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Constituents of the Roots of *Boerhaavia diffusa* L. II.[1] Structure and Stereochemistry of a New Rotenoid, Boeravinone C[2]

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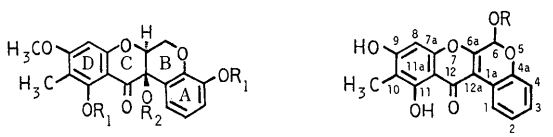
A new 12a-hydroxyrotenoid, boeravinone C, has been isolated from the roots of *Boerhaavia diffusa* L. (Nyctaginaceae) and its structure including the absolute configuration was determined based on chemical and spectral evidence. The ^{1}H-nuclear magnetic resonance of boeravinone C showed unusual splitting patterns due to ABC spin systems. These splitting patterns were analyzed by a simulation method.

Keywords *Boerhaavia diffusa*; Nyctaginaceae; 12a-hydroxyrotenoid; boeravinone C; 2D INADEQUATE; NMR simulation; NOE; ORD

In the preceding paper,[1] we reported the isolation and structure determination of two new rotenoids, boeravinones A (**2**) and B (**3**), from the roots of *Boerhaavia diffusa* L. (Nyctaginaceae), which is used as a traditional medicine in Nepal, Sri Lanka, India, and East Africa. In a continuing investigation of the oily fraction of the ether extract, we have isolated a new rotenoid and named it boeravinone C (**1a**). This paper describes the structure determination of this compound.

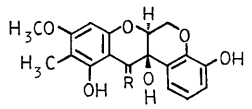
Boeravinone C (**1a**) was obtained as pale yellow needles (from $CHCl_3$), mp 248—249 °C, $[\alpha]_D$ −459.9° (acetone). It showed the molecular ion peak at *m/z* 344 in the mass spectrum (MS) and its molecular formula was determined to be $C_{18}H_{16}O_7$ by high-resolution MS. In the infrared (IR) spectrum, it revealed hydroxyl absorptions at 3550 and 3440 (OH) cm^{-1}, a carbonyl absorption at 1630 cm^{-1}, and aromatic absorptions at 1580, 1510, and 1480 cm^{-1}. The ultraviolet (UV) spectrum of **1a** showed absorption bands at 207.4, 212sh, 293.5, and 331sh nm (log ε: 4.03, 4.01, 3.94, and 3.05, respectively). On addition of 3 N NaOH (2 drops), bathochromic displacements of these absorptions were noticed to 219.5, 240.5, 295.5, and 370 nm (log ε: 4.38, 3.95, 3.85, and 2.93, respectively), suggesting that **1a** may be a phenolic compound.

The proton and carbon nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra of **1a** (in pyridine-d_5) analyzed with the aid of ^{1}H–^{1}H and ^{1}H–^{13}C shift correlation spectroscopies (COSY) indicated the presence of a carbonyl (δ_C 195.60), a hydroxyl proton (δ_H 12.56), four aromatic CH groups (δ_H 8.34, 7.27, 7.06, and 6.25; δ_C 122.23, 117.20, 121.41, and 90.23), a methoxyl group (δ_H 3.71; δ_C 55.97), and a vinyl methyl group (δ_H 2.15; δ_C 7.04) (Tables I and II). Further, the ^{1}H-NMR spectrum showed signals with a complex splitting pattern in the 4.67—4.93 ppm region, which were ascribed to an O-CH-CH_2 grouping (6a-H and 6-H_2) by means of the ^{1}H–^{13}C COSY experiment (Tables I and II). An interpretation of these ^{1}H-signals will be discussed later.

