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Unambiguous Assignment of ^{13}C Chemical Shifts of Some Hopane and Migrated Hopane Derivatives by 2D NMR

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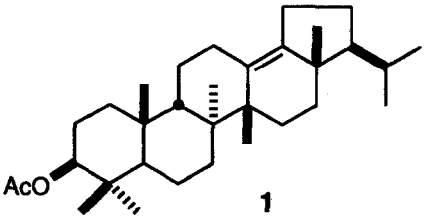
Abstract: ^{13}C NMR chemical shifts of some migrated hopane derivatives, *viz.* boehmeryl acetate (**1**), neohop-13(18)-en-3β-ol (**2**), neomotiol (**3**), arborinol (**4**), isoarborinyl acetate (**5**), fernenol (**6**), fernenyl acetate (**7**), and simiarenol (**8**), and a hopane derivative, hop-17(21)-en-3β-yl acetate (**9**) have been assigned unambiguously on the basis of detailed 2D NMR analyses. Heteronuclear Multiple Bond Correlation (HMBC) spectrum was found to be most informative not only in the assignment of signals to specific carbons but also in the elucidation of back-bone structure of triterpenoids. The relative stereochemistry of most of the chiral centres of the back-bone could also be established from the NOESY spectra.

^{13}C NMR spectroscopy is considered as a powerful tool in structure elucidation of natural products. Unambiguous assignment of ^{13}C NMR signals to specific carbons of the compounds is an important prerequisite in solving their structural problems. In compounds like triterpenes, even a tentative assignment of ^{13}C chemical shifts is very difficult unless the data of variously functionalised compounds of same skeleton or of skeleton of comparable three dimensional geometry are available. Most of the data so far reported in the literature are tentative assignments based on comparative studies. However, when dealing with a compound of a new rearranged skeleton, it becomes increasingly difficult to do a reasonable assignment of the ^{13}C chemical shifts because of the change in the three dimensional geometry of the molecule. Recently, during the structure elucidation of a rare triterpene, boehmeryl acetate (**1**) isolated[1] from *Pluchea indica*, it was found that ^{13}C NMR spectral assignment reported for **1**[2] and boehmerol[3] vary significantly. We, therefore, undertook assignment of ^{13}C chemical shifts of **1** by 2D NMR. On detailed analyses (*vide infra*), we could assign unambiguously all the ^{13}C NMR signals and found that the assignment reported by both the groups[2,3] were erroneous. This result prompted us to undertake assignment of ^{13}C NMR spectra of some other hopane and migrated hopane derivatives. We report herein assignment of ^{13}C NMR signals of boehmeryl acetate (**1**), neohop-13(18)-en-3β-ol (**2**)[4], neomotiol (**3**)[5], arborinol (**4**)[6], isoarborinyl acetate (**5**)[6], fernenol (**6**)[7], fernenyl acetate (**7**)[7],

simiarenol (**8**)[8] and hop-17(21)-en-3β-yl acetate (**9**)[9], whose ^{13}C NMR data are not known so far. In the process, ^{1}H NMR signals of methyl protons in particular have also been assigned.

Assignments of ^{13}C NMR chemical shifts for **1-9** are summarized in Table 1 and those of ^{1}H chemical shifts particularly of methyl protons of **1-9** are listed in Tables 2-10.



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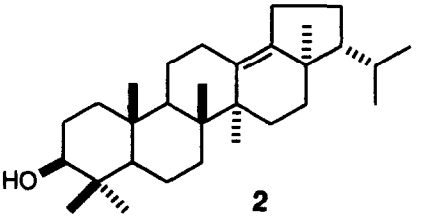

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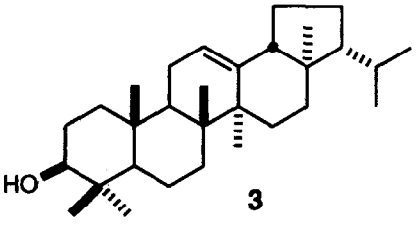

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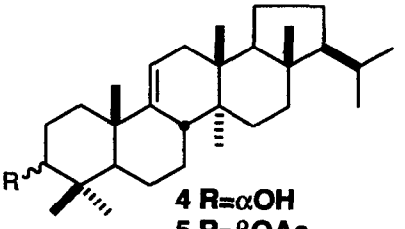

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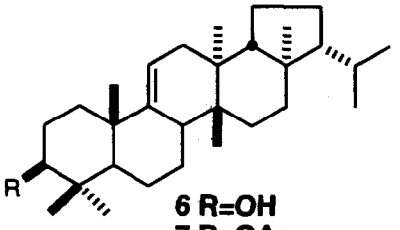

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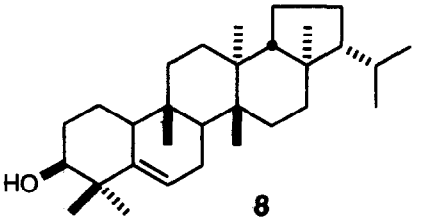
7 R=OAc



