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Supplementary Information

Assignment of absolute configurations of highly flexible linear diterpenes from the brown alga *Bifurcaria bifurcata* by VCD spectroscopy

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Experimental Section

IR and VCD spectroscopy. The IR and VCD spectra were recorded on a Bruker Vertex 70V spectrometer equipped with a PMA 50 module for polarization modulated measurements. Samples were held in a sealed BaF_2 IR cell with 100 µm path length (Specac). Both IR and VCD spectra were recorded at 4 cm^{-1} spectral resolution by accumulating 32 respectively ~20000 scans. Baseline correction of the spectra was done by subtraction of the solvent spectra measured under identical conditions.

Computational details. Force field (MMFF94[1]) based conformational analysis of **1** and its C9-C15 fragment were carried out using the implemented algorithms of Spartan 14.[2] DFT-based geometry optimizations and spectra calculations were carried out using Gaussian 09 D.01[3] employing the B3LYP functional and the 6-31G(2d,p) and 6-311++G(2d,p) basis set. All calculations were carried out considering implicit solvation with a polarizable continuum model[4] for chloroform. Lorentzian band shapes with 8 cm^{-1} half-width at half height were assigned to the calculated dipole and rotational strength, and the frequencies were scaled by a factor of 0.98 for better visual comparison. 3D-representations of the calculated conformers were generated using CylView.[5]

Plant Material. *Bifurcaria bifurcata* was collected from the intertidal rockpool at Kilkee, Co. Clare of Ireland, in May of 2009. A voucher specimen is kept at the Herbarium of the Biodiscovery Laboratory in the Irish Marine Institute (BDV0015).

Extraction, isolation and identification. The algal material was initially freeze-dried (132.4 g dry weight) and then exhaustively extracted with CH_2Cl_2 and MeOH at room temperature. The combined extracts were concentrated to give a dark green residue (12.0 g) that was subjected to a modified Kupchan partition scheme. Briefly, the crude extract was partitioned between 10% aqueous MeOH and *n*-hexane. The water concentration was increased to 35%, before extracting with $CHCl_3$. Evaporation of the solvent under reduced pressure afforded 7.6 g of the $CHCl_3$ subextract which was subjected to flash column chromatography on silica gel. Step gradient (1%) elution with increasing amounts of EtOAc in *n*-hexane as mobile phase yielded pure **2** (0.04 g, 1% EtOAc) and **1** (3.6 g, 3% EtOAc). The structures of the linear diterpenoids were elucidated on the basis of extensive NMR, IR, $[\alpha]_D$ and HRMS studies and by comparison with previously reported data.[6]

VCD spectral analysis

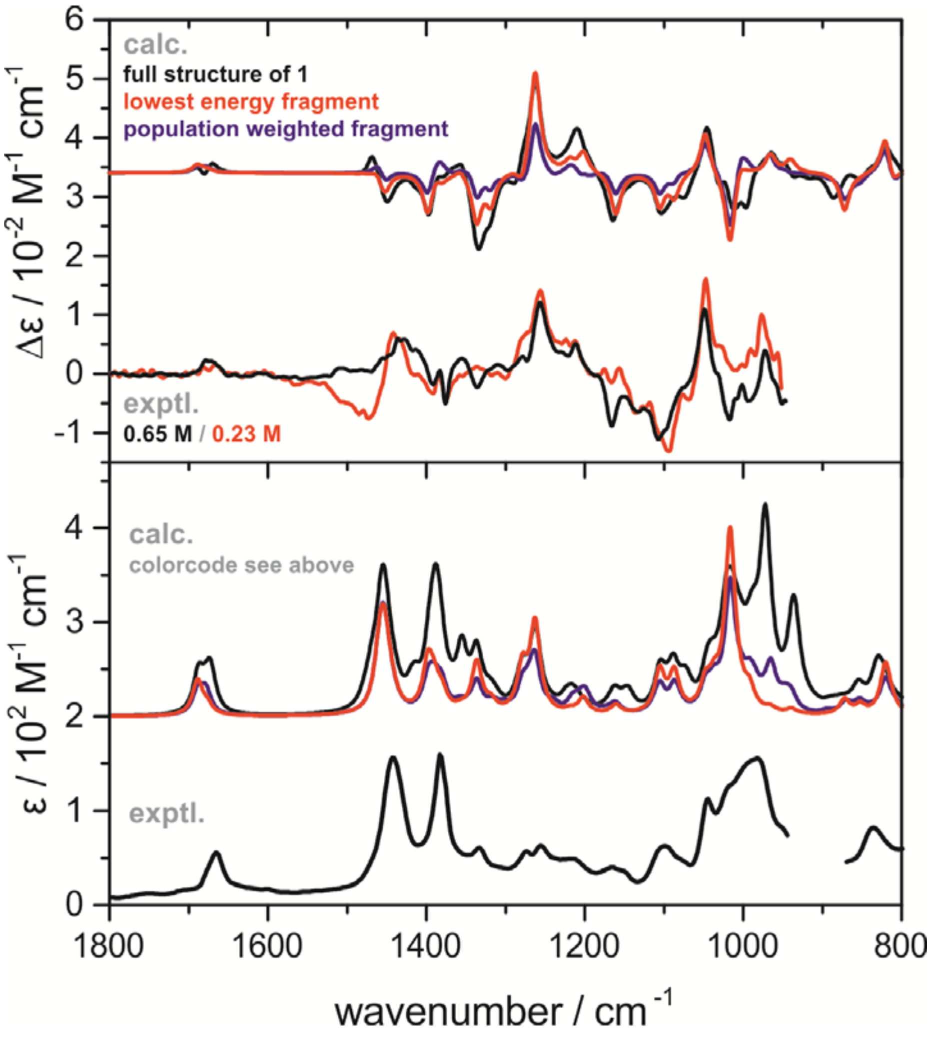


Figure S1. Comparison of the experimental IR and VCD spectra of **1** with calculations for the full diterpenoid structure **1**, the lowest energy fragment, and the population-weighted fragment spectrum. The experimental VCD spectrum taken for a 0.23 M solution (70 mg/ml) is shown as well.