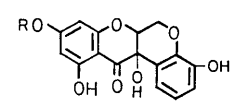


1a : $R_1=R_2=H$
1b : $R_1=COCH_3$, $R_2=H$
1c : $R_1=R_2=COCH_3$

2 : $R=CH_3$
3 : $R=H$



4 : R = 
5 : R = 



6 : $R=CH_3$
7 : $R=H$

Chart 1

Acetylation of **1a** with acetic anhydride–pyridine gave an amorphous diacetate (**1b**), $C_{22}H_{20}O_9$, and an amorphous triacetate (**1c**), $C_{24}H_{22}O_{10}$. The diacetate (**1b**) showed a strong IR band at 1760 cm^{-1} (CO) and ^{1}H-NMR signals at δ_H 2.27 and 2.53 due to two acetyl groups, while the triacetate (**1c**) showed IR bands at 1760 and 1745 cm^{-1} (CO) and ^{1}H-NMR signals at δ_H 1.79, 2.31, and 2.49 due to three acetyl groups (Table I). It was found that further acetylation of **1b** with acetic anhydride–pyridine proceeded slowly to give **1c** and that neither of the acetyl derivatives showed a ^{1}H-signal due to a proton geminal to the acetoxyl group (Table I). Therefore, **1a** has an aliphatic *tert*-hydroxyl and two phenolic hydroxyl groups.

Since **1a** has a number of quaternary carbons, a two dimensional incredible natural abundance double quantum transfer experiment (2D INADEQUATE)[3] on **1a** (in acetone-d_6)[4] was carried out to clarify the sequence of carbon atoms in the molecule. The result is reproduced in Fig. 1, revealing correlated peaks of all the ^{13}C–^{13}C pairs, except those between the carbons a and h, and h and q, leading to the partial structure A as depicted in Fig. 1.

Then, we measured the ^{1}H–^{13}C long-range COSY[5] of **1a** in order to elucidate the connectivities of the carbons a, h, and q, and substituent groups. As shown in Fig. 2, the carbon signal at δ_C 106.80 (h, C-10) is correlated with the proton signals at δ_H 1.97 (10-CH_3), 6.20 (8-H), and 11.98 (11-OH), while the carbon signal at δ_C 166.87 (q, C-9) is correlated with the proton signals at δ_H 1.97 (10-CH_3), 3.93 (9-OCH_3), and 6.20 (8-H). Some other proton–carbon long-range correlations observed are indicated by arrows in the structure in Fig. 2. It is therefore reasonable to conclude that carbon h is connected with carbons a and q and that the methoxyl group is connected with carbon q. Also, it is evident that one of the hydroxyl groups is linked to carbon p (C-11), because the proton signal at δ_H 11.98 (11-OH) is correlated with carbons h (C-10), p (C-11), and g (C-11a). On the other hand, the carbon signal at δ_C 144.20