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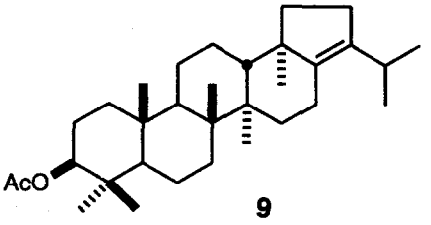

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Table 1. ^{13}C Chemical shifts (δ ppm, $CDCl_3$) of 1-9

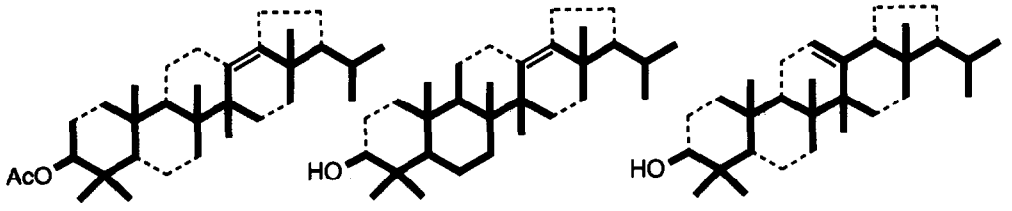
Carbons	1	2	3	4	5	6	7	8	9
1	32.89	39.02	38.01	30.39	35.68	39.35	39.00	18.06	38.53
2	25.32	27.44	27.14	25.69	24.17	28.14	24.64	27.78	23.72
3	81.07	78.98	79.11	76.28	80.91	79.16	81.06	76.36	80.99
4	38.17	38.87	38.81	37.84	37.97	39.28	38.14	40.82	37.81
5	48.20	55.65	55.54	46.55	52.41	44.30	44.47	141.97	55.33
6	18.82	18.52	18.61	21.35	21.30	19.15	18.94	121.99	18.28
7	34.84	34.53	32.54	26.62	26.57	18.00	17.84	24.05	33.41
8	41.36*	41.37*	39.28	41.03	40.93	39.99	39.94	44.25	41.72*
9	46.24	52.18	48.11	148.83	148.47	151.07	150.78	34.82	50.75
10	37.03	37.46	37.61	39.59	39.49	37.66	37.63	50.23	37.10
11	22.60	21.67	23.56	114.08	114.56	116.20	116.44	34.14	21.40
12	26.45	26.65	117.93	36.05	36.05	36.74	36.70	29.00	23.99
13	131.10	131.46	145.49	36.75	36.76	36.74	36.73	38.61	49.31
14	42.51*	42.16*	41.64	38.27	38.19	37.79	37.67	39.31	41.99*
15	30.35	29.35	25.06	29.62	29.65	29.28	29.28	29.10	31.83
16	37.46	37.90	34.61	35.94	35.92	36.16	36.16	35.41	19.82
17	42.76	42.67	40.06	42.86	42.85	42.95	42.95	42.79	139.91
18	141.83	141.83	52.64	52.08	52.06	51.97	51.98	51.74	49.81
19	26.39	26.50	22.83	20.19	20.18	20.14	20.14	19.91	41.65
20	27.59	27.57	28.40	28.23	28.21	28.21	28.21	28.32	27.50
21	59.04	59.17	60.10	59.64	59.63	59.66	59.67	60.03	136.09
22	29.83	29.81	31.73	30.80	30.79	30.78	30.77	30.79	26.36
23	28.94	27.97	28.06	28.30	28.16	27.45	27.39	29.07	27.97
24	17.18	15.41	15.39	22.53	16.79	15.05	16.14	25.48	16.51
25	22.93	16.76	15.28	21.93	22.17	25.22	25.24	17.87	16.29
26	25.68	18.62	16.32	17.05	17.03	15.85	15.76	15.75	16.29
27	26.70	26.65	22.22	15.30	15.30	15.38	15.38	15.00	14.91
28	17.90	17.85	18.57	14.00	13.99	13.99	13.98	16.07	19.08
29	22.88	22.88	22.51	22.13	22.13	22.13	22.12	21.96	21.30
30	23.08	23.08	22.65	23.01	23.00	23.00	23.01	22.93	21.91
OAc	21.32	-	-	-	21.34	-	21.35	-	21.35
	171.14	-	-	-	170.99	-	171.06	-	171.05

*Assignments in a vertical column may be interchanged.

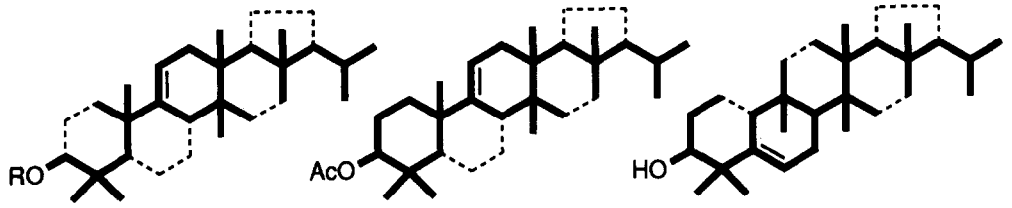
Initially, ^{13}C chemical shifts of the carbons of the compounds under study were obtained from their PND spectra. The multiplicities of each of the signals were determined by DEPT experiments. For assignment purposes, a number of 2D experiments *viz.* ^{1}H-^{1}H COSY, ^{1}H-^{13}C COSY, HSQC and HMBC were performed. Among these, HMBC (Heteronuclear Multiple Bond

