SUPPLEMENTARY MATERIAL

A new triterpenoid glycoside from the leaves and stems of *Duranta repens*

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Abstract

A new triterpenoid glycoside (**1**) was isolated from the methanol extract of the leaves and stems of *Duranta repens* L. (Verbenaceae) along with 14 known compounds consisting of eight triterpenoids, four iridoids, one phenylethanoid glycoside, and one flavonoid. The chemical structure of **1** was determined to be bayogenin 3-*O*-[β -D-glucopyranoside]-28-*O*-[α -L-rhamnopyranosyl-(1 $\rightarrow$ 5)-*O*- β -D-apiofuranosyl-(1 $\rightarrow$ 4)-*O*- α -L-rhamnopyranosyl-(1 $\rightarrow$ 2)-*O*- α -L-arabinopyranosyl] ester, based on spectroscopic data. In addition, the inhibitory effects on lipoxygenase activity of the isolates were examined. Among them, acteoside and apigenin resulted in 94 $\pm$ 3.6% and 82 $\pm$ 4.7% inhibition, respectively, at 0.5 mM.

4. Experimental

4.1. Plant material

D. repens was cultivated in Kumamoto prefecture, Japan, and was harvested in September 2006, and identified by one of authors (Prof. Dr. T. Nohara). A voucher specimen (DR 2006) has been deposited at the laboratory of Natural Products Chemistry, School of Agriculture, Tokai University.

4.2. General experimental procedures

Optical rotations were performed with a JASCO DIP-1000 KYU digital polarimeter (JASCO, Tokyo, Japan). FAB-MS and ESI-MS were recorded on a JEOL JMS-DX-303HF (JEOL, Tokyo, Japan) and JEOL JMS-T100 LP (JEOL), respectively. ¹H- and ¹³C-NMR spectra were recorded with a JEOL alpha-500 spectrometer (JEOL), and chemical shifts were given on a δ (ppm) scale with tetramethylsilane as an internal standard. Silica gel 60 (Merck, Art. 1.09385; Merck, Darmstadt, Germany), Sephadex LH-20 (Pharmacia Fine Chemicals, Uppsala, Sweden), and Chromatorex ODS (Fuji Silysia Chemical, Ltd., Aichi, Japan) were used for column chromatography. HPLC separation was run on a Shimadzu LC-10AS micro pump (Shimadzu, Kyoto, Japan) with a Shimadzu RID-10A RI-detector (Shimadzu). For HPLC column chromatography, COSMOSIL 5C18-AR- II (Nacalai Tesque, Inc., Kyoto, Japan, 20 mm i.d.×250 mm) was used. Lipxygenase type I-B and NDGA were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). All other chemicals were products from Nacalai Tesque, Inc.

4.3. Extraction and isolation of 1–15

The leaves and stems of *D. repens* (300.6 g) were extracted with MeOH (2000 mL) at room temperature, and the solvent was removed under reduced pressure to yield a MeOH extract (39.5 g). The MeOH extract was partitioned between hexane (2000 mL) and 90% MeOH (500 mL). The 90% MeOH-soluble fraction (fr.) (38.6 g) was chromatographed over silica gel column using gradient mixtures of CHCl₃–MeOH–H₂O (14:2:0.1, 10:2:0.1, 8:2:0.2, 7:3:0.5, 6:4:1, 0:1:0) as eluents to furnish fractions (frs.) 1–11. Fraction 2 (5.8 g) was subjected to Chromatorex ODS column

