Supporting Information

Stereochemical revision of brevipetins E and F: ellagitannin dimers with opposite hexahydroxydiphenoyl atropisomerism

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Figure S1. Optimized conformers of brevipetin B [(R_a)-**3**], with populations ≥1% at the B3LYP/6-31G(d,p)/PCM(MeOH) level.

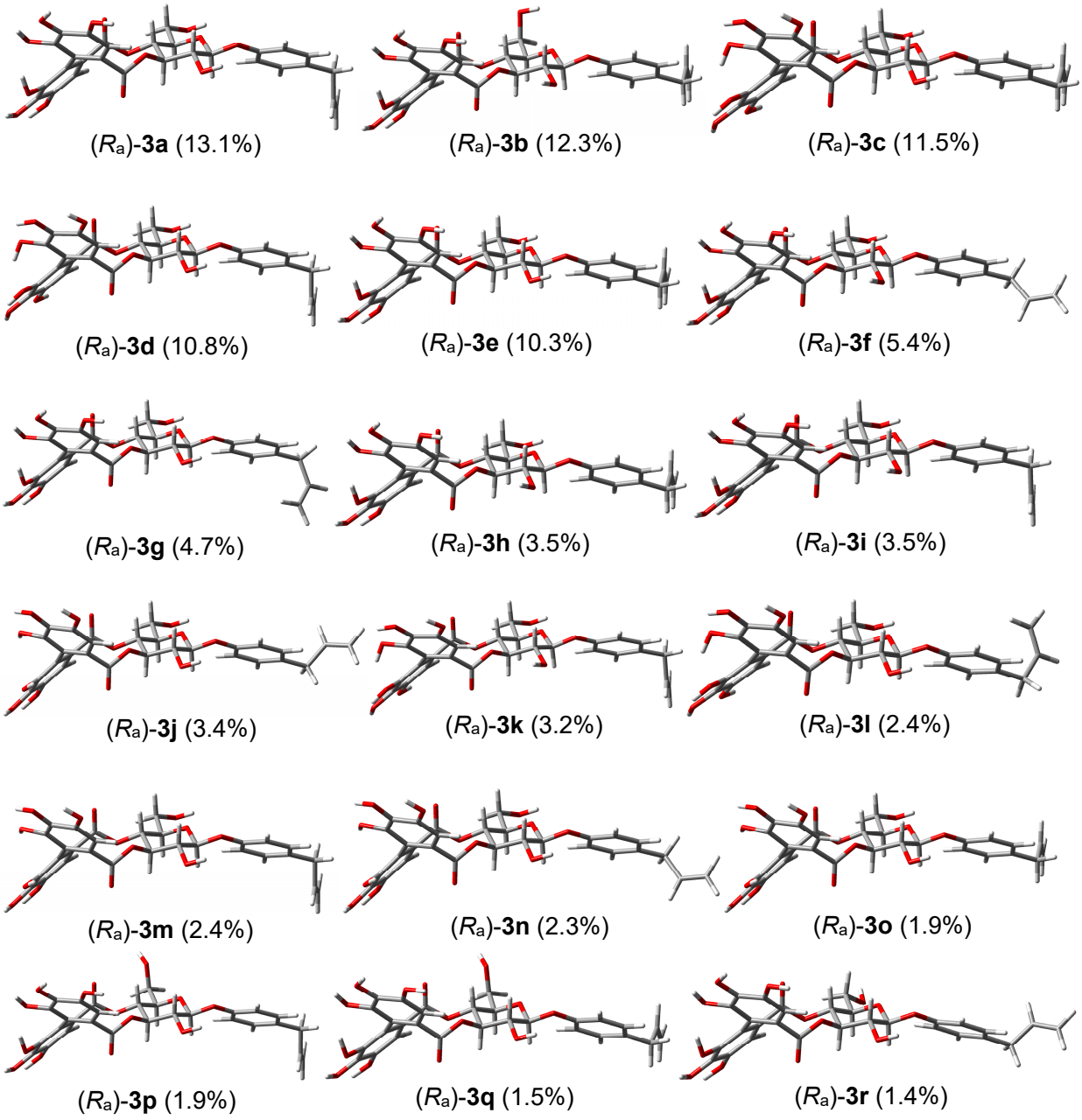
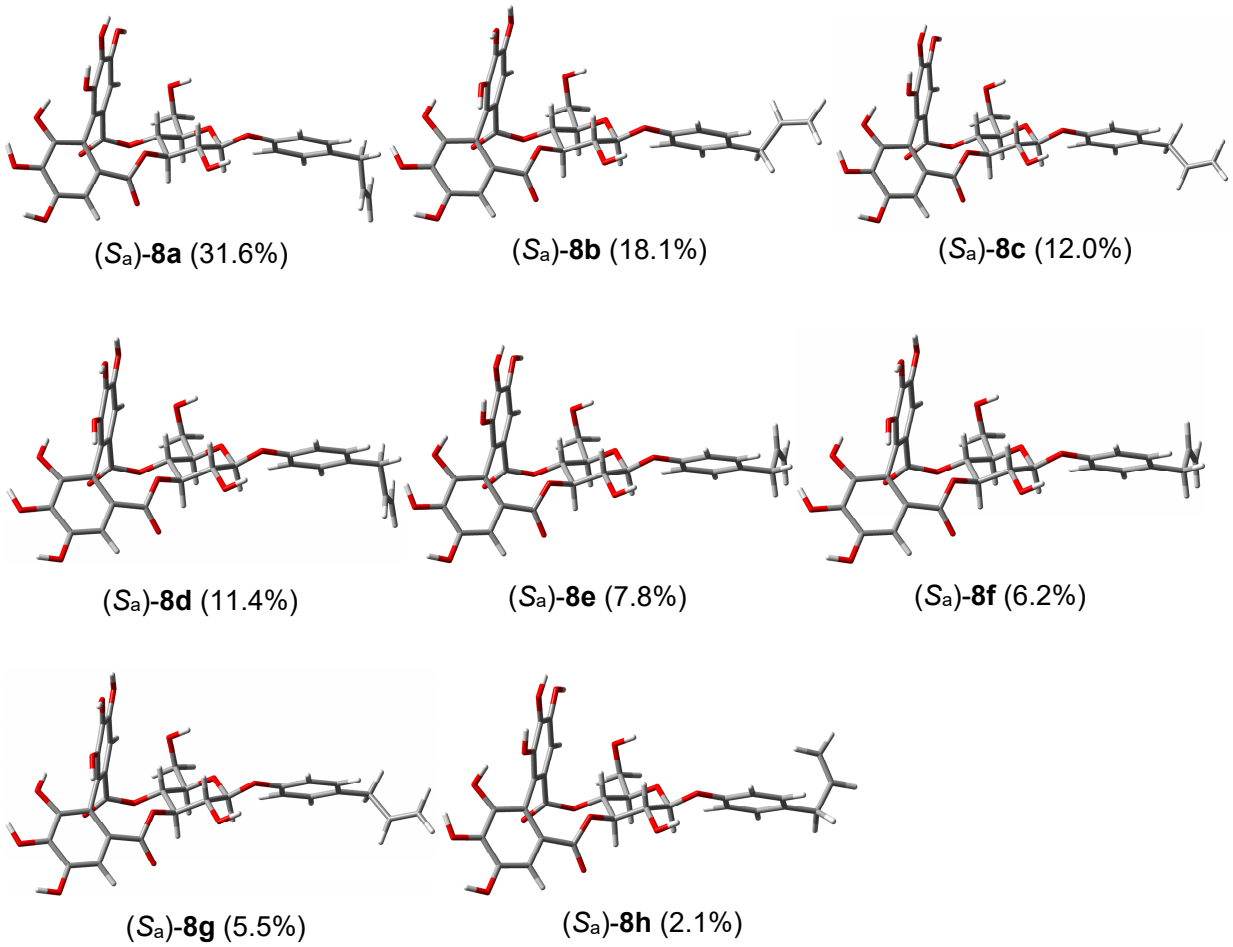
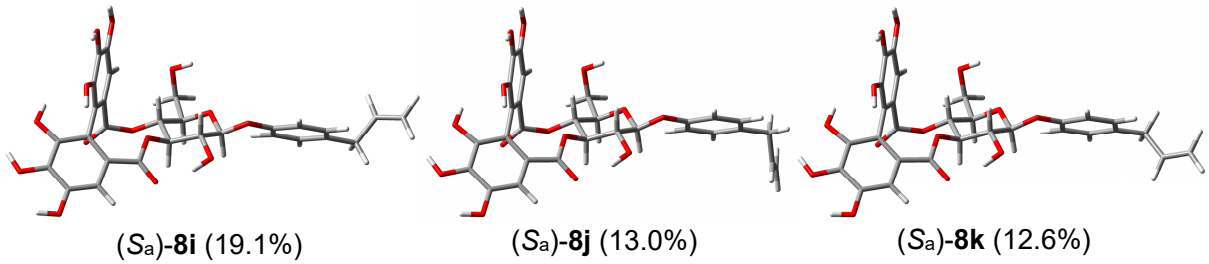


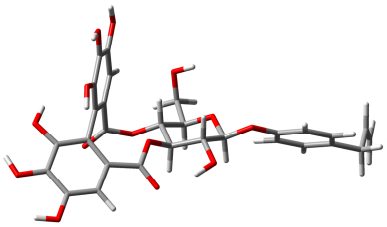
Figure S2. Optimized conformers of (S_a)-**8** at the B3LYP/6-31G(d,p)/PCM(MeOH) level.

(a) Conformers lacking the intramolecular hydrogen bond between the 2-hydroxy group and the 3-ester carbonyl of the glucose unit with populations ≥1%.

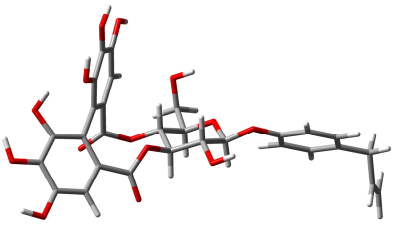


(b) All conformers including those with the intramolecular hydrogen bond between the 2-hydroxy group and the 3-ester carbonyl of the glucose unit with populations ≥1%.

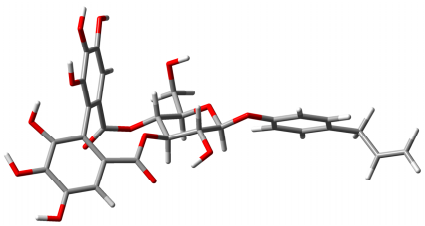




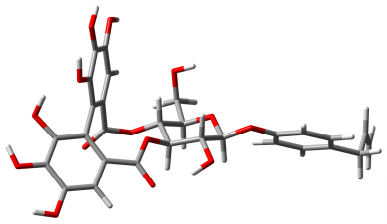
(*S*a)-**8l** (12.3%)



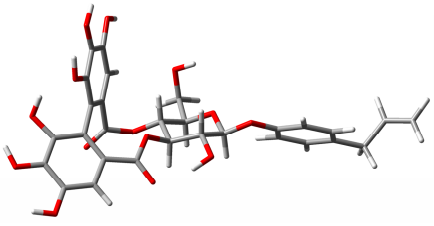
(*S*a)-**8a** (5.6%)



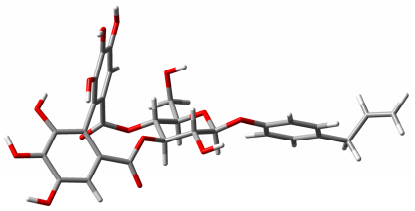
(*S*a)-**8m** (4.2%)



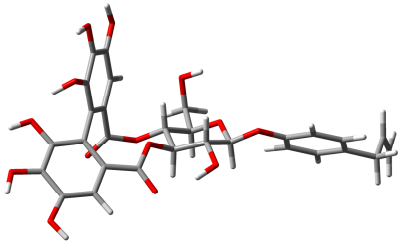
(*S*a)-**8n** (3.7%)