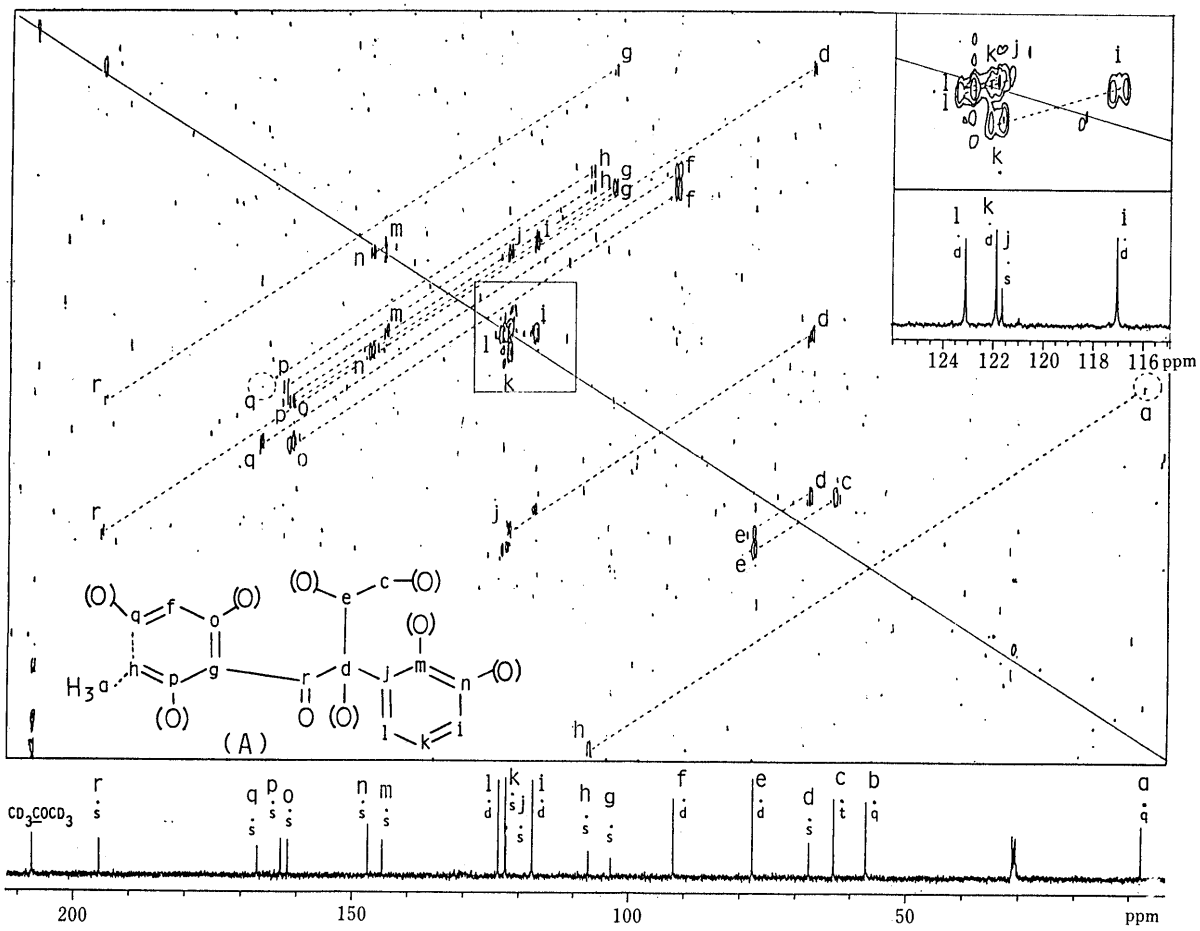


Fig. 1. 2D INADEQUATE Spectrum of Boeravinone C (**1a**) in Acetone-d_6 (Sample, 110 mg; J_{CC} = 60 Hz; 35 °C; 72 h Run)

Carbon signals are marked with small letters a—r in the order of increasing δ values. Dotted circles indicate expected correlation peaks which were not observed in this experiment.