Correlation) spectrum was found to be the most informative. Because of the unique back-bone structure of triterpenoids with several ring juncture methyl groups, only two and three bond correlation data (Tables 2-10) of the methyl protons and in some cases, a few well identified methine protons with different carbons, obtained from HMBC spectra, resulted in the unambiguous assignment of all the back-bone carbons besides peripheral methyl and some methylene carbons also (shown by heavy lines in structures **1a-9a**). In fact, based on the correlations obtained from the HMBC spectrum, we could establish[10] the structure of a novel rearranged hopane triterpenoids, chiratenol, which is the first representative of a new chiratane skeleton.

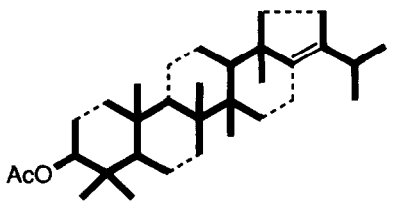
The ^1H chemical shifts of the methyl protons and other methylene and methine protons attached to the carbons, already assigned on the basis of HMBC spectra, could then be directly obtained from ^1H-^{13}C COSY or HSQC spectra. The assignment and connectivity of the remaining carbons of the part structures indicated by dotted lines in **1a-9a** were thereafter achieved by analyses of ^1H-^1H COSY and ^1H-^{13}C COSY spectra as in the sequel.



1a **2a** **3a**



4a, 6a, 7a **5a** **8a**



9a

Table 2. One bond (^{1}H-^{13}C COSY) and multiple bond (HMBC) ^{1}H-^{13}C correlation data of boehmeryl acetate (1)

δ_H ppm	One bond correlation δ_C ppm	Multiple bond correlation δ_C ppm			
0.866 (23-H_3)	28.94 (C-23)	17.18 (C-24)	38.17 (C-4)	48.20 (C-5)	81.07 (C-3)
0.857 (24-H_3)	17.18 (C-24)	28.94 (C-23)	38.17 (C-4)	48.20 (C-5)	81.07 (C-3)
0.959 (25-H_3)	22.93 (C-25)	32.89 (C-1)	37.03 (C-10)	46.24 (C-8)	48.20 (C-5)
0.998 (26-H_3)	25.68 (C-26)	34.84 (C-7)	41.36 (C-8)	42.51 (C-14)	46.24 (C-9)
1.069 (27-H_3)	26.70 (C-27)	30.35 (C-15)	41.36 (C-8)	42.51 (C-14)	131.10 (C-13)
0.786 (28-H_3)	17.90 (C-28)	37.46 (C-16)	42.76 (C-17)	59.04 (C-21)	141.83 (C-18)
0.942 d (29-H_3) (J=6.7 Hz)	22.88 (C-29)	23.08 (C-30)	29.83 (C-22)	59.04 (C-21)	
0.898 d (30-H_3) (J=6.7 Hz)	23.08 (C-30)	22.88 (C-29)	29.83 (C-22)	59.04 (C-21)	
4.505 dd (3-H) (J=11.6, 4.9 Hz)	81.07 (C-3)	17.18 (C-24) 171.14 (OAc)	25.32 (C-2)	28.94 (C-23)	38.17 (C-4)
1.18, 1.52 (6-H_2)	18.82 (C-6)				
0.94, 1.40 (11-H_2)	22.60 (C-11)				
2.18, 2.28 (19-H_2)	26.45 (C-19)				
1.37, 1.84 (20-H_2)	27.59 (C-20)				

Table 3. One bond (^{1}H-^{13}C COSY) and multiple bond (HMBC) ^{1}H-^{13}C correlation data of neohop-13(18)-en-3β-ol (2)

δ_H ppm	One bond correlation δ_C ppm	Multiple bond correlation δ_C ppm			
0.979 (23-H_3)	27.97 (C-23)	15.41 (C-24)	38.87 (C-4)	55.65(C-5)	78.98 (C-3)
0.761 (24-H_3)	15.41(C-24)	27.97 (C-23)	38.87 (C-4)	55.65 (C-5)	78.98 (C-3)
0.831 (25-H_3)	16.76 (C-25)	37.36 (C-10)	39.02 (C-1)	52.18 (C-9)	55.65 (C-5)
0.860 (26-H_3)	18.62 (C-26)	34.53 (C-7)	41.37 (C-8)	42.16 (C-14)	52.18 (C-9)
1.093 (27-H_3)	26.65 (C-27)	29.35 (C-15)	41.37 (C-8)	42.16 (C-14)	131.46 (C-13)
0.793 (28-H_3)	17.85(C-28)	37.90 (C-16)	42.67 (C-17)	59.17 (C-21)	141.35 (C-18)
0.937 d (29-H_3) (J=6.7 Hz)	22.88 (C-29)	23.08 (C-30)	29.81 (C-22)	59.17 (C-21)	
0.893 d (30-H_3) (J=6.7 Hz)	23.08 (C-30)	22.88 (C-29)	29.81 (C-22)	59.17 (C-21)	
0.73 (5-H)	55.65 (C-5)	15.41 (C-24) 38.87 (C-4)	18.52 (C-6)	34.53 (C-7)	37.46 (C-10)
1.34 (9-H)	52.18 (C-9)	16.76 (C-25)	18.62 (C-26)	21.67 (C-11)	37.46 (C-10)
1.56, 1.64 (2-H_2)	27.44 (C-2)				
1.89, 2.31 (12-H_2)	26.65 (C-12)				
2.20, 2.27 (19-H_2)	26.50 (C-19)				
1.35, 1.84 (20-H_2)	27.57 (C-20)				

