NMR Spectra of Triterpenoids. III. Oleanenes and Migrated Oleanenes

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The ^{1}H- and ^{13}C-NMR signals of nine triterpenoid hydrocarbons belonging to the oleanene and migrated oleanene groups together with friedelin were completely assigned by the application of modern NMR techniques, and the conformations of rings D and E are discussed on the basis of Chem3D Plus and MM2 calculations, and nuclear Overhauser effect spectroscopy spectra.

Key words ^{1}H-NMR; ^{13}C-NMR; triterpenoid; oleanene; migrated oleanene; conformation

In previous papers,[1] we have described the complete assignments of the ^{1}H- and ^{13}C-NMR signals of eleven hydrocarbons of the hopane and migrated hopane groups and have discussed the conformations of the side chain of these compounds. This paper deals similarly with nine hydrocarbons and a ketone belonging to the oleanene and migrated oleanene groups, olean-18-ene (**1**),[2] olean-13(18)-ene (**2**),[2b] olean-12-ene (**3**),[2] taraxer-14-ene (**4**),[2] multiflor-9(11)-ene (**5**),[2] multiflor-7-ene (**6**),[2] glutin-5(10)-ene (**7**),[2b] glutin-5-ene (**8**),[2b] and friedel-3-ene (**9**)[2] in addition to friedelin (**10**).[3] As a result, the *cis*-fused D and E rings of compounds **5**—**10** in CDCl$_3$ solution were found for the first time to be in boat–boat conformations.

Experimental

General Procedures ^{1}H- and ^{13}C-NMR spectra of the 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 and olefinic proton signals and related carbon signals were correlated by the heteronuclear multiple bond correlation (HMBC) method. The assignments of methyl signals determined by the CDCl$_3$–C$_6$D$_6$ solvent shift method[2] were confirmed by the HMBC spectra. Signals of methylene and methine protons were picked up from the C–H COSY spectra, and linkages to the same or the neighboring carbons were made by the ^{1}H–^{1}H correlated spectroscopy (H–H COSY) method. On the other hand, the most stable conformation of each compound with minimum steric energy was simulated by using the Chem3D Plus and MM2 programs[4] and finally the conformation was confirmed by obtaining nuclear Overhauser effect spectroscopy (NOESY) spectra. Signals of methyl, methylene and methine protons were also confirmed by the NOESY spectra including the stereochemistry of these protons.

Conditions for NMR Measurement The 1D and 2D NMR spectra were measured on a JEOL A-500 spectrometer equipped with a VAX station 3200 computer, using a CDCl$_3$ solution of *ca.* 10 mg in 0.8 ml with tetramethylsilane (TMS) 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, 32 K data points and a frequency width of 10000.0 Hz were used, giving a digital resolution of 0.3 Hz per point. For 1D ^{13}C-NMR at 125.65 MHz, 32 K data points and a frequency width of 33893.3 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. The frequency width was 4450.4 Hz and the initial t_1, t_2 matrix of 512 × 512 real data point was zero-filled to 1024 × 1024 data points to give a final resolution of 4.3 Hz per point. The NOESY spectrum was obtained using a mixing time of 1000 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 initial matrix of 1024 × 256 real data points was zero-filled to 2048 × 512 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.

Discussion of Conformations

To establish precise assignments of NMR signals of the compound, the conformation of the compound should be

