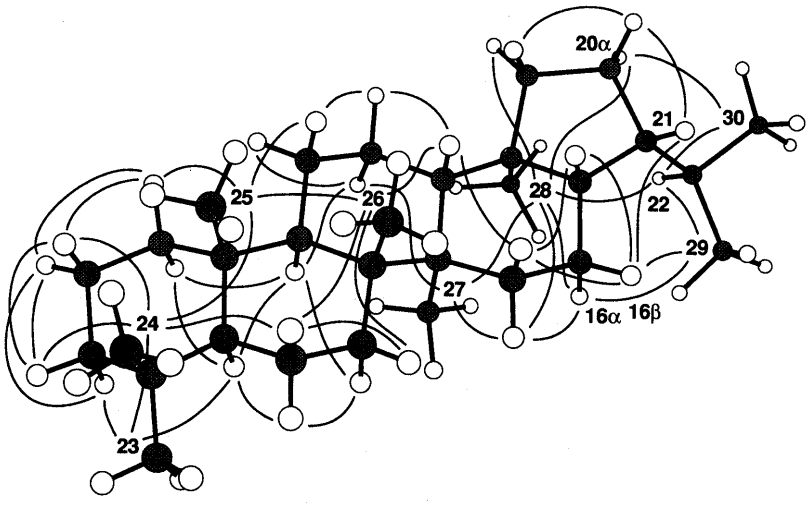

Fig. 1. Chem3D Plus Drawing of Hopane (**1**) and NOEs (—)

sides of the D, E rings of the molecule, such as H-21β, H-20α, H-20β, H-17β, H-16α, H-16β, H-28, H-27 and H-26 protons.

22-Hydroxyhopane (3) The correct assignment for the methyl protons of **3** were first reported from our laboratory on the basis of $CDCl_3$–C_6D_6 solvent shifts.[10] The H-26 and H-27 signals of **3** are superimposable, and thus assignments of the C-26 and C-27 signals, as well as the C-8 and C-14 signals, are very difficult. Other proton and carbon signals could be readily assigned as shown in Tables I—III. The conformation of this compound with minimum steric energy (93.465 kcal/mol) was simulated as partially shown in Fig. 2, and its validity was supported by cross peaks between H-29 and H-28, H-28 and H-27; H-29 and H-16α (δ 1.57), H-16α and H-28; H-30 and H-16β (δ 1.93), H-16β and H-17; H-30 and H-21, H-21 and H-17, H-21 and H-20β (δ 1.74); H-20β and 22-OH (Fig. 2). Accordingly the assignments of H-29 and H-30, and C-29 and C-30 were established.

29-Hydroxyhopane (Neriifoliol, 4) and 30-Hydroxyhopane (Dryocrassol, 5) Assignments of the ^1H- and ^{13}C-NMR signals of neriifoliol,[11] and the correct assignments of

