Dihydrostilbene Derivatives from the Mongolian Medicinal Plant *Scorzonera radiata*

Yao Wang,[†] RuAngelie Edrada-Ebel,[‡] Nanzad Tsevegsuren,[§] Jandirk Sendker,[†] Manfred Braun,[⊥] Victor Wray,[∥] Wenhan Lin,*[,Δ] and Peter Proksch*[,†]

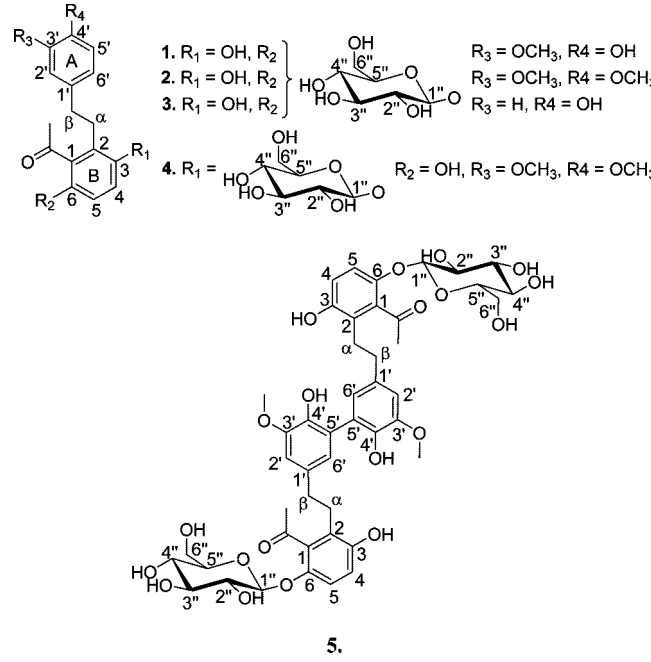
Institut für Pharmazeutische Biologie and Biotechnologie, Heinrich-Heine-Universität Düsseldorf, Universitätsstrasse 1, Geb. 26.23, 40225 Düsseldorf, Germany, Strathclyde Institute of Pharmacy and Biomedical Sciences, University of Strathclyde, The John Arbuthnott Building, 27 Taylor Street, Glasgow G4 0NR, U.K., Department of Organic and Food Chemistry, Faculty of Chemistry, National University of Mongolia, Ulaanbaatar, Mongolia, Institut für Organische and Makromolekulare Chemie I, Heinrich-Heine-Universität Düsseldorf, Universitätsstrasse 1, Geb. 26.33, 40225 Düsseldorf, Germany, Helmholtz-Zentrum für Infektionsforschung GmbH, Inhoffenstrasse 7, 38124 Braunschweig, Germany, and State Key Laboratory of Natural and Biomimetic Drugs, Peking University, 100083 Beijing, People's Republic of China

Received December 9, 2008

Chromatographic separation of a crude extract obtained from aerial parts of the Mongolian medicinal plant *Scorzonera radiata* yielded five new dihydrostilbenes, scorzodihydrostilbenes A−E (**1**−**5**). The structures were unambiguously elucidated on the basis of one- and two-dimensional NMR (^{1}H, ^{13}C, COSY, HMBC, HMQC, and ROESY) and mass spectrometric data. Compounds **1**−**5** exhibited antioxidative activity when analyzed in the DPPH (2,2-diphenyl-1-picrylhydrazyl) assay. For **1** and **5** the antioxidant activities were stronger than that of the well-known naturally occurring stilbene antioxidant resveratrol.

Scorzonera is a genus of the family Asteraceae that includes more than 150 species, which are distributed in the temperate zone of Eurasia.[1−3] Eleven species of *Scorzonera* are found on the Mongolian plateau, two of which are endemic.[4−6] Most of the Mongolian *Scorzonera* spp. are used in traditional medicine and as forage for livestock, especially in desert regions.[7] *Scorzonera radiata* Fisch. (Asteraceae) is a typical mesophyte and a perennial herbaceous rosette plant, which is widely distributed in Hangai, Douria, Kobodo, Mongolia-Altai, and East-Mongolia.[8] It grows at an elevation between 900 and 1800 m above sea level, on rubble slopes, in underbrush, in forest fringe, in meadows, and in the gravel zone of floodplains. All parts of the plant are used in Mongolian folk medicine for the treatment of poisonous ulcers, for fever caused by bacterial and viral infections, and for its diuretic and galactagogue properties.[9,10]

No phytochemical studies have been reported for *S. radiata*, although other species of this genus have been studied extensively, resulting in the isolation of sesquiterpenes,[11−16] lignans,[17,18] neolignans,[19,20] phenolic acids,[15,21] triterpene derivatives,[14,19,22] stilbene derivatives,[23−26] dihydroisocoumarins,[23,27] and flavonoids.[22] In this paper, we report the isolation, structure elucidation, and antioxidant activity of five new natural dihydrostilbene derivatives from the aerial parts of *S. radiata*.