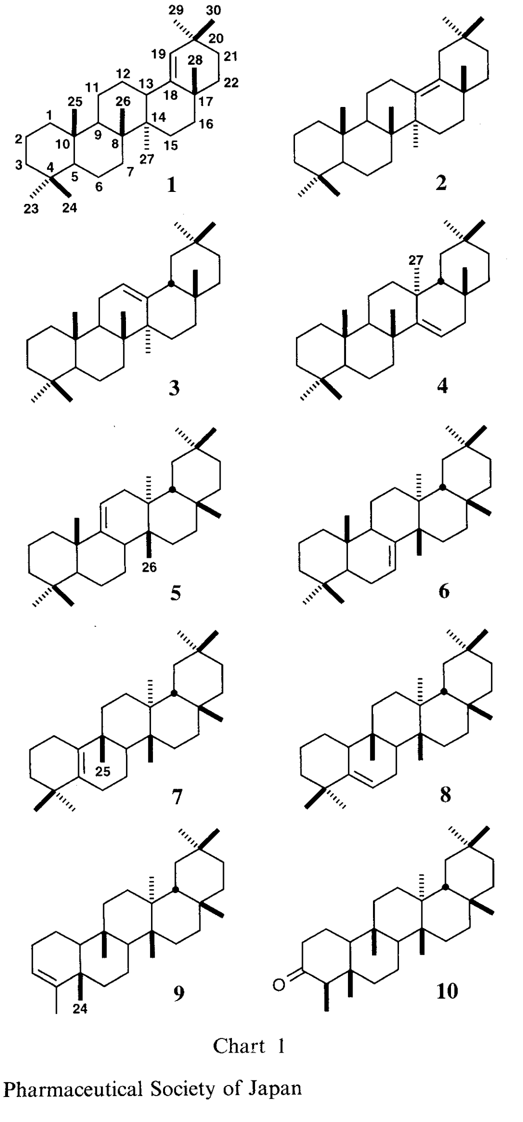

Chart 1

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firmly established. We tried to estimate the conformation with minimum steric energy by using the Chem3D Plus/MM2 programs, as has been done for hopane derivatives and migrated hopenes.[1] Compounds **1**—**4** gave one conformation (chair–chair in the D and E rings) as expected, while compounds **5**—**10** afforded two conformations (boat–boat and chair–chair in the D and E rings) with almost the same steric energies, as shown in Table I. X-ray crystallographic analyses of many friedelane derivatives have been reported. The *cis* fused D and E rings in most of the derivatives, such as 3-*O*-acetyl-16-bromobenzoylfriedelan-3β-ol,[5] friedelan-3β-ol,[6] 28,30-dihydroxyfriedelan-3-one,[7] and friedelan-3-one (friedelin),[8] had boat–boat form, while some of them, such as friedelan-3α-ol chloroacetate,[3] and methyl 3-oxofriedelan-29-oate,[9] as well as glutinan-3β,10β-oxide[10] had chair–chair form. For friedelan-3β-ol (**11**) and multiflor-7-en-3β-ol (**12**) in solution, we concluded that the D and E rings of these compounds are in boat–boat conformation, based on the precise assignments of ^{13}C- and ^{1}H-NMR signals and lanthanide shift studies.[11] As the ^{1}H- and ^{13}C-NMR signals of the D and E rings of compounds **5**—**10** are similar to each other except for the signals affected by the double bond (*e.g.*, C-13, 14 and 22 in **5**, H-15, C-14, 18 and 22 in **6**; Tables II, III and IV) and to those of **11** and **12**,[11] compounds **5**—**12** can be concluded to have the same boat–boat conformation at rings D and E in CDCl$_3$ solution.[12] It is noteworthy that the H-28 signal of compounds **1**—**4** appears at higher field than that of compounds **5**—**10**.

TABLE I. Conformations of Triterpenoid Hydrocarbons and a Ketone Belonging to the Oleanane and Migrated Oleanane Series with Steric Energies Calculated by Chem3D plus/MM2

Compound	Conformation	Steric energy (kcal/mol)
Olean-18-ene (**1**)	c–c–c–c–tw	68.479
Olean-13(18)-ene (**2**)	c–c–c–tw–c	69.672
Olean-12-ene (**3**)	c–c–tw–c–c	69.630
	c–c–tw–b–c	76.903
Taraxer-14-ene (**4**)	c–c–b–hb–c	75.946
	c–c–b–tw–c	77.736
Multiflor-9(11)-ene (**5**)	c–b–hb–b–b	75.914
	c–b–hb–c–c	75.209
Multiflor-7-ene (**6**)	c–hb–b–b–b	78.635
	c–hb–b–c–c	79.433
Glutin-5(10)-ene (**7**)	tw–hb–c–b–b	78.517
	tw–hb–c–c–c	78.805
Glutin-5-ene (**8**)	c–tw–c–b–b	79.482
	c–tw–c–c–c	79.164
Friedel-3-ene (**9**)	tw–c–c–b–b	84.323
	tw–c–c–c–c	84.348
Friedelin (**10**)	c–c–c–b–b	89.255
	c–c–c–c–c	89.024

Abbreviations: c, chair; b, boat; tw, twist; hb, half boat.