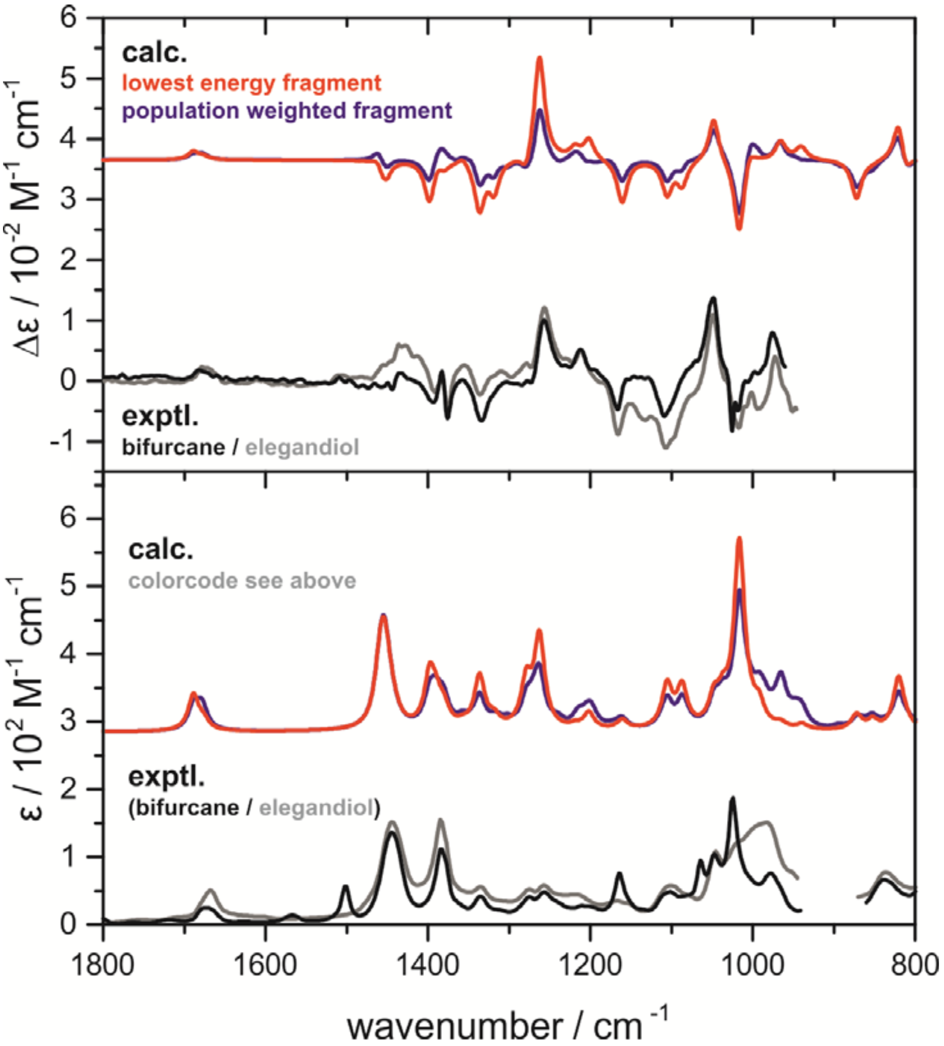


Figure S2. Comparison of the experimental IR and VCD spectra of **1** and **2** with calculations for the lowest energy fragment and the population-weighted fragment spectrum.

Table S1. Energies of conformers of **1** optimized at the B3LYP/6-311++G(2d,p) level of theory. The large changes in Boltzmann populations between ΔE_{ZPC} and ΔG are due to entropic effects.

conformer-id	**E_{ZPC} / hartree**	**G / hartree**	**ΔE_{ZPC} / kcal mol^{-1}**	**ΔG / kcal mol^{-1}**	**pop(ΔE) / %**	**pop(ΔG) / %**
elegandiol_c80	-932.789832	-932.852841	0.00	2.06	**18.22**	1.29
elegandiol_c83	-932.789652	-932.856118	0.11	0.00	**15.06**	**41.58**
elegandiol_c0	-932.789538	-932.850568	0.18	3.48	**13.34**	0.12
elegandiol_c72	-932.789382	-932.854098	0.28	1.27	**11.31**	4.89
elegandiol_c123	-932.788849	-932.854413	0.62	1.07	6.43	6.83
elegandiol_c78	-932.788728	-932.855477	0.69	0.40	5.66	**21.08**
elegandiol_c1	-932.788723	-932.850391	0.70	3.59	5.63	0.10
elegandiol_c57	-932.788525	-932.851821	0.82	2.70	4.56	0.44
elegandiol_c43	-932.788485	-932.85301	0.85	1.95	4.37	1.54
elegandiol_c73	-932.788429	-932.855252	0.88	0.54	4.12	**16.61**
elegandiol_c77	-932.78822	-932.851123	1.01	3.13	3.30	0.21
elegandiol_c3	-932.78793	-932.848608	1.19	4.71	2.43	0.01
elegandiol_c74	-932.787877	-932.854098	1.23	1.27	2.30	4.89
elegandiol_c54	-932.787221	-932.84971	1.64	4.02	1.15	0.05
elegandiol_c7	-932.786742	-932.847143	1.94	5.63	0.69	0.00
elegandiol_c5	-932.786429	-932.847242	2.14	5.57	0.49	0.00
elegandiol_c55	-932.786297	-932.851561	2.22	2.86	0.43	0.33
elegandiol_c6	-932.785934	-932.849345	2.45	4.25	0.29	0.03
elegandiol_c12	-932.784712	-932.846567	3.21	5.99	0.08	0.00
elegandiol_c23	-932.784711	-932.846575	3.21	5.99	0.08	0.00
elegandiol_c9	-932.784575	-932.846714	3.30	5.90	0.07	0.00

