

Article

Four New Sesquiterpenoids from the Roots of *Diarthron Tianschanica* with Their Antineoplastic Activity

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Received: 9 May 2018; Accepted: 26 May 2018; Published: 8 June 2018



Abstract: Four new sesquiterpenoids, known as diarthronchas A–D (1–4), and one known daphnauranol B (5) were isolated from the methanol extract of the roots of *Diarthron tianschanica*. The compounds structures were determined on the basis of spectroscopic data. All of the isolated compounds were profiled for their antineoplastic activity.

Keywords: thymelaeaceae; *Diarthron tianschanica*; sesquiterpenoids; antineoplastic activity

1. Introduction

Diarthron tianschanica (Pobed.) Kit Tanis, a member of the genus *Diarthron* (Thymelaeaceae), is only observed in the Zhaosu County of Xinjiang Uygur Autonomous Region, China [1]. The roots of *D. tianschanica* have been used in folk medicine to cure a wide variety of ailments, including coughs; asthma [2]; bronchitis [3]; and tuberculosis of the skin, bone, and epididymis [4]. Previously, our group examined the chemical constituents of *D. tianschanica*, resulting in the identification of lignans, coumarins, and diarylpentanol [5,6]. As part of our ongoing phytochemical study, we further investigated the chemical constituents from the roots of *D. tianschanica* and obtained four new sesquiterpenoids, known as diarthronchas A–D (1–4), and one known daphnauranol B (5) [7] (Figure 1). In this paper, we elucidate the structure of these new compounds and their antineoplastic activity.

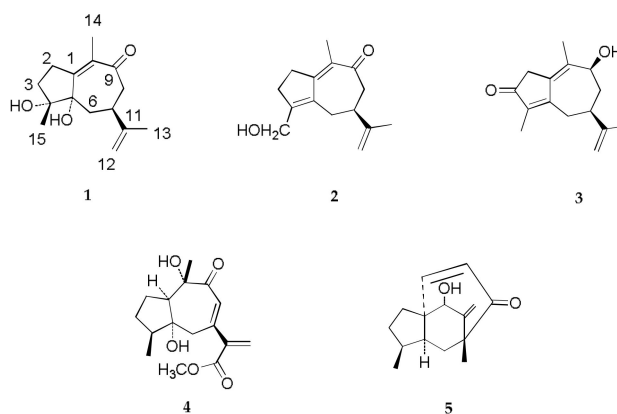


Figure 1. Structures of compounds diarthronchas A–D (1–4) and daphnauranol B (5).

2. Results and Discussion

2.1. Purification of Compounds 1–4

The roots of *D. tianschanica* (10 kg) were soaked with MeOH at room temperature and extracted three times under reflux. The sesquiterpenoids were isolated and purified via silica gel chromatography, Sephadex LH-20 gel chromatography, and semi-preparative high-performance liquid chromatography (HPLC).

