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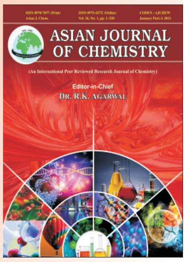

^{1}H and ^{13}C NMR Spectra of Natural Products Laurene-Type Sesquiterpenes: Theoretical and Experimental Studies

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Quantum chemical calculations for geometrical optimization of the natural products laurene-type sesquiterpenes, 12-hydroxy isolaurene (**1**), 8,11-dihydro-12-hydroxy isolaurene (**2**) and isolauraldehyde (**3**) isolated from the red alga *Laurencia obtusa* using density functional theory (DFT) were carried out. A comparable study between experimental ^{1}H and ^{13}C NMR spectral data and calculated with DFT and *ab initio* Hartree-Fock (HF) methods were used to confirm the spectral data assignments of compounds **1-3**. The calculated NMR spectral data showed good agreement with the experimental data supporting the obtained geometries. Among the studied methods, DFT/B3LYP method is most convenient one for prediction of ^{1}H and ^{13}C NMR spectra of such compounds.

Keywords: Terpenoids, Isolaurenes, NMR spectroscopy, DFT/B3LYP, DFT/LSDA, *ab initio* Calculation.

INTRODUCTION

^{1}H NMR and ^{13}C NMR are essential and one of the most powerful techniques used in structural elucidation of natural products having several stereoisomers. These compounds can be definitely distinguished by either their NMR spectra or through direct comparison of chemical shifts and coupling constants. Sometimes, this kind of difficulty leads even experienced and skilful researchers to make mistakes, reporting erroneous structures for newly isolated compounds[1]. Theoretical calculation of chemical shift has been under development for over three decades[2] and has achieved a high degree of agreement to experimental data. To solve a common difficulty in the calculation of magnetic properties, the gauge origin problem[3] several methods were developed, the most used one is the gauge-including atomic orbital (GIAO) method[4-6].

Laurene-type sesquiterpenes are aryl cyclopentanes substituted with three methyl groups in 1, 2 and 3 fashion. In addition to laurenes, two closely similar sesquiterpene families, cuparenes and laurokamurenes, differ from each other only in the methylation pattern (1,2,2 and 2,2,3 for cuparenes and laurokamurenes, respectively)[7]. Recently, three laurene-type sesquiterpenes, 12-hydroxy isolaurene (**1**), 8,11-dihydro-12-hydroxy isolaurene (**2**) and isolauraldehyde (**3**) were isolated previously by our group from the red alga *Laurencia obtusa*[7]. The chemical structures of isolates were determined by interpretation of their spectral data (1D and 2D NMR, UV, IR and MS).

To our best of knowledge, no paper reports for modeling and predicting the NMR spectra of laurene-type sesquiterpenes. In this study, we use the GIAO method to calculate chemical shifts for the three new laurenes (**1-3**) as a valuable aid to confirm the correct assignment of the structures of the natural products.

EXPERIMENTAL

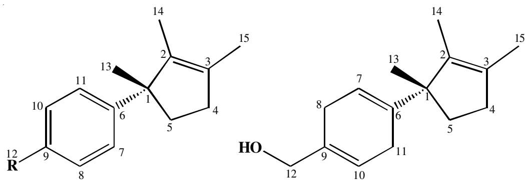
The three laurene-type sesquiterpenes, 12-hydroxy isolaurene (**1**), 8,11-dihydro-12-hydroxy isolaurene (**2**) and isolauraldehyde (**3**) were isolated and purified as previously reported[7]. The ^{1}H NMR spectra were recorded on Bruker AVANCE III WM 600 MHz spectrometers and ^{13}C NMR at 150 MHz. Chemical shifts are given in δ (ppm) relative to TMS as internal standard.

Computational details: Quantum chemical calculations used for geometry optimization of compounds **1-3** were carried out by Gaussian 03 W suite program[8] using density functional theory (DFT) at Becke3-Lee-Yang-Parr (B3LYP) with 6-311++G (d,p) basis set. For NMR calculations, after optimization,

^{1}H and ^{13}C NMR isotropic shielding constants were calculated in chloroform utilizing polarizable continuum model (PCM) with the gauge-invariant atomic orbital (GIAO) method[9] which is one of the most common approaches for calculating nuclear magnetic shielding tensors at *ab initio* Hartree-Fock (HF) and DFT levels using both Becke3-Lee-Yang-Parr (B3LYP)[10-12] and Local-Spin Density Approximation (LSDA)[13-16] exchange-correlation functional with standard 6-311++G (d,p) basis set. The isotropic shielding constants were used to calculate the isotropic chemical shifts (δ) with respect to tetramethylsilane by the relation $\delta_{iso} = \sigma_{TMS} - \sigma_{iso}$, where δ_{iso} isotropic chemical shift and σ_{TMS} isotropic shielding constant. The spectral data (^{1}H and ^{13}C NMR) were assigned by means of visual inspection using the GAUSS VIEW program[17].