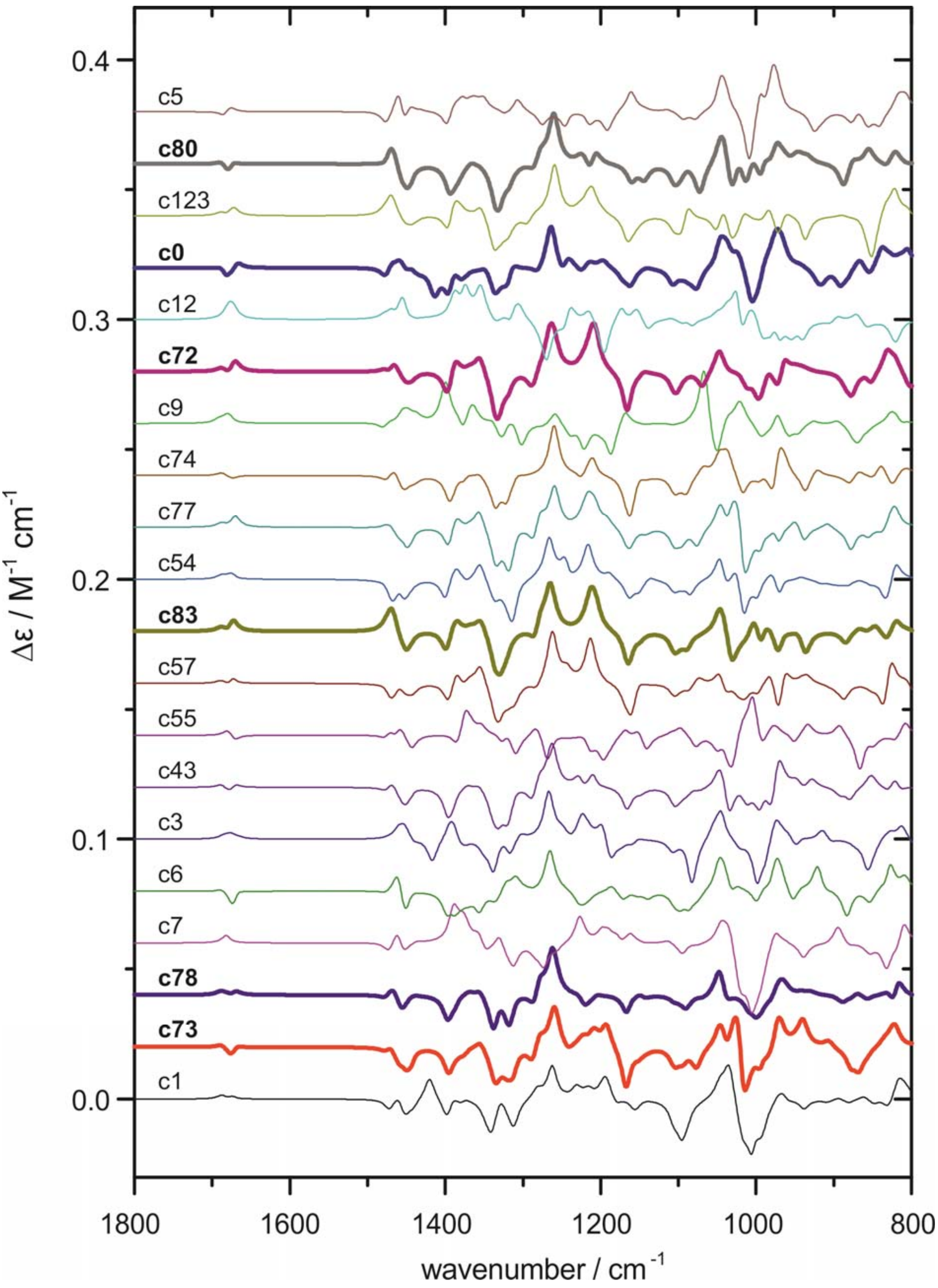


Figure S3. Single conformer spectra for the conformers of **1** obtained at B3LYP/6-311++G(2d,p) level of theory.