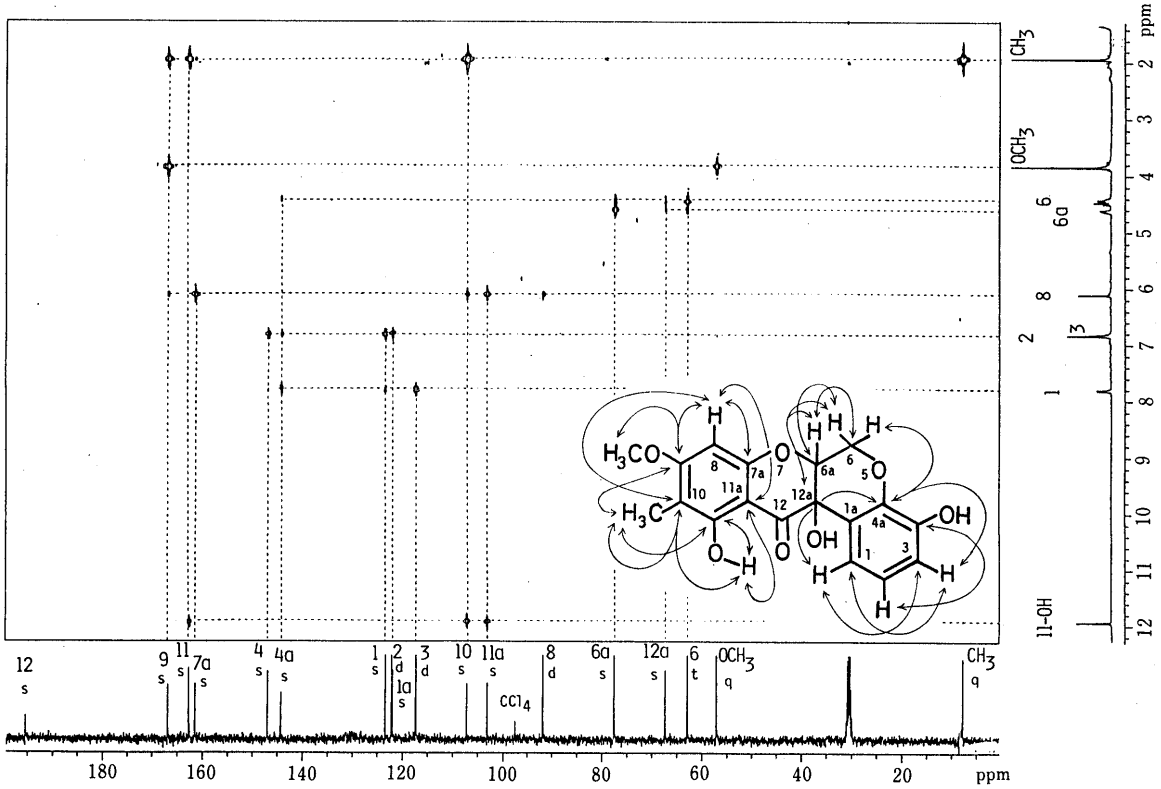


Fig. 2. ^1H–^{13}C Long-Range Shift Correlation Spectrum of Boeravinone C (**1a**) in Acetone-d_6 (J_{CH} = 10 Hz)

(m, C-4a) is correlated with the proton signals at δ_H 4.46 (6-H), 6.86 (3-H), and 7.81 (1-H), indicating that carbons m and c are connected through an ether linkage. Although no correlation could be detected between carbon o (C-7a) and 6a-H, an ether linkage should exist between carbons o (C-7a) and e (C-6a) in view of the molecular formula. Thus, the remaining two hydroxyl groups must be linked to the quaternary carbons d (C-12a) and n (C-4).

From the foregoing findings, the gross structure of boeravinone C should be represented by the formula **8** (Chart 2). In accordance with the proposed structure, the MS of **1a** showed significant fragment ion peaks at *m/z* 299 (a), 181 (b, base peak), and 163 (c), which may be assigned to the formulae a, b, and c, respectively.[6,7]

The B/C ring junction was considered to be *trans* from the chemical shift value of 1-H (δ 8.34 in pyridine-d_5).[8] This was supported by the results of nuclear Overhauser