Table 4. One bond (^1H-^{13}C COSY) and multiple bond (HMBC) ^1H-^{13}C correlation data of neomotiol (3)

δ_H ppm	One bond correlation δ_C ppm		Multiple bond correlation δ_C ppm		
0.992 (23-H_3)	28.06 (C-23)	15.39 (C-24)	38.81 (C-4)	55.54 (C-5)	79.11 (C-3)
0.788 (24-H_3)	15.39 (C-24)	28.06 (C-23)	38.81 (C-4)	55.54 (C-5)	79.11 (C-3)
0.885 (25-H_3)	15.28 (C-25)	37.61 (C-10)	38.01 (C-1)	48.11 (C-9)	55.54 (C-5)
0.733 (26-H_3)	16.32 (C-26)	32.54 (C-7)	39.28 (C-8)	41.64 (C-14)	48.11 (C-9)
1.111 (27-H_3)	22.22 (C-27)	25.06 (C-15)	39.28 (C-8)	41.64 (C-14)	145.49 (C-13)
0.755 (28-H_3)	18.57 (C-28)	34.61 (C-16)	40.06 (C-17)	52.64 (C-18)	60.10 (C-21)
0.937 d (29-H_3) (*J*=6.4 Hz)	22.51 (C-29)	22.65 (C-30)	31.73 (C-22)	60.10 (C-21)	
0.847 d (30-H_3) (*J*=6.4 Hz)	22.65 (C-30)	22.51 (C-29)	31.73 (C-22)	60.10 (C-21)	
3.227 dd (3-H) (*J*=10.8, 4.4 Hz)	79.11 (C-3)	15.39 (C-24)	28.06 (C-23)		
5.052 ddd (12-H) (*J*=2.1, 2.1, 5.2 Hz)	117.93 (C-12)	41.64 (C-14)	48.11 (C-9)	52.64 (C-18)	
1.58, 1.63 (2-H_2)	27.14 (C-2)				
1.43, 1.58 (6-H_2)	18.61 (C-6)				
1.81, 2.06 (11-H_2)	23.56 (C-11)				
1.27, 1.65 (19-H_2)	22.83 (C-19)				
1.23, 1.87 (20-H_2)	28.40 (C-20)				

The general strategy adopted was to find out the ^1H chemical shifts of the proton(s) attached to those unassigned carbons from ^1H-^1H COSY spectra taking advantage of the known ^1H chemical shifts of the vicinal protons. Thus, in case of $\Delta^{13(18)}$ compounds **1** and **2** for example, having known ^{13}C chemical shifts of C-5, C-7, C-9 and C-21, the ^1H chemical shifts of the protons attached to them could easily be obtained from their ^1H-^{13}C COSY or HSQC spectra. Careful examination of ^1H-^1H COSY spectra then resulted in the location of the corresponding vicinal proton signals through the cross peaks. In this way, 6-H_2, 11-H_2 and 20-H_2 proton chemical shifts could be identified (Tables 2 and 3). Similarly, 19-H_2 proton signal positions could then be located through correlations with 20-H_2 proton signals. The corresponding ^{13}C signals were then assigned from ^1H-^{13}C COSY spectra.

However, due to severe overlapping of cross peaks between δ 1.0-2.0 ppm in ^1H-^1H COSY spectra of triterpenoids, sometimes no well defined correlation peaks are obtained and therefore some proton signal positions are very difficult to determine correctly. For this reason, 12-H_2 signals of **1** and 19-H_2 signals of **5** and **6** could not be identified. Assignment of the carbons attached to these protons were, therefore, done on the basis of elimination since all other carbons were assigned unambiguously.

Table 5. One bond (^1H-^{13}C COSY) and multiple bond (HMBC) ^1H-^{13}C correlation data of arborinol (4)