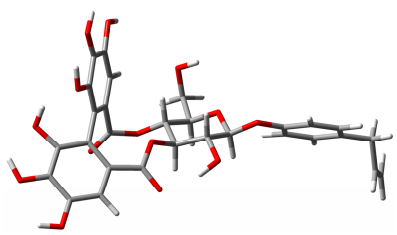
(*S*a)-**8o** (3.7%)



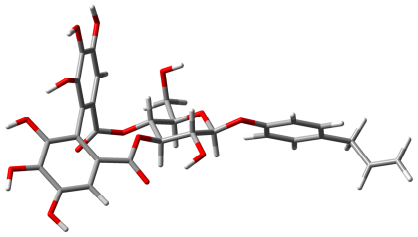
(*S*a)-**8b** (3.2%)



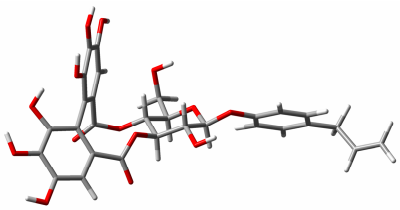
(*S*a)-**8p** (3.1%)



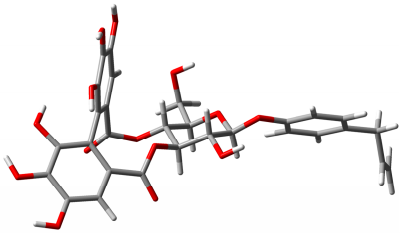
(*S*a)-**8q** (2.6%)



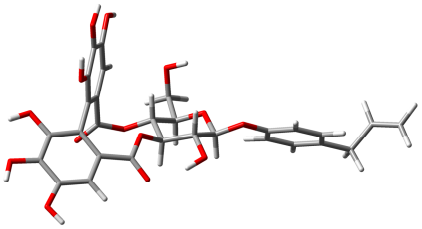
(*S*a)-**8r** (2.2%)



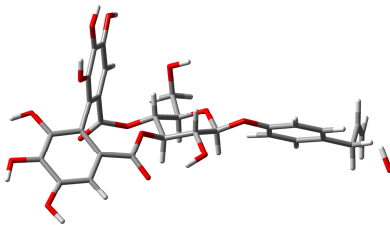
(*S*a)-**8c** (2.1%)



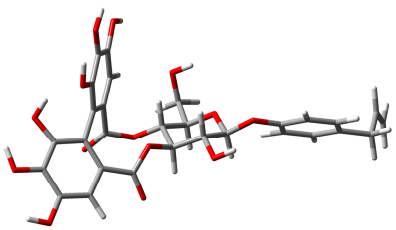
(*S*a)-**8d** (2.0%)



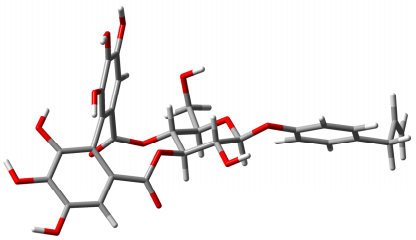
(*S*a)-**8s** (1.5%)



(*S*a)-**8t** (1.5%)

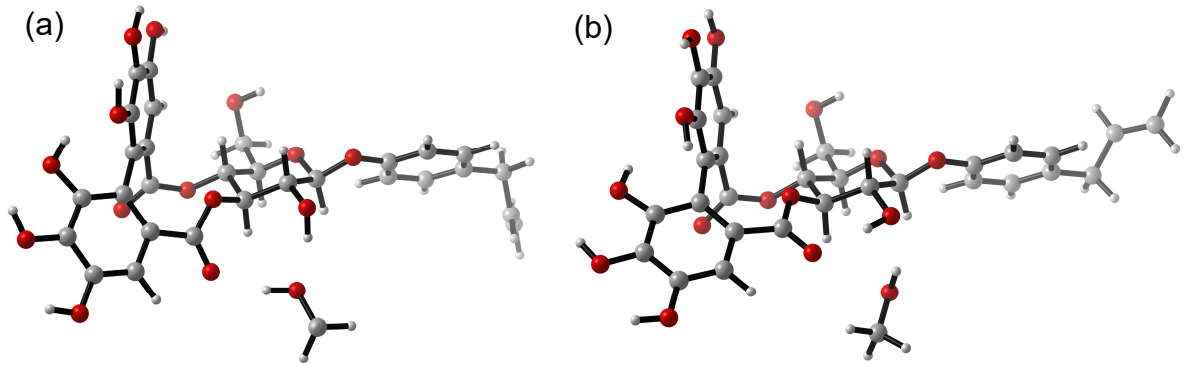


(*S*a)-**8e** (1.4%)



(*S*a)-**8f** (1.1%)

Figure S3. The two lowest-energy conformers of (*S*a)-**8** calculated with one explicit MeOH molecule at the B3LYP/6-31G(d,p)/PCM(MeOH) level. (a) The global minimum energy conformer, where the explicit MeOH forms a stabilizing hydrogen bonded bridge. (b) The higher-energy conformer, which retains the intramolecular hydrogen bond between the 2-hydroxy and 3-ester carbonyl of the glucose unit.



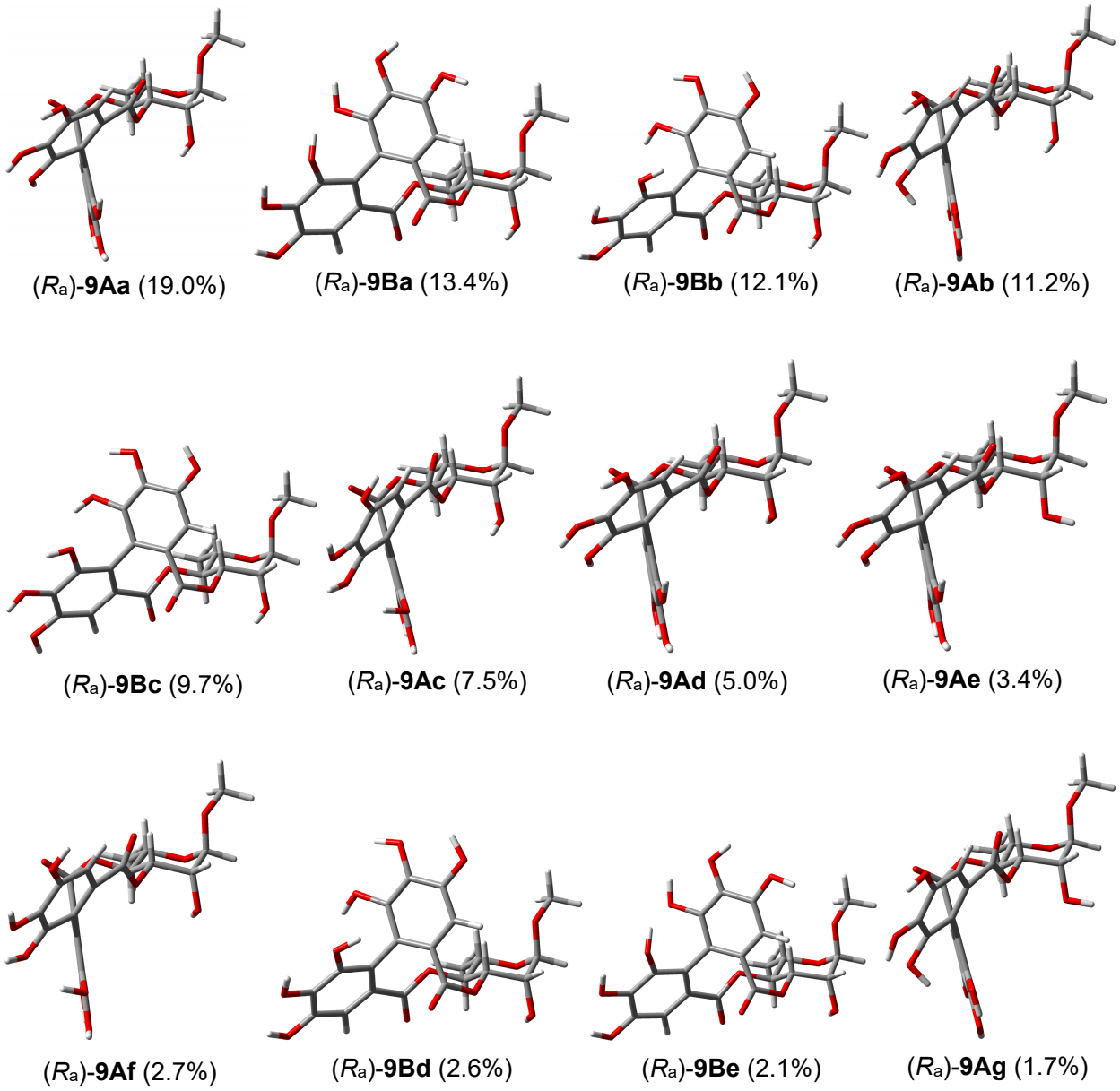
(*S*a)-**8·MeOH-a**
Δ*G* = 0.0 kcal/mol

(*S*a)-**8·MeOH-b**
Δ*G* = +2.1 kcal/mol

(*S*a)-**8·MeOH-a**: $E = -2289.644691$ a.u.; $E' = -2289.065954$ a.u.; $H = -2289.021773$ a.u.; $G = -2289.145573$ a.u.

(*S*a)-**8·MeOH-b**: $E = -2289.638751$ a.u.; $E' = -2289.061235$ a.u.; $H = -2289.016305$ a.u.; $G = -2289.142274$ a.u.

Figure S4. Optimized conformers of (R_a)-**9**, with populations ≥1% at the B3LYP/6-31G(d,p)/PCM(MeOH) level.



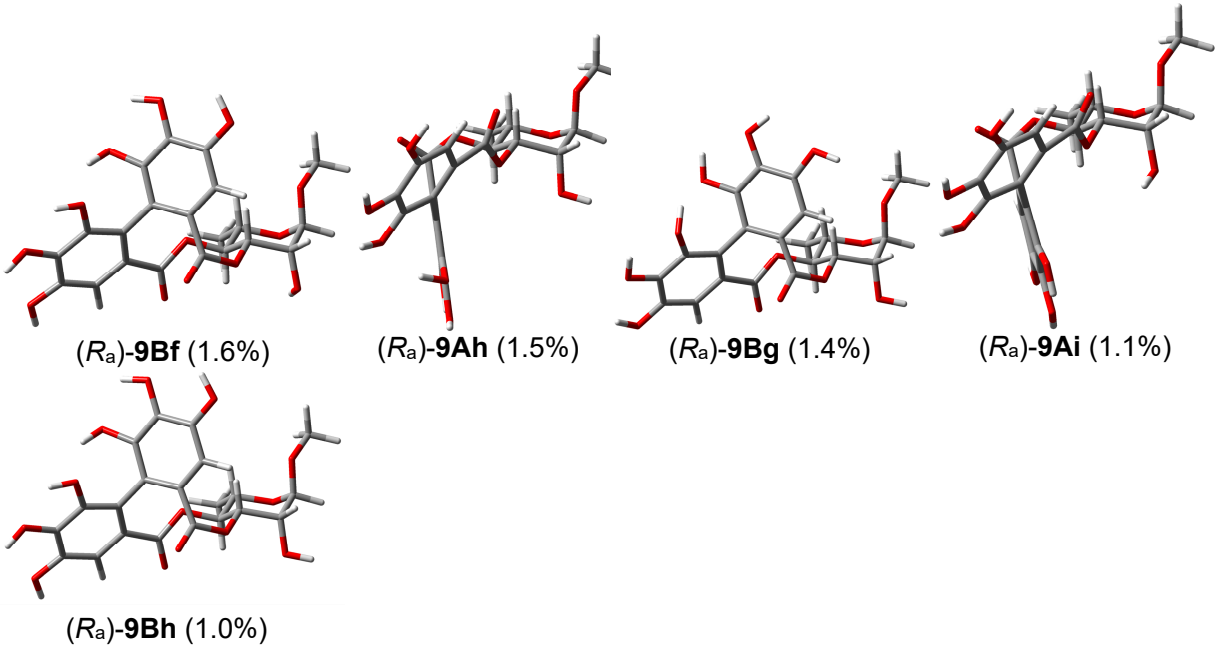


Figure S5. Optimized conformers of (S_a)-**10**, with populations ≥1% at the B3LYP/6-31G(d,p)/PCM(MeOH) level.