2.2. Structure Elucidation of Compounds 1–4

Compound **1** was obtained as a white powder. This compound's molecular formula was established to be $C_{15}H_{22}O_3$, based on the HRESIMS quasimolecular ion at m/z 273.1485 $[M + Na]^+$ (Calcd for. 273.1467 $C_{15}H_{22}O_3Na$). The infrared (IR) and ultraviolet (UV) spectra revealed absorptions for the hydroxyl (3365 cm^{-1}), and an α,β -unsaturated ketone moiety (216 nm; 1724 cm^{-1}) [8]. The 1H -NMR spectrum (Table 1) showed three tertiary methyl groups as singlets at δ_H 1.19 (3H, s, H₃-15), 1.54 (3H, s, H₃-14), and 1.72 (3H, s, H₃-13), and an exo-methylene as two broad doublets at δ_H 4.65 (1H, d, $J = 1.8\text{ Hz}$, H-12a) and 4.71 (1H, d, $J = 1.8\text{ Hz}$, H-12b). The ^{13}C -APT nmR spectrum revealed 15 carbon signals due to three methyls, five methylenes, one methine, and six quaternary carbons. Among these signals, the carbon signals at δ_C 136.8 (C-10), 172.1 (C-1), and 205.3 (C-9) indicated the presence of an α,β -unsaturated ketone group, and the carbon signals at δ_C 20.1 (C-13), 108.7 (C-12), and 151.0 (C-11) revealed the existence of an isopropenyl group [8]. The results described above suggested that compound **1** contained a guaiane-type skeleton [8]. All the signals and functional groups were confirmed by HSQC, HMBC, and 1H - 1H COSY spectra. In the HMBC spectrum (Figure 2A), the protons of δ_H 1.54 (s, H₃-14) were correlated with δ_C 136.8 (C-10), 172.1 (C-1), and 205.3 (C-9), indicating that the connection of H₃-14 is at C-10 and the presence of an α,β -unsaturated ketone group. Moreover, the proton signal at δ_H 1.19 (s, H₃-15) had long-range correlations with carbon signals at δ_C 39.5 (C-3), 73.9 (C-4), and 83.3 (C-5), suggesting that the methyl group of H₃-15 was located at the quaternary carbon C-4. The proton signal at δ_H 2.67 (1H, m, H-7) was interrelated with δ_C 151.0 (C-11) and 108.7 (C-12). The double bond protons at δ_H 4.65 (1H, d, $J = 1.8\text{ Hz}$, H-12a) and 4.71 (1H, d, $J = 1.8\text{ Hz}$, H-12b) and the methyl protons at δ_H 1.72 (3H, s, H-13) were connected with δ_C 42.2 (C-7) and 151.0 (C-11), respectively, suggesting the presence of an isopropenyl group at C-7. Furthermore, the HMBC correlations from δ_H 4.31 (1H, br s) to δ_C 73.9 (C-4) and δ_H 5.27 (1H, br s) to δ_C 83.3 (C-5) indicated that two OH groups were attached to C-4 and C-5, respectively. The relative stereochemistry of compound **1** was determined by the Nuclear Overhauser Effect Spectroscopy (NOESY) experiment (Figure 2B), in which correlations were observed between the following protons (OH-4/OH-5, H-7/OH-5). Finally, because of the $n-\pi$ electron transition effect of the α,β -unsaturated ketone group, the CD spectra of compound **1** showed the cotton effects at 325 nm ($\Delta\epsilon -0.7$) and 250 nm ($\Delta\epsilon + 2.0$); thus, the C-5 is in the *S* configuration [9]. Based on these results, compound **1** was elucidated as described and given the trivial name of diarthroncha A.

Table 1. 1H (600 MHz) and ^{13}C -NMR (150 MHz) spectral data for compounds **1** and **2** (in DMSO- d_6).

Position	1		Position	2	
	δ_C Type	δ_H (J in Hz)		δ_C Type	δ_H (J in Hz)
1	172.1		1	162.6	
2	27.6	1.50 (1H, dd, 10.8, 9.6) 1.52 (1H, dd, 10.8, 2.4)	2	39.9	2.26 (2H, m)
3	39.5	1.99 (1H, m) 2.48 (1H, m)	3	34.0	2.48 (2H, m)
4	73.9		4	145.5	

Table 1. Cont.

Position	1		Position	2	
	δ_C Type	δ_H (J in Hz)		δ_C Type	δ_H (J in Hz)
5	83.3		5	144.9	
6	34.7	2.53 (1H, m) 2.65 (1H, m)	6	39.6	2.48 (2H, m)
7	42.2	2.67 (1H, m)	7	41.5	3.28 (1H, m)
8	47.9	2.16 (1H, dd, 12.0, 1.8) 2.60 (1H, dd, 12.0, 10.8)	8	49.6	2.81 (2H, m)
9	205.3		9	199.0	
10	136.8		10	134.1	
11	151.0		11	147.3	
12	108.7	4.65 (1H, d, 1.8) 4.71 (1H, d, 1.8)	12	110.8	4.77 (1H, d, 1.8) 4.79 (1H, d, 1.8)
13	20.1	1.72 (3H, s)	13	20.1	1.75 (3H, s)
14	7.9	1.54 (3H, s)	14	2.3	1.80 (3H, s)
15 OH	27.5	1.19 (3H, s) 4.31 (br s) 5.27 (br s)	15 OH	58.8	4.15 (1H, dd, 11.5, 5.4)