RESULTS AND DISCUSSION

Geometrical structure parameters: The petroleum ether extract of the red alga *Laurencia obtusa* afforded three new sesquiterpenes which identified as 12-hydroxy isolaurene (**1**), 8,11-dihydro-12-hydroxy isolaurene (**2**) and isolaureldehyde (**3**)[7] (Fig. 1). Since the isolated laurene-type sesquiterpenes are oil and could not be obtained in a single crystal, geometrical optimization were carried out to at DFT/B3LYP level and the optimized structures are shown in Fig. 2.



1 R = CH_2OH
3 R = CHO
2

Fig. 1. Structures of compounds **1-3**

The comparison between optimized structures parameters of compounds **1-3** indicates that (Tables 1-2):

(i) The bond angle data show deviation from the ideal values of sp^3 and sp^2 hybridization by 5° (for C-1, C-4 and C-5) and 10° (for C-2 and C-3), respectively. Also, the dihedral angle data clearly indicate that the cyclopentene ring is not planer where C-5 lies below the plane of the other four carbon atoms in all compounds.

(ii) Compounds **1** and **3** contain a phenyl ring and so all carbon atoms have sp^2 hybridization with 120° for C-6- to C-11 but the bond angle data displayed a little angle distortion (0.8-2.5°). On the other hand, the compound **2** contains cyclohexdiene ring and so only C-8 and C-11 have sp^3 hybridization which showed more angle distortion than other C-atoms (5 and 1.5°, respectively).

(iii) In all compounds, the six and five membered ring are not co-planar where the five membered ring is tilted on the six membered ring as shown from the dihedral angles C7-C6-C1-C2 and C11-C6-C1-C2 are 50° while both C7-C6-C1-C5 and C11-C6-C1-C5 are 63°.

(iv) The C-13 bonded to C-1 showing almost ideal bond angle values (109.5°) as the angles C13-C1-C2, C13-C1-C5 and C13-C1-C6 are 108.90°, 109.55° and 112.60°, respectively. Meanwhile, C-13 is above the six membered ring by 8° and the five membered ring by 105°. On contrary, carbon atoms 14 and 15 which bonded to C-2 and C-3, respectively, with bond angles C14-C2-C1 (120.25°), C14-C2-C3 (127.50°), C15-C3-C2 (128.40°) and C15-C3-C4 (119.60°), are almost in the same plane of the five membered ring and below the C-13 plane as shown in the dihedral angles values (C13-C1-C2-C14-71.31°).

(v) For alcoholic branch (-CH_2OH), the dihedral angle data clearly showed that the C-12 is in the same plane of the

TABLE-1
SELECTED BOND ANGLE (°) AND DIHEDRAL ANGLE (°) DATA OF COMPOUNDS 1-3

Bond angle	Compound **1**	Compound **2**	Compound **3**	Dihedral Angle	Compound **1**	Compound **2**	Compound **3**
O-C12-C9	108.80	115.46	125.10	C10-C9-C12-O	81.61	-7.94	179.81
C6-C11-C10	121.56	114.80	120.94	C8-C9-C12-O	-97.17	172.63	-0.02
C11-C10-C9	120.83	124.32	120.67	C11-C10-C9-C12	-178.59	-179.71	-179.80
C8-C9-C10	118.02	121.44	118.95	C12-C9-C8-C7	178.84	-179.33	179.92
C7-C8-C9	121.10	114.11	120.08	C10-C9-C8-C7	0.03	1.23	0.09
C6-C7-C8	121.23	125.11	121.60	C7-C6-C11-C10	-0.23	0.48	0.25
C11-C6-C7	117.26	120.21	117.76	C11-C10-C9-C8	0.23	-0.31	0.03
C12-C9-C8	121.18	115.31	121.22	C8-C7-C6-C11	0.49	0.53	-0.13
C12-C9-C10	120.79	123.25	119.83	C9-C10-C11-C6	-0.12	-0.59	-0.21
C5-C1-C6	111.19	111.34	110.49	C9-C8-C7-C6	-0.39	-1.37	-0.04
C2-C1-C6	112.25	111.34	111.13	C1-C2-C3-C4	0.96	0.47	0.92
C1-C6-C11	119.31	116.31	123.16	C2-C3-C4-C5	13.03	7.07	4.20
C1-C6-C7	123.43	123.48	119.07	C3-C4-C5-C1	-21.18	-11.42	-7.36
C5-C1-C2	101.88	102.57	102.84	C2-C1-C5-C4	21.31	11.44	7.70
C3-C2-C1	111.82	112.50	112.50	C5-C1-C2-C3	-14.21	-7.61	-5.49
C4-C3-C2	111.77	112.16	112.38	C11-C6-C1-C13	172.94	173.62	-9.91
C4-C5-C1	105.74	106.72	106.83	C7-C6-C1-C13	-7.33	-6.33	171.12
C5-C4-C3	103.81	104.61	104.83	C13-C1-C2-C14	-74.23	-68.39	-66.20
				C14-C2-C3-C15	-0.41	-0.87	-0.17
				C13-C1-C2-C3	101.58	108.27	111.49
				C13-C1-C5-C4	-93.85	-104.16	-109.01
				C14-C2-C3-C4	176.39	176.83	178.41
				C5-C1-C2-C14	169.99	175.72	176.81
				C15-C3-C4-C5	-169.85	-174.99	-177.09
				C1-C2-C3-C15	-175.85	-177.24	-177.65