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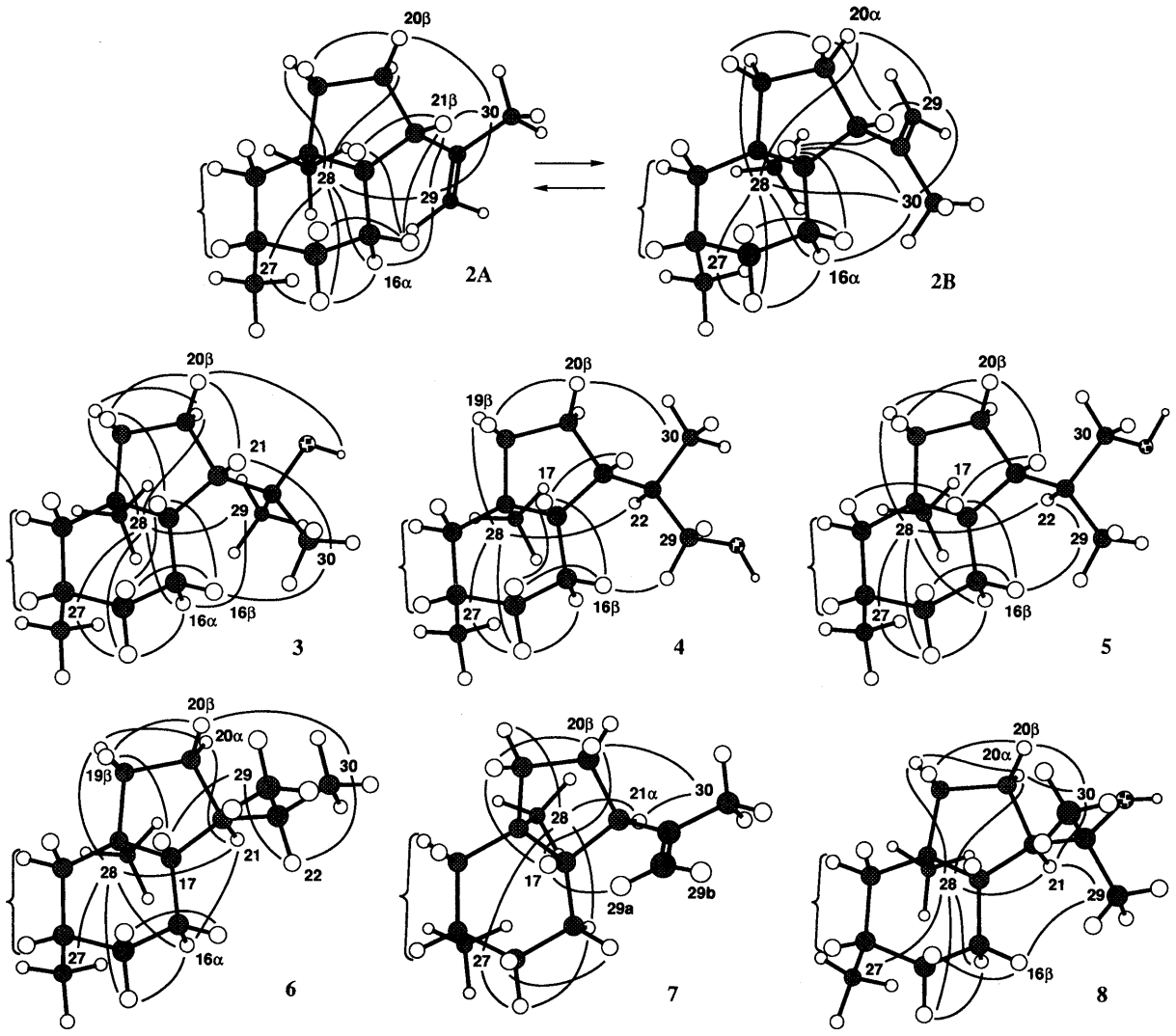

Fig. 2. Chem3D Plus Drawing and NOEs (—)

methyl protons[5,10] and carbon signals[11] for dryocrassol were reported from our laboratory. The absolute configuration at C-22 of both compounds has already been established by correlation with adiantol B, the structure of whose bromoacetate was established by X-ray studies.[12] Simulation of the conformations with minimum steric energy (**4**, 91.031 kcal/mol; **5**, 91.002 kcal/mol) indicated that the side chain of these two compounds has a similar conformation to that of hopane (**1**), as shown in Fig. 2. Thus, the chemical shifts of H-29 (**5**) and H-30 (**4**) may be compared with those of hopane (**1**). The difference between the chemical shifts of H-29 (**5**) and H-30 (**4**) (−0.123 ppm) is just the same as that between the chemical shifts of H-29 and H-30 (**1**) (−0.121 ppm). The conformations of both compounds are supported by the NOESY spectra, in which cross peaks were observed between H-22 and H-28, H-28 and H-27; H-30 and H-20β (δ 1.76); H-29a (δ 3.747) and H-16β (δ 1.63) and H-17 (**4**): and between H-22 and H-28, H-28 and H-27; H-29 and H-16β (δ 1.71), H-16β and H-17 (**5**) (Fig. 2). Unfortunately, assignments of the methylene protons, H-29 (**4**) and H-30 (**5**), could not be established because of rather poor cross peaks in the NOESY spectra.