5.

Results and Discussion

Analysis of a crude MeOH extract of the aerial parts of *S. radiata* by HPLC-DAD and LC-MS indicated the presence of several unknown phenolic compounds that exhibited UV spectra similar to that of the known stilbene derivative resveratrol. The compounds were isolated by chromatographic separation and identified as new dihydrostilbene derivatives (**1**−**5**).

Compound **1**, obtained as a pale yellow solid, was shown to have the molecular formula $C_{23}H_{28}O_{10}$ as determined by HRESIMS (*m/z* 482.2021 $[M + NH_4]^+$). The ^{1}H NMR spectrum measured in CD_3OD (Table 1) showed a pair of doublets with coupling constants of 8.8 Hz typical of *ortho*-coupled aromatic protons (H-4 and H-5). In the aromatic region, further resonances indicative for an ABX system [δ_H 6.64 (d, J = 1.6 Hz), 6.66 (d, J = 7.9 Hz), and 6.55 (dd, J = 7.9 and 1.6 Hz)] were observed, which were assigned to a 1,3,4-trisubstituted phenyl unit. Two methyl resonances (δ_H 3.77 and 2.31) indicated an aromatic *O*-methyl group and a methyl ketone function. From the ^{1}H NMR spectrum, along with analysis of the ^{13}C NMR data (Table 2), two aromatic rings, two methylene groups (δ_H 2.70, m), and one sugar unit (δ_H 4.76−3.33, m) were inferred to be present. The assignments were supported by analysis of the ^{1}H−^{1}H COSY and HMBC spectra of **1** (Figure 1). Assignment of the *O*-methyl group at C-3′ was determined from the HMBC cross-peak of the methyl singlet at δ_H 3.77 with δ_C 148.7, which further correlated with the *meta*-coupled proton at $\delta_{H\text{-}5'}$ 6.66 that was part of the ABX system. The methyl singlet at δ_H 2.31 gave a cross-peak with the carbonyl carbon at δ_C 208.7 and the aromatic carbon at $\delta_{C\text{-}1}$ 135.5, respectively. In the HMBC

* To whom correspondence should be addressed. (P.P.) Tel: +49-211-8114163. Fax: +49-211-8111923. E-mail: proksch@uni-duesseldorf.de. (W.L.) Tel: +86-10-82806188. Fax: +86-10-82806188. E-mail: whlin@bjmu.edu.cn.

† Institut für Pharmazeutische Biologie and Biotechnologie, Heinrich-Heine-Universität Düsseldorf.

‡ University of Strathclyde.

§ National University of Mongolia.

⊥ Institut für Organische and Makromolekulare Chemie I, Heinrich-Heine-Universität Düsseldorf.

∥ Helmholtz-Zentrum für Infektionsforschung GmbH (HZI).

Δ Peking University.

10.1021/np800782f CCC: $40.75
Published on Web 03/09/2009

Table 1. ^{1}H NMR Data (500 MHz, CD_3OD) for Compounds **1**−**5**, δ in ppm, J in Hz

position	1	2	3	4	5
4	6.79, d (8.8)	6.80, d (8.8)	6.78, d (8.8)	7.13, d (8.8)	6.83, d (8.8)
5	6.97, d (8.8)	6.97, d (8.8)	6.96, d (8.8)	6.65, d (8.8)	7.01, d (8.8)
C*H*$_3$CO-C(1)[b]	2.31, s	2.32, s	2.33, s	2.29, s	2.21, s
α-CH_2	2.70, m[a]	2.71, m[a]	2.66, m[a]	2.88, m[a], 2.78, m[a]	2.78, m[a]
β-CH_2	2.70, m[a]	2.75, m[a]	2.69, m[a]	2.78, m[a]	2.78, m[a]
2′	6.64, d (1.6)	6.68, d (1.9)	6.93, d (8.5)	6.72, d (1.9)	6.54, d (1.9)
3′			6.65, d (8.5)		
5′	6.66, d (7.9)	6.80, d (8.2)	6.65, d (8.5)	6.81, d (7.9)	
6′	6.55, dd (7.9, 1.6)	6.66, dd (8.2, 1.9)	6.93, d (8.5)	6.70, dd (7.9, 1.9)	6.53, d (1.9)
C*H*$_3$O-C(3′)	3.77, s	3.76, s		3.77, s	3.75, s
C*H*$_3$O-C(4′)		3.75, s		3.77, s	
1″	4.76, d (7.6)	4.76, d (7.6)	4.76, d (7.6)	4.80, d (7.6)	4.73, d (7.8)
2″	3.36, m[a]	3.37, m[a]	3.37, m[a]	3.44, dd (9.1, 8.5)	3.33, m[a]
3″	3.40, m[a]	3.40, m[a]	3.40, m[a]	3.49, dd (9.1, 7.3)	3.38, m[a]
4″	3.34, m[a]	3.34, m[a]	3.34, m[a]	3.38, m[a]	3.31, m[a]
5″	3.33, m[a]	3.33, m[a]	3.33, m[a]	3.38, m[a]	3.30, m[a]
6″	3.85, dd (12.0, 1.3)	3.85, dd (12.0, 0.6)	3.85, dd (12.0, 1.3)	3.88, dd (12.0, 1.6)	3.80, dd (12.0, 2.1)
	3.66, dd (12.0, 5.4)	3.66, dd (12.0, 5.1)	3.65, dd (12.0, 5.1)	3.70, dd (12.0, 5.4)	3.63, dd (12.0, 5.3)