δ_H ppm	One bond correlation δ_C ppm		Multiple bond correlation δ_C ppm		
0.957 (23-H_3)	28.30 (C-23)	22.53 (C-24)	37.84 (C-4)	46.55 (C-5)	76.28 (C-3)
0.877 (24-H_3)	22.53 (C-24)	28.30 (C-23)	37.84 (C-4)	46.55 (C-5)	76.28 (C-3)
1.051 (25-H_3)	21.93 (C-25)	30.39 (C-1)	39.59 (C-10)	46.55 (C-5)	148.83 (C-9)
0.820 (26-H_3)	17.05 (C-26)	29.62 (C-15)	36.75 (C-13)	38.27 (C-14)	41.03 (C-8)
0.770 (27-H_3)	15.30 (C-27)	36.05 (C-12)	36.75 (C-13)	38.27 (C-14)	52.08 (C-18)
0.756 (28-H_3)	14.00 (C-28)	35.94 (C-16)	42.86 (C-17)	52.08 (C-18)	59.64 (C-21)
0.890 d (29-H_3) (J=6.4 Hz)	22.13 (C-29)	23.01 (C-30)	30.80 (C-22)	59.64 (C-21)	
0.829 d (30-H_3) (J=6.4 Hz)	23.01 (C-30)	22.13 (C-29)	30.80 (C-22)	59.64 (C-21)	
3.425 dd (3-H) (J=2.8, 2.8 Hz)	76.28 (C-3)	22.53 (C-24)	30.39 (C-1)	46.55 (C-5)	
5.264 ddd (11-H) (J=6.1, 1.8, 1.8 Hz)	114.08 (C-11)	36.05 (C-12)	36.75 (C-13)	39.59 (C-10)	41.03 (C-9)
1.43, 1.58 (6-H_2)	21.35 (C-2)				
1.24, 1.82 (7-H_2)	26.62 (C-7)				
1.23, 1.37 (19-H_2)	20.19 (C-19)				
1.23, 1.85 (20-H_2)	28.23 (C-20)				

It is also important to point out that a lower level contour plot of HMBC spectrum sometimes gives additional information though the spectrum is full of noise peaks. Thus a careful examination of the lower level HMBC spectrum of **2** revealed a number of correlations involving the methine protons 5-H and 9-H (Table 3) which indeed helped us in assigning C-6 and C-11 chemical shifts. Similarly, C-6 and C-12 of **9** could be assigned from correlations involving the methine protons 5-H and 13-H respectively (Table 10).

Now, having assignments of ^{13}C chemical shifts in hand, the data (Table 1) of isoarborinyl acetate (**5**) and fernenyl acetate (**7**), which are antipodal with respect to part of the structures comprising C, D and E rings, may be compared. It can be seen that C-5 and C-7 signals of **7** experienced up-field shift by 8-9 ppm. Moreover, shielding of C-6 and C-10, and deshielding of C-1, C-9, C-11 and C-25 signals by smaller magnitudes of 2-3 ppm were also observed. In general, these changes may be attributed to the *boat* conformation of ring B in **7**. But the strong shielding of C-5 and C-7 must be due to their pronounced steric interaction with C-8 and C-25 carbons respectively. Similarly, comparison of chemical shifts of boehmeryl acetate (**1**) and neohop-13(18)-en-3β-ol (**2**) having similar antipodal part structures revealed up-field shift of C-1, C-5 and C-9 signals of **1** by 6-7 ppm and down-field shift of C-25 and C-26 signals by approximately the same amount. It seems, therefore, that unlike the case of **7**, the ^{13}C chemical

Table 6. One bond (^1H-^{13}C COSY) and multiple bond (HMBC) ^1H-^{13}C correlation data of isoarborinyl acetate (5)

δ_H ppm	One bond correlation δ_C ppm		Multiple bond correlation δ_C ppm		
0.862 (23-H_3)	28.16 (C-23)	16.79 (C-24)	37.97 (C-4)	52.41 (C-5)	80.91 (C-3)
0.887 (24-H_3)	16.79 (C-24)	28.16 (C-23)	37.97 (C-4)	52.41 (C-5)	80.91 (C-3)
1.055 (25-H_3)	22.17 (C-25)	35.68 (C-1)	39.49 (C-10)	148.47 (C-9)	52.41 (C-5)
0.804 (26-H_3)	17.03(C-26)	29.65 (C-15)	36.76 (C-13)	38.19 (C-14)	40.93 (C-8)
0.763 (27-H_3)	15.30 (C-27)	36.05 (C-12)	36.76 (C-13)	38.19 (C-14)	52.06 (C-18)
0.755 (28-H_3)	13.99 (C-28)	35.92 (C-16)	42.85 (C-17)	52.06 (C-18)	59.63 (C-21)
0.890 d (29-H_3) (*J*=6.4 Hz)	22.13 (C-29)	23.00 (C-30)	30.79 (C-22)	59.63 (C-21)	
0.830 d (30-H_3) (J=6.4 Hz)	23.00 (C-30)	22.13 (C-29)	30.79 (C-22)	59.63 (C-21)	
4.481 dd (3-H) (*J*=11.6, 3.9 Hz)	80.91 (C-3)	16.79 (C-24) 37.97 (C-4)	24.17 (C-2)	28.16 (C-23)	35.68 (C-1)
5.230 ddd (11-H) (*J*=6.1, 1.8, 1.8 Hz)	114.56 (C-11)	36.76 (C-13)	39.49 (C-10)	40.93 (C-8)	36.05 (C-12)
1.46, 1.66 (6-H_2)	21.30 (C-6)				
1.25, 1.82 (7-H_2)	26.57 (C-7)				
1.23, 1.84 (20-H_2)	28.21 (C-20)				