Assignments of NMR Signals and Discussion

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

Olean-18-ene (1) The correct assignments of methyl proton signals were reported by us[2] using the solvent shift method. Carbon signals for C-1, 3, 4, 5, 7, 8, 9, 10, 13, 14, 15, 17, 18, 19, 20 and 21 were assigned from the HMBC spectrum with the H-23, 24, 25, 26, 27, 28, 29, 30 and 19 signals, without ambiguity. Confirmations of the carbon signals for C-16 and C-22 and assignments of other carbon signals (C-2, 6, 11 and 12) were established from the corresponding proton signals, which were confirmed by the H–H COSY spectra with the signals of proton(s) attached to the neighboring carbon(s). Assignments of all other methylene and methine protons were also confirmed by this method. The conformations of the compounds with minimum steric energy, simulated by Chem3D plus/MM2, are shown in Fig. 1, and all cross peaks observed in the NOESY spectrum except the peaks between two protons attached to the same carbon are also shown in Fig. 1. The signals for C-23 and 24, and C-29 and 30 were clearly distinguished by NOEs. The NOE peaks, observed between H-27 and H-29, 15α (δ 1.09) and 16α (δ 1.31); H-28 and H-30, 13, 15β (δ 1.79) and 16β (δ 1.37); H-29 and H-19; H-30 and H-19 and H-21β (δ 1.32); H-16α and H-22α (δ 1.47); and H-21α (δ 1.40) and H-22β (δ 1.40), strongly supported the chair–twist conformation of rings

TABLE II. ^{1}H-Chemical Shifts for Methyl and Olefinic Protons of Triterpenoid Hydrocarbons and a Ketone Belonging to the Oleanane and Migrated Oleanene Series (500 MHz, CDCl$_3$)

Compd. -ene	**1** 18	**2** 13(18)	**3** 12	**4** 14	**5** 9(11)	**6** 7	**7** 5(10)	**8** 5	**9** 3	**10** 3-one
H-23	0.846	0.860	0.870	0.849	0.845	0.850	0.960	1.001	1.554	0.877 (d, 6.7)
H-24	0.801	0.794	0.819	0.829	0.890	0.886	0.945	1.061	0.991	0.725
H-25	0.876	0.854	0.932	0.921	1.052	0.738	0.913	0.791	0.855	0.871
H-26	1.079	0.854	0.968	1.089	0.780	1.073	1.006	1.082	0.999	1.007
H-27	0.746	1.165	1.144	0.913	0.906 (d, 0.6)	1.097	1.009	1.001	0.995	1.050
H-28	1.019	1.007	0.833	0.821	1.049	1.056	1.183	1.158	1.172	1.180
H-29	0.937	0.699	0.870	0.950	0.971	0.975	0.945	0.951	0.943	0.954
H-30	0.941	0.932	0.870	0.910	0.979	0.967	0.999	0.986	0.995	1.001
C=CH (1H)	4.858 (dd, 1.4, 1.4)	—	5.188 (dd, 3.7, 3.7)	5.525 (dd, 6.0, 3.0)	5.300 (ddd, 5.5, 2.1, 2.1)	5.460 (ddd, 2.5, 2.4, 2.4)	—	5.526 (ddd, 6.1, 1.9, 1.9)	5.158 (s, $w\frac{1}{2}$h, 9.0)	

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

Table III. ^{1}H-Chemical Shifts for Methylene and Methine Protons of Triterpenoid Hydrocarbons and a Ketone Belonging to the Oleanane and Migrated Oleanane Series (500 MHz, $CDCl_3$)