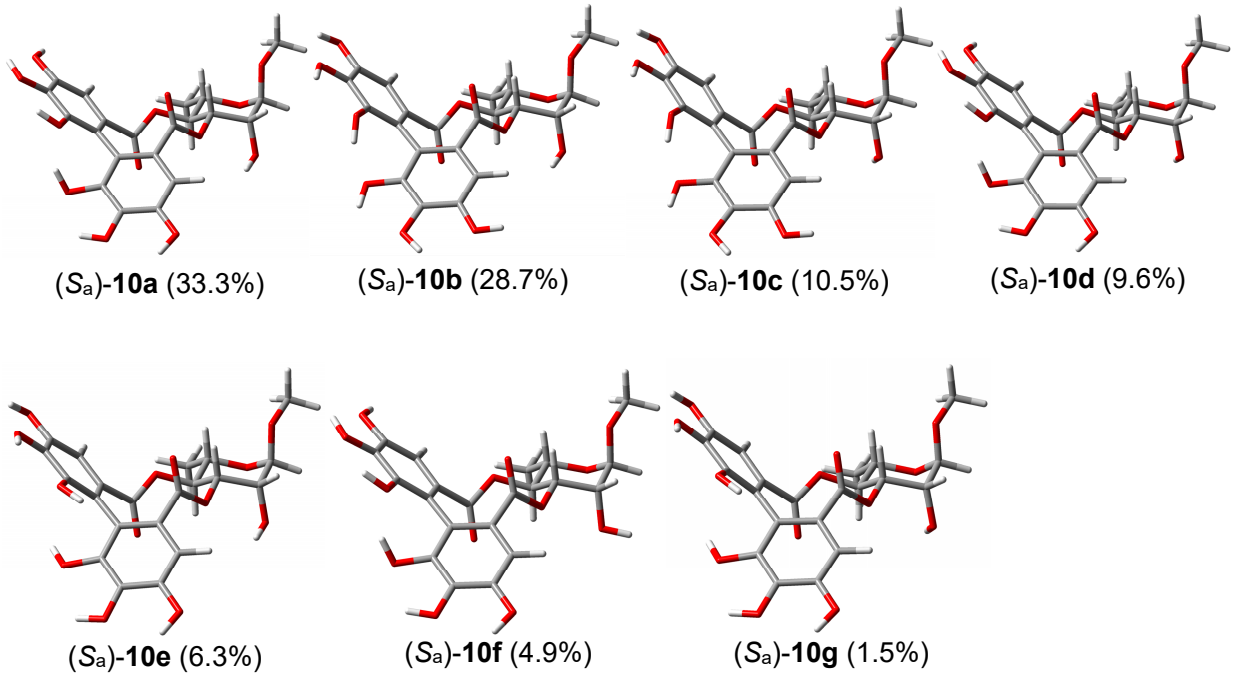


Table S1. Thermodynamic parameters (electronic, enthalpy, and free energies) and Boltzmann populations of the conformers of brevipetin B [(R_a)-**3**] at the B3LYP/6-31G(d,p)/PCM(MeOH) level ($P_G \geq 1\%$).

conformers	E (a.u.)	E' (a.u.)	H (a.u.)	G (a.u.)	ΔG (kcal/mol)	P_G (%)
3a	-2173.901228	-2173.376824	-2173.336716	-2173.449451	0.00	13.1
3b	-2173.900157	-2173.376142	-2173.335950	-2173.449388	0.04	12.3
3c	-2173.901119	-2173.376692	-2173.336610	-2173.449323	0.08	11.5
3d	-2173.901139	-2173.376704	-2173.336604	-2173.449268	0.11	10.8
3e	-2173.901220	-2173.376699	-2173.336646	-2173.449219	0.15	10.3
3f	-2173.899686	-2173.375612	-2173.335406	-2173.448609	0.53	5.4
3g	-2173.900432	-2173.376128	-2173.336045	-2173.448487	0.60	4.7
3h	-2173.899654	-2173.375415	-2173.335243	-2173.448213	0.78	3.5
3i	-2173.899662	-2173.375445	-2173.335268	-2173.448209	0.78	3.5
3j	-2173.897920	-2173.374446	-2173.333765	-2173.448177	0.80	3.4
3k	-2173.899722	-2173.375455	-2173.335295	-2173.448126	0.83	3.2
3l	-2173.900360	-2173.375894	-2173.335868	-2173.447859	1.00	2.4
3m	-2173.897878	-2173.374343	-2173.333701	-2173.447837	1.01	2.4
3n	-2173.897925	-2173.374386	-2173.333733	-2173.447802	1.03	2.3
3o	-2173.897874	-2173.374222	-2173.333623	-2173.447633	1.14	1.9
3p	-2173.898495	-2173.374615	-2173.334298	-2173.447608	1.16	1.9
3q	-2173.898478	-2173.374532	-2173.334265	-2173.447382	1.30	1.5
3r	-2173.898353	-2173.374440	-2173.334167	-2173.447353	1.32	1.4

E: electronic energy; E': electronic energy with zero point energy; H: enthalpy; G: Gibbs free energy; ΔG: relative Gibbs free energy. P_G : conformational distribution calculated from relative Gibbs free energy.

Table S2. Thermodynamic parameters (electronic, enthalpy, and free energies) and Boltzmann populations of the conformers of (S_a)-**8** at the B3LYP/6-31G(d,p)/PCM(MeOH) level.

(a) Conformers lacking the intramolecular hydrogen bond between the 2-hydroxy group and the 3-ester carbonyl of the glucose unit with populations ≥1%.

conformers	*E* (a.u.)	*E′* (a.u.)	*H* (a.u.)	*G* (a.u.)	Δ*G* (kcal/mol)	P_G (%)
8a	-2173.898958	-2173.374499	-2173.334405	-2173.448150	0.00	31.6
8b	-2173.897242	-2173.373421	-2173.332924	-2173.447624	0.33	18.1
8c	-2173.899053	-2173.374263	-2173.334292	-2173.447235	0.57	12.0
8d	-2173.897198	-2173.373375	-2173.332890	-2173.447186	0.60	11.4
8e	-2173.899001	-2173.374094	-2173.334235	-2173.446826	0.83	7.8
8f	-2173.897209	-2173.373280	-2173.332847	-2173.446615	0.96	6.2
8g	-2173.897273	-2173.373185	-2173.332789	-2173.446501	1.03	5.5
8h	-2173.898239	-2173.373319	-2173.333499	-2173.445585	1.61	2.1

E: electronic energy; E′: electronic energy with zero point energy; H: enthalpy; G: Gibbs free energy; ΔG: relative Gibbs free energy. P_G *: conformational distribution calculated from relative Gibbs free energy.*

(b) All conformers including those with the intramolecular hydrogen bond between the 2-hydroxy group and the 3-ester carbonyl of the glucose unit with populations ≥1%.

conformers	*E* (a.u.)	*E′* (a.u.)	*H* (a.u.)	*G* (a.u.)	Δ*G* (kcal/mol)	P_G (%)
8i	-2173.899630	-2173.375812	-2173.335483	-2173.449301	0.00	19.1
8j	-2173.899598	-2173.375588	-2173.335324	-2173.448939	0.23	13.0
8k	-2173.899653	-2173.375651	-2173.335391	-2173.448906	0.25	12.6
8l	-2173.899576	-2173.375617	-2173.335371	-2173.448888	0.26	12.3
8a	-2173.898958	-2173.374499	-2173.334405	-2173.448150	0.72	5.6
8m	-2173.900161	-2173.375288	-2173.335534	-2173.447876	0.89	4.2
8n	-2173.900072	-2173.375225	-2173.335460	-2173.447754	0.97	3.7
8o	-2173.900159	-2173.375335	-2173.335555	-2173.447742	0.98	3.7
8b	-2173.897242	-2173.373421	-2173.332924	-2173.447624	1.05	3.2
8p	-2173.899700	-2173.374932	-2173.335151	-2173.447586	1.08	3.1
8q	-2173.900105	-2173.375105	-2173.335391	-2173.447417	1.18	2.6
8r	-2173.899809	-2173.374843	-2173.335152	-2173.447246	1.29	2.2
8c	-2173.899053	-2173.374263	-2173.334292	-2173.447235	1.30	2.1
8d	-2173.897198	-2173.373375	-2173.332890	-2173.447186	1.33	2.0
8s	-2173.896670	-2173.373209	-2173.332570	-2173.446910	1.50	1.5
8t	-2173.896591	-2173.373136	-2173.332504	-2173.446881	1.52	1.5
8e	-2173.899001	-2173.374094	-2173.334235	-2173.446826	1.55	1.4
8f	-2173.897209	-2173.373280	-2173.332847	-2173.446615	1.69	1.1

E: electronic energy; E′: electronic energy with zero point energy; H: enthalpy; G: Gibbs free energy; ΔG: relative Gibbs free energy. P_G *: conformational distribution calculated from relative Gibbs free energy.*

Table S3. Thermodynamic parameters (electronic, enthalpy, and free energies) and Boltzmann populations of the conformers of (R_a)-**9** at the B3LYP/6-31G(d,p)/PCM(MeOH) level ($P_G \geq 1\%$).

conformers	E (a.u.)	E' (a.u.)	H (a.u.)	G (a.u.)	ΔG (kcal/mol)	P_G (%)
9Aa	-1790.223253	-1789.818072	-1789.785522	-1789.878972	0.00	19.0
9Ba	-1790.224816	-1789.818577	-1789.786602	-1789.878647	0.20	13.4
9Bb	-1790.223568	-1789.818207	-1789.785728	-1789.878550	0.26	12.1
9Ab	-1790.224488	-1789.818334	-1789.786351	-1789.878475	0.31	11.2
9Bc	-1790.224845	-1789.818497	-1789.786610	-1789.878336	0.40	9.7
9Ac	-1790.224385	-1789.818157	-1789.786232	-1789.878102	0.55	7.5
9Ad	-1790.222449	-1789.817018	-1789.784565	-1789.877715	0.79	5.0
9Ae	-1790.221326	-1789.816324	-1789.783653	-1789.877343	1.02	3.4
9Af	-1790.223432	-1789.817070	-1789.785173	-1789.877128	1.16	2.7
9Bd	-1790.222285	-1789.816768	-1789.784342	-1789.877080	1.19	2.6
9Be	-1790.223555	-1789.817052	-1789.785171	-1789.876883	1.31	2.1
9Ag	-1790.222508	-1789.816511	-1789.784421	-1789.876681	1.44	1.7
9Bf	-1790.223475	-1789.816841	-1789.785039	-1789.876610	1.48	1.6
9Ah	-1790.222416	-1789.816462	-1789.784388	-1789.876577	1.50	1.5
9Bg	-1790.222298	-1789.816365	-1789.784223	-1789.876540	1.53	1.4
9Ai	-1790.220069	-1789.815175	-1789.782344	-1789.876303	1.67	1.1
9Bh	-1790.222278	-1789.816212	-1789.784147	-1789.876233	1.72	1.0

E: electronic energy; E': electronic energy with zero point energy; H: enthalpy; G: Gibbs free energy; ΔG: relative Gibbs free energy. P_G : conformational distribution calculated from relative Gibbs free energy.