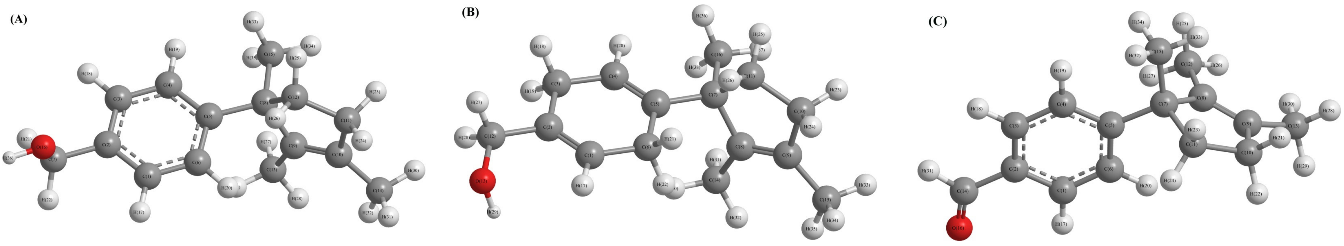


Fig. 2. DFT optimized structures of compounds **1** **(A)**, **2** **(B)** and **3** **(C)**

TABLE-2
SELECTED DFT BOND LENGTH (Å) DATA OF COMPOUNDS **1-3**

Bond	Compound **1**	Compound **2**	Compound **3**	Bond	Compound **1**	Compound **2**	Compound **3**
O-H	0.963	0.963	-	C1-C2	1.541	1.539	1.538
C15-H	1.091	1.091	1.090	C1-C5	1.565	1.570	1.573
C15-H	1.097	1.096	1.096	C1-C13	1.545	1.544	1.544
C15-H	1.097	1.097	1.097	C2-C3	1.342	1.340	1.341
C14-H	1.091	1.091	1.095	C2-C14	1.500	1.502	1.501
C14-H	1.095	1.095	1.091	C3-C4	1.513	1.512	1.510
C14-H	1.096	1.096	1.096	C3-C15	1.499	1.499	1.499
C13-H	1.093	1.093	1.093	C4-C5	1.541	1.545	1.546
C13-H	1.093	1.093	1.093	C6-C1	1.534	1.535	1.536
C13-H	1.094	1.093	1.094	C6-C7	1.398	1.337	1.409
C12-H	1.097	1.096	1.110	C6-C11	1.405	1.516	1.399
C12-H	1.098	1.101	-	C7-C8	1.396	1.505	1.384
C12-O	1.437	1.421	1.200	C9-C8	1.393	1.507	1.403
C11-H	1.085	1.099	1.082	C9-C10	1.399	1.333	1.396
C10-H	1.086	1.087	1.086	C9-C12	1.505	1.511	1.475
C8-H	1.086	1.101	1.084	C10-C11	1.388	1.503	1.394
C7-H	1.082	1.084	1.085				
C5-H	1.091	1.090	1.091				
C5-H	1.093	1.092	1.092				
C4-H	1.096	1.097	1.097				
C4-H	1.099	1.099	1.098				

six membered ring (C11-C10-C9-C12 and C12-C9-C8-C7 ~180°) while the oxygen atom of is out of the plane where C10-C9-C12-O and C8-C9-C12-O are 82.0° for compound **1** and 7.5° for compound **2**.

(vi) In compound **3**, the aldehyde group (-CHO) clearly planar with the phenyl ring where the dihedral angle C10-C9-C12-O and C8-C9-C12-O-80°

(vii) Generally, the bond length data show good agreement with ideal values for C-H and slightly less for C-C bonds (average difference ± 0.024 and ± 0.850 Å for compound **1**, ± 0.014 Å and ± 0.026 Å for compound **2**, respectively)[18].