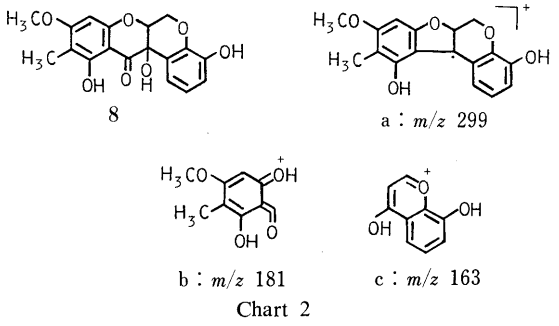


Chart 2

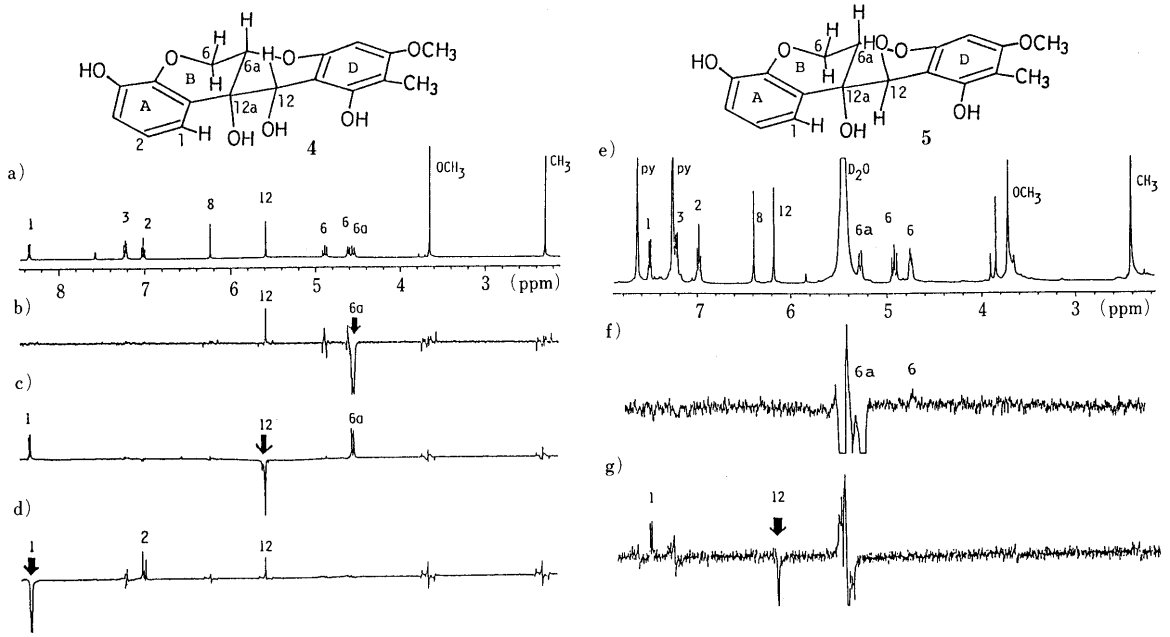


Fig. 3. Normal ^{1}H-NMR and NOE Difference Spectra of the Reduction Products (**4** and **5**) of Boeravinone C (**1a**) in Pyridine-d_5
a—d) Spectra of **4**, e—g) spectra of **5**.

TABLE I. The 400 MHz ^{1}H-NMR Data for Boeravinone C (**1a**) and Its Derivatives (Coupling Constants in Parenthesis)

Position	**1a**[a] δ	**1a**[b] δ	**1a**[c] δ	**1a**[d] δ	**1b**[a] δ	**1c**[a] δ	**4**[a] δ	**5**[e] δ
1	8.34 dd (7.5, 1.9)	7.89[f] (8.83, 0.66)	7.81[f] (8.20, 1.35)	7.80[f] (8.82, 0.84)	8.42 br d (8.0)	8.51 dd (8.0, 1.5)	8.36 dd (8.0, 1.5)	7.52 dd (8.0, 1.0)
2	7.06 t (7.5)	6.99[f] (8.83, 8.08)	6.87[f] (8.20, 7.98)	6.85[f] (8.82, 8.39)	7.01 t (8.0)	7.05 t (8.0)	7.02 t (8.0)	6.98 t (8.0)
3	7.27 dd (7.5, 1.9)	6.98[f] (8.08, 0.66)	6.86[f] (7.98, 1.35)	6.86[f] (8.39, 0.84)	7.23 dd (8.0, 1.8)	7.31 dd (8.0, 1.5)	7.23 dd (8.0, 1.5)	7.22 dd (8.0, 1.0)
6α	4.67[f] (4.66, −10.23)	4.52[f] (4.62, −9.93)	4.46[f] (4.44, −10.02)	4.47[f] (6.66, −9.98)	4.58 (complex)	4.64 dd (10.0, 5.5)	4.62 dd (9.5, 4.5)	4.74 dd (9.6, 4.5)
6β	4.92[f] (11.64, −10.23)	4.54[f] (11.48, −9.93)	4.49[f] (11.50, −10.02)	4.48[f] (9.95, −9.98)	4.77 m	4.68 t (10.0)	4.89 dd (11.0, 9.5)	4.92 dd (11.5, 9.6)
6a	4.93[f] (11.64, 4.66)	4.68[f] (11.48, 4.62)	4.80[f] (11.50, 4.44)	4.76[f] (9.95, 6.66)	4.77 m	4.84 br dd (10.0, 5.5)	4.56 dd (11.0, 4.5)	5.27 dd (11.5, 4.5)
8	6.25 s	6.12 s	6.20 s	6.22 s	6.44 s	6.49 s	6.24 s	6.39 s
12	—	—	—	—	—	—	5.59 s	6.17 s
9-OMe	3.71 s	3.88 s	3.93 s	3.93 s	3.67 s	3.71 s	3.65 s	3.72 s
10-Me	2.15 s	2.03 s	1.97 s	1.97 s	2.05 s	2.01 s	2.30 s	2.41 s
11-OH	12.56 s	11.80 s	11.98 s	—	—	—	—	—
CH_3CO–	—	—	—	—	2.29 s 2.53 s	1.74 s 2.31 s 2.49 s	—	—

δ values in ppm and coupling constants in Hz. *a*) In pyridine-d_5. *b*) In chloroform-d_1. *c*) In acetone-d_6. *d*) In acetone-d_6 + D_2O. *e*) In pyridine-d_5 + D_2O. *f*) Chemical shifts and coupling constants were determined by means of simulation and rounded to three decimal figures.