chromatography using gradient mixtures of H₂O–MeOH (40% MeOH, 50% MeOH, 60% MeOH, 70% MeOH, 80% MeOH, 90% MeOH, MeOH) as eluents to yield frs. 2.1–2.32. HPLC of fr. 2.12 (156 mg) with 40% MeOH as eluent furnished **12** (43 mg). Fractions 2.13 (1.4 g) and 2.14 (1.9 g) were each subjected to HPLC with 50% MeOH as eluent to yield **12** (26 mg) and **11** (44 mg) from fr. 2.13 and **11** (528 mg) from fr. 2.14. Fraction 2.16 (62 mg) was subjected to HPLC with 55% MeOH as eluent to furnish **15** (7 mg). HPLC of fr. 2.25 (173 mg) using 90% MeOH as eluent yielded **9** (33 mg) and **8** (58 mg). Chromatography of fr. 3 (1.5 g) over Chromatorex ODS column using gradient mixtures of H₂O–MeOH (40% MeOH, 50% MeOH, 60% MeOH, 70% MeOH, 80% MeOH, 90% MeOH, MeOH) as eluents furnished frs. 3.1–3.28. Fractions 3.11 (56 mg), 3.13 (32 mg), and 3.14 (67 mg) were each subjected to HPLC with 40% MeOH as eluent to yield **13** (28 mg) from fr. 3.11, **12** (13 mg) from fr. 3.13, and **11** (12 mg) from fr. 3.14. Chromatography of fr. 5 (12.8 g) over silica gel column using gradient mixtures of CHCl₃–MeOH–H₂O (10:2:0.1, 8:2:0.1, 7:3:0.5, 6:4:1, 0:1:0) as eluents furnished frs. 5.1–5.9. Fraction 5.6 (9.2 g) was chromatographed over silica gel column using gradient mixtures of CHCl₃–MeOH–H₂O (8:2:0.1, 7:3:0.5, 6:4:1, 0:1:0) as eluents to yield frs. 5.6.1–5.6.8. Fraction 5.6.5 (6.9 g) was subjected to Chromatorex ODS column using gradient mixtures of H₂O–MeOH (10% MeOH, 20% MeOH, 30% MeOH, 40% MeOH, 50% MeOH, 60% MeOH, 70% MeOH, 80% MeOH, 90% MeOH, MeOH) as eluents to yield frs. 5.6.5.1–5.6.5.8. HPLC of fr. 5.6.5.4 (1.4 g) with 20% MeOH as eluent yielded **10** (119 mg). Chromatography of fr. 5.6.5.7 (2.2 g) over Sephadex LH-20 column with MeOH as eluent furnished frs. 5.6.5.7.1–5.6.5.7.5. Fraction 5.6.5.7.4 (1.4 g) was subjected to HPLC using 40% MeOH as eluent to yield **14** (794 mg). Fraction 8 (2.0 g) was chromatographed over silica gel column using gradient mixtures of CHCl₃–MeOH–H₂O (7:3:0.5, 6:4:1, 0:1:0) as eluents to afford frs. 8.1–8.6. HPLC of fr. 8.4 (227 mg) with 70% MeOH as eluent yielded **2** (56 mg). Fraction 8.5 (1.4 g) was subjected to HPLC with 60% MeOH as eluent to furnish **1** (43 mg) and **4** (3 mg). Fraction 9 (3.6 g) was chromatographed over silica gel column using gradient mixtures of CHCl₃–MeOH–H₂O (8:2:0.2, 7:3:0.5, 6:4:1, 0:1:0) as eluents to yield frs. 9.1–9.20. Fraction 9.7 (9.2 g) was subjected to Chromatorex ODS column using gradient mixtures of H₂O–MeOH (20% MeOH, 30% MeOH, 40% MeOH, 50% MeOH, 60% MeOH, 70%

MeOH, 80% MeOH, MeOH) as eluents to furnish frs. 9.7.1–9.7.12. Fractions 9.7.9 (676 mg), 9.7.10 (194 mg), and 9.7.11 (64 mg) were each subjected to HPLC with 60% MeOH as eluent to yield **4** (406 mg), **6** (132 mg), and frs. 9.7.9.1–9.7.9.3 from fr. 9.7.9, **5** (24 mg) and **7** (5 mg) from fr. 9.7.10, and **3** (7 mg) from fr. 9.7.11. HPLC of fr. 9.7.9.3 (112 mg) with 55% MeOH as eluent furnished **4** (2mg), **6** (77 mg), and **5** (19 mg).