^{1}H NMR spectra: The chemical shifts are frequently used as an aid in identification of different chemical species. The ^{1}H NMR spectrum of compound **1** showed three sets of signals as shown in Fig. 3. The first set appeared in the region 1.13-2.35 ppm in which the methyl groups (C-atom 13, 14 and 15) displayed broad signals at 1.36, 1.44 and 1.72 ppm, respectively, in addition to two multiplet at 1.90 and 2.30 ppm attributed to carbon atom no. 5 and 4, respectively. The spectral data compounds **2** and **3** clearly indicate that the methyl groups and carbon atoms protons appeared at more or less same position of compound **1** (Table-3).

The 2nd set appeared in the region 4-5 ppm and displayed a singlet signal at 4.62 ppm for two protons attributed to the CH_2 alcoholic group (C-12) while it appeared at 4 ppm in the spectrum of compound **2** (Fig. 4). On contrary, the spectrum

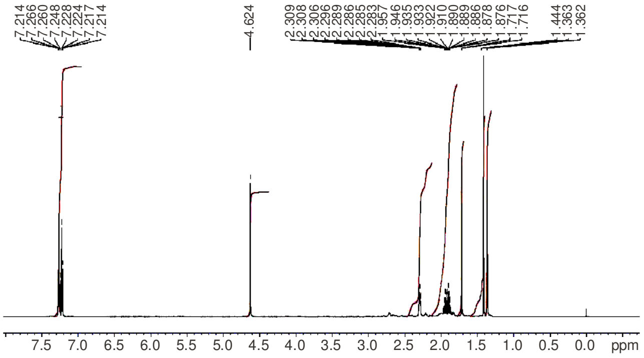


Fig. 3. ^{1}H NMR spectrum of Compound **1**

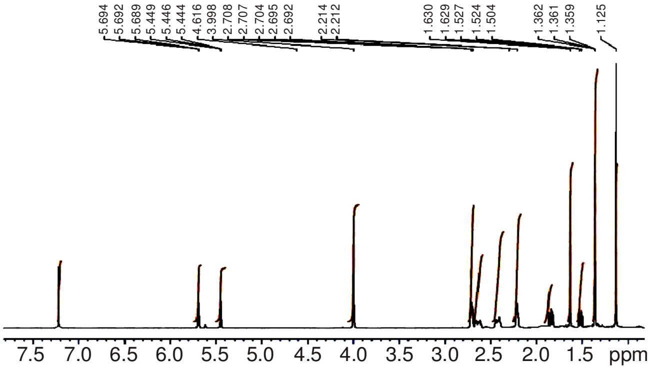


Fig. 4. ^{1}H NMR spectrum of Compound **2**

TABLE-3
EXPERIMENT AND CALCULATED ^{1}H-NMR CHEMICAL SHIFTS OF COMPOUNDS **1-3**.

C-atom No	Exper.	HF	DFT	
			B3LYP	LSDA
Compound 1				
4	2.30	1.95	2.46	3.26
5	1.91	1.55	1.95	2.69
7	7.27	7.39	7.64	8.44
8	7.21	7.46	7.68	8.38
10	7.21	7.60	7.75	8.42
11	7.27	7.35	7.52	8.27
12	4.62	4.14	4.69	5.48
13	1.36	1.10	1.36	2.00
14	1.44	1.00	1.26	1.89
15	1.72	1.52	1.74	2.35
Compound 2				
4	2.21	1.87	2.38	3.16
5	1.83, 1.52	1.42, 1.03	1.91, 1.37	2.64, 2.09
7	5.45	5.52	5.79	6.5
8	2.70, 2.66	2.1, 2.08	2.73, 2.68	3.54, 3.50
10	5.69	5.69	5.98	6.63
11	2.62, 2.40	2.17, 1.73	2.89, 2.37	3.75, 3.21
12	4.00	3.51	4.14	4.96
13	1.13	0.99	1.11	1.86
14	1.36	1.08	1.33	1.94
15	1.63	1.40	1.66	2.28
Compound 3				
4	2.34, 2.30	2.08, 2.07	2.64, 2.55	3.46, 3.36
5	1.95, 1.88	1.56, 1.51	1.94, 1.93	2.74, 2.67
7	7.40	7.48	7.52	8.47
8	7.80	7.96	8.20	8.52
10	7.80	8.39	7.78	8.83
11	7.40	7.35	7.71	8.32
12	9.98	9.37	10.05	10.92
13	1.36	1.20	1.46	2.09
14	1.45	1.02	1.29	1.92
15	1.72	1.54	1.80	2.36

of compound **3** does not show signals at this region which indicates absence of alcoholic group.