Compd.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
-ene	18	13(18)	12	14	9(11)	7	5(10)	5	3	3-one
H-1	0.77; 1.69	0.83; 1.68	0.80; 1.57	0.80; 1.55	1.13; 1.88	0.93; 1.65	2.07; 2.05	1.68; 1.03	1.56; 1.38	1.96; 1.67
H-2	1.38; 1.61	1.39; 1.57	1.38; 1.57	1.36; 1.58	1.42; 1.48	1.45; 1.53	1.54; 1.38	1.55; 1.60	2.01; 2.01	2.39; 2.29
H-3	1.13; 1.36	1.17; 1.36	1.15; 1.36	1.12; 1.35	1.11; 1.37	1.16; 1.40	1.37; 1.40	1.36; 1.20	(5.16)	—
H-4	—	—	—	—	—	—	—	—	—	2.24; —
H-5	0.73	0.76	0.77	0.82	1.28	1.26	—	—	—	—
H-6	1.47; 1.32	1.50; 1.28	1.52; 1.35	1.58; 1.38	1.72; 1.56	2.13; 1.88	1.84; 1.92	(5.53)	1.24; 1.81	1.28; 1.75
H-7	1.33; 1.43	1.41; 1.41	1.32; 1.50	1.33; 2.00	1.60; 1.33	(5.46)	1.58; 1.52	1.80; 1.91	1.28; 1.46	1.33; 1.47
H-8	—	—	—	—	2.09	—	1.53	1.49	1.32	1.37
H-9	1.29	1.48	1.58	1.45	—	2.16	—	—	—	—
H-10	—	—	—	—	—	—	—	1.93	1.18	1.54
H-11	1.56; 1.25	1.47; 1.20	1.87; 1.87	1.62; 1.48	(5.30)	1.57; 1.39	1.37; 1.42	1.42; 1.50	1.18; 1.42	1.30; 1.45
H-12	1.17; 1.48	1.82; 2.64	(5.19)	1.63; 1.52	1.82; 1.56	1.62; 1.37	1.32; 1.32	1.34; 1.34	1.32; 1.32	1.40; 1.34
H-13	2.26	—	—	—	—	—	—	—	—	—
H-14	—	—	—	—	—	—	—	—	—	—
H-15	1.09; 1.79	1.06; 1.76	0.97; 1.76	(5.53)	1.48; 1.43	1.76; 1.67	1.46; 1.30	1.46; 1.33	1.47; 1.29	1.48; 1.33
H-16	1.31; 1.37	1.31; 1.31	1.99; 0.80	1.92; 1.64	1.35; 1.46	1.48; 1.48	1.36; 1.42	1.38; 1.52	1.35; 1.53	1.37; 1.55
H-17	—	—	—	—	—	—	—	—	—	—
H-18	—	—	1.95	0.95	1.45	1.45	1.55	1.57	1.53	1.54
H-19	(4.86)	2.27; 1.65	1.67; 1.02	0.97; 1.32	1.42; 1.24	1.45; 1.38	1.37; 1.21	1.38; 1.25	1.35; 1.21	1.36; 1.20
H-20	—	—	—	—	—	—	—	—	—	—
H-21	1.40; 1.32	1.44; 1.13	1.35: 1.10	1.32; 1.24	1.24; 1.53	1.23; 1.57	1.28; 1.43	1.25; 1.50	1.26; 1.48	1.28; 1.47
H-22	1.47; 1.40	1.38; 1.30	1.23; 1.40	1.01; 1.36	0.87; 1.53	0.87; 1.62	0.93; 1.52	0.92; 1.52	0.91; 1.50	0.94; 1.53