1: Amorphous powder. $[\alpha]_D^{17} -39.2^\circ$ ($c = 1.2$, MeOH). $^1\text{H-NMR}$ (pyridine- d_5 , 500 MHz) δ : 2.25 (1H, d, $J = 13.0$ Hz, aglycone (Agl)-1a), 4.29 (1H, br s, Agl-2), 5.43 (1H, br s, Agl-12), 3.25 (1H, dd, $J = 3.0, 13.0$ Hz, Agl-18), 3.63 (1H, d, $J = 11.0$ Hz), 1.31 (3H, s, Agl-24), 1.55 (3H, s, Agl-25), 1.11 (3H, s, Agl-26), 1.23 (3H, s, Agl-27), 0.90 (3H, s, Agl-29), 0.95 (3H, s, Agl-30), 5.14 (1H, d, $J = 7.5$ Hz, glucopyranosyl (Glc)-1), 4.01 (1H, dd, $J = 7.5, 9.0$ Hz, Glc-2), 4.16 (1H, dd, $J = 9.0, 9.0$ Hz, Glc-3), 4.21 (1H, dd, $J = 9.0, 9.0$ Hz, Glc-4), 6.44 (1H, d, $J = 3.0$ Hz, arabinopyranosyl (Ara)-1), 3.92 (1H, dd, $J = 3.0, 10.5$ Hz, Ara-5b), 5.85 (1H, s, rhamnopyranosyl (Rha)-1), 1.64 (3H, d, $J = 6.0$ Hz, Rha-6), 6.31 (1H, s, apiofuranosyl (Api)-1), 5.35 (1H, s, Rha'-1), 1.64 (3H, d, $J = 6.0$ Hz, Rha'-6). $^{13}\text{C-NMR}$ (pyridine- d_5 , 125 MHz) δ : 44.1, 70.4, 83.0, 42.7, 47.7, 18.0, 33.0, 40.0, 48.5, 36.9, 24.0, 123.1, 144.2, 42.3, 28.3, 23.2, 47.3, 41.7, 46.2, 30.9, 34.1, 32.7, 65.5, 15.0, 17.3, 17.5, 26.1, 176.2, 33.1, 23.7 (Agl-1–30), 105.6, 75.3, 78.5, 71.5, 78.2, 62.6 (Glc-1–6), 93.5, 75.4, 70.8, 66.5, 63.4 (Ara-1–5), 101.4, 72.5, 72.6, 79.6, 68.5, 18.6 (Rha-1–6), 111.3, 78.2, 79.0, 75.0, 71.0 (Api-1–5), 102.0, 72.0, 72.7, 73.9, 69.8, 18.6 (Rha'-1–6). Negative HR-ESI-MS m/z : 1205.59455 (Calcd for $\text{C}_{58}\text{H}_{93}\text{O}_{26}$: 1205.59550)]. Positive HR-ESI-MS m/z : 1229.59403 (Calcd for $\text{C}_{58}\text{H}_{94}\text{O}_{26}\text{Na}$: 1229.59310)]. Positive FAB-MS m/z : 1229 $[\text{M}+\text{Na}]^+$, 673 $[(\text{deoxyhexosyl unit})\times 2 - 132 (\text{pentosyl unit})\times 2]^+$. Positive HR-FAB-MS m/z : 1229.5886 (Calcd for $\text{C}_{58}\text{H}_{94}\text{O}_{26}\text{Na}$: 1229.5931).

4.4. Sugar analysis of **1**

Compound **1** (5 mg) was heated in 2 M HCl–dioxane (3:2, 2.5 mL) at a temperature of 95° for 2 h. The reaction mixture was extracted with EtOAc (2 mL $\times$ 5). The aqueous layer was neutralized with Amberlite MB-3 column (Organo Co., Tokyo, Japan, 18 mm i.d. $\times$ 120 mm) and then evaporated under reduced pressure to give a

monosaccharide fr. This fr. was analyzed by HPLC under the following conditions: column, Shodex RS-Pac DC-613 (Showa Denko, Tokyo, Japan, 6.0 mm i.d.×150 mm; solvent, CH₃CN-H₂O (4:1); flow rate, 1.0 mL/min; column temperature, 70 °C; detector, JASCO OR-2090 plus (JASCO Co., Tokyo, Japan); pump, JASCO PU-2080; and column oven, JASCO CO-2060. The retention time (t_R) and optical activity of each of the monosaccharides were detected as follows. L-rhamnose [t_R , 4.2 min; optical activity, negative], D-apiose [t_R 5.3 min; optical activity, positive], L-arabinose [t_R , 7.5 min; optical activity, positive], and D-glucose [t_R , 9.8 min; optical activity, positive].