The 3rd set in compound **1** spectrum appeared in the region 7-8 ppm showing two doublet signals for four protons attributed to the aromatic protons (C-7 and C-11 at 7.27 ppm, C-8 and C-10 at 7.27 ppm). The compound **3** spectrum showed the same feature as that of compound **1** with little downfield shift of aromatic protons as shown in Table-3 (Fig. 5). On the other hand, the compound **2** spectrum does not exhibit signals in this region but showed another four multiplet signals at 2.40, 2.70, 5.45 and 5.69 ppm attributed the cyclohexadiene ring. Moreover, the spectrum of compound **3** displayed a signal at 9.98 ppm assigned to the aldehydic proton (C-12).

Calculated ^{1}H NMR spectral data of the optimized structure for isolated laurene-type sesquiterpenes **1-3** are shown in Table-3 in comparison with the experimental data. The experimental and calculated spectral data showed good agreement. Examination of the relationship between the experimental and the calculated chemical shifts shows good linear relationship which expressed by the general equation, $\delta_{exp.} = a\ \delta_{Calcd} + b$ as shown in Fig. 6. The values of intercept (b), slope (a) and regression coefficient (R^2) of the linear fitting are shown in Table-4. Generally, the data confirms the good linearity where the linear fit has slope values near to unity (1.0136-1.0931), intercept in the range 0.0637-0.7481 and regression coefficient ranged from 0.9817 to 0.9984. On comparison of the values of different methods, it is obviously noted that the DFT/B3LYP method is the most coincided one than other methods where it show a, b and R^2 values 0.0637-0.1361, 1.0136-1.0777 and 0.9965-0.9984, respectively.

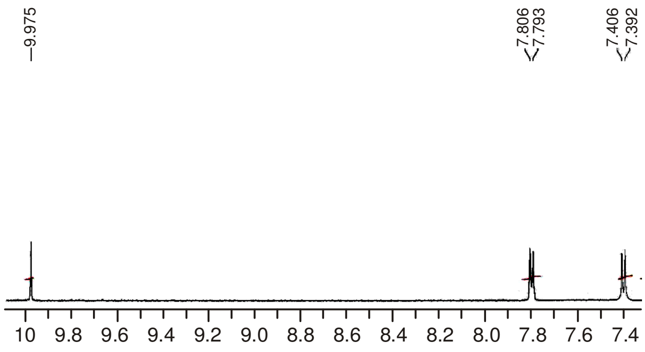


Fig. 5. ^{1}H NMR spectrum of Compound **3**

^{13}C NMR spectra: The ^{13}C NMR spectrum of compound **1** shows three signals at 24.2, 10.3 and 14.3 ppm attributed to the carbon of methyl branches (C-13, C-14 and C-15), respectively. Also, the spectrum displayed five signals at 54.8, 137.1, 132.1, 35.8 and 41.5 ppm assigned to the carbon atoms of the cyclopentene ring (C-1, 2, 3, 4 and 5, respectively). On comparison with spectra of the other two compounds, it is clear that the methyl and cyclopentene carbons signals appeared at more or less the same position (Table-5).

Moreover, the compound **1** spectrum displayed a signal at 65.2 ppm assigned to the alcoholic carbon (C-12) which shown at 66.8 in compound **2** spectrum while the spectrum of compound **3**, no signal observed in this region but a new one at 192.1 ppm is observed and attributed to aldehydic carbon (C-12) (Fig. 7-9). Both of compound **1** and **3** spectra are almost coincided with each other in the region from 126 to 149 ppm in which six signals were observed and attributed to the carbon atoms of the phenyl ring. On the other hand, the spectrum of compound **2** showed only four signals at 116.4, 121.1, 135.9 and 139.7 ppm in addition to two signals at 22.7 and 26.2 ppm which were attributed to C-7, C10, C-6, C-9, C-8 and C-11, respectively, confirming the existence of cyclohexadiene ring.