Table S2. Energies of the conformers of the C9-C15 fragment optimized at the B3LYP/6-311++G(2d,p) level of theory.

conformer-id	E_{ZPC} / hartree	G / hartree	ΔE_{ZPC} / kcal mol^{-1}	ΔG / kcal mol^{-1}	pop(ΔE) / %	pop(ΔG) / %
fragment	-466.994148	-467.035826	0.00	0.00	47.14	35.11
fragment_c17	-466.9929	-467.034884	0.78	0.59	12.56	12.94
fragment_c21	-466.992799	-467.035256	0.85	0.36	11.29	19.19
fragment_c34	-466.992089	-467.03391	1.29	1.20	5.32	4.61
fragment_c42	-466.992025	-467.034314	1.33	0.95	4.97	7.07
fragment_c18	-466.991791	-467.033816	1.48	1.26	3.88	4.17
fragment_c25	-466.991696	-467.033927	1.54	1.19	3.51	4.69
fragment_c8	-466.991029	-467.033167	1.96	1.67	1.73	2.10
fragment_c41	-466.990651	-467.032968	2.19	1.79	1.16	1.70
fragment_c38	-466.990605	-467.032778	2.22	1.91	1.10	1.39
fragment_c29	-466.990591	-467.032671	2.23	1.98	1.09	1.24
fragment_c32	-466.990418	-467.032495	2.34	2.09	0.91	1.03
fragment_c27	-466.99039	-467.032137	2.36	2.31	0.88	0.70
fragment_c11	-466.990173	-467.031988	2.49	2.41	0.70	0.60
fragment_c31	-466.989697	-467.031385	2.79	2.79	0.42	0.32
fragment_c12	-466.989323	-467.031188	3.03	2.91	0.28	0.26
fragment_c4	-466.98882	-467.030636	3.34	3.26	0.17	0.14
fragment_c16	-466.988337	-467.029947	3.65	3.69	0.10	0.07
fragment_c7	-466.987989	-467.029963	3.86	3.68	0.07	0.07
fragment_c20	-466.987912	-467.029898	3.91	3.72	0.06	0.07
fragment_c35	-466.987678	-467.02968	4.06	3.86	0.05	0.05
fragment_c19	-466.986715	-467.028327	4.66	4.71	0.02	0.01
fragment_c9	-466.986385	-467.028276	4.87	4.74	0.01	0.01
fragment_c3	-466.98622	-467.02827	4.97	4.74	0.01	0.01
fragment_c10	-466.985415	-467.027306	5.48	5.35	0.00	0.00
fragment_c24	-466.985213	-467.02727	5.61	5.37	0.00	0.00
fragment_c14	-466.985039	-467.026313	5.72	5.97	0.00	0.00
fragment_c30	-466.984828	-467.027025	5.85	5.52	0.00	0.00
fragment_c33	-466.984224	-467.026623	6.23	5.77	0.00	0.00
fragment_c13	-466.98414	-467.025323	6.28	6.59	0.00	0.00
fragment_c28	-466.981209	-467.022913	8.12	8.10	0.00	0.00

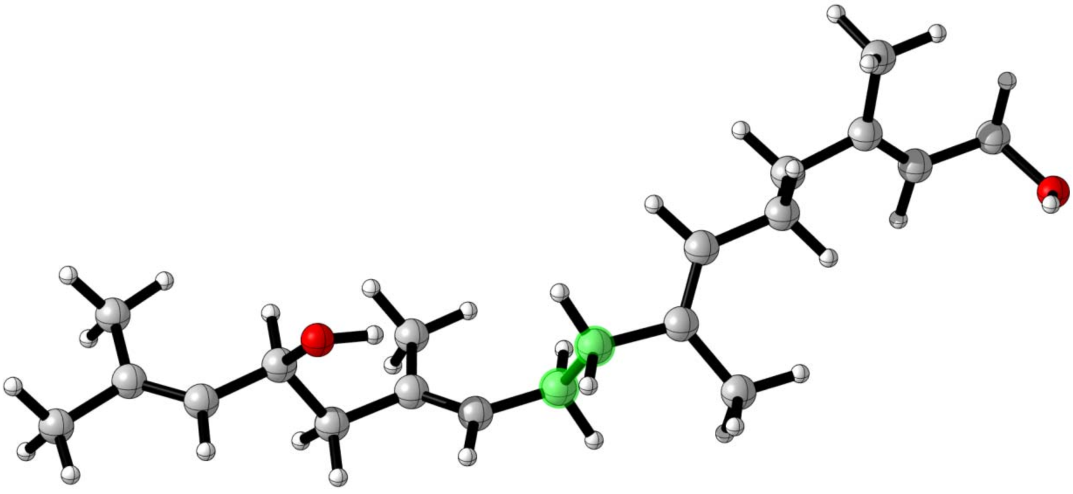


Figure S4. Lowest energy structure of **1** (c83). Further lowest energy conformations are shown in Tab. S1.