Table 7. One bond (^1H-^{13}C COSY) and multiple bond (HMBC) ^1H-^{13}C correlation data of fernenol (6)

δ_H ppm	One bond correlation δ_C ppm		Multiple bond correlation δ_C ppm		
0.963 (23-H_3)	27.45 (C-23)	15.05 (C-24)	39.28 (C-4)	44.30 (C-5)	79.16 (C-3)
0.870 (24-H_3)	15.05 (C-24)	27.45 (C-23)	39.28 (C-4)	44.30 (C-5)	79.16 (C-3)
1.065 (25-H_3)	25.22 (C-25)	37.66 (C-10)	39.35 (C-1)	44.30 (C-5)	151.07 (C-9)
0.732 (26-H_3)	15.38 (C-26)	29.28 (C-15)	36.74 (C-13)	37.79 (C-14)	39.99 (C-8)
0.813 (27-H_3)	15.85 (C-27)	36.74 (C-12)	36.74 (C-13)	37.79 (C-14)	51.97 (C-18)
0.757 (28-H_3)	13.99 (C-28)	36.16 (C-16)	42.95 (C-17)	51.97 (C-18)	59.66 (C-21)
0.891 d (29-H_3) (*J*=6.4 Hz)	22.13 (C-29)	23.00 (C-30)	30.78 (C-22)	59.66 (C-21)	
0.830 d (30-H_3) (J=6.4 Hz)	23.00 (C-30)	22.13 (C-29)	30.78 (C-22)	59.66 (C-21)	
3.210 dd (3-H) (*J*=10.6, 5.5 Hz)	79.16 (C-3)	15.05 (C-24)	27.45 (C-23)	39.28 (C-4)	39.35 (C-1)
5.296 ddd (11-H) (*J*=5.2, 2.5, 2.5 Hz)	116.20 (C-11)	36.74 (C-12)	37.66 (C-10)	39.99 (C-8)	
1.58, 1.64 (2-H_2)	28.14 (C-2)				
1.34, 1.59 (7-H_2)	18.00 (C-7)				
1.23, 1.84 (20-H_2)	28.21 (C-20)				

Table 8. One bond (^1H-^{13}C COSY) and multiple bond (HMBC) ^1H-^{13}C correlation data of fernenyl acetate (7)

δH ppm	One bond correlation δC ppm		Multiple bond correlation δC ppm		
0.845 (23-H_3)	27.39 (C-23)	16.14 (C-24)	38.14 (C-4)	44.47 (C-5)	81.06 (C-3)
0.941 (24-H_3)	16.14 (C-24)	27.39 (C-23)	38.14 (C-4)	44.47 (C-5)	81.06 (C-3)
1.084 (25-H_3)	25.24 (C-25)	37.63 (C-10)	39.00 (C-1)	44.47 (C-5)	150.78 (C-9)
0.729 (26-H_3)	15.76 (C-26)	29.28 (C-15)	36.73 (C-13)	37.67 (C-14)	39.94 (C-8)
0.804 (27-H_3)	15.38 (C-27)	36.70 (C-12)	36.73 (C-13)	37.67 (C-14)	51.98 (C-18)
0.758 (28-H_3)	13.98 (C-28)	36.16 (C-16)	42.95 (C-17)	51.98 (C-18)	59.67 (C-21)
0.890 d (29-H_3) (*J*=6.4 Hz)	22.12 (C-29)	23.01 (C-30)	30.77 (C-22)	59.67 (C-21)	
0.829 d (30-H_3) (J=6.4 Hz)	23.01 (C-30)	22.12 (C-29)	30.77 (C-22)	59.67 (C-21)	
4.481 dd (3-H) (*J*=9.3, 6.9 Hz)	81.06 (C-3)	16.14 (C-24)	27.39 (C-23)	171.06 (OAc)	
5.295 ddd (11-H) (*J*=5.5, 2.5, 2.5 Hz)	116.44 (C-11)	36.70 (C-12)			
1.62, 1.67 (2-H_2)	24.64 (C-2)				
1.64, 1.71 (6-H_2)	18.94 (C-6)				
1.34, 1.61 (7-H_2)	17.84 (C-7)				
1.24, 1.34 (19-H_2)	20.14 (C-19)				
1.23, 1.83 (20-H_2)	28.21 (C-20)				

shifts of some of the A and B ring carbons and the attached methyl carbons of **1** were influenced by not only the *boat* conformation of ring B but also the stereochemical disposition of 9-H with respect to 8α-H and 10β-Me. Though the structure of boehmerol was established[3] by X-ray crystallography, the orientation of 9-H is not specifically mentioned. Examination of molecular model (Dreiding) of both the C-9 epimers of **1**, in terms of interactions considered important in assignment of ^{13}C chemical shifts, also could not conclusively distinguish between the epimers. However, the relative configuration of 9-H in **1** could be easily established to be β on the basis of a number of NOE interactions involving 9-H (Chart 1) in the NOESY spectrum. Similarly, the NOE interactions involving methyl protons as well as methine protons of all the compounds under study, summarized in Chart 1, also clearly determined the relative stereochemistry of most of the chiral centres of the back-bone of each of the compounds **1-9**. Some of the expected NOE cross peaks particularly due to interaction between (i) 25-H_3 and 26-H_3 in **2**, (ii) 18-H and 21-H in **3** and **7**, (iii) 27-H_3 and 28-H_3 in **4** and **5**, (iv) 25-H_3 and 7β-H in **6**, and (v) 24-H_3 and 25-H_3 in **9**, however, could not be identified or observed at all. This may be attributed to either of the two reasons, *viz.* (i) the resonance frequencies of two interacting protons were very close and (ii) either or both of the interacting proton signals showed complex splitting pattern.