[a] Overlapped signals assigned by ^{1}H−^{1}H COSY, HMBC, and HMQC spectra without designating multiplicity. [b] A time-dependent H/D exchange was observed for this signal in CD_3OD but not in DMSO-d_6. The original singlet decreased in intensity and new signals corresponding to CH_2D and CHD_2 appeared to high-field of the original, while all other signals remained unchanged.

Table 2. ^{13}C NMR Data (δ in ppm, 125 MHz, CD_3OD) for Compounds **1**−**5**

position	1	2	3	4	5
1	135.5, qC	135.5, qC	135.5, qC	132.4, qC	136.1, qC
2	126.5, qC	126.4, qC	126.6, qC	130.8, qC	126.9, qC
3	152.4, qC	152.4, qC	152.4, qC	150.7, qC	152.7, qC
4	117.1, CH	117.1, CH	117.1, CH	119.6, CH	117.2, CH
5	116.4, CH	116.5, CH	116.4, CH	114.8, CH	116.7, CH
6	147.8, qC	147.8, qC	147.8, qC	150.3, qC	147.9, qC
CH_3*C*O-C(1)	208.7, qC	208.5, qC	208.6, qC	208.4, qC	208.6, qC
CH_3CO-C(1)	33.1, CH_3	33.1, CH_3	33.1, CH_3	33.1, CH_3	34.4, CH_3
α-CH_2	31.3, CH_2	31.1, CH_2	31.4, CH_2	30.9, CH_2	31.4, CH_2
β-CH_2	36.5, CH_2	36.5, CH_2	36.2, CH_2	37.1, CH_2	36.5, CH_2
1′	135.2, qC	136.7, qC	134.6, qC	137.0, qC	131.7, qC
2′	113.3, CH	113.6, CH	130.5, CH	114.0, CH	111.6, CH
3′	148.7, qC	150.2, qC	116.1, CH	150.4, qC	151.3, qC
4′	145.6, qC	148.7, qC	156.5, qC	148.7, qC	148.4, qC
5′	116.0, CH	113.1, CH	116.1, CH	113.2, CH	130.5, qC
6′	121.9, CH	121.8, CH	130.5, CH	122.0, CH	124.1, CH
CH_3O-C(3′)	56.3, CH_3	56.6, CH_3		56.6, CH_3	56.3, CH_3
CH_3O-C(4′)		56.3, CH_3		56.5, CH_3	
1″	103.7, CH	103.7, CH	103.7, CH	103.8, CH	104.0, CH
2″	74.9, CH	74.9, CH	74.9, CH	75.3, CH	75.0, CH
3″	78.2, CH	78.2, CH	78.3, CH	78.5, CH	78.2, CH
4″	71.4, CH	71.4, CH	71.4, CH	71.5, CH	71.4, CH
5″	78.1, CH	78.1, CH	78.1, CH	78.2, CH	78.0, CH
6″	62.7, CH_2	62.7, CH_2	62.7, CH_2	62.7, CH_2	62.6, CH_2

spectrum, carbons C-1′ and C-2 correlated with methylene protons Hα and H*β* at δ_H 2.70, which in turn showed HMBC connectivities with C-1 (δ 135.5)/C-3 (δ 152.4) and C-2′ (δ 113.3)/C-6′ (δ 121.9), respectively. These HMBC correlations allowed the carbon and proton assignments of the dihydrostilbene framework in compound **1**.