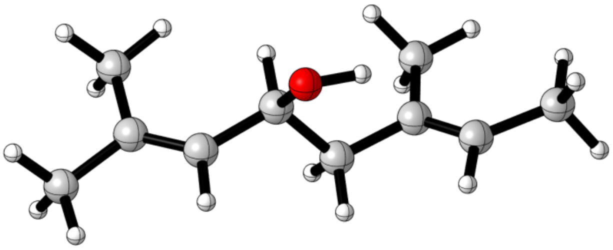
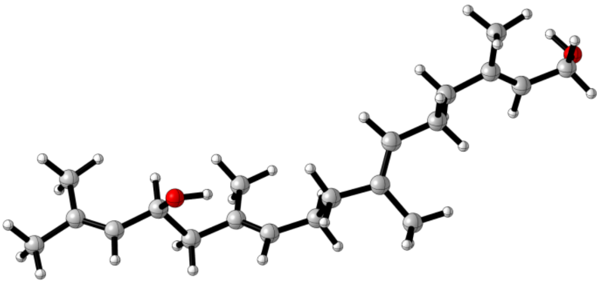
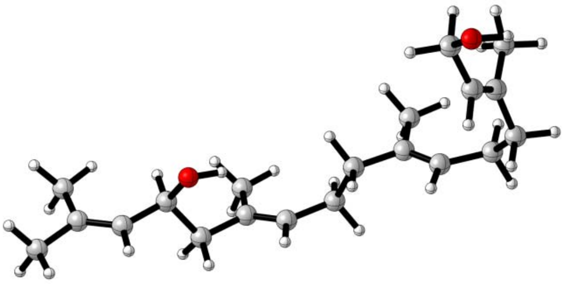
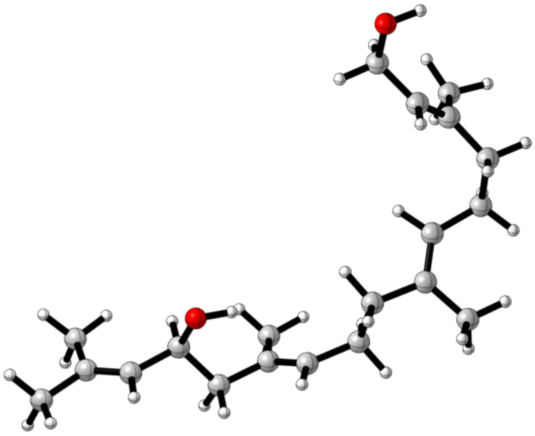
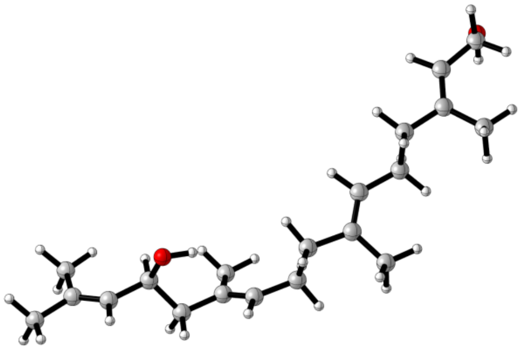
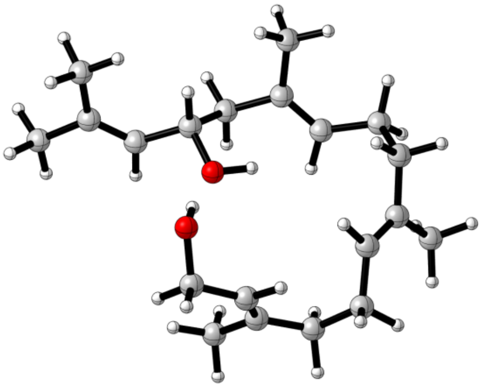


Figure S5. Fragment of C9-C15 considered in the calculation.

Table S3. Further highly populated conformers

c80	
c78	
c73	
c72	
c0	

Analytical data for compounds 1 and 2

Eleganediol (1):

Colorless oil; $[\alpha]_D$ = -1.3 (c 0.3, $CHCl_3$); $[\alpha]_D$ = -5.9 (c 0.7, MeOH); ^1H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) data, see Table S4; HRESIMS *m/z* $[M+Na]^+$ 329.2452 (calcd for $C_{20}H_{34}O_2Na^+$, 329.2451, Δ=0.25ppm).

Table S4. NMR data for eleganediol (**1**) in $CDCl_3$ (^1H, 500 MHz; ^{13}C, 125 MHz; chemical shifts expressed in ppm, *J* values in Hz).

No.	**^1H (δ)**	**mult (*J*)**	**^{13}C (δ)**	**mult**
1	4.10	d 6.9	59.3	CH_2
2	5.37	t 6.9	123.5	CH
3	-		139.4	C
4	2.00	m	39.4	CH_2
5	2.09	m	26.1	CH_2
6	5.08	t 6.7	124.3	CH
7	-		135.0	C
8	2.00	m	39.4	CH_2
9	2.10	m	26.3	CH_2
10	5.19	t 6.9	128.5	CH
11	-		131.6	C
12	2.09	m	48.2	CH_2
13	4.36	ddd 8.4, 8.4, 4.8	65.6	CH
14	5.12	br. d 8.4	127.3	CH
15	-		134.8	C
16	1.69	br. s	25.7	CH_3
17	1.66	br. s	18.2	CH_3
18	1.62	br. s	16.1	CH_3
19	1.57	br. s	15.9	CH_3
20	1.64	br. s	16.2	CH_3