TABLE-4
LINEAR RELATIONSHIP PARAMETERS BETWEEN EXPERIMENT AND DFT CALCULATED ^{1}H-NMR DATA

Compounds	Compound **1**			Compound **2**			Compound **3**		
	B3LYP	LSDA	HF	B3LYP	LSDA	HF	B3LYP	LSDA	HF
A	1.0733	1.0837	1.0931	1.0777	1.0780	1.0688	1.0136	1.0244	1.0378
B	-0.1361	0.5327	-0.5190	-0.1226	0.6243	-0.5408	0.0637	0.7481	-0.3221
R^2	0.9984	0.9981	0.9962	0.9965	0.9930	0.9817	0.9976	0.9968	0.9918

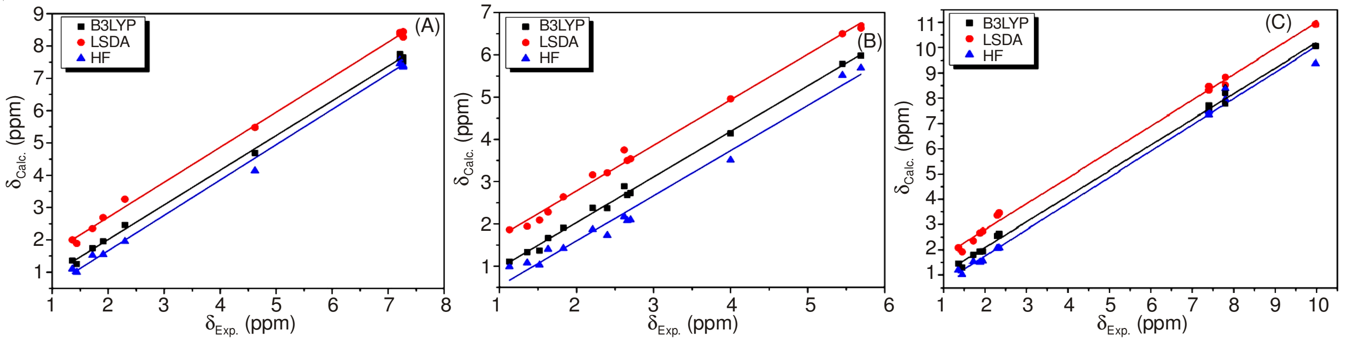


Fig. 6. A linear regression plot of experimental and calculated ^{1}H NMR spectral data of compound **1 (A)**, compound **2 (B)** and compound **3 (C)**

TABLE-5
EXPERIMENT AND CALCULATED ^{13}C-NMR CHEMICAL SHIFTS OF COMPOUNDS **1-3**

C-atom No.	Exper.	HF		DFT			
		Calc	Scaled	B3LYP		LSDA	
				Calc	Scaled	Calc	Scaled
Compound **1**							
1	54.80	39.32	37.65	62.10	59.30	66.57	63.54
2	137.20	135.23	128.77	148.15	141.04	150.96	143.71
3	132.10	129.36	123.19	141.64	134.86	144.99	138.04
4	35.80	22.52	21.69	38.90	37.26	40.73	38.99
5	41.50	30.24	29.03	46.57	44.54	48.36	46.24
6	148.90	147.36	140.29	158.37	150.75	162.01	154.21
7	126.50	120.39	114.67	129.75	123.56	132.72	126.38
8	127.10	125.29	119.33	134.62	128.19	138.13	131.52
9	137.80	132.25	125.94	142.71	135.87	144.36	137.44
10	127.10	126.71	120.67	135.32	128.85	138.75	132.11
11	126.50	125.45	119.48	134.06	127.66	136.44	129.92
12	65.20	50.16	47.95	69.28	66.12	72.50	69.18
13	24.20	10.54	10.31	21.53	20.75	20.47	19.75
14	10.30	-1.22	-0.86	10.36	10.14	9.65	9.47
15	14.30	2.85	3.01	14.71	14.27	14.18	13.77
Compound **2**							
1	55.40	39.82	38.13	63.04	60.19	67.64	64.56
2	134.20	132.96	126.61	146.15	139.14	148.87	141.73
3	131.70	129.18	123.02	141.42	134.65	144.58	137.65
4	35.90	22.69	21.86	39.73	38.04	41.58	39.80
5	36.20	21.04	20.29	36.44	34.92	37.36	35.79
6	135.90	137.71	131.12	151.00	143.75	154.52	147.09
7	116.40	112.71	107.37	123.24	117.38	125.79	119.80
8	22.70	14.35	13.93	31.25	29.99	33.11	31.75
9	139.70	130.91	124.66	143.95	137.05	146.88	139.84
10	121.10	111.19	105.93	121.01	115.26	122.56	116.73
11	26.20	12.48	12.16	29.31	28.14	31.10	29.85
12	66.80	49.59	47.41	69.37	66.20	72.70	69.37
13	23.90	12.76	12.42	24.38	23.46	23.57	22.69
14	10.00	-1.25	-0.89	10.55	10.32	9.74	9.55
15	14.40	2.69	2.86	14.61	14.18	14.13	13.72
Compound **3**							
1	55.00	40.64	38.91	63.96	61.06	68.85	65.71
2	137.00	133.45	127.08	147.02	139.97	150.12	142.91
3	133.00	130.6	124.37	142.52	135.69	145.57	138.59
4	35.90	22.88	22.04	40.25	38.54	42.10	40.30
5	41.40	27.61	26.53	44.00	42.10	45.49	43.52
6	143.00	159.50	151.83	168.74	160.60	172.26	163.95
7	127.00	117.88	112.29	133.58	127.20	133.21	126.85
8	129.70	132.90	126.56	131.10	124.85	142.74	135.90
9	134.40	125.55	119.57	138.67	132.04	141.62	134.84
10	129.70	125.73	119.74	139.79	133.10	132.94	126.59
11	127.00	122.65	116.82	129.69	123.51	136.64	130.11
12	192.10	183.88	174.99	193.76	184.37	200.01	190.31
13	24.00	13.28	12.92	25.14	24.18	24.45	23.53
14	10.30	-1.27	-0.91	10.56	10.33	9.98	9.78
15	14.10	2.76	2.92	14.63	14.20	14.16	13.75