The *β*-glucose moiety was evident from the ^{1}H NMR resonances of four oxymethine protons at δ_H 3.40, 3.36, 3.34, and 3.33, together with one pair of methylene protons at δ_H 3.85 and 3.66 for H_2-6″ and an anomeric proton at δ_H 4.76 as shown in Table 1. By inspection of the ^{13}C NMR spectrum, these resonances were in agreement with four oxymethine resonances at δ_C 78.2, 78.1, 74.9, and 71.4; one methylene cabon at δ_C 62.7; and an anomeric carbon at δ_C 103.7, all of which are characteristic of a *β*-glucopyranose unit. Butanolysis followed by capillary glc of the trimethylsilylated (−)-2-butyl derivatives established the sugar as *β*-D-glucose. The assignments for the glucose moiety were corroborated by analysis of the ^{1}H−^{1}H COSY and HMBC spectra of **1**. Attachment of the glucose at C-6 was deduced from the HMBC correlation between the anomeric proton H-1″ and the oxygenated aromatic carbon (C-6) at δ_C 147.8, which in turn gave two cross-peaks with H-4 at δ_H 6.79 and H-5 at δ_H 6.97, respectively. Moreover, H-5 correlated with C-1, and H-4 correlated with C-2, as observed in the HMBC spectrum. The connectivity of the glucose to C-6 of ring B was also evident from the ^{13}C NMR chemical shift of the C-6-oxygenated carbon, which was shielded at δ_C 147.8 compared to tyrolobibenzyl C, which has a free OH group at C-6 (δ_C 150.4).[25] The chemical shift of C-3 (δ_C 152.4) bearing an OH group was deshielded compared to tyrolobibenzyl C (δ_C 150.5), which is substituted with a glucose moiety at this position.

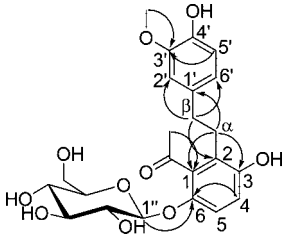


Figure 1. Key HMBC correlations of compound **1**.

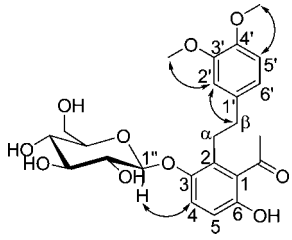


Figure 2. Key ROESY correlations of compound **4**.

Congener **2** was isolated as a pale yellow solid with the molecular formula $C_{24}H_{30}O_{10}$, as determined by HRESIMS (*m*/*z* 496.2177 [M + NH_4]$^+$), indicating the presence of an additional CH_3 group compared to **1**. Compound **2** is a derivative of **1**, which was deduced from inspection of the ^{1}H and ^{13}C NMR spectra of **2** (Tables 1 and 2), which are almost superimposable to those of **1**. The only obvious difference in the NMR spectra between **1** and **2** was observed for the second *O*-methyl resonance at δ_H 3.75 in the ^{1}H NMR spectrum of **2**. This methoxy group was assigned at C-4′ of ring A, as suggested by the HMBC spectrum of **2**. This assignment was corroborated by the 3.1 ppm downfield shift of the C-4′ resonance of **2** as compared to that of **1**. Moreover the resonances for H-5′ were shifted downfield by 0.14 ppm compared to that of **1**, because of the inductive effect of the methoxy group at C-4′.

Congener **3** was obtained from the aerial parts of *S. radiata* as a pale yellow solid showing the molecular formula $C_{22}H_{26}O_9$, as determined from the positive HRESI mass spectrum (*m*/*z* 457.1469 [M + Na]$^+$). The main difference in the NMR spectra of **3** compared to those of **1** and **2** was observed with regard to the proton and carbon signals of the A-ring. The ^{1}H NMR spectrum of **3** (Table 1) exhibited signals for the A-ring protons, which are typical of an AA′BB′ system instead of an ABX system as present in compounds **1** and **2**. These differences in the ^{1}H NMR spectrum are mirrored by equally clear differences in the ^{13}C NMR spectrum of **3** (Table 2) compared to those of **1** and **2**. Attachment of the β-glucose moiety to ring B at C-6 rather than at C-3 (as found for the known compound tyrolobibenzyl C) was confirmed on the basis of the HMBC cross-peak of the anomeric proton (H-1″) at δ_H 4.76 with the aromatic carbon C-6 at δ 147.8. Compared with tyrolobibenzyl C, compound **3** differs from the latter only by the linkage of the β-glucose moiety in ring B.[25]

