

Computational Methods and Points for Attention in Absolute Configuration Determination

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Table S1. Experimental ^{13}C NMR shifts obtained for the natural product compared to the calculated data of the possible diastereomers.

C. No	$\delta_{\text{Exp.}}$ (ppm)	$\delta_{\text{calcd.}}$ 9a	δ_{calcd} 9b	δ_{calcd} 9c	δ_{calcd} 9d
C16	15.83	13.88	14.64	14.31	13.84
C20	21.32	18.97	19.36	21.05	19.30
C17	21.54	16.52	10.97	19.16	20.95
C19	21.59	19.44	20.36	20.16	18.97
C9	21.86	26.07	22.86	23.43	24.26
C5	23.11	25.13	30.85	31.69	30.10
C18	27.03	23.69	27.00	24.66	24.54
C13	27.27	27.57	29.40	28.04	27.92
C15	27.67	30.26	31.17	31.00	29.84
C7	30.31	37.33	41.00	44.00	38.63
C8	32.89	31.00	33.01	33.18	33.33
C4,	37.26	38.39	38.98	37.99	36.76
C12	39.17	39.27	43.51	34.97	33.92
C1	39.81	39.64	42.84	40.78	39.21
C11	52.23	55.94	54.41	56.12	55.80
C6	55.33	53.58	60.28	53.81	59.90
C3	132.75	137.41	137.59	136.00	137.66
C14	137.75	141.09	142.42	140.36	144.37
C2	140.31	137.61	137.85	139.32	138.82
C10	141.14	142.56	142.13	142.59	139.09
Mean		2.59	2.79	3.47	3.01
deviation					
R ²		99.55	99.22	99.10	99.35
DP4		99.6	0.4	0.0	0.0
assigned ^a					
DP4		5.1	94.9	0.0	0.0
unassigned					
^b					

The table correlates the experimental and predicted chemical shift of the same carbon assigned by its connectivity. ^a ^{13}C -shifts assigned based on connectivity information. ^b ^{13}C -shifts compared in order of appearance in the spectra.

Please see the original report at: Merten, C.; Dirkmann, M.; Schulz, F. (2017) Stereochemical assignment of fusicocadiene from NMR shielding constants and vibrational circular dichroism spectroscopy. *Chirality*. 29, 409-414.

Table S2. The computed ^{13}C NMR for the three pairs of stereoisomers using four quantum methods.

C- No.	Uncorr. $\Delta\delta_{\text{calcd.}}$ / Method A ^b	corr. $\Delta\delta_{\text{calcd.}}$ / Method B	(ppm) ^a ($\delta_{17} - \delta_{18}$) Method C	(ppm) ^a ($\delta_{17} - \delta_{18}$) Method D	$\Delta\delta$ exp. ($\delta_{17} - \delta_{18}$) (ppm) A ^c	B	C
12	-0.1 / - 0.1	0.1 / 0	-0.3 / -0.3	-0.2 / -0.2	-0.4	-0.4	-0.4
13	-0.1 / - 0.1	-0.2 / - 0.2	-0.4 / 0.4	-0.3 / -0.3	-0.2	-0.2	-0.3
14	0.1 / 0.1	0 / 0	0.2 / 0.2	0.1 / 0.1	0.1	0.1	0.0
16	1.7 / 1.7	1.3 / 1.3	1.5 / 1.5	1.2 / 1.3	1.0	1.1	1.1
17	-0.7 / - 0.7	-0.1 / 0.6	0.2 / 0.2	0.3 / 0.4	0	0	-0.1
20	0.2 / 1.2	0.6 / 1.1	1.1 / 1.1	0.6 / 0.7	0.4	0.4	0.5
21	-0.9 / - 0.8	-0.6 / - 0.6	-1.0 / -1.0	-0.7 / -0.8	-0.4	-0.4	-0.3
22	0.4 / 0.5	0.3 / 0.3	0.7 / 0.7	0.6 / 0	0	0	0.1
23	-0.6 / -0.6	-0.9 / - 0.9	-0.7 / -0.7	-0.7 / -0.6	-0.6	-0.5	-0.3

^a The uncorr. $\Delta\delta_{\text{calcd}}$ values were obtained directly from the computed chemical shifts after Boltzmann statistics. Corr. $\Delta\delta_{\text{calcd}}$ values means the computed chemical shifts after Boltzmann statistics were corrected using the linear fits using the methods listed in Ref. 30a. ^b ^{13}C NMR data were obtained via the B3LYP/6-311+G(2d,p) level of theory on the basis of the B3LYP/6-31+G(d,p)-optimized geometries [B3LYP/6-311+G(2d,p)//B3LYP/6-31+G(d,p)]. Method B: B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d). Method C: B3LYP/6-311+G(2d,p)//HF/6-31G(d). Method D: HF/6-31G(d)//HF/6-31G (d). ^c The chemical shift differences between **17** and **18** were obtained for the corresponding three compounds **17A**, **17B** and **17C** via **18A**, **18B** and **18C**.

Please see the original report at:

Hua, Y.; Han, L. D.; Chen, C. X. (2004) Six novel 5 α -adynerin-type cardenolides from *Parepigynum funingense*. *Helvetica Chimica Acta*. 87, 516-523.

Table S3 Model combinations used in the calculations

Models	Config at C1	Config of X-part
151A <i>S-S</i>	151A , <i>S</i>	<i>S</i>
151A <i>R-S</i>	151A , <i>R</i>	<i>S</i>
151A <i>S-R</i>	151A , <i>S</i>	<i>R</i>
151A <i>R-R</i>	151A , <i>R</i>	<i>R</i>
151B-S	151B , -	<i>S</i>
151B-S	151B , -	<i>R</i>
152-S	152 , -	<i>S</i>
152-R	152 , -	<i>R</i>

Please see the original report at:

Tanaka, S.; Honmura, Y.; Uesugi, S.; Fukushi, E.; Tanaka, K.; Maeda, H.; Kimura, K.; Nehira, T.; Hashimoto, M. (2017) Cyclohelminthol X, a hexa-substituted spirocyclopropane from *Helminthosporium velutinum* yone96: structural elucidation, electronic circular dichroism analysis, and biological properties. *J. Org. Chem.* 82, 5574-5582.