Isohopane (6) Assignments for methyl protons were reported by us,[2,6,9] and those for carbons by Wilkins *et al.*,[7] without discrimination between H-29 and H-30, C-2 and C-6, and C-29 and C-30. Although some ambiguity remains in the assignment of C-8 and C-14, most of the other carbons and protons were readily assigned as shown in the tables. The conformation of **6** with minimum steric energy (85.227 kcal/mol) indicated that C-29, C-22 and C-30 (Fig. 2) are similar to those of hopane (**1**), and this was clearly demonstrated by the NOESY spectrum. Cross peaks were observed between H-29 and H-17, H-17 and H-19β (δ 0.89); H-30 and H-20β (δ 1.27), H-20β and H-19β, H-20β and H-21, H-21 and H-28. Cross peaks were also observed between H-20α (δ 1.59) and H-21, H-21 and H-28, H-28 and H-27; H-21 and H-16α (δ 1.22), H-16α and H-28. In addition, the difference between the chemical shifts of H-29 and H-30 (−0.094) is similar to that of hopane (**1**), and 30- and 29-hydroxyhopane (**5** and **4**). The assignments of C-29 and C-30, as well as H-29 and H-30 were thus clearly established.

Isohop-22(29)-ene (7) Assignments for the methyl protons were reported by us[2,6] without discrimination of H-29 and H-30. The ^{13}C-NMR spectrum was reported by Wilkins *et al.*,[7] who left ambiguity in the assignments of C-8 and C-14, and C-26 and C-27. As H-26 and H-27 gave independent signals in the ^{1}H-NMR spectrum, the C-26

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and C-27 signals could be firmly assigned by the C–H COSY and HMBC methods. Unlike **2**, **7** has only one conformation with minimum steric energy (83.440 kcal/mol), and thus the H-29 endomethylene protons were observed as two correlated signals (H-29a δ 4.671 dd and H-29b δ 4.694 dq). The other carbon signals except for C-8 and C-14, and all the other proton signals were also firmly assigned as shown in the tables. The conformation of the side chain was simulated as shown in Fig. 2, and this was supported by the NOESY spectrum, in which cross peaks were observed between H-29a and H-17; H-29b and H-30, H-30 and H-21, H-21 and H-28, H-28 and H-27; H-30 and H-20β (δ 1.43), H-20β and H-17. The NOESY spectrum also firmly established the assignments of H-29a and H-29b (Fig. 2 and Table I).

22-Hydroxyisohopane (8) Assignments of the methyl signals were reported by us.[6] As the NMR spectra of this compound gave independent signals for H-26 and H-27, as well as C-26 and C-27, all proton signals and carbon signals except for C-8 and C-14 were assigned without ambiguity as shown in the tables. For the C-8 signals of the compounds **6**, **7** and **8**, rather constant values, 41.89, 41.89 and 41.87, respectively, were adopted as shown in Table III. In the simulated conformation of **8** with minimum steric energy (86.367 kcal/mol), the side chain is similar to that of hopane (**1**), when the OH group in the former is substituted with H in the latter, as shown in Fig. 2. This was supported by the NOESY spectrum, in which cross peaks were observed between H-29 and H-16β (δ 1.77); H-30 and both H-20α (δ 1.74) and H-20β (δ 1.31). Cross peaks were also observed between both H-29 and H-30, and H-21; H-21 and H-28, H-28 and H-27; H-20α and H-28 (Fig. 2). Accordingly, the assignments of C-29 and C-30, as well as H-29 and H-30, are firmly established.

All the conformations of the side chain (C-22, C-29 and C-30) of the eight compounds simulated by Chem3D Plus and MM2 were supported by NOESY spectra in solution. There were five different types of conformation, as follows. Type A: hopane (**1**), 29-hydroxyhopane (**4**), 30-hydroxyhopane (**5**), 22-hydroxyisohopane (**8**); type B: 22-hydroxyhopane (**3**); type C: isohopane (**6**), type D: hop-22(29)-ene (**2**); type E: isohop-22(29)-ene (**7**). Type A is very common among compounds belonging to the migrated hopane series.[13] Type B is very interesting because the conformation of **3** is different from that of **1**. Type C also has a different conformation at the side chain. Type D is very characteristic because the side chain of compound **2** can rotate rather freely in solution at room temperature, and thus the H-29 endomethylene protons gave a singlet signal, and NOEs between H-30 methyl protons and many protons of the upper and lower sides of rings D and E were observed. Type E is the preferred conformation of compound **7**, and the direction of the isopropenyl group is very characteristic. We recommend that these preferred conformations should be used in drawing the structures of the corresponding compounds as shown in Chart 1.

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