Congener **4** was obtained as a pale yellow solid with the molecular formula $C_{24}H_{30}O_{10}$, as indicated from the negative HRESI mass spectrum (*m*/*z* 523.1819 [M − H + HCOOH]$^-$), which was identical to the molecular formula of **2**. The compounds differed only with regard to the position of attachment of the glucose unit on ring B. An aromatic proton at δ_H 7.13 (H-4) showed a HMBC correlation with C-2 (δ_C 130.8), which implied the B-ring of **4** to be different from that of **2**. The attachment of the β-glucose moiety of compound **4** was inferred to be at C-3 rather than at C-6 as previously observed for **2**, which was confirmed from the ROESY correlation of the anomeric proton (H-1″) at δ_H 4.80 with H-4 at δ_H 7.13 (Figure 2). The presence of the glucose substituent at C-3 was also indicated by the downfield shift of H-4 by −0.33 ppm and the upfield shift of H-5 by +0.32 ppm, compared to the respective signals in the ^{1}H NMR spectrum of compound **2**. Furthermore, when the ^{13}C NMR data of **4** were compared to those of **2**, the C-1, C-3, and C-5 signals of **4** were shifted upfield by +3.1, +1.7, and +1.7 ppm, while the C-2, C-4, and C-6 signals were shifted downfield by −4.4, −2.5, and −2.5 ppm, respectively, which implied that glycosylation had occurred at C-3 instead of at C-6.

Compound **5** was isolated as a pale yellow solid. Its molecular formula was determined as $C_{46}H_{54}O_{20}$ by HRESIMS (*m*/*z* 949.3101 [M + Na]$^+$). Compound **5** was a dimer of **1**, which was inferred from inspection of the ^{1}H NMR (Table 1) and mass spectra of **5**.

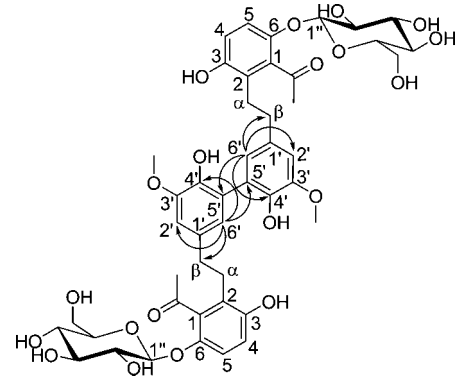


Figure 3. Key HMBC correlations of compound **5**.

Table 3. IC_{50} values of Compounds **1**−**5** and Resveratrol in DPPH Assay

	1	**2**	**3**	**4**	**5**	resveratrol
IC_{50} (μM)	105.51	663.13	486.38	730.99	102.90	149.52

Only one set of NMR resonances was displayed in the ^{1}H NMR spectrum of **5**, indicating that it was a symmetrical dimer. The only difference in the ^{1}H NMR spectrum of **5** compared to **1** was observed with regard to a pair of doublets [δ_H 6.54 (d, J = 1.9 Hz) and 6.53 (d, J = 1.9 Hz)] resonating close to each other instead of an ABX system in the aromatic region. The resonances of the two doublets were assigned to H-2′ and H-6′, which exhibited direct correlations to carbons at δ_C 111.6 (C-2′) and 124.1 (C-6′), as shown in the HMQC spectrum of **5**. The nature and position of the linkage between the two monomers was determined from the HMBC spectrum (Figure 3) and ^{13}C chemical shifts. The strong cross-peak observed between δ_C 130.5 (C-5′) and δ_H 6.53 (H-6′), which further correlated with C-2′ (δ_C 111.6) and C-4′ (δ_C 148.4) of ring A, and the deshielding of the aromatic ring carbons C-5′, C-4′, C-6′, and C-3′ by −14.5, −2.8, −2.2, and −2.6 ppm, respectively, compared to the signals in the ^{13}C NMR spectrum of **1**, were indicative of a symmetrical dimer linked through C-5′.

Radical-scavenging activity of compounds **1**−**5** was assessed using the DPPH assay. As a reference compound, the well-known naturally occurring antioxidative stilbene resveratrol was included. IC_{50} values were determined for each of these compounds and are presented in Table 3. Compounds **1** and **5** were more active than resveratrol or compounds **2**−**4**. Methoxy substitution at the *ortho* position relative to an OH group (C-4′) of the phenol moiety as found for **1** and **5** induced an increase in the scavenging reaction. The electron-donating methoxy group allows stabilization of the resulting aryloxy radical through electron delocalization after hydrogen donation by the OH group.[28] The structure−activity relationships of the phenolic compounds were also comfirmed by theoretical studies, which indicated that the O−H bond dissociation enthalpy (BDE) value is reduced by an *ortho* substitution of a methoxy group, and the weaker the OH bond, the faster the reaction with free radicals.[29,30] Compounds **1** and **2** were also tested for their cytotoxicity toward the mouse lymphoma cell line (L5175Y), but neither was active when assayed at a concentration of 10 μg/mL.