Table S4. Thermodynamic parameters (electronic, enthalpy, and free energies) and Boltzmann populations of the conformers of (S_a)-**10** at the B3LYP/6-31G(d,p)/PCM(MeOH) level ($P_G \geq 1\%$).

conformers	E (a.u.)	E' (a.u.)	H (a.u.)	G (a.u.)	ΔG (kcal/mol)	P_G (%)
10a	-1790.228320	-1789.822507	-1789.790397	-1789.882199	0.00	33.3
10b	-1790.228248	-1789.822438	-1789.790351	-1789.882060	0.09	28.7
10c	-1790.227560	-1789.821540	-1789.789521	-1789.881109	0.68	10.5
10d	-1790.227407	-1789.821403	-1789.789359	-1789.881027	0.74	9.6
10e	-1790.225029	-1789.820087	-1789.787462	-1789.880626	0.99	6.3
10f	-1790.226125	-1789.820514	-1789.788269	-1789.880386	1.14	4.9
10g	-1790.224205	-1789.818943	-1789.786428	-1789.879282	1.83	1.5

E: electronic energy; E': electronic energy with zero point energy; H: enthalpy; G: Gibbs free energy; ΔG: relative Gibbs free energy. P_G : conformational distribution calculated from relative Gibbs free energy.

Table S5. Calculated ^{1}H NMR chemical shifts of (R_a)-**3** and comparison with reported experimental data of brevipetin B (**3**) and brevipetin E (**1′**).

Position	shielding tensors (calculated)[a]																			chemical shifts (ppm)				
	3a	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**	**3h**	**3i**	**3j**	**3k**	**3l**	**3m**	**3n**	**3o**	**3p**	**3q**	**3r**	**3** (averaged)	**3** (calcd)[b]	**3**		**1'**	
																					3 (exptl)[c]	$\Delta\delta$ (vs **3**) ($\delta_{calcd} - \delta_{exptl}$)	**1'** (exptl)[c]	$\Delta\delta$ (vs **1'**) ($\delta_{calcd} - \delta_{exptl}$)
glucose																								
1	26.58	26.41	26.57	26.58	26.56	26.44	26.52	26.44	26.46	26.59	26.46	26.56	26.60	26.59	26.58	26.64	26.62	26.71	26.53	4.94	5.10	-0.16	5.10	-0.16
2	27.59	27.56	27.57	27.57	27.59	27.54	27.58	27.53	27.53	27.63	27.51	27.56	27.62	27.63	27.61	27.61	27.62	27.62	27.57	3.97	3.86	0.11	3.87	0.10
3	26.22	26.24	26.21	26.22	26.21	26.26	26.20	26.26	26.26	26.27	26.26	26.19	26.29	26.28	26.27	26.21	26.20	26.22	26.23	5.22	5.22	0.00	5.20	0.02
4	26.57	26.00	26.57	26.56	26.57	26.57	26.56	26.58	26.57	26.64	26.56	26.56	26.64	26.63	26.64	25.91	25.91	26.59	26.48	4.99	5.08	-0.09	5.05	-0.06
5	27.54	27.68	27.56	27.56	27.54	27.55	27.52	27.55	27.54	27.58	27.56	27.54	27.59	27.58	27.59	27.65	27.65	27.51	27.57	3.98	3.85	0.13	4.09	-0.11
6a	27.80	27.57	27.83	27.83	27.81	27.81	27.80	27.81	27.81	27.83	27.84	27.82	27.83	27.83	27.83	27.45	27.47	27.55	27.77	3.79	3.85	-0.06	4.02	-0.23
6b	27.92	27.91	27.93	27.92	27.93	27.94	27.91	27.94	27.93	27.93	27.94	27.91	27.93	27.93	27.94	27.53	27.54	27.78	27.91	3.66	3.70	-0.04	3.73	-0.07
HHDP																								
3	24.74	24.71	24.54	24.55	24.74	24.74	24.74	24.72	24.73	24.61	24.53	24.53	24.61	24.61	24.60	24.72	24.71	24.74	24.66	6.68	6.70	-0.02	6.67	0.01
3'	24.61	24.58	24.80	24.82	24.59	24.60	24.61	24.59	24.61	24.63	24.83	24.79	24.65	24.64	24.65	24.61	24.59	24.58	24.66	6.68	6.58	0.10	6.55	0.13
chavicol																								
2, 6	24.26	24.29	24.27	24.25	24.28	24.30	24.23	24.31	24.29	24.31	24.28	24.24	24.26	24.30	24.28	24.24	24.26	24.11	24.27	7.04	7.05	-0.01	7.04	0.00
3, 5	24.09	24.10	24.09	24.09	24.09	24.09	24.13	24.10	24.10	24.10	24.10	24.14	24.10	24.10	24.10	24.10	24.10	24.11	24.10	7.20	7.11	0.09	7.12	0.08
7	28.23	28.22	28.21	28.23	28.21	28.21	28.17	28.22	28.23	28.22	28.24	28.18	28.22	28.23	28.21	28.22	28.21	28.22	28.22	3.38	3.32	0.06	3.30	0.08
8	25.40	25.40	25.41	25.40	25.41	25.44	24.96	25.41	25.39	25.42	25.39	24.96	25.41	25.46	25.41	25.41	25.40	25.43	25.38	6.02	5.94	0.08	5.93	0.09
9	26.22	26.23	26.23	26.22	26.23	26.24	26.82	26.23	26.22	26.22	26.23	26.81	26.22	26.23	26.23	26.21	26.22	26.23	26.27	5.19	5.03	0.16	5.02	0.17

[a] Calculated by the GIAO method at the mPW1PW91/6-311+G(2d,p)/PCM(MeOH) level. [b] NMR chemical shifts were obtained from shielding tensors using the reported scaling factors. [c] Measured in CD_3OD (400 MHz).

Table S6. Calculated ^{1}H NMR chemical shifts of (S_a)-**8** and comparison with reported experimental data of brevipetin E (**1′**).

(a) Conformers lacking the intramolecular hydrogen bond between the 2-hydroxy group and the 3-ester carbonyl of the glucose unit with populations ≥1%.

Position	shielding tensors (calculated)[a]									chemical shifts (ppm)		
	8a	**8b**	**8c**	**8d**	**8e**	**8f**	**8g**	**8h**	**8** (averaged)	**8** (calcd)[b]	**1'** (exptl)[c]	$\Delta\delta$ ($\delta_{calcd} - \delta_{exptl}$)
glucose												
1	26.63	26.63	26.59	26.65	26.61	26.64	26.62	26.60	26.63	4.85	5.10	-0.25
2	28.12	28.17	28.11	28.17	28.11	28.17	28.17	28.10	28.14	3.45	3.87	-0.42
3	26.15	26.44	26.14	26.46	26.14	26.45	26.44	26.13	26.27	5.18	5.20	-0.02
4	26.57	26.60	26.56	26.59	26.57	26.60	26.59	26.55	26.58	4.90	5.05	-0.15
5	27.77	27.79	27.75	27.80	27.76	27.80	27.78	27.74	27.78	3.79	4.09	-0.30
6a	27.52	27.52	27.50	27.53	27.52	27.53	27.51	27.50	27.52	4.03	4.02	0.01
6b	27.72	27.72	27.71	27.73	27.71	27.73	27.72	27.70	27.72	3.84	3.73	0.11
HHDP												
3	23.65	23.69	23.65	23.69	23.65	23.69	23.69	23.63	23.66	7.61	6.67	0.94
3'	24.54	24.39	24.53	24.39	24.54	24.39	24.39	24.52	24.47	6.86	6.55	0.31
chavicol												
2, 6	24.34	24.35	24.34	24.34	24.34	24.34	24.34	24.29	24.34	6.98	7.04	-0.06
3, 5	24.10	24.10	24.10	24.10	24.11	24.10	24.08	24.14	24.10	7.20	7.12	0.08
7	28.20	28.23	28.22	28.20	28.24	28.24	28.21	28.20	28.21	3.38	3.30	0.08
8	25.45	25.41	25.45	25.45	25.43	25.42	25.46	24.98	25.43	5.97	5.93	0.04
9	26.23	26.23	26.25	26.23	26.23	26.22	26.25	26.80	26.24	5.21	5.02	0.19

[a] Calculated by the GIAO method at the mPW1PW91/6-311+G(2d,p)/PCM(MeOH) level. [b] NMR chemical shifts were obtained from shielding tensors using the reported scaling factors. [c] Measured in CD_3OD (400 MHz).

(b) All conformers including those with the intramolecular hydrogen bond between the 2-hydroxy group and the 3-ester carbonyl of the glucose unit with populations ≥1%.

Position	shielding tensors (calculated)[a]																			chemical shifts (ppm)		
	8i	**8j**	**8k**	**8l**	**8a**	**8m**	**8n**	**8o**	**8b**	**8p**	**8q**	**8r**	**8c**	**8d**	**8s**	**8t**	**8e**	**8f**	**8** (averaged)	**8** (calcd)[b]	**1'** (exptl)[c]	$\Delta\delta$ ($\delta_{calcd} - \delta_{exptl}$)
glucose																						
1	26.62	26.63	26.60	26.61	26.63	26.59	26.59	26.61	26.63	26.58	26.61	26.59	26.59	26.65	26.63	26.62	26.61	26.64	26.61	4.87	5.10	-0.23
2	28.11	28.11	28.10	28.10	28.12	28.09	28.09	28.09	28.17	28.07	28.09	28.08	28.11	28.17	28.12	28.12	28.11	28.17	28.11	3.48	3.87	-0.39
3	27.12	27.13	27.12	27.13	26.15	26.97	26.97	26.97	26.44	26.97	26.97	26.97	26.14	26.46	27.15	27.14	26.14	26.45	26.95	4.55	5.20	-0.65
4	26.52	26.52	26.50	26.52	26.57	26.44	26.43	26.43	26.60	26.35	26.44	26.35	26.56	26.59	26.54	26.54	26.57	26.60	26.51	4.97	5.05	-0.08
5	27.83	27.84	27.82	27.84	27.77	27.81	27.81	27.81	27.79	27.82	27.81	27.81	27.75	27.80	27.85	27.85	27.76	27.80	27.82	3.74	4.09	-0.35
6a	27.51	27.52	27.51	27.54	27.52	27.50	27.52	27.50	27.52	27.51	27.51	27.49	27.50	27.53	27.53	27.55	27.52	27.53	27.52	4.03	4.02	0.01
6b	27.70	27.71	27.70	27.72	27.72	27.70	27.71	27.70	27.72	27.68	27.70	27.68	27.71	27.73	27.72	27.73	27.71	27.73	27.71	3.85	3.73	0.12
HHDP																						
3	23.65	23.66	23.65	23.64	23.65	23.53	23.50	23.52	23.69	23.68	23.52	23.69	23.65	23.69	23.89	23.88	23.65	23.69	23.64	7.63	6.67	0.96
3'	24.46	24.47	24.46	24.47	24.54	24.66	24.64	24.64	24.39	24.41	24.64	24.41	24.53	24.39	24.76	24.77	24.54	24.39	24.50	6.83	6.55	0.28
chavicol																						
2, 6	24.35	24.36	24.36	24.36	24.34	24.35	24.36	24.35	24.35	24.36	24.35	24.35	24.34	24.34	24.36	24.37	24.34	24.34	24.36	6.97	7.04	-0.07
3, 5	24.14	24.12	24.11	24.13	24.10	24.11	24.13	24.13	24.10	24.13	24.12	24.10	24.10	24.10	24.14	24.14	24.11	24.10	24.12	7.18	7.12	0.06
7	28.25	28.23	28.22	28.23	28.20	28.23	28.23	28.25	28.23	28.23	28.24	28.22	28.22	28.20	28.25	28.23	28.24	28.24	28.23	3.36	3.30	0.06
8	25.41	25.46	25.45	25.44	25.45	25.44	25.44	25.41	25.41	25.43	25.46	25.45	25.45	25.45	25.41	25.44	25.43	25.42	25.43	5.96	5.93	0.03
9	26.21	26.24	26.26	26.23	26.23	26.26	26.22	26.21	26.23	26.23	26.24	26.26	26.25	26.23	26.22	26.23	26.23	26.22	26.23	5.22	5.02	0.20

[a] Calculated by the GIAO method at the mPW1PW91/6-311+G(2d,p)/PCM(MeOH) level. [b] NMR chemical shifts were obtained from shielding tensors using the reported scaling factors. [c] Measured in CD_3OD (400 MHz).