4.5. Lipoxygenase inhibition

The lipoxygenase assay was performed based on the decolorisation of methyleneblue during the enzymatic reaction (Nishida et al. 2014). Linoleic acid solution as a 50 mM stock was first prepared in a volume of 1.0 mL, containing linoleic acid (56 mg), Tween 20 (112 mg), 1 M NaOH (24 µL), and water (811.2 µL), and stored at -20°C under N₂ gas. Lipoxygenase was prepared in 0.1 M phosphate buffer (pH 6.0). The standard assay mixture, in a final volume of 350 µL, contained the sample solution (17.5 µL) at varying concentrations, 0.2 M phosphate buffer (pH 6.0) (140 µL), 25 mM linoleic acid solution (5.6 µL), 250 µM methyleneblue (14 µL), water (102.9 µL) and 212 kU/mL lipoxygenase (70 µL). The reaction was started by the addition of the enzyme, allowed to proceed for 0 min and 30 min at room temperature in a 96-well multiplate. The assay mixture was allowed to a colorimetric measurement at 660 nm using a grating microplate reader (SH-1000Lab, Corona Electric, Ibaraki, Japan). The lipoxygenase inhibitory activity was expressed as the percentage inhibition:

$$\text{Lipoxygenase inhibition (\%)} = [1 - \{(\Delta\text{OD}_{\text{Sample}} - \Delta\text{OD}_{\text{Blank}}) / (\Delta\text{OD}_{\text{Control}} - \Delta\text{OD}_{\text{Blank}})\}] \times 100$$

References

- Nishida Y, Sugahara S, Wada K, Toyohisa D, Tanaka T, Ono M, Yasuda S. 2014. Inhibitory effects of the ethyl acetate extract from bulbs of *Scilla scilloides* on

lipoxygenase and hyaluronidase activities. *Pharm Biol.* 52: 1351–1357.

Supplementary Table

Table S1. ¹H-NMR Data for Aglycone Moiety of **1**, **3**, and **4** (in pyridine-*d*₅. 500 MHz)

	1	3	4
1	2.25 d(13.0)	2.25 dd(3.0, 14.5)	2.29
1	1.23	1.23	1.28 dd(4.0, 13.5)
2	4.80 br s	4.80 br ddd(3.0, 3.0, 3.0)	4.81 ddd(4.0, 4.0, 4.0)
3	4.29	4.31	4.32
5	1.72	1.74	1.75
6	1.77	1.78	1.79
6	1.55	1.60	1.56
7	1.72	1.67	1.78
7	1.45	1.37	1.45 br d(12.0)
9	1.68	1.71	1.87 dd(4.0, 12.0)
11	2.10	2.09	2.20
11	1.97	2.01	2.04 ddd(4.0, 4.0, 17.0)
12	5.43 br s	5.45 dd(3.5, 3.5)	5.63 dd(4.0, 4.0)
15	2.10	2.09	2.34
15	1.23	1.14	1.75
16	2.10	2.09	5.22 ddd(3.5, 4.0, 4.0)
16	1.97	1.98	
18	3.25 dd(3.0, 13.0)	3.30 dd(4.5, 14.5)	3.59 dd(4.0, 13.5)
19	1.77	1.76	2.74 dd(13.5, 13.5)
19	1.23	1.25	1.34
21	1.42	1.39	2.39 ddd(4.5, 12.5, 12.5)
21	1.15	1.15	1.31
22	1.97	1.99	2.29
22	1.72	1.71	2.16
23	4.31	4.33	4.34
23	3.63 d(11.0)	3.68 d(10.5)	3.67 d(11.0)
24	1.31 s	1.34 s	1.34 s
25	1.55 s	1.55 s	1.60 s
26	1.11 s	1.13 s	1.15 s
27	1.23 s	1.23 s	1.77 s
29	0.90 s	0.91 s	1.00 s
30	0.95 s	1.02 s	1.15 s

δ in ppm from TMS.