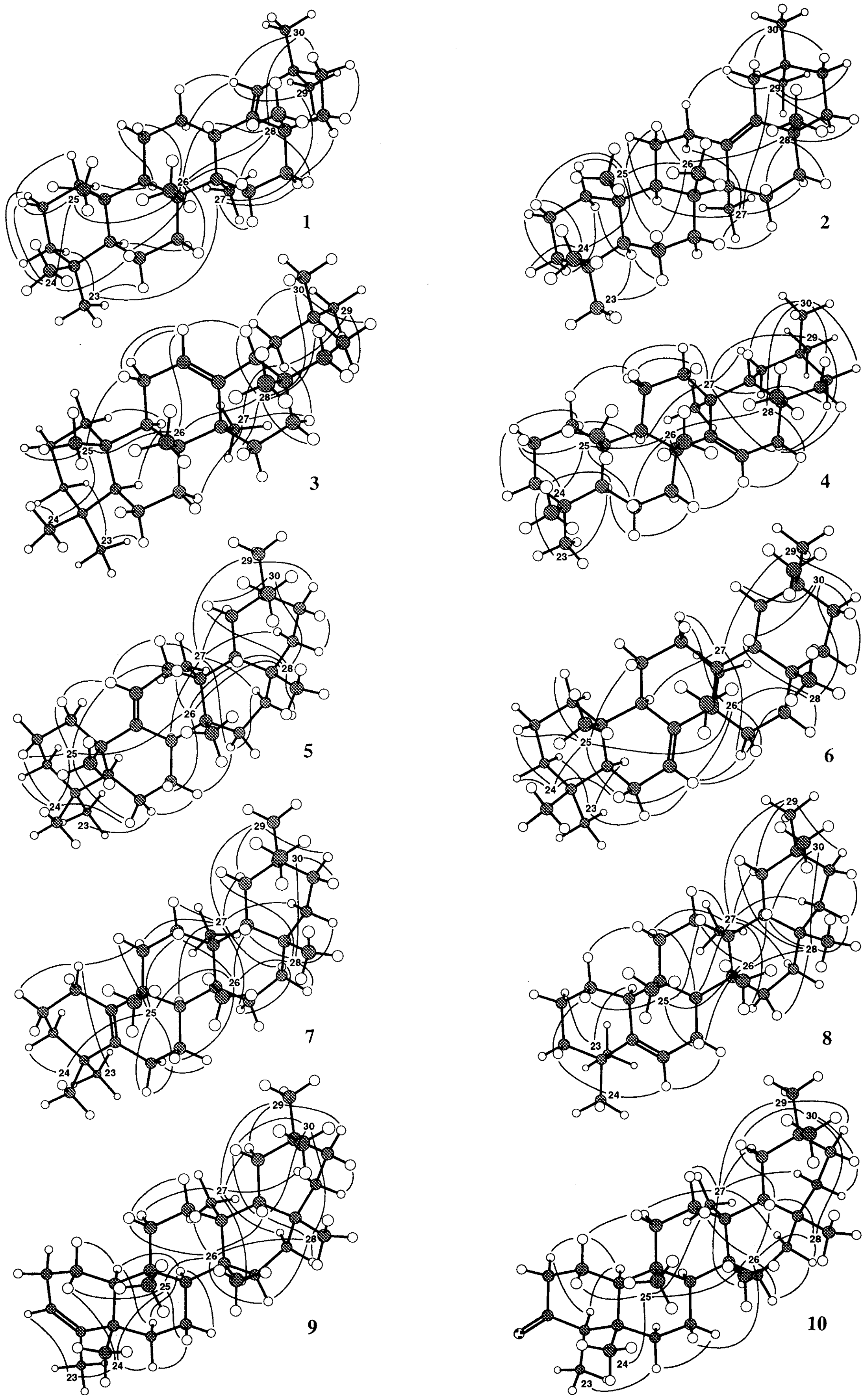
Methylene signals are listed as α-H; β-H in each column; assignments were confirmed by NOESY spectra, splitting pattern and a consideration of the relation to the double bond.

Table IV. ^{13}C-Chemical Shifts for Triterpenoid Hydrocarbons and a Ketone Belonging to the Oleanane and Migrated Oleanane Series (125 MHz, $CDCl_3$)