Table S7. Calculated ^{1}H NMR chemical shifts of (R_a)-**9** and comparison with reported experimental data of brevipetin E (**1′**).

Position	shielding tensors (calculated)[a]																		chemical shifts (ppm)		
	9Aa	**9Ba**	**9Bb**	**9Ab**	**9Bc**	**9Ac**	**9Ad**	**9Ae**	**9Af**	**9Bd**	**9Be**	**9Ag**	**9Bf**	**9Ah**	**9Bg**	**9Ai**	**9Bh**	**9** (averaged)	**9** (calcd)[b]	**1'** (exptl)[c]	$\Delta\delta$ ($\delta_{calcd} - \delta_{exptl}$)
rhamnose																					
1	26.94	26.92	26.94	26.93	26.91	26.94	26.97	27.09	26.95	26.94	26.94	27.10	26.93	27.10	27.10	26.95	27.10	26.95	4.55	4.80	-0.25
2	27.49	27.28	27.29	27.53	27.25	27.55	27.74	27.45	27.84	27.58	27.59	27.51	27.56	27.53	27.29	27.51	27.26	27.44	4.09	4.07	0.02
3	26.64	26.73	26.75	26.17	26.63	26.19	26.71	26.60	26.21	26.71	26.71	26.09	26.60	26.12	26.64	26.58	26.53	26.55	4.93	5.35	-0.42
4	26.87	26.34	26.63	26.79	26.36	26.71	27.06	26.85	26.92	26.83	26.51	26.77	26.53	26.69	26.29	26.88	26.32	26.67	4.81	5.06	-0.25
5	27.61	27.99	28.04	27.57	28.00	27.58	27.60	27.67	27.57	28.06	28.01	27.62	28.03	27.63	28.00	27.63	28.01	27.79	3.78	4.09	-0.31
6	30.37	30.61	30.60	30.34	30.63	30.31	30.33	30.36	30.29	30.56	30.57	30.35	30.60	30.31	30.60	30.38	30.63	30.46	1.29	1.24	0.05
1-OMe	28.29	28.33	28.33	28.28	28.32	28.29	28.22	28.28	28.22	28.29	28.30	28.28	28.29	28.28	28.33	28.29	28.33	28.30	3.30	–	–
HHDP																					
3	23.71	24.98	24.79	23.66	24.72	23.84	23.72	23.72	23.83	24.82	25.01	23.67	24.76	23.85	25.01	23.97	24.77	24.24	7.07	6.66	0.41
3'	24.78	23.62	23.68	24.96	23.83	24.69	24.78	24.78	24.69	23.69	23.64	24.97	23.85	24.70	23.64	25.10	23.85	24.31	7.01	6.48	0.53

[a] Calculated by the GIAO method at the mPW1PW91/6-311+G(2d,p)/PCM(MeOH) level. [b] NMR chemical shifts were obtained from shielding tensors using the reported scaling factors. [c] Measured in CD_3OD (400 MHz).

Table S8. Calculated ^{1}H NMR chemical shifts of (S_a)-**10** and comparison with reported experimental data of brevipetin E (**1′**).

Position	shielding tensors (calculated)[a]								chemical shifts (ppm)		
	10a	**10b**	**10c**	**10d**	**10e**	**10f**	**10g**	**10** (averaged)	**10** (calcd)[b]	**1'** (exptl)[c]	$\Delta\delta$ ($\delta_{calcd} - \delta_{exptl}$)
rhamnose											
1	26.84	26.84	26.87	26.88	26.83	26.99	26.88	26.86	4.64	4.80	-0.16
2	27.41	27.43	27.66	27.64	27.42	27.38	27.67	27.47	4.07	4.07	0.00
3	26.25	26.24	26.19	26.20	26.29	26.16	26.25	26.24	5.22	5.35	-0.13
4	26.38	26.38	26.53	26.53	26.44	26.37	26.58	26.42	5.05	5.06	-0.01
5	27.53	27.51	27.49	27.52	27.54	27.55	27.54	27.52	4.02	4.09	-0.07
6	30.46	30.44	30.42	30.43	30.45	30.45	30.43	30.44	1.30	1.24	0.06
1-OMe	28.25	28.25	28.19	28.19	28.26	28.23	28.20	28.24	3.35	–	–
HHDP											
3	24.50	24.72	24.71	24.49	24.59	24.49	24.58	24.60	6.74	6.66	0.08
3'	24.84	24.64	24.65	24.85	24.72	24.85	24.73	24.75	6.60	6.48	0.12

[a] Calculated by the GIAO method at the mPW1PW91/6-311+G(2d,p)/PCM(MeOH) level. [b] NMR chemical shifts were obtained from shielding tensors using the reported scaling factors. [c] Measured in CD_3OD (400 MHz).

Table S9. Calculated ^{13}C NMR chemical shifts of (R_a)-**3** and comparison with reported experimental data of brevipetin B (**3**) and brevipetin E (**1′**).

Position	shielding tensors (calculated)[a]																			chemical shifts (ppm)				
																					3		**1'**	
	3a	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**	**3h**	**3i**	**3j**	**3k**	**3l**	**3m**	**3n**	**3o**	**3p**	**3q**	**3r**	**3** (averaged)	**3** (calcd)[b]	**3** (exptl)[c]	$\Delta\delta$ (vs **3**) ($\delta_{calcd} - \delta_{exptl}$)	**1'** (exptl)[c]	$\Delta\delta$ (vs **1'**) ($\delta_{calcd} - \delta_{exptl}$)
glucose																								
1	81.4	82.9	81.4	81.3	81.5	83.1	81.5	83.0	82.8	81.4	82.7	81.4	81.4	81.4	81.5	81.0	81.2	80.2	81.8	100.8	102.5	-1.7	102.5	-1.7
2	111.8	112.1	111.8	111.9	111.8	111.8	111.8	111.8	111.8	111.9	111.8	111.9	111.8	111.8	111.8	111.9	112.0	111.8	111.9	71.9	72.0	-0.1	72.0	-0.1
3	104.5	101.8	104.8	104.8	104.4	101.5	104.4	101.6	101.6	105.0	101.9	104.7	105.0	105.0	105.0	104.4	104.3	104.2	103.8	79.6	80.3	-0.7	80.3	-0.7
4	109.2	112.5	108.9	108.9	109.2	109.8	109.1	109.8	109.8	109.5	109.6	108.9	109.6	109.5	109.6	111.6	111.5	109.5	109.7	73.9	73.5	0.4	74.2	-0.3
5	109.5	110.1	109.6	109.5	109.5	109.8	109.5	109.7	109.7	109.6	109.7	109.5	109.6	109.6	109.6	110.1	110.2	109.4	109.7	74.0	74.7	-0.7	73.2	0.8
6	120.9	123.6	120.9	120.9	120.9	120.9	120.9	120.9	120.9	120.9	120.9	120.9	120.9	120.9	120.9	123.6	123.6	121.2	121.3	62.8	61.6	1.2	67.7	-4.9
HHDP																								
1	66.7	66.4	64.9	64.9	66.7	66.4	66.7	66.5	66.5	73.4	64.6	64.9	73.4	73.4	73.3	66.7	66.6	66.7	66.8	115.2	115.3	-0.1	115.4	-0.2
2	53.9	54.1	54.7	54.8	53.9	54.3	53.9	54.2	54.3	53.0	55.1	54.7	52.9	53.1	52.9	53.7	53.7	53.9	54.1	127.4	126.7	0.7	126.8	0.6
3	75.6	75.5	73.2	73.2	75.5	75.7	75.6	75.5	75.5	74.4	73.2	73.2	74.4	74.5	74.4	75.6	75.5	75.7	74.8	107.6	107.9	-0.3	107.9	-0.3
4	38.8	38.8	36.6	36.7	38.7	38.8	38.9	38.7	38.9	35.3	36.8	36.6	35.3	35.3	35.3	38.9	38.7	38.7	37.8	143.1	145.7	-2.6	145.8	-2.7
5	47.5	47.2	42.8	43.0	47.4	47.2	47.5	47.2	47.3	46.9	42.8	42.8	46.8	46.9	46.9	47.6	47.4	47.3	46.0	135.2	137.3	-2.1	137.5	-2.3
6	40.0	39.9	39.2	39.4	39.9	39.8	39.9	39.9	40.0	40.1	39.3	39.1	40.0	40.1	40.1	40.0	39.9	39.8	39.7	141.2	144.7	-3.5	144.9	-3.7
7	8.5	8.0	8.0	8.0	8.5	8.1	8.4	8.1	8.1	8.6	7.7	8.0	8.6	8.6	8.6	8.3	8.3	8.4	8.2	171.5	171.0	0.5	171.1	0.4
1'	65.2	65.2	66.7	66.7	65.1	65.2	65.2	65.2	65.2	73.0	66.8	66.6	73.1	73.1	73.1	65.1	65.1	65.1	66.4	115.5	115.5	0.0	115.6	-0.1
2'	55.4	55.1	54.5	54.7	55.2	55.3	55.4	55.2	55.4	53.3	54.7	54.5	53.7	53.3	53.5	55.1	54.9	55.1	54.9	126.7	126.4	0.3	126.3	0.4
3'	73.2	73.0	75.4	75.7	73.0	73.1	73.2	73.0	73.1	74.2	75.6	75.4	74.5	74.3	74.3	73.3	73.1	73.1	73.9	108.3	107.7	0.6	107.7	0.6
4'	36.7	36.5	38.6	38.8	36.6	36.6	36.7	36.5	36.6	35.3	38.8	38.6	35.3	35.3	35.3	36.8	36.6	36.6	37.1	143.8	145.7	-1.9	145.8	-2.0
5'	43.2	43.1	47.4	47.7	43.0	42.9	43.0	42.9	43.2	46.8	47.7	47.3	46.7	46.7	46.7	43.3	43.1	42.9	44.8	136.4	137.3	-0.9	137.4	-1.0
6'	39.5	39.4	40.0	40.1	39.4	39.4	39.4	39.4	39.5	40.1	40.1	40.0	40.0	40.0	40.1	39.5	39.4	39.4	39.7	141.3	144.6	-3.3	144.8	-3.5
7'	8.5	8.4	8.9	8.9	8.5	8.4	8.4	8.5	8.5	9.0	8.9	8.8	9.0	9.0	9.0	8.4	8.4	8.4	8.6	171.1	170.2	0.9	170.4	0.7
chavicol																								
1	23.6	23.4	23.5	23.6	23.6	23.7	23.5	23.6	23.6	23.6	23.5	23.6	23.6	23.6	23.6	23.3	23.3	22.8	23.5	156.8	157.1	-0.3	157.0	-0.2
2, 6	66.6	66.7	66.6	66.6	66.7	66.8	66.7	66.8	66.7	66.7	66.7	66.6	66.6	66.7	66.6	66.5	66.6	65.4	66.6	115.4	117.8	-2.4	117.9	-2.5
3, 5	51.0	51.1	50.9	51.0	50.9	51.2	49.6	51.0	51.0	51.1	51.0	49.7	51.0	51.1	50.9	51.1	51.1	51.2	50.9	130.5	130.5	0.0	130.6	-0.1
4	45.4	45.9	45.5	45.4	45.5	45.8	47.6	45.9	45.9	45.5	45.9	47.7	45.4	45.4	45.5	45.6	45.6	45.3	45.7	135.5	135.5	0.0	135.8	-0.3
7	143.1	143.0	143.0	143.1	143.0	142.9	144.8	143.0	143.0	142.9	143.0	144.9	143.1	143.0	143.0	143.1	143.0	142.9	143.2	41.8	40.2	1.6	40.3	1.5
8	38.9	38.7	38.8	38.8	38.9	38.7	36.3	38.7	38.7	38.8	38.7	36.5	38.9	38.8	38.8	38.8	38.8	38.7	38.6	142.3	139.0	3.3	139.1	3.2
9	66.3	66.5	66.4	66.3	66.3	66.6	67.4	66.5	66.4	66.4	66.5	67.5	66.2	66.8	66.3	66.3	66.3	66.6	66.5	115.5	115.7	-0.2	115.7	-0.2

[a] Calculated by the GIAO method at the mPW1PW91/6-311+G(2d,p)/PCM(MeOH) level. [b] NMR chemical shifts were obtained from shielding tensors using the reported scaling factors. [c] Measured in CD_3OD (100 MHz).