Table S2. ¹H-NMR Data for Sugar Moiety of **1**, **3**, and **4** (in pyridine-*d*₅, 500 MHz)

	1	3	4
Glc-1	5.14 d(7.5)	5.15 d(8.0)	5.14 d(7.5)
2	4.01 dd(7.5, 9.0)	4.02 dd(8.0, 9.0)	4.02 dd(7.5, 9.0)
3	4.16 dd(9.0, 9.0)	4.16 dd(9.0, 9.0)	4.15 dd(9.0, 9.0)
4	4.21 dd(9.0, 9.0)	4.22 dd(9.0, 9.0)	4.21
5	3.88	3.89 ddd(2.5, 5.0, 9.0)	3.90
6	4.45	4.46 dd(2.5, 11.0)	4.44
6	4.32	4.33	4.32
Ara-1	6.44 d(3.0)	6.55 s	6.56 d(1.5)
2	4.57	4.49	4.50
3	4.50	4.58	4.54
4	4.31	4.42 m	4.51
5	4.46	4.58	4.54
5	3.92 dd(3.0, 10.5)	3.97 dd(5.5, 9.5)	3.93 dd(4.0, 10.5)
Rha-1	5.85 s	5.58 s	5.65 d(1.0)
2	4.50	4.73	4.49
3	4.58	4.38 dd(3.0, 10.0)	4.56 dd(3.5, 9.5)
4	4.39	4.49	4.38 dd(9.5, 9.5)
5	4.39	4.33	4.41
6	1.64 d(6.0)	1.74 d(6.5)	1.66 d(6.5)
Api-1	6.31 s	5.90 d(4.5)	6.27 d(2.5)
2	4.59	4.78 d(4.5)	4.62 d(2.5)
4	4.38	4.57 d(9.5)	4.35
4	4.23 d(10.0)	4.18 d(9.5)	4.22 d(10.0)
5	4.30	4.09 d(10.5)	4.28 d(10.5)
5	3.93 d(10.5)	4.03 d(10.5)	3.89 d(10.5)
Xyl-1		5.27 d(8.0)	
2		3.94	
3		4.25 dd(8.5, 8.5)	
4		4.08	
5		4.14 dd(7.5, 10.5)	
5		3.39 dd(10.5, 10.5)	
Rha'-1	5.35 s	6.16 s	5.33 d(1.0)
2	4.50	4.75	4.47
3	4.45	4.57 dd(3.0, 9.5)	4.42
4	4.23	4.30	4.21
5	4.30	4.94 dq (9.5, 6.5)	4.29
6	1.64 d(6.0)	1.65 d (6.5)	1.65 d(6.5)

δ in ppm from TMS. Glc, glucopyranosyl; Ara, Arabinopyranosyl; Rha, rhamnopyranosyl; Api, apiofuranosyl; Xyl, xylopyranosyl.

Table S3. ¹³C-NMR Data for **1**, **3**, and **4** (in pyridine-*d*₅, 125 MHz)

	1	3	4		1	3	4
Agl-1	44.1	44.1	44.2	Glc-1	105.6	105.7	105.6
2	70.4	70.5	70.5	2	75.3	75.5	75.4
3	83.0	83.0	83.1	3	78.5	78.6	78.5
4	42.7	42.8	42.7	4	71.5	71.6	71.6
5	47.7	47.7	47.9	5	78.2	78.3	78.2
6	18.0	18.1	18.1	6	62.6	62.7	62.6
7	33.0	33.0	33.2	Ara-1	93.5	93.0	93.3
8	40.0	40.0	40.2	2	75.4	75.7	76.1
9	48.5	48.5	47.7	3	70.8	68.6	69.9
10	36.9	37.0	37.0	4	66.5	65.2	65.7
11	24.0	24.0	24.0	5	63.4	61.9	62.5
12	123.1	123.3	123.0	Rha-1	101.4	100.9	101.6
13	144.2	144.2	144.4	2	72.5	71.6	72.5
14	42.3	42.2	42.2	3	72.6	82.6	72.6
15	28.3	28.2	36.1	4	79.6	77.7	79.9
16	23.2	23.2	74.1	5	68.5	68.7	68.7
17	47.3	47.4	49.6	6	18.6	18.6	18.6
18	41.7	41.7	41.2	Api-1	111.3	112.0	111.3
19	46.2	46.2	47.0	2	78.2	77.5	78.2
20	30.9	30.9	30.9	3	79.0	79.8	78.9
21	34.1	34.1	35.9	4	75.0	74.7	75.0
22	32.7	32.8	32.0	5	71.0	64.3	70.7
23	65.5	65.6	65.6	Xyl-1		104.9	
24	15.0	15.1	15.1	2		75.8	
25	17.3	17.3	17.4	3		83.3	
26	17.5	17.6	17.6	4		69.9	
27	26.1	26.2	27.2	5		67.0	
28	176.2	176.3	175.9	Rha'-1	102.0	102.8	102.0
29	33.1	33.2	33.2	2	72.0	72.7	72.0
30	23.7	23.7	24.9	3	72.7	72.5	72.7
				4	73.9	74.2	73.9
				5	69.8	69.6	69.6
				6	18.6	18.7	18.6