Experimental Section

General Experimental Procedures. Optical rotations were recorded on a Perkin-Elmer 241 MC polarimeter. 1D and 2D NMR spectra (chemical shifts in ppm, coupling constants in Hz) were recorded on Bruker ARX 500 and DMX 600 NMR spectrometers using the standard Bruker software and CD_3OD as solvent. NMR spectra were referenced to the solvent signal. ESI mass spectra were obtained on a ThermoFinnigan LCQ DECA mass spectrometer coupled to an Agilent 1100 HPLC system that included an online photodiode array detector.

HRESIMS spectra were determined on a ThermoFinnigan LTQ-Orbitrap FT-ESIMS. For HPLC analysis, 20 μL samples were injected into an HPLC system (Dionex, Munich, Germany) equipped with a photodiode array detector, employing a linear gradient from 0.1% phosphoric acid to MeOH (HPLC grade, Merck) at 35 min. Routine detection was at 254 nm. The separation column (125 × 4 mm, i.d.) was prefilled with 5 μm Eurospher-100 C18 (Knauer, Berlin, Germany). The temperature of the column oven was set at 20 °C. The compounds were eluted at 17.79 min (**3**), 18.24 min (**1**), 19.48 min (**4**), 20.74 min (**2**), and 21.12 min (**5**). Semipreparative HPLC was performed on a Merck-Hitachi Eurospher-100-C18, L-7100 pump and L-7400 UV detector. TLC was performed on TLC plates precoated with Si 60 F_{254} (Merck, Darmstadt, Germany) using EtOAc/HCO_2H/ H_2O, 85:10:5, as solvent. The compounds were detected from their UV absorbance and by spraying the TLC plates with anisaldehyde reagent. The absolute configuration of glucose linked to the dihydrostilbenes (**1**−**5**) was determined as β-D-glucose by butanolysis and capillary glc of the trimethylsilylated (−)-2-butyl derivatives.[31] Radical-scavenging activities by DPPH were measured on a Perkin-Elmer Lambda 25 UV/vis spectrometer.

Plant Material. Aerial parts of *S. radiata* were collected in July 2004 in Khandgait am forest, Ulaanbaatar region, Mongolia. The plant was identified by Prof. Sc. D. Sh. Darijmaa (Mongolian State University of Education). Voucher specimens (ts-15-02072004-khandgaitUB) have been deposited in the herbarium section of the Department of Organic and Food Chemistry, National University of Mongolia, Ulaanbaatar, Mongolia.

Extraction and Isolation. The air-dried, powdered plant material of *S. radiata* (300 g) was extracted exhaustively by maceration with MeOH (3 × 400 mL) at room temperature. The total extract was concentrated to dryness under vacuum. The concentrated solids (32.0 g) were reconstituted with 100 mL of MeOH/H_2O (3:7) and then partitioned successively with hexane (5 × 100 mL), EtOAc (5 × 100 mL), and *n*-BuOH (5 × 100 mL) to give the hexane, EtOAc, *n*-BuOH, and aqueous fractions. Solvents (technical grade) were distilled prior to use, and spectral grade solvents (Merck) were used for spectroscopic measurements.

Aliquot amounts of the EtOAc fractions of the MeOH extract derived from the aerial parts of *S. radiata* (1.98 g) were separated by HP-20 resin CC with gradient elution using H_2O and MeOH as solvents to afford 10 fractions. Compounds **1** (34.7 mg, 0.018% yield) and **2** (55.3 mg, 0.028% yield) were separated by Sephadex LH-20 CC using MeOH as mobile phase. Compounds **3** (14.1 mg, 0.007% yield), **4** (3.4 mg, 0.002% yield), and **5** (1.1 mg, 0.0006% yield) were purified by semipreparative HPLC utilizing RP-18 as stationary phase and mixtures of MeOH/H_2O as solvent.

Scorzodihydrostilbene A (1): amorphous solid; $[\alpha]^{20}_D$ −19 (*c* 0.12, MeOH); UV (MeOH/H_2O) λ_{max} 224, 285 nm; ^{1}H and ^{13}C NMR data, Tables 1 and 2; (+)ESIMS *m/z* 482.1 $[M + NH_4]^+$; (−)ESIMS *m/z* 463.1 $[M - H]^-$; HRESIMS *m/z* 482.2021 $[M + NH_4]^+$ (482.2026 calc for $C_{23}H_{32}O_{10}N$).

Scorzodihydrostilbene B (2): amorphous solid; $[\alpha]^{20}_D$ −20 (*c* 0.12, MeOH); UV (MeOH/H_2O) λ_{max} 225, 284 nm; ^{1}H and ^{13}C NMR data, Tables 1 and 2; (+)ESIMS *m/z* 496.1 $[M + NH_4]^+$; (−)ESIMS *m/z* 477.2 $[M - H]^-$; HRESIMS *m/z* 496.2177 $[M + NH_4]^+$ (496.2183 calc for $C_{24}H_{34}O_{10}N$).