Table S10. Calculated ^{13}C NMR chemical shifts of (S_a)-**8** and comparison with reported experimental data of brevipetin E (**1′**).

(a) Conformers lacking the intramolecular hydrogen bond between the 2-hydroxy group and the 3-ester carbonyl of the glucose unit with populations ≥1%.

Position	shielding tensors (calculated)[a]									chemical shifts (ppm)		
	8a	**8b**	**8c**	**8d**	**8e**	**8f**	**8g**	**8h**	**8** (averaged)	**8** (calcd)[b]	**1'** (exptl)[c]	$\Delta\delta$ ($\delta_{calcd} - \delta_{exptl}$)
glucose												
1	81.2	81.4	81.2	81.3	81.2	81.2	81.3	81.1	81.2	101.3	102.5	-1.2
2	111.5	111.2	111.5	111.1	111.4	111.2	111.2	111.4	111.3	72.4	72.0	0.4
3	106.6	105.7	106.6	105.6	106.7	105.7	105.7	106.7	106.2	77.3	80.3	-3.0
4	109.6	110.0	109.6	110.0	109.6	110.0	110.0	109.6	109.8	73.9	74.2	-0.3
5	109.4	109.3	109.3	109.3	109.4	109.3	109.2	109.3	109.3	74.3	73.2	1.1
6	123.1	123.2	123.1	123.2	123.1	123.2	123.1	123.1	123.1	61.0	67.7	-6.7
HHDP												
1	60.9	70.0	60.9	70.0	60.9	70.0	70.1	60.8	64.9	117.1	115.4	1.7
2	63.1	61.0	63.1	61.2	63.1	61.0	61.1	63.1	62.2	119.6	126.8	-7.2
3	65.4	66.9	65.3	66.8	65.4	66.8	66.8	65.3	66.0	115.9	107.9	8.0
4	37.3	36.0	37.2	36.0	37.3	35.9	35.9	37.2	36.7	144.2	145.8	-1.6
5	39.3	43.7	39.3	43.6	39.4	43.6	43.6	39.2	41.2	139.8	137.5	2.3
6	39.6	39.6	39.6	39.6	39.5	39.6	39.6	39.5	39.6	141.4	144.9	-3.5
7	10.9	11.8	10.9	11.8	10.9	11.7	11.8	10.9	11.3	168.6	171.1	-2.5
1'	63.9	70.4	64.0	70.5	64.1	70.5	70.5	64.1	66.8	115.2	115.6	-0.4
2'	57.3	55.7	57.4	55.7	57.4	55.7	55.8	57.4	56.6	125.0	126.3	-1.3
3'	75.2	74.4	75.4	74.4	75.2	74.4	74.6	75.3	74.9	107.4	107.7	-0.3
4'	39.6	36.2	39.7	36.1	39.6	36.1	36.3	39.6	38.1	142.8	145.8	-3.0
5'	47.5	47.3	47.5	47.1	47.3	47.2	47.5	47.3	47.4	133.9	137.4	-3.5
6'	39.3	39.5	39.3	39.3	39.2	39.3	39.5	39.2	39.3	141.6	144.8	-3.2
7'	8.5	8.3	8.6	8.3	8.5	8.3	8.4	8.5	8.4	171.3	170.4	0.9
chavicol												
1	23.6	23.6	23.6	23.6	23.6	23.5	23.6	23.6	23.6	156.7	157.0	-0.3
2, 6	66.7	66.8	66.7	66.7	66.8	66.7	66.7	66.6	66.7	115.3	117.9	-2.6
3, 5	51.1	51.1	51.1	51.1	51.0	51.1	51.1	49.7	51.1	130.3	130.6	-0.3
4	45.5	45.5	45.5	45.5	45.6	45.5	45.5	47.7	45.5	135.6	135.8	-0.2
7	142.9	142.9	142.9	143.0	143.0	143.0	142.9	144.8	143.0	41.9	40.3	1.6
8	38.9	38.6	38.7	39.0	38.7	38.8	38.7	36.1	38.7	142.2	139.1	3.1
9	66.6	66.6	66.7	66.4	66.6	66.5	66.8	67.5	66.6	115.4	115.7	-0.3

[a] Calculated by the GIAO method at the mPW1PW91/6-311+G(2d,p)//PCM(MeOH) level. [b] NMR chemical shifts were obtained from shielding tensors using the reported scaling factors. [c] Measured in CD_3OD (100 MHz).

(b) All conformers including those with the intramolecular hydrogen bond between the 2-hydroxy group and the 3-ester carbonyl of the glucose unit with populations ≥1%.

Position	shielding tensors (calculated)[a]																		chemical shifts (ppm)		
	8i	**8j**	**8k**	**8l**	**8a**	**8m**	**8n**	**8o**	**8b**	**8p**	**8q**	**8r**	**8c**	**8d**	**8s**	**8t**	**8e**	**8f**	**8** (averaged)	**8** (calcd)[b]	**1'** (exptl)[c]	$\Delta\delta$ ($\delta_{calcd} - \delta_{exptl}$)
glucose																						
1	81.0	81.1	81.1	81.1	81.2	80.9	81.0	80.8	81.4	81.1	80.8	80.9	81.2	81.3	81.1	81.2	81.2	81.2	81.1	101.5	102.5	-1.0
2	111.8	111.7	111.8	111.7	111.5	111.9	111.8	111.8	111.2	111.8	111.8	111.9	111.5	111.1	111.8	111.7	111.4	111.2	111.7	72.0	72.0	0.0
3	98.7	98.7	98.7	98.7	106.6	99.2	99.3	99.2	105.7	98.9	99.3	98.8	106.6	105.6	98.8	98.9	106.7	105.7	100.0	83.3	80.3	3.0
4	111.0	111.0	111.0	111.0	109.6	110.9	111.0	110.9	110.0	111.1	110.9	111.0	109.6	110.0	111.2	111.2	109.6	110.0	110.8	72.9	74.2	-1.3
5	110.0	110.0	110.0	110.0	109.4	109.8	109.8	109.8	109.3	109.7	109.8	109.7	109.3	109.3	110.0	110.0	109.4	109.3	109.8	73.8	73.2	0.6
6	123.3	123.3	123.3	123.3	123.1	123.3	123.2	123.2	123.2	123.3	123.3	123.3	123.1	123.2	123.3	123.3	123.1	123.2	123.3	60.9	67.7	-6.8
HHDP																						
1	68.7	68.6	68.6	68.6	60.9	58.3	58.2	58.3	70.0	61.3	58.4	61.3	60.9	70.0	61.6	61.6	60.9	70.0	65.8	116.2	115.4	0.8
2	62.5	62.4	62.4	62.5	63.1	65.2	65.2	65.2	61.0	64.4	65.1	64.3	63.1	61.2	64.0	64.1	63.1	61.0	63.0	118.9	126.8	-7.9
3	66.8	66.8	66.7	66.6	65.4	65.0	64.8	65.0	66.9	68.1	64.8	68.3	65.3	66.8	71.2	70.9	65.4	66.8	66.5	115.4	107.9	7.5
4	35.9	35.8	35.7	35.9	37.3	37.1	37.2	37.2	36.0	38.9	36.9	39.0	37.2	36.0	38.8	38.7	37.3	35.9	36.4	144.4	145.8	-1.4
5	42.6	42.3	42.3	42.4	39.3	37.5	37.5	37.6	43.7	42.7	37.4	42.6	39.3	43.6	42.9	42.9	39.4	43.6	41.5	139.5	137.5	2.0
6	38.7	38.5	38.6	38.6	39.6	39.0	39.1	39.0	39.6	39.0	39.1	38.9	39.6	39.6	36.1	36.1	39.5	39.6	38.8	142.1	144.9	-2.8
7	8.3	8.4	8.2	8.4	10.9	7.5	7.7	7.6	11.8	7.9	7.7	7.7	10.9	11.8	7.6	7.7	10.9	11.7	8.6	171.1	171.1	0.0
1'	71.0	71.0	71.2	71.0	63.9	64.4	64.1	64.2	70.4	60.9	64.3	61.2	64.0	70.5	64.1	64.2	64.1	70.5	68.5	113.5	115.6	-2.1
2'	54.4	54.5	54.5	54.4	57.3	56.0	56.0	56.0	55.7	56.7	56.0	56.7	57.4	55.7	56.8	56.8	57.4	55.7	55.2	126.3	126.3	0.0
3'	74.9	74.9	75.0	75.0	75.2	76.0	76.1	76.1	74.4	73.2	75.9	73.3	75.4	74.4	78.8	78.9	75.2	74.4	75.1	107.2	107.7	-0.5
4'	36.0	35.9	36.0	35.9	39.6	39.6	39.5	39.6	36.2	37.4	39.4	37.5	39.7	36.1	39.8	39.7	39.6	36.1	37.0	143.8	145.8	-2.0
5'	47.4	47.1	47.4	47.1	47.5	47.8	47.1	47.4	47.3	42.0	47.3	42.6	47.5	47.1	47.8	47.7	47.3	47.2	47.1	134.2	137.4	-3.2
6'	38.8	38.7	38.9	38.6	39.3	38.9	38.4	38.6	39.5	38.1	38.5	38.8	39.3	39.3	36.5	36.4	39.2	39.3	38.7	142.2	144.8	-2.6
7'	8.3	8.4	8.4	8.3	8.5	8.7	8.6	8.7	8.3	8.1	8.7	8.1	8.6	8.3	8.0	8.0	8.5	8.3	8.4	171.4	170.4	1.0
chavicol																						
1	23.4	23.5	23.4	23.4	23.6	23.4	23.5	23.3	23.6	23.5	23.5	23.4	23.6	23.6	23.4	23.5	23.6	23.5	23.5	156.9	157.0	-0.1
2, 6	66.6	66.7	66.7	66.7	66.7	66.7	66.7	66.6	66.8	66.7	66.6	66.7	66.7	66.7	66.7	66.7	66.8	66.7	66.7	115.3	117.9	-2.6
3, 5	51.2	51.1	51.2	51.1	51.1	51.2	51.0	51.2	51.1	51.0	51.1	51.2	51.1	51.1	51.2	51.1	51.0	51.1	51.1	130.3	130.6	-0.3
4	46.1	46.1	46.0	46.1	45.5	46.0	46.1	46.1	45.5	46.1	46.1	46.0	45.5	45.5	46.2	46.1	45.6	45.5	46.0	135.2	135.8	-0.6
7	142.9	142.9	142.9	143.0	142.9	142.8	143.0	142.9	142.9	143.0	142.9	142.9	142.9	143.0	142.9	143.0	143.0	143.0	142.9	42.0	40.3	1.7
8	38.6	38.7	38.6	38.7	38.9	38.6	38.7	38.6	38.6	38.6	38.6	38.7	38.7	39.0	38.6	38.6	38.7	38.8	38.7	142.3	139.1	3.2
9	66.6	66.7	66.8	66.8	66.6	66.8	66.8	66.6	66.6	66.9	66.8	66.8	66.7	66.4	66.6	66.8	66.6	66.5	66.7	115.3	115.7	-0.4

[a] Calculated by the GIAO method at the mPW1PW91/6-311+G(2d,p)/PCM(MeOH) level. [b] NMR chemical shifts were obtained from shielding tensors using the reported scaling factors. [c] Measured in CD_3OD (100 MHz).