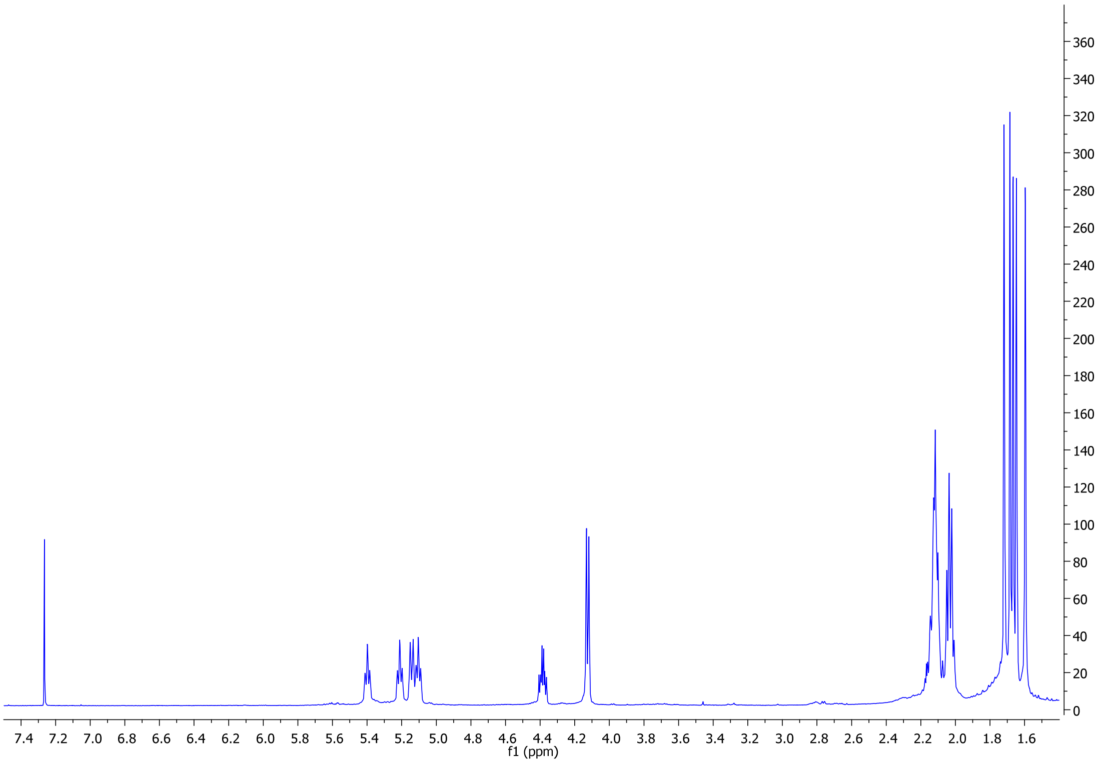


Figure S6. ^{1}H NMR spectrum of eleganediol (**1**) in $CDCl_3$ (500 MHz)

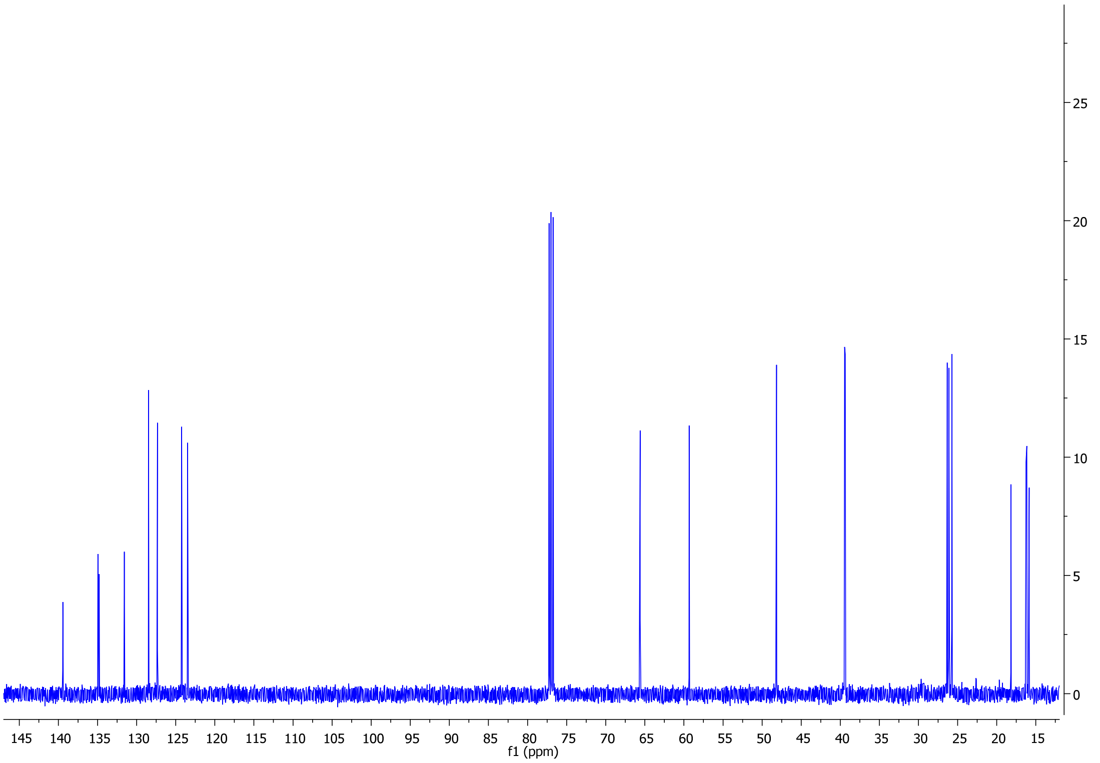


Figure S7. ^{13}C NMR spectrum of eleganediol (**1**) in $CDCl_3$ (125 MHz)

Bifurcane (2):

Colorless oil; $[\alpha]_D$ = -1.5 (c 1.2, $CHCl_3$); $[\alpha]_D$ = -3.5 (c 4.1, EtOH); ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) data, see Table S5; HRESIMS *m/z* $[M+Na]^+$ 325.2142 (calcd for $C_{20}H_{30}O_2Na^+$, 325.2438, Δ=1.24ppm).

Table S5. NMR data for bifurcane (**2**) in $CDCl_3$ (^{1}H, 500 MHz; ^{13}C, 125 MHz; chemical shifts expressed in ppm, *J* values in Hz).