Compd.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
-ene	18	13(18)	12	14	9(11)	7	5(10)	5	3	3-one
C-1	40.51	40.43	40.22	39.39	41.37	39.01	26.79	26.04	17.48	22.28
C-2	18.73	18.67	18.53	18.45	19.54	19.08	18.57	21.88	27.18	41.52
C-3	42.14	42.07	41.99	42.11	42.44	42.37	39.87	40.83	120.30	213.22
C-4	33.32	33.23	33.11	33.10	33.62	33.03	33.80	35.69	144.34	58.21
C-5	56.65	56.42	56.13	56.59	44.87	50.71	132.35	145.20	38.47	42.14
C-6	18.60	18.73	18.67	19.11	19.72	24.56	24.55	117.57	38.96	41.28
C-7	34.57	34.81	32.66	41.38	17.93	117.81	20.05	23.37	18.17	18.24
C-8	43.40	41.22	39.99	39.20	43.30	147.67	48.01	47.45	53.02	53.10
C-9	51.31	50.79	47.68	49.33	151.08	48.91	37.49	34.75	37.10	37.44
C-10	37.57	37.59	37.21	38.31	37.94	35.35	137.91	51.10	56.93	59.46
C-11	20.99	21.65	23.54	17.50	115.69	17.08	31.42	34.70	35.23	35.62
C-12	26.31	25.11	121.99	33.82	38.80	36.25	31.02	30.48	30.62	30.50
C-13	38.41	134.61	145.12	37.57	35.86	36.99	38.21	37.88	38.36	38.29
C-14	40.99	44.71	41.77	158.45	37.44	41.63	39.48	39.31	39.75	39.69
C-15	27.49	26.47	26.11	116.62	30.67	31.67	32.28	32.12	32.32	32.42
C-16	37.77	39.42	26.97	37.74	36.04	36.62	36.05	36.07	36.09	36.00
C-17	34.39	34.56	32.51	35.81	31.60	30.97	30.06	30.11	30.05	29.99
C-18	142.90	132.93	47.26	48.75	43.87	46.84	42.67	43.11	42.87	42.78
C-19	129.64	38.65	46.84	36.68	35.01	34.60	35.44	35.10	35.34	35.34
C-20	32.36	33.31	31.09	28.81	28.47	28.23	28.16	28.27	28.18	28.16
C-21	33.38	35.46	34.75	33.12	33.70	33.89	32.81	33.15	32.83	32.76
C-22	37.42	36.69	37.17	35.14	36.22	36.07	39.34	38.98	39.27	39.24
C-23	33.35	33.45	33.45	33.37	32.81	33.05	28.01	29.79	17.96	6.83
C-24	21.58	21.65	21.77	21.63	21.68	21.49	29.09	29.73	20.72	14.65
C-25	16.68	16.34	15.46	15.37	25.10	13.14	20.99	16.25	18.32	17.95
C-26	16.17	17.77	16.88	25.99	18.42	27.14	20.56	19.64	20.09	20.26
C-27	14.60	21.38	26.04	21.31	18.12	26.22	18.81	18.44	18.60	18.66
C-28	25.30	23.78	28.42	29.83	30.02	30.95	32.15	32.05	32.12	32.09
C-29	31.36	24.09	33.36	33.37	33.14	33.68	35.07	34.54	35.03	35.03
C-30	29.23	32.37	23.71	29.93	34.00	34.12	31.76	32.42	31.84	31.78

D and E.

Olean-13(18)-ene (2) The appropriate assignments of methyl signals were reported by us.[2] Carbon signals for C-1, 3, 4, 5, 7, 8, 9, 10, 13, 14, 15, 17, 18 and 20 were assigned from the HMBC spectrum with the H-23, 24, 15, 26, 27, 28, 29 and 30 signals, without ambiguity.



1 2 3 4 5 6 7 8 9 10

Fig. 1. Chem 3D Plus Drawing and NOEs (−)

Discrimination of the signals for C-16 and C-22, and C-19 and 21, and assignments of other carbon signals for C-2, 6, 11, and 12 were based on by the corresponding proton signals, confirmed by the H–H COSY spectrum with the signals of proton(s) attached to the neighboring carbon(s), while signals for C-8 and 14 were difficult to assign because the HMBC method was not applicable. The conformation with minimum steric energy was obtained as shown in Fig. 1, and all cross peaks observed in the NOESY spectrum are also shown in Fig. 1. NOE peaks were found between H-27 and H-29, H-12α (δ 1.82) and H-16α (δ 1.31); H-28 and H-26, 15β (δ 1.76), 16β (δ 1.31) and 22β (δ 1.30); H-29 and H-19α (δ 2.27), 21α (δ 1.44) and 22α (δ 1.38); H-30 and H-19β (δ 1.65) and H-21β (δ 1.13). Thus, the twist–chair conformation of the rings D and E was clearly established.

Olean-12-ene (3) Our assignments of methyl protons[2] using the solvent shift method were found to be correct. As three methyl proton signals (C-23, 29 and 30) were superimposed, only the carbon signals for C-1, 3, 4, 5, 7, 9, 10, 13, 15, 17, 18 and 20 were unambiguously assigned from the HMBC spectrum with the remaining five methyl signals. Carbon signals for C-11, 12, 14, 17, 18 and 19 were firmly assigned from the HMBC spectrum with the H-12 olefinic proton signal. Other carbon signals (C-2, 6, 16 and 22) 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). The conformation of this compound with minimum steric energy was simulated as shown in Fig. 1, and all cross peaks observed in the NOESY spectrum are shown in the figure. As NOE peaks were observed between H-27 and H-16α (δ 1.99) and 19α (δ 1.67); H-28 and H-30, 15β (δ 1.76), 16β (δ 0.80), 18, 22β (δ 1.40); H-29 and H-19α and 21α (δ 1.35); and H-30 and H-19β (δ 1.02) and 21β (δ 1.10), the *cis*-fused D and E rings were indicated to be in the chair–chair conformation. The fact that the signals of 30-methyl (axial) were observed at higher field than those of 29-methyl (equatorial) is similar to the case of 24-methyl (axial) and 23-methyl (equatorial).