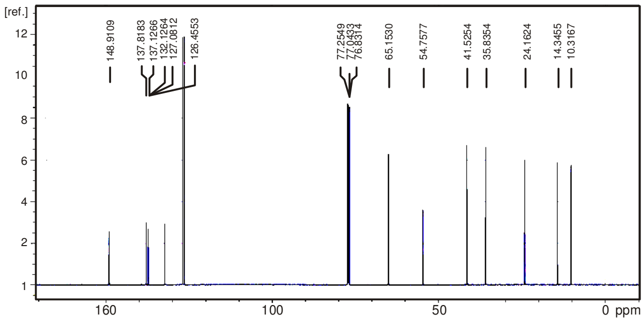


Fig. 7. ^{13}C NMR spectrum of Compound **1**

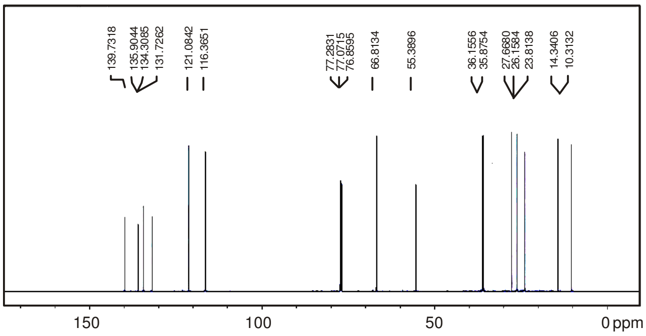


Fig. 8. ^{13}C NMR spectrum of Compound **2**

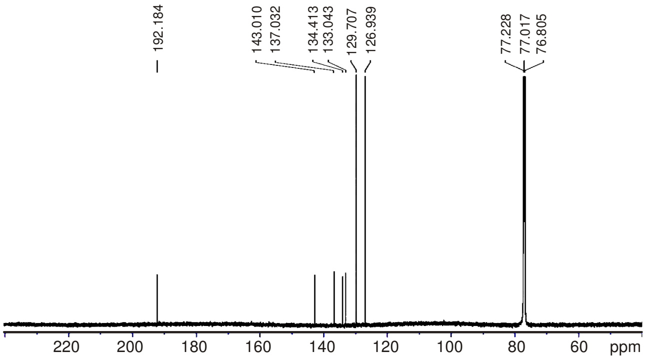


Fig. 9. ^{13}C NMR spectrum of Compound **3**

The comparison of the calculated and experimental ^{13}C NMR spectral data of compounds **1-3** indicates that the DFT/B3LYP data is more coincided with experimental than DFT/LSDA and HF methods (Table-5). The root mean square (RMS) and mean absolute deviation (MAD) values confirm that the DFT/B3LYP is more agreed than the others where it has RMS = 6.48-8.70 ppm and MAD = 3.17-4.66 ppm, while the other methods have 9.02-11.14, 4.28-5.45 and 9.33-10.92, 4.52-5.82 ppm, respectively (Table-6).

Predictions of ^{13}C shifts are rather poor than relatively accurate values of ^{1}H chemical shifts were achieved using this technique. So, linear scaling of the calculated ^{13}C chemical shifts is used in order to account for the differences in the conditions of the experimental measurements and computational predictions, as well as for possible systematic errors either at the geometry optimization or NMR stages of the calculations. For the calculation of the linearly scaled values of the ^{13}C chemical shift, the following equation was used[19,20]: $\delta_{scalc} = 0.95\ \delta_{calc} + 0.30$. As shown in Table-6, applying scaling procedure on the calculated data leads to improvement in the root mean square (RMS) and mean absolute deviation (MAD) values by about two folds. According to the RMS and MAD values, methods may be ordered as DFT/B3LYP, DFT/LSDA and HF, respectively, according to its agreement with the experimental data.