No.	**^{1}H (*δ*)**	**mult (*J*)**	**^{13}C (*δ*)**	**mult**
1	7.30	br. s	142.5	CH
2	6.25	br. s	111.0	CH
3	-		124.9	C
4	2.42	t 7.4	24.9	CH_2
5	2.22	td 7.4, 7.0	28.4	CH_2
6	5.14	t 7.3	124.1	CH
7	-		135.4	C
8	2.00	t 7.1	39.4	CH_2
9	2.11	m	26.4	CH_2
10	5.19	t 6.8	128.4	CH
11	-		131.6	C
12	2.10	m	48.1	CH_2
13	4.38	td 8.0, 5.5	65.6	CH
14	5.13	d 8.0	127.5	CH
15	-		134.7	C
16	1.70	br. s	25.7	CH_3
17	1.67	br. s	18.1	CH_3
18	1.63	br. s	16.1	CH_3
19	1.56	br. s	15.9	CH_3
20	7.18	br. s	138.8	CH

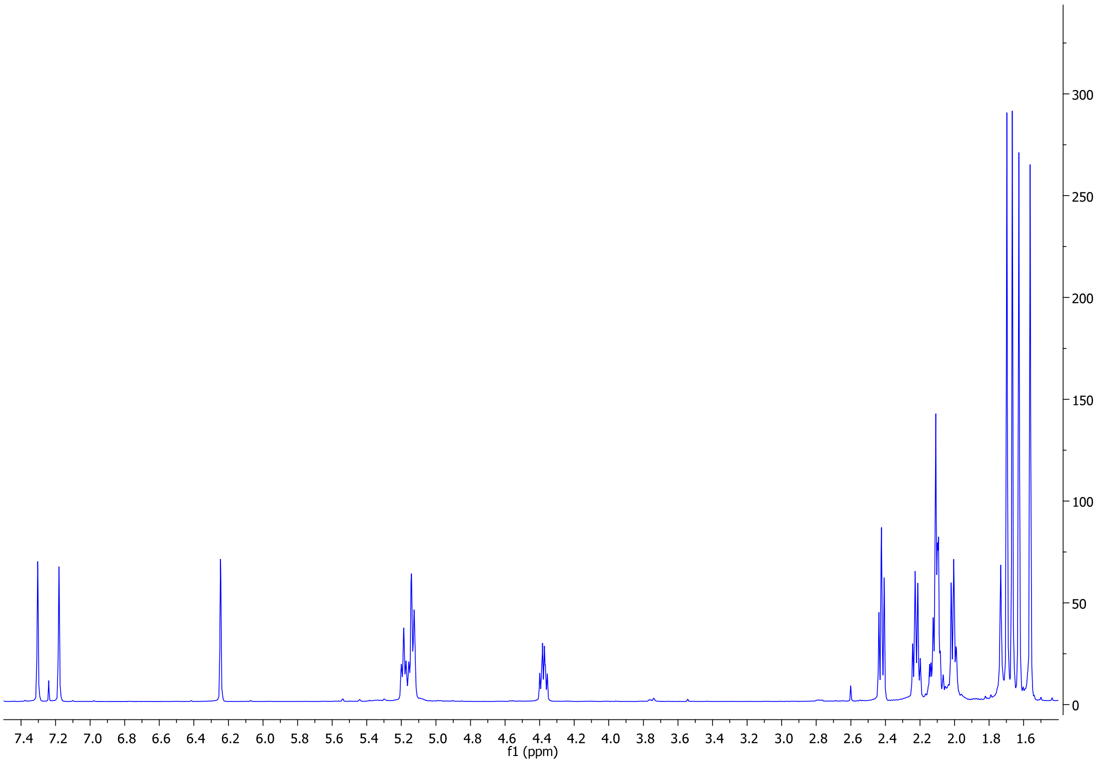


Figure S8. ^{1}H NMR spectrum of bifurcane (**2**) in $CDCl_3$ (500 MHz)