Taraxer-14-ene (4) Assignments of methyl protons for H-26 and H-27 published by us[2a] must be revised. Carbon signals for C-1, 3, 4, 5, 7, 8, 9, 10, 12, 13, 14, 15, 16, 17, 18, 20 and 22 were assigned from the HMBC spectrum with the H-23, 24, 25, 26, 27, 28, 29, 30 and 15, without ambiguity. Carbon signals for C-2, 6, 11, 19 and 21 were assigned from the corresponding proton signals, confirmed by the H–H COSY spectrum with the signals of protons(s) attached to the neighboring carbon(s). The conformation of this compound with minimum steric energy was simulated as shown in Fig. 1, and all cross peaks observed in the NOESY spectrum are also shown in the figure. NOE peaks were observed between H-27 and H-29, 19α (δ 0.97) and 19β (δ 1.32); H-28 and H-30; H-15 and 16β (δ 1.64); H-16α (δ 1.92) and H-21α (δ 1.32); H-18 and H-30; H-29 and H-21α; H-30 and H-21β (δ 1.24) and H-22β (δ 1.36). Thus, the twist–chair conformation of rings D and E was clearly demonstrated.

Multiflor-9(11)-ene (5) The correct assignment of methyl protons was reported by us.[2] Carbon signals for C-1, 3, 4, 5, 8, 9, 10, 11, 12, 13, 14, 15, 17, 18 and 20 were assigned from the HMBC spectrum with H-23, 24, 25, 26, 27, 28, 29, 30 and 11, without ambiguity. Distinction of signals for C-16 from 22, and 19 from 21, and assignments of C-2, 6, and 7 was based on the corresponding proton signals, confirmed by the H–H COSY spectrum with the signals of proton(s) attached to the neighboring carbon(s). The boat–boat conformation in the D and E rings was simulated as shown in Fig. 1, and all cross peaks observed in the NOESY spectrum are shown in the figure. NOE peaks, observed between H-26 and H-28 and 18; H-27 and H-29, 16α (δ 1.48), 19α (δ 1.42) and 22α (δ 0.87); H-28 and H-30, 18, and 19β; H-29 and H-21α (δ 1.24); and H-30 and H-19β, were more consistent with this conformation than that with the chair–chair form of the D and E rings.

Multiflor-7-ene (6) The assignment[2] of methyl protons based on the solvent shift method was found to be correct. Carbon signals for C-1, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13, 14, 15, 17, 18 and 20 were assigned from the HMBC spectrum with the H-23, 24, 25, 26, 27, 28, 29, 30 and 7, without ambiguity. Other carbon signals for C-2, 11, 16, 19, 21 and 22 were fixed or 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). The boat–boat conformation of the D and E rings in this compound was simulated as shown in Fig. 1, and all cross peaks observed in the NOESY spectrum are shown in the figure. NOE peaks, observed between H-26 and H-28 and 15β (δ 1.67); H-27 and H-29, 15α (δ 1.76) and 22α (δ 0.87); H-28 and H-16β (δ 1.48) and 18; H-29 and H-21α (δ 1.23); H-30 and H-18, 19β (δ 1.38) and 21β (δ 1.57), firmly supported the boat–boat conformation of rings D and E.

Glutin-5(10)-ene (7) Our published data[2b] for methyl proton signals, H-23, 25, 29 and 30, must be corrected. Carbon signals for C-3, 4, 5, 8, 9, 10, 11, 12, 15, 17, 18 and 20 were assigned from the HMBC spectrum with the H-23, 24, 25, 26, 27, 28, 29 and 30, without ambiguity. Distinction of signals for C-16 from 22, and 19 from 21, and assignments of C-1, 2, 6, and 7 were established by the corresponding proton signals, confirmed by the H–H COSY spectrum with the signals of proton(s) attached to the neighboring carbon(s). Specification of the signals of C-13 and 14 was difficult in the case of compounds **7**—**10**, because the HMBC method is not applicable. Comparing the fixed signals of C-13 (δ 35.86) of **5** and C-14 (δ 41.63) of **6**, the C-13 signals of **7**—**10** might also be observed at higher field than the C-14 signals. The boat–boat conformation of the D and E rings in this compound was simulated as shown in Fig. 1, and all cross peaks observed in the NOESY spectrum are shown in the figure. NOE peaks, observed between H-26 and H-28 and 18; H-27 and H-29, 16α (δ 1.36), 19α (δ 1.37) and 22α (δ 0.93); H-28 and H-30, 16β (δ 1.42), 18, 19β (δ 1.21) and 22β (δ 1.52); and H-29 and H-19α and 21α (δ 1.28), were more consistent with this conformation than with the chair–chair form of the D and E rings.