Table S11. Calculated ^{13}C NMR chemical shifts of (R_a)-**9** and comparison with reported experimental data of brevipetin E (**1′**).

Position	shielding tensors (calculated)[a]																		chemical shifts (ppm)		
	9Aa	**9Ba**	**9Bb**	**9Ab**	**9Bc**	**9Ac**	**9Ad**	**9Ae**	**9Af**	**9Bd**	**9Be**	**9Ag**	**9Bf**	**9Ah**	**9Bg**	**9Ai**	**9Bh**	**9** (averaged)	**9** (calcd)[b]	**1'** (exptl)[c]	$\Delta\delta$ ($\delta_{calcd} - \delta_{exptl}$)
glucose																					
1	82.7	82.8	82.7	82.5	82.7	82.5	81.5	81.0	81.2	81.8	81.7	80.8	81.7	80.8	81.2	82.6	81.2	82.3	100.3	102.4	-2.1
2	112.2	112.5	112.3	111.8	112.4	111.9	112.7	112.1	112.5	112.8	113.1	111.7	113.0	111.8	112.4	112.1	112.4	112.3	71.5	70.5	1.0
3	104.9	103.7	104.2	106.7	103.9	106.1	105.5	107.2	106.8	105.1	104.6	109.0	104.8	108.3	105.4	105.3	105.5	105.2	78.3	76.5	1.8
4	105.5	107.8	106.3	105.2	107.3	105.3	105.2	105.6	104.9	106.1	107.5	105.3	107.0	105.4	108.5	105.7	108.0	106.2	77.4	77.0	0.4
5	116.6	116.8	116.7	116.4	117.0	116.3	116.8	116.1	116.6	116.6	116.9	115.9	117.0	115.8	116.2	116.5	116.3	116.6	67.3	67.4	-0.1
6	169.1	169.0	168.5	169.1	169.0	169.1	169.1	168.9	169.1	168.5	169.0	169.0	169.1	169.0	168.9	169.1	168.9	169.0	16.9	17.7	-0.8
1-OMe	130.6	130.8	130.8	130.6	130.8	130.7	130.0	130.5	130.1	130.2	130.2	130.5	130.2	130.5	130.6	130.6	130.6	130.6	53.8	–	–
HHDP																					
1	69.3	64.0	70.1	60.6	61.4	63.3	69.5	69.3	63.4	70.4	64.2	60.7	61.5	63.3	64.1	62.9	61.5	65.6	116.4	115.5	0.9
2	61.7	56.8	55.5	63.6	57.8	62.7	61.5	61.4	62.3	55.2	56.6	63.1	57.5	62.2	56.6	63.2	57.5	59.7	122.0	126.8	-4.8
3	67.0	75.5	75.2	65.3	72.9	68.3	67.2	67.2	68.5	75.4	75.7	65.6	73.1	68.5	75.9	71.7	73.4	70.5	111.6	108.3	3.3
4	36.4	38.9	36.1	37.3	37.2	39.0	36.7	36.6	39.2	36.0	39.0	37.4	37.2	39.1	39.0	39.5	37.3	37.4	143.5	145.7	-2.2
5	43.8	46.8	47.1	39.2	41.2	44.4	44.3	44.2	44.5	47.3	47.0	39.4	41.4	44.5	47.0	45.5	41.5	44.0	137.1	137.5	-0.4
6	39.7	39.0	39.7	40.0	38.3	40.0	39.9	39.8	39.9	39.6	38.9	39.9	38.3	39.9	38.9	37.3	38.2	39.4	141.5	144.9	-3.4
7	12.0	9.1	9.0	11.5	8.5	11.5	11.7	11.9	11.1	8.2	8.4	11.1	7.8	11.1	8.5	11.2	7.9	10.4	169.5	171.0	-1.5
1'	70.3	60.7	70.2	63.7	63.6	61.1	70.3	70.4	61.0	70.1	60.6	63.8	63.5	61.3	60.7	63.7	63.6	65.7	116.3	115.3	1.0
2'	55.2	63.6	61.3	56.8	62.6	57.8	55.2	55.0	57.9	61.4	63.7	56.7	62.7	57.6	63.4	57.4	62.4	59.1	122.6	126.8	-4.2
3'	74.7	65.1	66.7	75.4	67.9	72.5	74.9	74.8	72.8	66.7	65.2	75.6	68.0	72.8	65.3	78.6	68.1	70.9	111.3	107.7	3.6
4'	36.0	37.2	35.7	39.1	39.1	37.3	36.1	36.1	37.4	35.7	37.2	39.3	39.1	37.5	37.2	39.3	39.1	37.2	143.7	145.8	-2.1
5'	46.9	39.0	43.6	47.4	44.1	41.9	47.0	47.0	42.0	43.6	38.9	47.6	44.0	42.2	39.1	47.7	44.1	44.2	137.0	137.3	-0.3
6'	39.5	40.0	39.8	39.3	40.1	38.8	39.4	39.5	38.8	39.8	40.0	39.4	40.1	38.9	40.0	36.4	40.1	39.6	141.4	144.8	-3.4
7'	8.3	11.0	11.8	8.7	11.0	8.0	8.4	8.2	8.1	11.8	11.0	8.6	11.1	7.9	11.2	7.9	11.3	9.7	170.1	170.8	-0.7

[a] Calculated by the GIAO method at the mPW1PW91/6-311+G(2d,p)/PCM(MeOH) level. [b] NMR chemical shifts were obtained from shielding tensors using the reported scaling factors. [c] Measured in CD_3OD (100 MHz).

Table S12. Calculated ^{13}C NMR chemical shifts of (S_a)-**10** and comparison with reported experimental data of brevipetin E (**1′**).

Position	shielding tensors (calculated)[a]								chemical shifts (ppm)		
	10a	**10b**	**10c**	**10d**	**10e**	**10f**	**10g**	**10** (averaged)	**10** (calcd)[b]	**1'** (exptl)[c]	$\Delta\delta$ ($\delta_{calcd} - \delta_{exptl}$)
glucose											
1	82.5	82.5	81.5	81.5	82.6	80.8	81.6	82.2	100.4	102.4	-2.0
2	111.9	111.9	112.8	112.8	111.8	112.1	112.7	112.1	71.6	70.5	1.1
3	106.1	105.7	106.9	107.3	106.3	108.3	107.5	106.3	77.2	76.5	0.7
4	106.8	107.0	106.6	106.4	107.3	106.8	106.9	106.8	76.7	77.0	-0.3
5	117.2	117.1	117.2	117.3	117.1	116.7	117.3	117.1	66.8	67.4	-0.6
6	169.0	169.0	168.9	169.0	169.0	168.8	169.0	169.0	16.9	17.7	-0.8
1-OMe	130.6	130.6	130.0	130.0	130.6	130.3	130.0	130.4	54.0	–	–
HHDP											
1	64.5	66.6	66.7	64.5	72.8	64.6	72.9	66.1	115.9	115.5	0.4
2	54.8	54.1	53.5	54.3	53.1	54.3	52.5	54.2	127.3	126.8	0.5
3	72.7	75.2	75.1	72.6	74.3	72.6	74.2	73.8	108.4	108.3	0.1
4	36.6	38.7	38.7	36.5	35.7	36.6	35.7	37.4	143.5	145.7	-2.2
5	42.9	47.4	47.4	42.9	47.2	42.9	47.3	45.1	136.1	137.5	-1.4
6	39.5	40.0	40.0	39.5	40.6	39.5	40.6	39.8	141.2	144.9	-3.7
7	8.8	9.2	8.5	8.1	9.3	8.1	8.6	8.8	170.9	171.0	-0.1
1'	67.1	65.2	65.0	66.8	73.4	67.1	73.2	66.8	115.2	115.3	-0.1
2'	54.1	54.7	54.8	54.2	53.7	54.0	53.9	54.3	127.2	126.8	0.4
3'	76.0	73.4	73.5	76.1	75.2	76.2	75.2	74.9	107.4	107.7	-0.3
4'	38.8	36.7	36.8	38.8	35.7	38.8	35.7	37.7	143.2	145.8	-2.6
5'	48.3	43.4	43.4	48.2	47.6	48.3	47.5	46.2	135.0	137.3	-2.3
6'	40.4	39.5	39.5	40.4	40.4	40.5	40.4	40.0	140.9	144.8	-3.9
7'	8.6	8.2	8.3	8.7	8.7	8.8	8.8	8.5	171.3	170.8	0.5

[a] Calculated by the GIAO method at the mPW1PW91/6-311+G(2d,p)/PCM(MeOH) level. [b] NMR chemical shifts were obtained from shielding tensors using the reported scaling factors. [c] Measured in CD_3OD (100 MHz).

Figure S6. Correlation plots of experimental ^{1}H and ^{13}C NMR chemical shifts of brevipetin B (**3**) versus corresponding calculated ^{1}H and ^{13}C NMR chemical shifts of (R_a)-**3**.

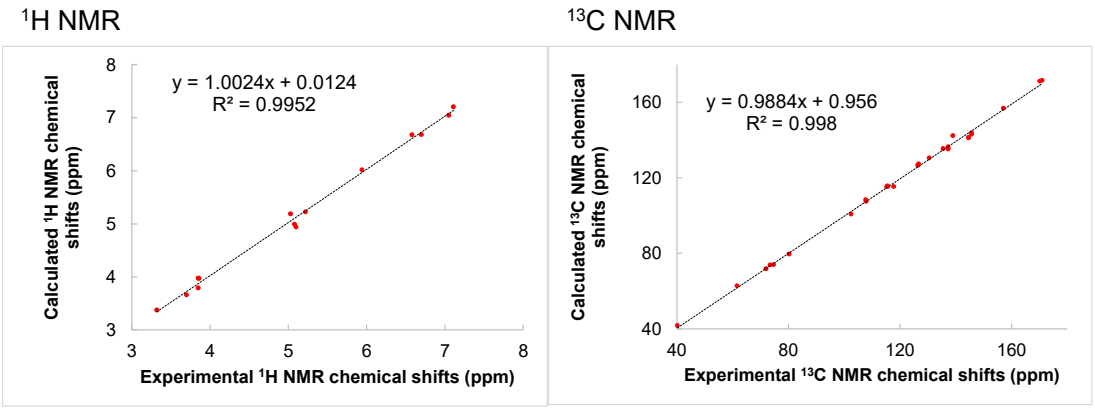
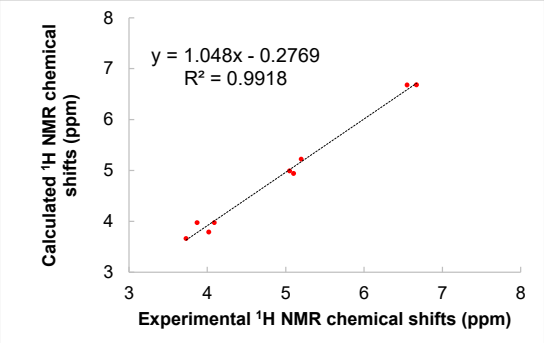
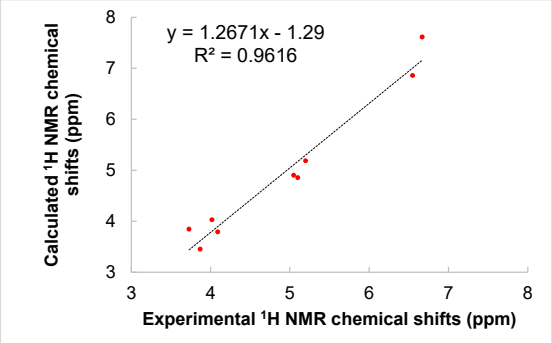


Figure S7. Correlation plots of experimental ^{1}H NMR chemical shifts of **1′** versus corresponding calculated ^{1}H NMR chemical shifts of (R_a)-**3** and (S_a)-**8** for the glucopyranose moiety and (R_a)-**9** and (S_a)-**10** for the rhamnopyranose moiety, except for the chavicol moiety.