A comparison of linear relationship between the experimental and both of calculated and scaled calculated ^{13}C NMR chemical shifts showed a good linearity which could be expressed by the equation, $\delta_{exp.} = a\ \delta_{Calcd} + b$. Comparison of the linear relationship parameters, slope (a), intercept (b) and linear regression (R^2) for calculated data indicate i) the good linearity of both scaled and unscaled data, ii) but the scaled is more linear than unscaled, iii) confirms that DFT/B3LYP data is most agreed with the experimental data (Fig. 10).

Conclusion

The study of the calculation of chemical shifts by *ab initio* and DFT methods is a convenient aid in the structure elucidation of laurene-type sesquiterpenes **1-3** showing good correlation between calculated and experimental data. The DFT/B3LYP method is the most convenient method than other those for prediction of ^{1}H and ^{13}C NMR. The calculated ^{1}H NMR chemical shifts show more coincidence with the experi-mental data than ^{13}C NMR. Thus, the NMR calculation can reinforce the structure elucidation.

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TABLE-6
LINEAR RELATIONSHIP PARAMETERS BETWEEN EXPERIMENT AND CALCULATED ^{13}C NMR DATA*

Linear Parameter	Compound **1**			Compound **2**			Compound **3**		
	B3LYP	LSDA	HF	B3LYP	LSDA	HF	B3LYP	LSDA	HF
A	1.0588 (1.0059)	1.0809 (1.0268)	1.0946 (1.0399)	1.0536 (1.0009)	1.0734 (1.0197)	1.0768 (1.0229)	1.0439 (0.9917)	1.0700 (1.0165)	1.0785 (1.0246)
B	0.1182 (0.4123)	0.3762 (0.6574)	-15.7825 (-14.6934)	1.1718 (1.4132)	1.6736 (1.8899)	-14.9232 (-13.8770)	1.7957 (2.0059)	1.7478 (1.9604)	-13.8759 (-12.8821)
R^2	0.9980 (0.9980)	0.9962 (0.9962)	0.9974 (0.9974)	0.9945 (0.9945)	0.9925 (0.9925)	0.9943 (0.9943)	0.9896 (0.9896)	0.9891 (0.9891)	0.9884 (0.9884)
RMS	6.48 (2.42)	9.10 (4.53)	9.33 (11.68)	6.80 (3.86)	9.02 (5.48)	10.92 (12.85)	8.70 (5.67)	11.14 (6.86)	10.03 (12.22)
MAD	3.17 (1.75)	4.28 (2.84)	5.20 (2.69)	3.98 (2.87)	4.94 (3.66)	4.52 (3.36)	4.66 (3.75)	5.45 (4.34)	5.82 (4.02)

*Values between parentheses correspond to scaled calculated data

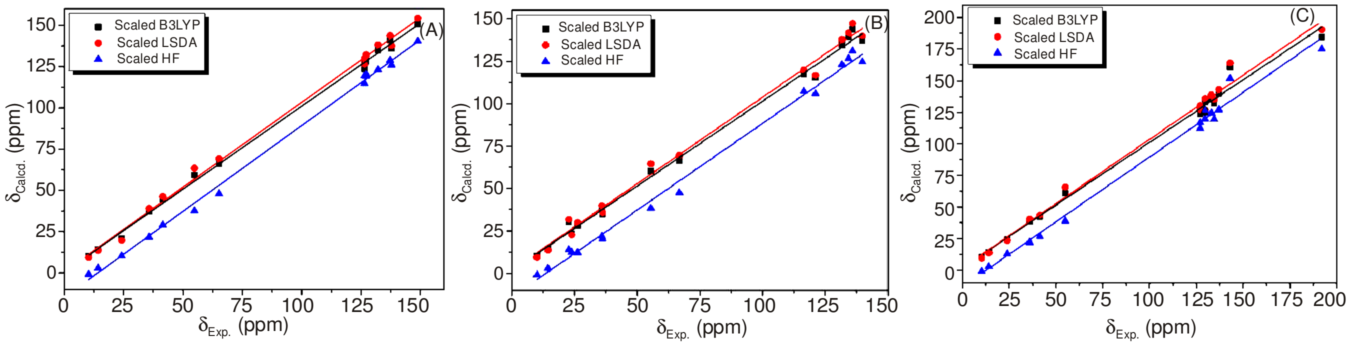

Fig. 10. A linear regression plot of experimental and scaled calculated ^{13}C NMR spectral data of compound **1 (A)**, compound **2 (B)** and Compound **3 (C)**.

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