δ in ppm from TMS. Agl, aglycone; Glc, glucopyranosyl; Ara, Arabinopyranosyl; Rha, rhamnopyranosyl; Api, apiofuranosyl; Xyl, xylopyranosyl.

Table S4. Inhibitory Effects on Lipoxygenase Activity (%) of **1–15** and NDGA

sample	Inhibition (%)
1	24.5±1.4
2	6.4±1.4
3	2.1±1.7
4	22.1±4.3
5	24.5±2.9
6	12.6±5.1
7	0.7±0.3
8	24.8±3.2
9	20.5±4.9
10	16.6±3.3
11	10.2±0.9
12	20.6±2.9
13	5.1±1.1
14	94.0±3.6
15	82.2±4.7
NDGA	96.2±3.1

The final concentration of each sample tested was 0.5 mM. Data shown represent mean ± S.D. derived from four determinations.

Table S5. Pea List of Signals in ¹H-NMR Spectrum of 1

	Pos X [ppm]	Pos X [kHz]	Integral [abn]	Intensity [abn]	Histogram
1:	6.4455	3.2238	3.1185	2.3641E-01
2:	6.4398	3.2209	2.3036	2.1994E-01
3:	6.3092	3.1556	7.6718	3.0806E-01
4:	5.8523	2.9271	2.5736	2.7499E-01
5:	5.4274	2.7146	2.8672	1.8149E-01
6:	5.3461	2.6739	3.1846	3.3624E-01
7:	5.1503	2.5760	22.7275	5.5358E-01
8:	5.1365	2.5691	18.4704	5.2128E-01
9:	4.8010	2.4013	4.5493	1.5608E-01
10:	4.5891	2.2953	4.1395	3.3645E-01
11:	4.5674	2.2844	4.9356	2.7768E-01
12:	4.5285	2.2650	3.5420	2.1724E-01
13:	4.4975	2.2495	6.9413	3.5366E-01
14:	4.4586	2.2300	3.9247	2.6522E-01
15:	4.4391	2.2203	5.9268	3.2739E-01
16:	4.4128	2.2071	1.6223	1.7750E-01
17:	4.4025	2.2019	5.2944	3.7723E-01
18:	4.3842	2.1928	4.8691	3.5278E-01
19:	4.3613	2.1813	9.2647E-01	1.0287E-01
20:	4.3464	2.1739	1.8841	1.4511E-01
21:	4.3086	2.1550	9.6436	4.4945E-01
22:	4.2971	2.1492	1.6834	2.5233E-01
23:	4.2891	2.1452	3.5820	2.6402E-01
24:	4.2387	2.1200	3.2898	3.0925E-01
25:	4.2204	2.1109	3.5051	3.3922E-01
26:	4.2089	2.1051	2.2045	1.9897E-01
27:	4.1906	2.0960	1.4141	1.5019E-01
28:	4.1757	2.0885	1.3550	1.3483E-01
29:	4.1574	2.0794	1.6617	1.6769E-01
30:	4.1402	2.0708	7.5701E-01	8.2255E-02
31:	4.0303	2.0158	9.5720E-01	1.0427E-01
32:	4.0143	2.0078	1.5567	1.5724E-01
33:	3.9982	1.9998	7.1618E-01	8.1136E-02
34:	3.9375	1.9694	1.6925	1.7083E-01
35:	3.9169	1.9591	2.9871	2.3755E-01
36:	3.8963	1.9488	4.6121	1.8143E-01
37:	3.8906	1.9459	1.9238	1.6682E-01
38:	3.8791	1.9402	5.2151E-01	1.0835E-01
39:	3.8723	1.9367	9.3799E-01	9.4609E-02
40:	3.6421	1.8216	1.3866	1.0726E-01
41:	3.6203	1.8107	1.5568	1.0927E-01
42:	3.5825	1.7918	2.9607	4.6546E-01
43:	3.2653	1.6332	5.8433E-01	7.3977E-02