TABLE II. The 100 MHz ^{13}C-NMR Data for Boeravinone C (**1a**) and Its Derivatives

Position	**1a**[a] δ[c]	**1a**[b] δ[c]	**1b**[a] δ[c]	**1c**[a] δ[c]	**4**[a] δ[c]
1	122.23 d	123.21 d	130.40 d	132.33 d	121.69 d
1a	122.13 s	121.91 s	120.70 s	122.34 s	127.02 s
2	121.41 d	121.95 d	120.70 d	125.08 d	119.61 d
3	117.20 d	117.12 d	123.76 d	120.69 d	116.73 d
4	147.50 s	146.97 s	147.42 s	147.77 s	147.25 s
4a	144.31 s	144.20 s	139.81 s	139.83 s	143.25 s
6	62.25 t	62.72 t	62.30 t	62.38 t	62.98 t
6a	77.16 d	77.40 d	76.33 d	74.80 d	74.01 d
7a	160.69 s	161.52 s	150.64 s	150.14 s	153.17 s
8	90.93 d	91.64 d	96.92 d	96.52 d	91.21 d
9	165.76 s	166.87 s	163.66 s	163.66 s	158.80 s
10	106.18 s	106.80 s	114.74 s	117.86 s	106.31 s
11	162.02 s	162.68 s	160.96 s	159.14 s	157.50 s
11a	102.57 s	102.98 s	107.66 s	115.41 s	105.33 s
12	195.60 s	195.59 s	187.16 s	183.33 s	71.33 d
12a	66.67 s	67.23 s	66.82 s	72.46 s	64.66 s
9-OMe	55.97 q	57.00 q	56.04 q	56.13 q	55.39 q
10-Me	7.04 q	7.62 q	8.40 q	8.52 q	8.35 q
$\underline{C}H_3CO$–	—	—	20.54 q	20.49 q	—
			21.04 q	20.60 q	
				20.80 q	
$CH_3\underline{C}O$–	—	—	168.93 s	168.80 s	—
			169.18 s	169.16 s	
				169.60 s	

δ values in ppm. The multiplicities of carbon signals were determined by means of the DEPT method and are indicated as s, d, t, and q. *a*) In pyridine-d_5. *b*) In acetone-d_6. *c*) ^{1}H–^{13}C and ^{1}H–^{13}C long-range correlation spectra were measured.