Glutin-5-ene (8) Assignments of the methyl protons for C-26 and C-27 reported by us[2b] must be revised. Carbon signals for C-3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 15, 17, 18 and 20 were assigned from the HMBC spectrum with H-23, 24, 25, 26, 27, 28, 29, 30 and 6, without ambiguity.

Distinction of signals for C-16 from 22, and 19 from 21, and assignments of C-1 and 2 were established by the corresponding proton signals, confirmed by the H–H COSY spectrum with the signals of proton(s) attached to the neighboring carbon(s). The boat–boat conformation of the D and E rings in this compound was simulated as shown in Fig. 1, and all cross peaks observed in the NOESY spectrum are shown in the figure. NOE peaks, observed between H-26 and H-28 and 18; H-27 and H-29, 15α (δ 1.46), 16α (δ 1.38), 19α (δ 1.38) and 22α (δ 0.92); H-28 and H-30, 15β (δ 1.33), 18 and 19β (δ 1.25); and H-30 and H-18, were more consistent with this conformation than with the chair–chair form of the D and E rings. The conformation of ring A is different from those of **1**—**7**.

Friedel-3-ene (9) Assignments of methyl protons reported by us[2)] were found to be correct. Carbon signals for C-1, 2, 4, 5, 6, 8, 9, 10, 11, 12, 15, 17, 18 and 20 were assigned from the HMBC spectrum with the H-23, 24, 25, 26, 27, 28, 29, 30 and 3, without ambiguity. Distinction of signals for C-16 from 22, and 19 from 21, and assignments of C-7 were based on the corresponding proton signals, confirmed by the H–H COSY spectrum with the signals of proton(s) attached to the neighboring carbon(s). The boat–boat conformation of the D and E rings in this compound was simulated as shown in Fig. 1, and all cross peaks observed in the NOESY spectrum are shown in the figure. NOE peaks, observed between H-26 and H-28, 15β (δ 1.29) and 18; H-27 and H-29, 16α (δ 1.35), 19α (δ 1.35) and 22α (δ 0.91); H-28 and H-30, 15β and 18; H-29 and H-19α and 21α (δ 1.26); H-30 and H-19β (δ 1.21); and H-18 and H-19β, were more consistent with this conformation than with the chair–chair form of the D and E rings.

Friedelin (10) The structure of **10** was first established by Corey and Ursprung,[3)] but the conformation proposed is not believed to be correct in the crystalline state.[6,8a)] Although many reports has dealt with assignments of the ^{1}H- and ^{13}C-NMR signals, even the latest[13)] differes in part from ours. Carbon signals for C-4, 5, 6, 8, 9, 10, 11, 12, 15, 17, 18 and 20 were assigned from the HMBC spectrum with H-23, 24, 25, 26, 27, 28, 29 and 30, without ambiguity. Distinction of signals for C-16 from 22, and 19 from 21, and assignments of C-1, 2 and 7 were based on the corresponding proton signals, confirmed by the H–H COSY spectrum with the signals of proton(s) attached to the neighboring carbon(s). Assignments of C-13 and 14 were made according to those of **7**—**9**. The boat–boat conformation of the D and E rings in this compound was simulated as shown in Fig. 1, and all cross peaks observed in the NOESY spectrum are shown in the figure. NOE peaks, observed between H-26 and H-28, 15β (δ 1.33) and 18; H-27 and H-29, 16α (δ 1.37), 19α (δ 1.36) and 22α (δ 0.94); H-28 and H-30 and 16β (δ 1.55); H-29 and H-19α and 21α (δ 1.28); H-30 and H-19β (δ 1.20) and 21β (δ 1.47); and H-18 and H-19β, are more consistent with this conformation than with the chair–chair form of the D and E rings.

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