Table S5 continue

	Pos X [ppm]	Pos X [kHz]	Integral [abn]	Intensity [abn]	Histogram
44:	3.2596	1.6303	1.3825	7.4005E-02	■
45:	3.2390	1.6200	1.4001	7.5773E-02	■
46:	3.2332	1.6171	5.1941E-01	7.3445E-02	■
47:	2.2587	1.1297	1.2477	8.3124E-02	■
48:	2.2323	1.1165	1.3131	9.0743E-02	■
49:	2.1236	1.0621	2.0646	1.0129E-01	■
50:	2.1041	1.0524	3.0904	1.9988E-01	■
51:	2.0835	1.0421	3.7592	1.2505E-01	■
52:	1.9907	9.9568E-01	2.3887	1.2458E-01	■
53:	1.9712	9.8594E-01	4.4146	2.0015E-01	■
54:	1.9380	9.6933E-01	2.1579	9.2051E-02	■
55:	1.8075	9.0403E-01	9.1764E-01	7.6831E-02	■
56:	1.7915	8.9601E-01	1.6957	1.4441E-01	■
57:	1.7800	8.9028E-01	1.6253	1.7647E-01	■
58:	1.7685	8.8456E-01	2.9950	2.1479E-01	■
59:	1.7525	8.7654E-01	1.5043	1.4275E-01	■
60:	1.7319	8.6623E-01	2.9161	1.8706E-01	■
61:	1.7182	8.5935E-01	4.3031	2.1637E-01	■
62:	1.7136	8.5706E-01	1.7469	2.1189E-01	■
63:	1.6975	8.4904E-01	4.2204	1.8389E-01	■
64:	1.6414	8.2098E-01	13.5568	8.2083E-01	■
65:	1.6346	8.1754E-01	2.6593	6.7304E-01	■
66:	1.6311	8.1582E-01	4.8035	6.4104E-01	■
67:	1.5487	7.7458E-01	11.3343	7.6855E-01	■
68:	1.5120	7.5625E-01	1.6595	8.6563E-02	■
69:	1.4651	7.3277E-01	3.2992	1.3058E-01	■
70:	1.4387	7.1960E-01	3.1682	1.3298E-01	■
71:	1.4101	7.0528E-01	1.0301	5.8678E-02	■
72:	1.3070	6.5373E-01	9.5547	8.5524E-01	■
73:	1.2853	6.4285E-01	2.4082	1.5166E-01	■
74:	1.2624	6.3139E-01	2.6775	1.5894E-01	■
75:	1.2326	6.1650E-01	15.9364	8.7690E-01	■
76:	1.2028	6.0161E-01	2.4550	1.5754E-01	■
77:	1.1650	5.8270E-01	2.3562	1.0655E-01	■
78:	1.1375	5.6896E-01	1.9400	1.1407E-01	■
79:	1.1135	5.5693E-01	9.8224	7.5884E-01	■
80:	9.5432E-01	4.7731E-01	9.3958	7.7961E-01	■
81:	9.0164E-01	4.5096E-01	10.3506	7.1591E-01	■