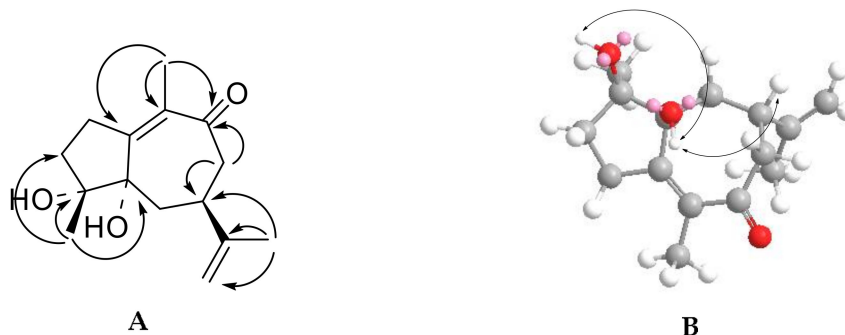


Figure 2. (A) Key HMBC (arrows) and (B) NOESY (arrows) correlations of compound 1.

Compound **2** yielded the molecular formula of $C_{15}H_{20}O_2$, based on the HRESIMS analysis of m/z 255.1348 $[M + Na]^+$ (Calcd for. 255.1361 $C_{15}H_{20}O_2Na$). Its 1H and ^{13}C -NMR (Table 1) data were very similar to **1**, except for the additional double bond and hydroxymethyl groups in **2**. In contrast to **1**, the signal for C-4 and C-5 of compound **2** showed strong downfield chemical shifts to δ_C 145.5 (C-4) and 144.9 (C-5), indicating a sp^2 double bond between C-4 and C-5 in **2**. Additionally, in the HMBC spectrum, the methylene protons at δ_H 4.15 (H-15a) and 4.24 (H-15b) had direct correlations with δ_C 145.5 (C-4), indicating that the methyl group at C-4 in **1** was oxidized to a hydroxymethyl group in **2**. Thus, the structure of **2** was determined as shown and named diarthroncha B.

Compound **3** was obtained as a white powder with the molecular formula of $C_{15}H_{20}O_2$, in agreement with the positive HRESIMS ion peak at m/z 255.1349 $[M + Na]^+$ (Calcd for. 255.1361 $C_{15}H_{20}O_2Na$). Comparison of this compound's 1H and ^{13}C -NMR data (Table 2) revealed that its structure was similar to that of oleodaphnoic acid [10], except for the additional hydroxyl group at C-9 and methyl group at C-10 in **3**. In the HMBC spectrum, the correlations from δ_H 4.33 (1H, m, H-9) to δ_C 41.0 (C-8) and 130.4 (C-10), together with the signal for C-9, revealed a powerful downfield shift to δ 70.0 (+ 44.4 ppm), confirming the presence of a hydroxy group at C-9. Additionally, the HMBC correlations of δ_H 1.87 (H₃-14) with δ_C 138.2 (C-1), 70.0 (C-9), and 130.4 (C-10) suggested that the

carboxyl group at C-10 in the oleodaphnoic acid was reduced to a methyl group in **3**. In the NOESY spectrum, the cross-peaks of H-7 and H-9 indicated the 9-OH was in α,β -orientation. Therefore, the structure of **3** was established as shown and named diarthroncha C.

Table 2. ^1H (600 MHz) and ^{13}C -NMR (150 MHz) spectral data for compounds **3** and **4** (in $\text{DMSO}-d_6$).

Position	3		Position	4	
	δc Type	δH (J in Hz)		δc Type	δH (J in Hz)
1	138.2		1	47.6	2.33 (1H, m)
2	40.4	2.90 (1H, m) 3.20 (1H, m)	2	29.1	1.09 (1H, m) 1.23 (1H, m)
3	202.8		3	30.9	1.43 (1H, m) 1.85 (1H, m)
4	137.3		4	34.7	2.56 (1H, m)
5	165.5		5	78.4	
6	35.3	2.63 (1H, m) 2.80 (1H, m)	6	35.5	1.76 (2H, m)
7	37.2	2.65 (1H, m)	7	154.3	
8	41.0	1.93 (1H, m) 1.89 (1H, m)	8	124.5	5.63 (1H, d, 1.2)
9	70.0	4.33 (1H, m)	9	202.1	
10	130.4		10	84.3	
11	149.8		11	146.3	
12	110.1	4.71 (1H, s) 4.76 (1H, s)	12	125.6	6.09 (1H, d, 1.2) 6.12 (1H, d, 0.6)
13	20.2	1.75 (1H, s)	13	165.8	
14	17.0	1.87 (1H, s)	14	15.9	1.92 (3H, s)
15	8.2	1.66 (1H, s)	15 MeO	22.2 51.7	0.90 (3H, d, 7.2) 3.62 (3H, s)