Scorzodihydrostilbene C (3): amorphous solid; $[\alpha]^{20}_D$ −33 (*c* 0.12, MeOH); UV (MeOH/H_2O) λ_{max} 221, 283 nm; ^{1}H and ^{13}C NMR data, Tables 1 and 2; (+)ESIMS *m/z* 457.3 $[M + Na]^+$; (−)ESIMS *m/z* 433.3 $[M - H]^-$; HRESIMS *m/z* 457.1469 $[M + Na]^+$ (457.1475 calc for $C_{22}H_{26}O_9Na$).

Scorzodihydrostilbene D (4): amorphous solid; $[\alpha]^{20}_D$ −20 (*c* 0.12, MeOH); UV (MeOH/H_2O) λ_{max} 221, 280 nm; ^{1}H and ^{13}C NMR data, Tables 1 and 2; (+)ESIMS *m/z* 501.3 $[M + Na]^+$; (−)ESIMS *m/z* 477.3 $[M - H]^-$; HRESIMS *m/z* 523.1819 $[M - H + HCOOH]^-$ (523.1816 calc for $C_{25}H_{31}O_{12}$).

Scorzodihydrostilbene E (5): amorphous solid; $[\alpha]^{20}_D$ −19 (*c* 0.12, MeOH); UV (MeOH/H_2O) λ_{max} 223, 292 nm; ^{1}H and ^{13}C NMR data, Tables 1 and 2; (+)ESIMS *m/z* 949.3 $[M + Na]^+$; (−)ESIMS *m/z* 925.3 $[M - H]^-$; HRESIMS *m/z* 949.3101 $[M + Na]^+$ (949.3106 calc for $C_{46}H_{54}O_{20}Na$).

Measurement of Radical-Scavenging Activity by DPPH. Qualitative analysis of radical-scavenging activity of the extracts and fractions was carried out by spraying the TLC plates after development in an appropriate solvent system (EtOAc/HCO_2H/H_2O, 85:10:5) with 1% 2,2-diphenyl-1-picrylhydrazyl (DPPH) reagent. Active components were observed as yellow bands against a violet background.

To quantify the antioxidative capacity, absorption at 517 nm was determined after a test sample dissolved in 10 μL of MeOH had reacted with 490 μL of DPPH solution (100 μM) at room temperature. Incubation time was 5 min. Prior to measurement, the difference in absorption between a DPPH blank solution and the positive control (propylgallate, 100 μM) was determined. This difference was then taken as 100% antioxidative activity. The percent antioxidative activity could be calculated from the difference in absorption between the test sample at 100 μM and the DPPH blank as follows:[15]

$$a_A(\%) = [(A_B - A_P)/(A_B - A_{Pos})] \times 100$$

where a_A = % antioxidative activity in comparison with the positive control, A_B = absorption of DPPH solution as blank, A_P = absorption of test sample, and A_{Pos} = absorption of positive control (propylgallate). Measurements were performed in triplicate, and IC_{50} values were calculated by linear regression.

Cell Proliferation Assay. Cytotoxicity was examined against L1578Y mouse lymphoma cells and was determined by a microculture tetrazolium (MTT) assay as described previously.[15] All experiments were carried out in triplicate and repeated three times.

Acknowledgment. We are grateful to Prof. Sc. D. Sh. Darijmaa from the Mongolian State University of Education for collection and identification of the plant material. We also thank C. Kakoschke and B. Jaschok-Kentner for NMR data (HZI, Braunschweig). Financial support of this project by grants of the BMBF and of MOST to P.P. and W.L. is gratefully acknowledged. N.T. thanks the Humboldt Foundation for a scholarship and ARC-NUM project.