Table S6. Pea List of Signals in ^{13}C -NMR Spectrum of 1

	Pos X [ppm]	Pos X [kHz]	Integral [abn]	Intensity [mabn]	Histogram
1:	176.2498	22.1661	1.0696E-01	66.9318	■
2:	144.2010	18.1355	7.3127E-02	73.1270	■
3:	123.5029	15.5324	7.8290	2.9546E+03	■
4:	123.0641	15.4772	2.5529E-01	83.6958	■
5:	111.2747	13.9945	1.7462E-01	93.8973	■
6:	105.6090	13.2819	1.5444E-01	77.8244	■
7:	102.0416	12.8333	2.1000E-01	116.2236	■
8:	101.3740	12.7493	1.4652E-01	82.6728	■
9:	93.4953	11.7585	1.2337E-01	66.1777	■
10:	82.9841	10.4365	1.0006E-01	61.4612	■
11:	79.6075	10.0119	1.2621E-01	74.4499	■
12:	79.0352	9.9399	1.5897E-01	114.4627	■
13:	78.5010	9.8727	2.0003E-01	103.9509	■
14:	78.2149	9.8367	4.4466E-01	211.8113	■
15:	75.4297	9.4864	2.0977E-01	97.7210	■
16:	75.2389	9.4624	1.2643E-01	63.6792	■
17:	75.0100	9.4337	1.2313E-01	71.0513	■
18:	73.9036	9.2945	2.1734E-01	128.3846	■
19:	72.6636	9.1386	3.2119E-01	108.4843	■
20:	72.6254	9.1338	2.1039E-01	97.8535	■
21:	72.5301	9.1218	1.7425E-01	95.9291	■
22:	71.9768	9.0522	2.1769E-01	119.8483	■
23:	71.4808	8.9898	1.9828E-01	112.4379	■
24:	71.0230	8.9322	1.6390E-01	75.4790	■
25:	70.8132	8.9058	1.4454E-01	64.7867	■
26:	70.4698	8.8627	1.1017E-01	56.9843	■
27:	69.8212	8.7811	1.9982E-01	116.7691	■
28:	68.4858	8.6131	1.2380E-01	73.5839	■
29:	66.5209	8.3660	1.4617E-01	72.2059	■
30:	65.4335	8.2293	1.2189E-01	49.3651	■
31:	63.4877	7.9846	1.0886E-01	45.5931	■
32:	62.5530	7.8670	1.7922E-01	92.6515	■
33:	48.4553	6.0940	1.1462E-01	74.4693	■
34:	47.6732	5.9956	1.2014E-01	68.4608	■
35:	47.3107	5.9500	1.1750E-01	117.5003	■
36:	46.1661	5.8061	1.2675E-01	56.7645	■
37:	44.0868	5.5446	1.4107E-01	62.5240	■
38:	42.7132	5.3718	1.4761E-01	103.1277	■
39:	42.3126	5.3215	1.3473E-01	104.7880	■
40:	41.7022	5.2447	1.5351E-01	79.3162	■
41:	39.9853	5.0288	1.3956E-01	103.5702	■
42:	36.9330	4.6449	1.4751E-01	99.6281	■
43:	34.0906	4.2874	1.2719E-01	53.0327	■

Table S6 continue

	Pos X [ppm]	Pos X [kHz]	Integral [abn]	Intensity [mabn]	Histogram
44:	33.0986	4.1627	3.0860E-01	148.6875
45:	32.9651	4.1459	1.3496E-01	56.6924
46:	32.6789	4.1099	1.3490E-01	61.4128
47:	30.8666	3.8820	1.6697E-01	125.5975
48:	28.2913	3.5581	1.3803E-01	61.4305
49:	26.0593	3.2774	1.6218E-01	107.8678
50:	23.9800	3.0158	1.5339E-01	69.2054
51:	23.6938	2.9799	2.6767E-01	143.8675
52:	23.1787	2.9151	9.8810E-02	50.0154
53:	18.6194	2.3417	6.3897E-01	176.5130
54:	18.0281	2.2673	9.2393E-02	51.6643
55:	17.5130	2.2025	1.4431E-01	109.0667
56:	17.2841	2.1737	2.2126E-01	134.5811
57:	15.0330	1.8906	2.2872E-01	133.4688

Figure S1. Negative ESI-MS of new compound **1**

Figure S2. Positive ESI-MS of new compound **1**

Figure S3. ^1H -NMR spectrum of new compound **1** (in pyridine- d_5 , 500 MHz)

Figure S4. ^{13}C -NMR spectrum of new compound **1** (in pyridine- d_5 , 125 MHz)

Figure S5. ^1H - ^1H COSY spectrum of new compound **1** (in pyridine- d_5 , 500 MHz)

Figure S6. HMQC spectrum of new compound **1** (in pyridine-*d*₅, 500 MHz)

Figure S7. HMBC spectrum of new compound **1** (in pyridine- d_5 , 500 MHz)

Figure S8. TOCSY spectrum of **1** (in pyridine- d_5 , 500 MHz)

Figure S9. ^1H - ^{13}C long-range correlations (arrows) observed in the HMBC spectrum of new compound **1** (in pyridine- d_5 , 500 MHz)

Figure S10. Positive FAB-MS of new compound **1**