Compound **4** was obtained as a white powder. The compound's molecular formula of $\text{C}_{16}\text{H}_{22}\text{O}_5$ was determined via HRESIMS analysis of m/z 317.1348 $[\text{M} + \text{Na}]^+$ (*Calcd for*. 317.1365 $\text{C}_{16}\text{H}_{22}\text{O}_5\text{Na}$). The ^1H -NMR spectrum (Table 2) showed two methyl groups as signals at δ_{H} 1.92 (3H, s, H₃-14) and 0.90 (3H, d, $J = 7.2$ Hz, H₃-15), an exo-methylene resonance as two broad doublets at δ_{H} 6.09 (1H, d, $J = 1.2$ Hz, H-12a) and 6.12 (1H, d, $J = 1.2$ Hz, H-12b), an olefinic proton signal at δ_{H} 5.63 (1H, s, H-8), and a methoxy signal at δ_{H} 3.62 (3H, s, 13-OMe). Aside from the single methoxy group, the ^{13}C -NMR spectrum exhibited 15 carbon resonances, including two methyls, four methylenes, three methines, and six quaternary carbons (one ketone, one carboxymethyl, two olefinic carbons, and two oxygenated carbons). The ^1H and ^{13}C -NMR data of **4** were characteristic of the guaiane-type skeleton with an α,β -unsaturated ketone (δc 124.5, 154.3, 202.1) and an acrylic ester group (δc 125.6, 146.3, 165.8). In the HMBC spectrum, the correlations of δ_{H} 6.09 (1H, d, $J = 1.2$ Hz, H-12a) and 6.12 (1H, d, $J = 1.2$ Hz, H-12b) with δc 146.3 (C-11), 154.3 (C-7), and 165.8 (C-13) suggested that the isopropenyl group at C-7 in the reported guaiane-type skeletons had been oxidized to an acrylic ester group in **4** [8]. Moreover, the proton of δ_{H} 5.63 (1H, s, H-8) was interrelated with δc 154.3 (C-7), and 202.1 (C-9) revealed the presence of an α,β -unsaturated ketone moiety at C-7/8/9. Furthermore, the ^1H - ^{13}C long-range signals from δ_{H} 3.62(-OCH₃) to δc 165.8 (C-13) and from δ_{H} 1.92 (H₃-14) to δc 84.3 (C-10) placed the methoxy group at C-13 and the methyl group at C-10. The downfield chemical shifts of C-5 (δc 78.4) and C-10 (δc 84.3), together with the molecular formula above, indicated the presence of OH groups at C-5 and C-10. The CD spectrum of **4** displayed strong cotton effects at

334 nm ($\Delta\epsilon -1.2$) and 287 nm ($\Delta\epsilon + 2.8$), which corresponded to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the unsaturated dienone. On the basis of the CD excitation chirality method for the unsaturated dienone, C-10 possessed the *S* absolute configuration. Taken together with the NOESY spectrum, the structure of **4** was defined as shown and given the trivial name diarthroncha D.

2.3. Antineoplastic Activity of Compounds 1–5

All of the isolated compounds were tested in vitro for their cytotoxic activity against HepG-2, MCF-7, and HeLa human cancer cell lines, with paclitaxel serving as a positive control. The results (Table 3) showed that compounds **1**, **3**, and **5** were moderately cytotoxic against HepG-2 cells with inhibitory concentration 50% (IC₅₀) values at 18.9, 22.5, and 20.3 μ M, respectively, while compound **2** was weakly cytotoxic with an IC₅₀ value of 41.3 μ M. Furthermore, compounds **2** and **5** exhibited weak cytotoxicity against HeLa cells with IC₅₀ values of 39.6 and 29.6 μ M, respectively. None of the compounds had activity against MCF-7 cell lines.

Table 3. IC₅₀ values of compounds 1–5 against HepG-2, MCF-7, and HeLa.