Table 9. One bond (^1H-^{13}C COSY) and multiple bond (HMBC) ^1H-^{13}C correlation data of simiarenol (8)

δH ppm	One bond correlation δC ppm		Multiple bond correlation δC ppm		
1.045 (23-H_3)	29.07 (C-23)	25.48 (C-24)	40.82 (C-4)	76.36 (C-3)	141.97 (C-5)
1.141 (24-H_3)	25.48 (C-24)	29.07 (C-23)	40.82 (C-4)	76.36 (C-3)	141.97 (C-5)
0.895 (25-H_3)	17.87 (C-25)	34.14 (C-11)	34.82 (C-9)	44.25 (C-8)	50.23 (C-10)
1.005 (26-H_3)	15.75 (C-26)	29.10 (C-15)	38.61 (C-13)	39.31 (C-14)	44.25 (C-8)
0.925 (27-H_3)	15.00 (C-27)	29.00 (C-12)	38.61 (C-13)	39.31 (C-14)	51.74 (C-18)
0.780 (28-H_3)	16.07 (C-28)	35.41 (C-16)	42.79 (C-17)	51.74 (C-18)	60.03 (C-21)
0.888 d (29-H_3) (J=6.7 Hz)	21.96 (C-29)	22.93 (C-30)	30.79 (C-22)	60.03 (C-21)	
0.829 d (30-H_3) (J=6.7 Hz)	22.93 (C-30)	21.96 (C-29)	30.79 (C-22)	60.03 (C-21)	
3.469 br. s (3-H)	76.36 (C-3)	18.06 (C-1)	141.97 (C-5)		
5.616 ddd (6-H) (J=6.0, 2.0, 2.0 Hz)	121.99 (C-6)	24.05 (C-7)	40.82 (C-4)	44.25 (C-8)	50.23 (C-10)
1.70, 1.86 (2-H_2)	27.78 (C-2)				
1.26, 1.36 (19-H_2)	19.91 (C-19)				
1.19, 1.82 (20-H_2)	28.32 (C-20)				

Table 10. One bond (^1H-^{13}C COSY) and multiple bond (HMBC) ^1H-^{13}C correlation data of hop-17(21)-en-3β-yl acetate (9)

δH ppm	One bond correlation δC ppm		Multiple bond correlation δC ppm		
0.853 (23-H_3)	27.97 (C-23)	16.51 (C-24)	37.81 (C-4)	55.33 (C-5)	80.99 (C-3)
0.835 (24-H_3)	16.51(C-24)	27.97 (C-23)	37.81 (C-4)	55.33 (C-5)	80.99 (C-3)
0.853 (25-H_3)	16.29 (C-25)	37.10 (C-10)	38.53 (C-1)	50.75 (C-9)	55.33 (C-5)
0.929 (26-H_3)	16.29 (C-26)	33.41 (C-7)	41.72 (C-8)	41.99 (C-14)	50.75 (C-9)
1.028 (27-H_3)	14.91 (C-27)	31.83 (C-15)	41.72 (C-8)	41.99 (C-14)	49.31 (C-13)
0.837 (28-H_3)	19.08 (C-28)	41.65 (C-19)	49.31 (C-13)	49.81 (C-18)	139.91 (C-17)
0.975 d (29-H_3) (J=7.0 Hz)	21.30 (C-29)	21.91 (C-30)	26.36 (C-22)	136.09 (C-21)	
0.916 d (30-H_3) (J=7.0 Hz)	21.91 (C-30)	21.30 (C-29)	26.36 (C-22)	136.09 (C-21)	
2.638 m (22-H)	26.36 (C-22)	21.30 (C-29) 139.91 (C-17)	21.91 (C-30)	27.50 (C-20)	136.09 (C-21)
4.487 dd (3-H) (J=10.9, 5.7 Hz)	80.99 (C-3)	16.51 (C-24) 171.05 (OAc)	23.72 (C-2)	27.97 (C-23)	37.81(C-4)
0.799 (5-H)	55.33 (C-5)	16.51 (C-24)	18.28 (C-6)	37.10 (C-10)	50.75 (C-9)
1.43 (13-H)	49.31 (C-13)	14.91 (C-27) 41.99 (C-14)	19.08 (C-28) 41.81 (C-18)	23.99 (C-12)	41.72 (C-8)
1.29, 1.52 (11-H_2)	21.40 (C-11)				
1.92, 2.26 (16-H_2)	19.82 (C-16)				