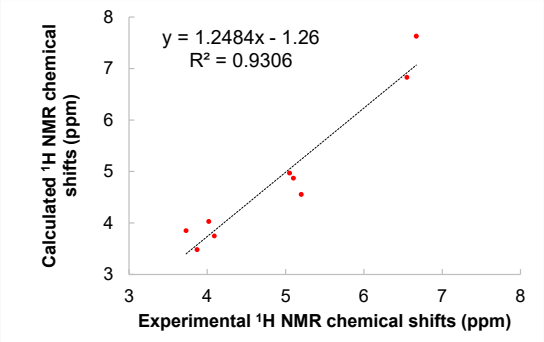
(R_a)-**3**



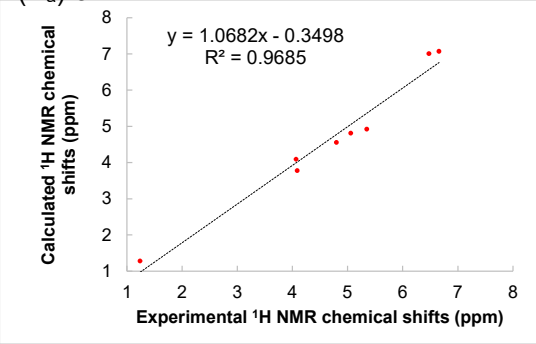
(S_a)-**8** (conformers lacking the intramolecular hydrogen bond between the 2-hydroxy group and the 3-ester carbonyl of the glucose unit)



(S_a)-**8** (all conformers including those with the intramolecular hydrogen bond between the 2-hydroxy group and the 3-ester carbonyl of the glucose unit)



(R_a)-**9**



(S_a)-**10**

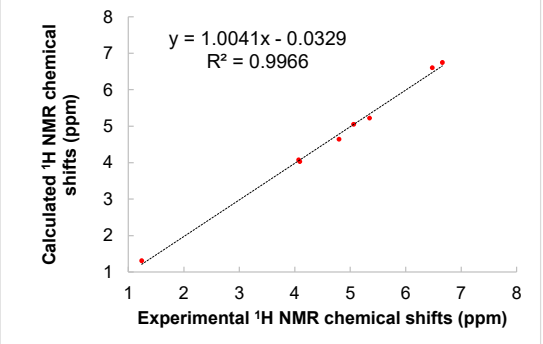
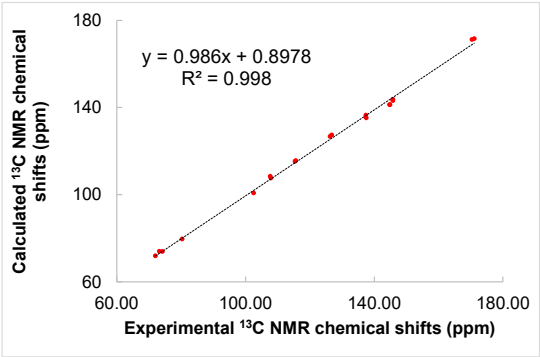
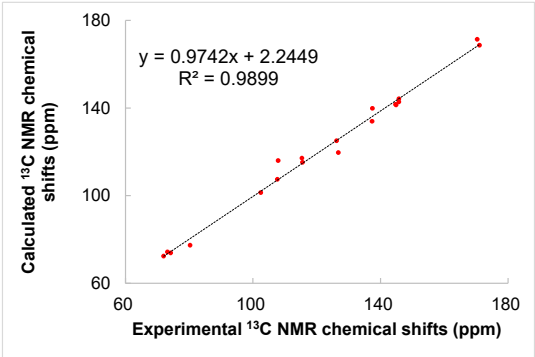


Figure S8. Correlation plots of experimental ^{13}C NMR chemical shifts of **1′** versus corresponding calculated ^{13}C NMR chemical shifts of (R_a)-**3** and (S_a)-**8** for the glucopyranose moiety, except for the chavicol moiety, and (R_a)-**9** and (S_a)-**10** for the rhamnopyranose moiety. The C-6 signal of the glucopyranose moiety was excluded from the plot for **3** and **8**.

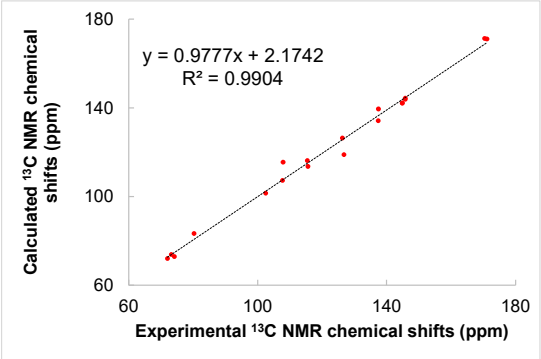
(R_a)-**3**



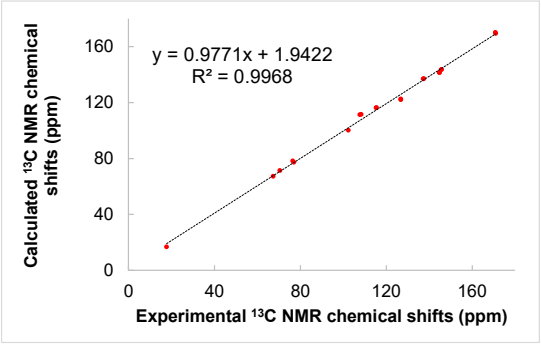
(S_a)-**8** (conformers lacking the intramolecular hydrogen bond between the 2-hydroxy group and the 3-ester carbonyl of the glucose unit)



(S_a)-**8** (all conformers including those with the intramolecular hydrogen bond between the 2-hydroxy group and the 3-ester carbonyl of the glucose unit)



(R_a)-**9**



(S_a)-**10**

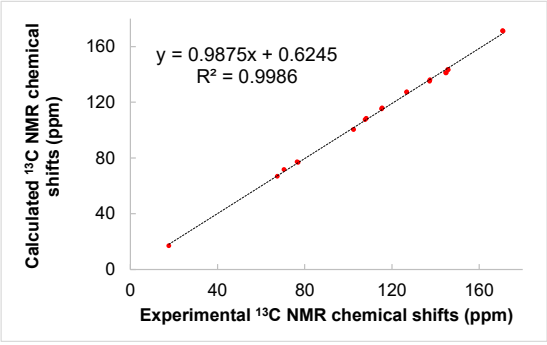


Figure S9. Representative optimized conformers of brevipetin E (**1**) within 5 kcal/mol at the B3LYP/6-31G(d,p)/PCM(MeOH) level.

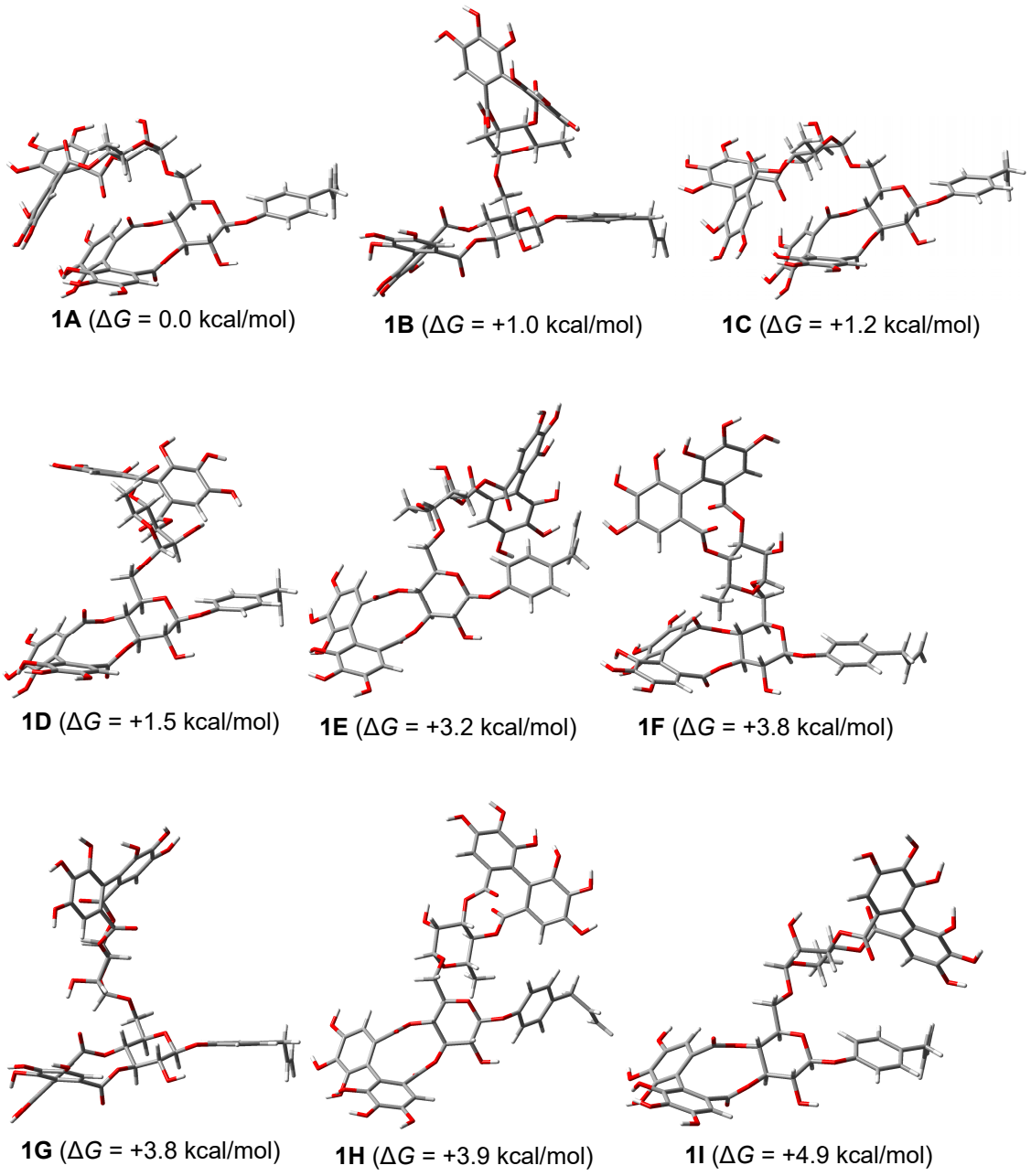


Table S13. Thermodynamic parameters (electronic, enthalpy, and free energies) of the representative conformers of **1** at the B3LYP/6-31G(d,p)/PCM(MeOH) level (within 5 kcal/mol).

conformers	*E* (a.u.)	*E′* (a.u.)	*H* (a.u.)	*G* (a.u.)	Δ*G* (kcal/mol)
1A	-3848.403903	-3847.525454	-3847.457207	-3847.629083	0.00
1B	-3848.396969	-3847.519221	-3847.450361	-3847.627446	1.03
1C	-3848.403067	-3847.524809	-3847.456389	-3847.627137	1.22
1D	-3848.395921	-3847.518222	-3847.449324	-3847.626695	1.50
1E	-3848.396501	-3847.518322	-3847.449703	-3847.623949	3.22
1F	-3848.394135	-3847.516054	-3847.447361	-3847.623020	3.80
1G	-3848.394252	-3847.516190	-3847.447495	-3847.622951	3.85
1H	-3848.394423	-3847.516632	-3847.447846	-3847.622806	3.94
1I	-3848.393127	-3847.515293	-3847.446561	-3847.621318	4.87

E: electronic energy; E': electronic energy with zero point energy; H: enthalpy; G: Gibbs free energy; ΔG: relative Gibbs free energy.

Figure S10. Calculated ECD spectra of representative conformers for **1**. All spectra were calculated at the CAM-B3LYP/6-31G(d,p)/PCM(MeOH) level.