Compound	HepG-2	MCF-7	HeLa
	IC ₅₀ (μ M) *		
Paclitaxel	1.80 \pm 0.26	3.80 \pm 0.31	4.25 \pm 0.52
1	18.9 \pm 0.02	48.7 \pm 0.39	>50
2	41.3 \pm 0.13	>50	39.6 \pm 0.53
3	22.5 \pm 0.09	>50	>50
4	>50	>50	>50
5	20.3 \pm 0.24	>50	29.6 \pm 0.61

* IC₅₀ = inhibitory concentration 50%.

3. Materials and Methods

3.1. General Experimental Procedures

Optical rotation data were obtained using a Perkin-Elmer 341 digital polarimeter (PerkinElmer, Norwalk, CT, USA). CD spectra were obtained using a JASCO J-815 spectropolarimeter (JASCO, Easton, Md., USA). UV and IR spectra were obtained using Shimadzu UV2550 and FTIR-8400S spectrometers (Shimadzu, Kyoto, Japan), respectively. nmR spectra were obtained using a Bruker AV III 600 nmR spectrometer (Bruker, Billerica, German) with chemical shift values presented as δ values and TMS (Tetramethylsilane) as the internal standard. HRESIMS was performed using an LTQ-Orbitrap XL spectrometer (Thermo Fisher Scientific, Boston, MA, USA). Column-chromatography (CC) was performed using silica gel (100–200 mesh, Qingdao Marine Chemical Plant, Qingdao, China) and Sephadex LH-20 (Pharmacia, Uppsala, Sweden). Precoated silica gel GF254 plates (Zhi Fu Huang Wu Pilot Plant of Silica Gel Development, Yantai, China) were used for TLC. All of the solvents used were of analytical grade (Beijing Chemical Plant, Beijing, China).

3.2. Plant Material

The roots of *Diarthron tianschanica* were collected in September 2013 from Zhaosu city, Xinjiang Autonomous Region, China, and were identified by Prof Xiao-Guang Jia, Department of Pharmaceutical Chemistry, Xinjiang Institute of Chinese and Ethnic Medicine. A voucher specimen (NO. 13094) was deposited at the Xinjiang Institute of Chinese and Ethnic Medicine.

3.3. Isolation and Purification of Compounds 1–5

The roots of *D. tianschanica* (10 kg) were soaked with MeOH at room temperature (3 \times 40 L, 3 h each) and were extracted three times under reflux. Removal of the MeOH under reduced

pressure yielded a methanol extract (2189 g). The residue was dissolved in water and extracted with petroleum ether (3×1000 mL), chloroform (3×1000 mL), ethyl acetate (3×1000 mL), and *n*-butanol (3×1000 mL), successively. The petroleum ether fraction (108 g) was subjected to CC (column-chromatography) over a silica gel (100–200 mesh, 15×60 cm) eluting with a stepwise gradient of CH_2Cl_2 -MeOH (from 1:0 to 0:1, that is, 100:0, 100:1, 80:1, 50:1, 30:1, 20:1, 15:1, 0:1, *v/v*) to yield fractions A–H. Fr. B was prepared using a Sephadex LH-20 column with MeOH to remove pigments, and purified by semi-preparative HPLC of MeOH- H_2O (60:40, *v/v*) as the mobile phase to yield compounds **1** (5.8 mg, $t_R = 18.8$ min) and **2** (2.5 mg, $t_R = 31.2$ min). Fr. C was purified by semi-preparative HPLC with MeOH- H_2O (70:30, *v/v*) as the mobile phase to yield compounds **3** (3.1 mg, $t_R = 16.7$ min), **4** (4.2 mg, $t_R = 28.3$ min), and **5** (3.5 mg, $t_R = 37.5$ min).

3.4. Characterization of Compounds 1–4

Diarthroncha A (**1**): white powder (MeOH); $[\alpha]_D^{20} + 11.6$ (c 0.1, MeOH); UV (MeOH) λ_{max} ($\log \epsilon$): 216 (3.62) nm, CD (MeOH) 325 nm ($\Delta \epsilon -0.7$) and 250 nm ($\Delta \epsilon + 2.0$); IR (film) ν_{max} : 3365, 2923, 2845, 1724, 1782 cm^{-1} ; ^1H and ^{13}C -NMR data (DMSO- d_6), (see Table 1); HR-ESI-MS m/z 273.1485 $[\text{M} + \text{Na}]^+$ (Calcd for. 273.1467 $\text{C}_{15}\text{H}_{22}\text{O}_3\text{Na}$).