References and Notes

(1) Mabberley, D. J. *The Plant Book (A Portable Dictionary of the Vascular Plants)*, 2 ed.; Cambridge University Press: Cambridge, 1997; p 652.
(2) Malyschev, L. I.; Peschkova, G. A. *Central Sibirian Flora Novosibisk: Aedibs*; Nauka Divisid: Sibirica, 1979; Vol. 2, pp 893−894.
(3) Tulin, T. G.; Heywood, V. H.; Burges, N. A.; Moore, D. M.; Valentine, D. H.; Walters, S. M.; Webb, D. A. *Flora Europaea*; Cambridge University Press: London, 1976; Vol. 4, pp 317−322.
(4) GrubovV. I. *Key to the Vascular Plants of Mongolia*; Nauka: Leningrad, 1982; pp 263−264.
(5) Gubanov, I. A. *Conspectus of Flora of Outer Mongolia (Vascular Plants)*; Valang: Moscow, 1996; p 106.
(6) Liu, G. X.; Zhao, Y. Z.; Xu, J. *Grassland China* **2001**, *23*, 12–18.
(7) Sancher, C.; Batkhuu, J.; Komatsu, K. *Picture handbook of useful plants from Mongolia*; KSA Press: Ulaanbaatar, 2003; p 60.
(8) Liu, G. X.; Zhao, Y. Z.; Liu, L. H.; Liu, D. Q. *Acta Prataculturae Sin.* **2002**, *11*, 37–44.
(9) He, X. L. *J. Hebei Univ. (Nat. Sci. Ed.)* **2004**, *24*, 65–73.
(10) Ligaa, U. *Medicinal Plants from Mongolia Used in Mongolian Traditional Medicine*; KSA Press: Ulaanbaatar, 1996; p 337.
(11) Bryanskii, O. V.; Tolstikhina, V. V.; Zinchenko, S. V.; Semenov, A. A. *Chem. Nat. Compd.* **1992**, *28*, 556–560.
(12) Li, J.; Wu, Q. X.; Shi, Y. P.; Zhu, Y. *Chin. Chem. Lett.* **2004**, *15*, 1309–1310.
(13) MacLeod, G.; Ames, J. M. *Phytochemistry* **1991**, *30*, 883–888.
(14) Öksüz, S.; Gören, N.; Ulubelen, A. *Fitoterapia* **1990**, *61*, 92–93.
(15) Tsevegsuren, N.; Edrada, R.; Lin, W.; Ebel, R.; Torre, C.; Ortlepp, S.; Wray, V.; Proksch, P. *J. Nat. Prod.* **2007**, *70*, 962–967.
(16) Zidorn, C.; Ellmerer-Muller, E. P.; Stuppner, H. *Pharmazie* **2000**, *55*, 550–551.
(17) Bryanskii, O. V.; Tolstikhina, V. V.; Semenov, A. A. *Chem. Nat. Compd.* **1992**, *25*, 519–520.
(18) Tolstikhina, V. V.; Semenov, A. A.; Ushakov, I. A. *Rastit. Resur.* **1999**, *35*, 87–90.
(19) Tolstikhina, V. V.; Bryanskii, O. V.; Syrchina, A. I.; Semenov, A. A. *Chem. Nat. Compd.* **1988**, *24*, 655.
(20) Tolstikhina, V. V.; Semenov, A. A. *Rastit. Resur.* **1998**, *34*, 77–80.
(21) Zidorn, C.; Petersen, B. O.; Udovièiã, V.; Larsen, T. O.; Duus, J.Ø.; Rollinger, J. M.; Ongania, K. H.; Ellmerer, E. P.; Stuppner, H. *Tetrahedron Lett.* **2005**, *46*, 1291–1294.
(22) Menichini, F.; Statti, G.; Delle, M. F. *Fitoterapia* **1994**, *65*, 555–556.
(23) Sari, A.; Zidorn, C.; Ellmerer, E. P.; Özgökçe, F.; Ongania, K. H.; Stuppner, H. *Helv. Chim. Acta* **2007**, *90*, 311–317.
(24) Zidorn, C.; Ellmerer, E. P.; Sturm, S.; Stuppner, H. *Phytochemistry* **2003**, *63*, 61–67.

(25) Zidorn, C.; Ellmerer-Müller, E. P.; Stuppner, H. *Helv. Chim. Acta* **2000**, *83*, 2920–2925.
(26) Zidorn, C.; Spitaler, R.; Ellmerer-Muller, E. P.; Perry, N. B.; Gerhauser, C.; Stuppner, H. *Z. Naturforsch. C* **2002**, *57*, 614–619.
(27) Paraschos, S.; Magiatis, P.; Kalpoutzakis, E.; Harvala, C.; Skaltsounis, A. L. *J. Nat. Prod.* **2001**, *64*, 1585–1587.
(28) Rice-Evans, C. A.; Miller, N. J.; Paganga, G. *Free Radical Biol. Med.* **1996**, *20*, 933–956.
(29) Ordoudi, S. A.; Tsimidou, M. Z.; Vafiadis, A. P.; Bakalbassis, E. G. *J. Agric. Food. Chem.* **2006**, *54*, 5763–5768.
(30) Wright, J. S.; Johnson, E. R.; DiLabio, G. A. *J. Am. Chem. Soc.* **2001**, *123*, 1173–1183.
(31) Gerwig, G. J.; Kamerling, J. P.; Vliegenthart, J. F. G. *Carbohydr. Res.* **1978**, *62*, 349–357.

NP800782F