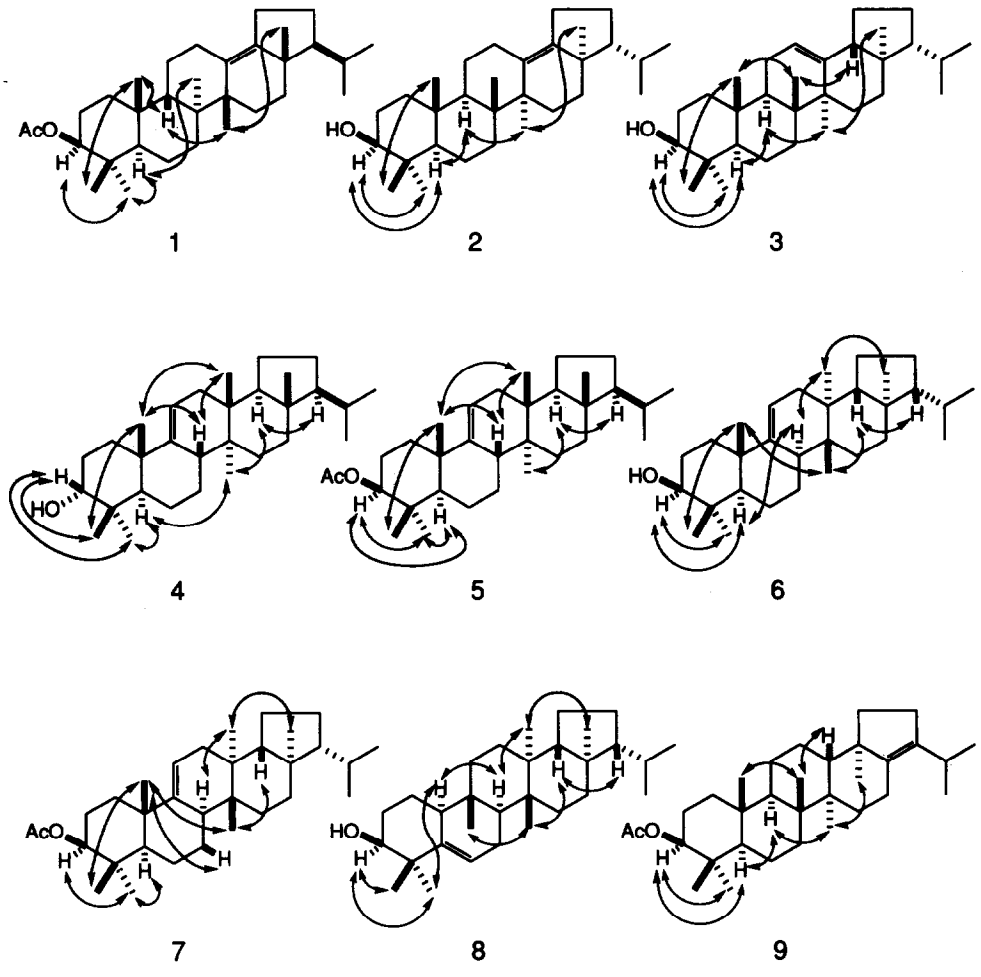


Chart 1

Thus, the 2D NMR methods can be successfully used not only to unambiguously assign ^{13}C chemical shifts but also to determine the complete structure and stereochemistry of triterpenoids even though this class of compounds display unresolved and severely overlapped ^{1}H-NMR signals for most of the methylene and methine protons.

Experimental

The 1D and 2D NMR spectra were measured on a JEOL A500 spectrometer equipped with a VAX station 3,200 computer using a solution of *ca.* 10 mg of sample in 0.8 ml of $CDCl_3$ with TMS as the internal standard at 24 °C. The chemical shifts are expressed on the δ scale. For 1D ^1H NMR (500 MHz), 32 K data points and a frequency width of 10,000.0 Hz were used giving a digital resolution of 0.3 Hz per point. For 1D ^{13}C NMR (125.65 MHz), 32 K data points and a frequency width of 33,898.3 Hz were used giving a digital resolution of 1.1 Hz per point. DEPT and 2D NMR spectra were obtained with the standard JEOL pulse sequences. For ^1H-^1H COSY and NOESY spectra, the frequency width was 4,450.4 Hz and the initial t_1, t_2 matrix of 512 x 512 real data points was zero-filled to 1024 x 1024 data points to give a final resolution of 4.3 Hz per point. The NOESY spectra were obtained using a mixing time of 800 ms. The ^1H-^{13}C COSY spectra were obtained using the frequency ranges of 25,773.2 Hz and 4,449.6 Hz for ^{13}C and ^1H respectively. The initial matrix of 1024 x 256 real data points was zero-filled to 2048 x 512 data points, thus giving a 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 Frourier transformation. 64 scans were acquired per t_1 increment. In some cases, for sensitivity reasons, the ^1H detected Heteronuclear Single-Quantum Coherence (HSQC) spectrum with ^{13}C decoupling during acquisition was used. The HMBC spectra were recorded with 128 scans (128 dummy scans). The delay τ_1 was set to 3.6 ms and τ_2 to 60 ms.

The compounds used in this study were available with us. These were isolated from various sources at different times.

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