Diarthroncha B (**2**): white powder (MeOH); $[\alpha]_D^{20} + 16.4$ (c 0.1, MeOH); UV (MeOH) λ_{max} ($\log \epsilon$): 214 (4.83) nm; IR (film) ν_{max} : 3372, 2930, 2848, 1721, 1776 cm^{-1} ; ^1H and ^{13}C -NMR data (DMSO- d_6), (see Table 1); HR-ESI-MS m/z 255.1348 $[\text{M} + \text{Na}]^+$ (Calcd for. 255.1361 $\text{C}_{15}\text{H}_{20}\text{O}_2\text{Na}$).

Diarthroncha C (**3**): white powder (MeOH); $[\alpha]_D^{20} + 14.2$ (c 0.1, MeOH); UV (MeOH) λ_{max} ($\log \epsilon$): 212 (3.71) nm; IR (film) ν_{max} : 3368, 2932, 2846, 1729, 1786 cm^{-1} ; ^1H and ^{13}C -NMR data (DMSO- d_6), (see Table 2); HR-ESI-MS m/z 255.1349 $[\text{M} + \text{Na}]^+$ (Calcd for. 255.1361 $\text{C}_{15}\text{H}_{20}\text{O}_2\text{Na}$).

Diarthroncha D (**4**): white powder (MeOH); $[\alpha]_D^{20} + 17.5$ (c 0.1, MeOH); UV (MeOH) λ_{max} ($\log \epsilon$): 210 (4.56) nm; CD (DMSO- d_6) 334 nm ($\Delta \epsilon -1.2$) and 287 nm ($\Delta \epsilon + 2.8$); IR (film) ν_{max} 3364, 2927, 2839, 1736, 1783, 1233 cm^{-1} ; ^1H and ^{13}C -NMR data (DMSO- d_6), (see Table 2); HR-ESI-MS m/z 317.1348 $[\text{M} + \text{Na}]^+$ (Calcd for. 317.1365 $\text{C}_{16}\text{H}_{22}\text{O}_5\text{Na}$).

3.5. Cytotoxicity Assay of Compounds 1–5

The tested human cancer cell lines were seeded in 96-well plates (10^7 cells/well), and the compounds were added at various concentrations (2.5, 5, 10, 25, and 50 μM , respectively). Keeping the treatment on for 48 h, MTT (0.5 mg/mL) solution was added to each well, which were incubated for a further 4 h at 37 °C. The supernatant was removed, and the formazan crystals were dissolved in DMSO (150 mL) with gentle shaking at room temperature. Finally, the optical density of each well was measured at 570 nm with a microplate reader.

4. Conclusions

In conclusion, five sesquiterpenoids were isolated and characterised by spectrometric analysis (1 and 2D-NMR, HRESIMS). Among the isolated compounds, compounds **1**, **3**, and **5** showed moderate cytotoxicity against HepG cells with IC_{50} values at 18.9, 20.3, and 22.5 μM , respectively. Therefore, we believed that this plant was an important source for the diverse structure of sesquiterpenoids and should be further investigated for biological activities.

Author Contributions: L.-L.S. conceived and designed the experiments; D.Z., L.-L.S., D.-X.S., and H.-Y.W. performed the experiments; H.-Y.W. and X.-L. guided the experiments and analyzed the data; L.-L.S. designed main ideas of this paper; J.Z. guided the writing of this paper; D.-X.S. and D.Z. wrote the paper. The authors read and approved the final manuscript.

Funding: This research was funded by the Natural Science Foundation of XinJiang Uygur Autonomous Region [grant number 2017D01A72] and the Urumqi science & technology bureau [grant number G161320012].

Acknowledgments: The work was financially supported by the Natural Science Foundation of XinJiang Uygur Autonomous Region [grant number 2017D01A72]. Urumqi science and technology project (G161320012).

Conflicts of Interest: There is no conflict of interest associated with the authors of this paper.

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Sample Availability: Samples of the compounds 1–4 and 5 are available from the authors.



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