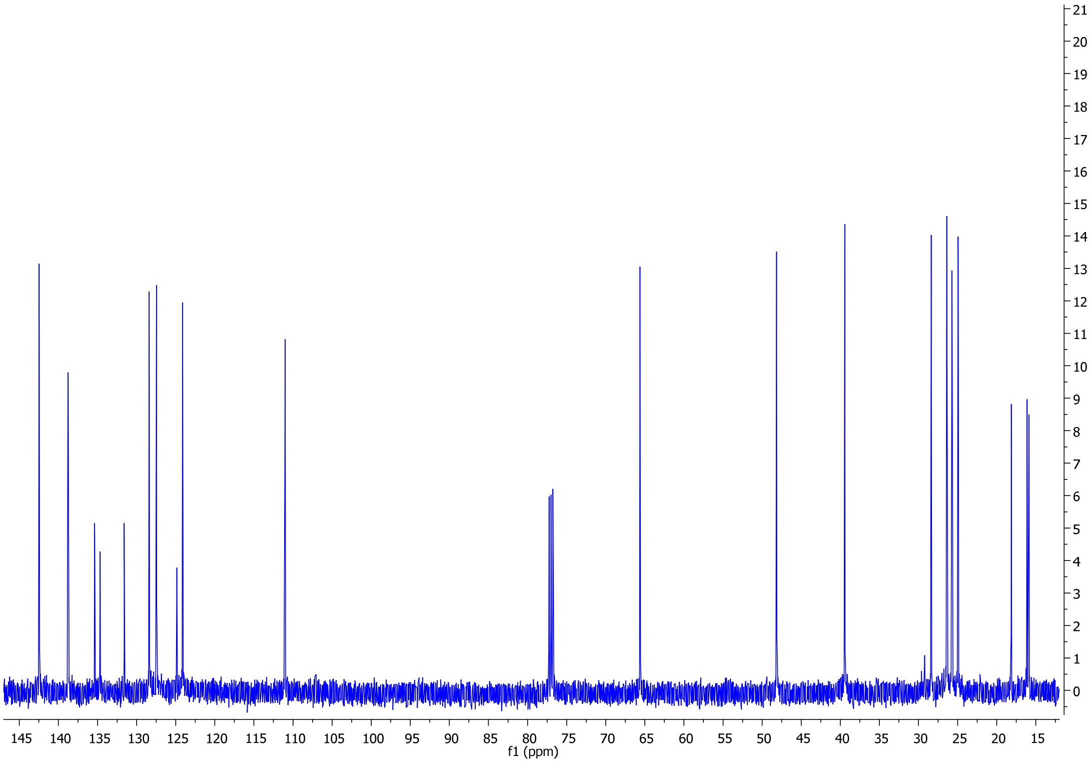


Figure S9. ^{13}C NMR spectrum of bifurcane (**2**) in $CDCl_3$ (125 MHz)

Cartesian coordinates

Diterpenoid c80

C	6.39011300	0.08158700	0.37635000
C	4.93238400	-0.21419300	0.19805700
C	4.32083800	0.64178400	-0.93490900
C	2.83375800	0.42220500	-1.11494700
C	1.96179200	1.33344500	-0.66198700
C	0.46118300	1.31039200	-0.72006600
C	-0.18059900	1.33278600	0.68783000
C	-1.69323300	1.39702000	0.67513800
C	-2.41156500	0.33378600	1.05381300
C	-3.90472600	0.17515200	1.10265200
C	-4.40657800	-0.91254800	0.12202300
C	-5.89623400	-1.16773300	0.20115100
C	-6.70012200	-0.73621200	-0.77895900
C	-8.18789400	-0.86713100	-0.87853600
O	-8.83821500	0.41830400	-0.94756400
C	-6.35589800	-1.93175500	1.41592600
C	-2.28056700	2.71235400	0.23099400
C	2.45208500	-0.85733000	-1.81435200
O	4.28140900	0.07537800	1.44989200
C	7.42997200	-0.73570000	0.18567800
C	8.83914500	-0.24337700	0.39527500
C	7.33614200	-2.17553600	-0.24641400
H	6.59091000	1.10235600	0.69561300
H	4.78088500	-1.27125800	-0.03736100
H	4.52205400	1.69293800	-0.71160900
H	4.85049900	0.39504200	-1.86097700
H	2.37804600	2.22486100	-0.19408000
H	0.12397600	2.19016300	-1.27930200
H	0.09266700	0.43848400	-1.26245900
H	0.14278000	0.44122500	1.23141600
H	0.21468100	2.19733000	1.23555000
H	-1.85777400	-0.55249000	1.36197800
H	-4.19486900	-0.10198700	2.12220100
H	-4.41620800	1.11238600	0.87838300
H	-4.13828600	-0.61368800	-0.89402400
H	-3.86853500	-1.84507600	0.33072600
H	-6.24523100	-0.20837800	-1.61486200
H	-8.46402500	-1.36286400	-1.81222300
H	-8.60807200	-1.45410100	-0.05858300
H	-8.55492300	0.93150800	-0.18108700
H	-5.98884200	-1.46377400	2.33344100
H	-7.43867700	-2.01219900	1.49224300
H	-5.94452400	-2.94660100	1.39903300
H	-1.92434400	3.52359100	0.87512400
H	-1.96561200	2.96305600	-0.78633700
H	-3.36881300	2.72262300	0.25032700
H	2.83522600	-0.85491300	-2.84040600
H	2.89855700	-1.72507400	-1.31942100
H	1.37648300	-1.01745400	-1.85801100
H	3.34025500	0.20528900	1.26172600
H	8.86332200	0.80195200	0.70545700
H	9.34858500	-0.84157900	1.15824200
H	9.42782000	-0.34337000	-0.52308400
H	6.31406800	-2.54300400	-0.31811600
H	7.81333600	-2.31258100	-1.22274300
H	7.87904700	-2.81583600	0.45629400

Fragment C9-C15

C	-1.74083700	-0.66449000	-0.10860400
C	-0.39234800	-0.20439200	0.35433400
C	0.59672100	-0.08355500	-0.82794500
C	1.99220300	0.31771400	-0.40003500
C	2.96668600	-0.60014800	-0.34708300
C	4.39963300	-0.42261600	0.06117600
C	2.16589200	1.77280600	-0.04796000
O	0.08543000	-1.17267200	1.30771800
C	-2.90154900	-0.00396400	-0.06283100
C	-4.16089600	-0.63078700	-0.60439000
C	-3.09228500	1.38045600	0.49895700
H	-1.73584000	-1.66526900	-0.53607300
H	-0.46754300	0.76642300	0.85193100
H	0.62376700	-1.04577700	-1.34641700
H	0.19128900	0.65548400	-1.52676800
H	2.70843200	-1.61117500	-0.65698000
H	5.06900100	-0.66670400	-0.77044500
H	4.63289700	0.58887500	0.39132700
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H	1.46073300	2.07874400	0.73095600
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H	1.04784100	-1.07596800	1.35785800
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H	-4.59077900	-0.01554200	-1.40226400
H	-2.19382800	1.79351600	0.95384200
H	-3.41951600	2.06914900	-0.28738000
H	-3.88419500	1.37471500	1.25487500
H	4.65598800	-1.10839500	0.87501000

Additional references

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