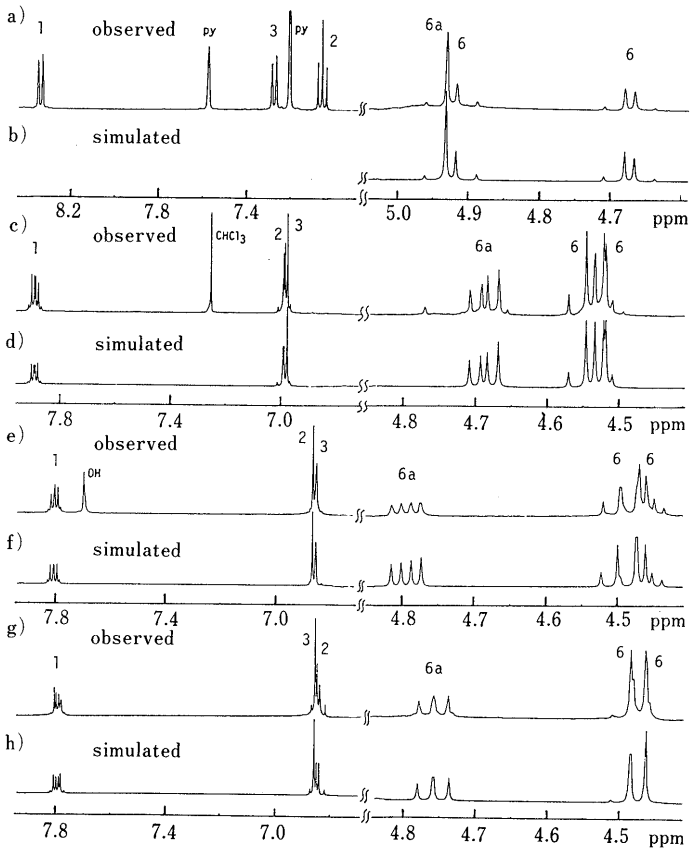


Fig. 4. Comparison of the Observed and Simulated ^{1}H-NMR Patterns of 1-, 2-, 3-, 6a-, and 6-Protons in Boeravinone C (**1a**)

a, b): Observed and simulated spectra in pyridine-d_5; c, d): in $CDCl_3$; e, f): in acetone-d_6; and g, h): in acetone-$d_6 + D_2O$.

effect (NOE) experiments on the reduction products (**4** and **5**) of **1a**.

Treatment of boeravinone C (**1a**) with sodium borohydride in methanol yielded an alcohol (**4**), $C_{18}H_{18}O_7$, mp 208—209 °C, as a sole product, which showed a ^{1}H-NMR signal due to the newly produced carbinol methine proton (12-H) at δ 5.59 (s) (Table I). On the other hand, reduction of **1a** with lithium borohydride in anhydrous ether afforded epimeric alcohols. The major alcohol (**5**), mp 203—205 °C, $C_{18}H_{18}O_7$, exhibited a ^{1}H-NMR signal due to the carbinol methine (12-H) at δ 6.17 (s), while the minor product, mp 208—209 °C, was identified as **4**.

As shown in Fig. 3, irradiation at 12-H (δ 5.59) in **4** enhanced the signal intensity of 6a-H (δ 4.56) and 1-H (δ 8.36) due to the NOE. In turn, irradiation at 6a-H enhanced the signal intensity of 12-H, indicating a 1,3-diaxial relation between 6a-H and 12-H. Also, irradiation at 1-H gave rise to an NOE increase of the signal of 12-H. On the other hand, irradiation at 6a-H (δ 5.27) and 12-H (δ 6.17) in **5** caused NOE's on the signals of 6-H (δ 4.74) and 1-H (δ 7.61), respectively. Since the proton 6a-H in **4** had the coupling constants of 11 Hz and 4.5 Hz, it should take an axial conformation with respect to both the B and C rings. This unambiguously revealed the B/C *trans* system in **1a**.

The absolute stereochemistry of the B/C ring junction in boeravinone C was determined to be 6a*S*,12a*R* (**1a**) based on the negative Cotton effect at around 340 nm in the optical rotatory dispersion (ORD) spectrum, which agreed with that of 6aα,12aβ-rotenolone.[9]

As mentioned before, the ^{1}H-NMR spectrum of boeravinone C (**1a**) in pyridine-d_5 showed a complicated splitting pattern due to an ABC spin system. This spectral pattern and that of the aromatic protons changed markedly when the solvent was changed from pyridine-d_5 to chloroform-d_1[10] or acetone-d_6 or acetone-$d_6 + D_2O$. Since these splitting patterns could not be interpreted in the first-order analysis, a simulative approach by calculation of the positions and intensities of respective resonance lines in these three spin systems was applied. For this purpose, the JEOL program COMIC was employed and the results are reproduced in Fig. 4. Comparison of observed and simulated splitting patterns reveals excellent agreement. It is noteworthy that 6β-H in **1a** showed a marked downfield shift in pyridine-d_5 compared with other solvents (Table I). Also, a significant change of the coupling constants between 6a-H and 6-H_2 was noticed when D_2O was added to the acetone-d_6 solution. This is probably due to a change of the solvation state, which may cause a conformational change of the molecule.

Nyctaginaceae plants seem to be a source of simple natural rotenoids. It should be mentioned that two 12a-hydroxyrotenoids (**6** and **7**) having structures closely related to **1a** have recently been isolated from *Boerhaavia coccinea*.[11] Occurrence of rotenoids in other plants of this family would be of particular interest from the biogenetic viewpoint.

Experimental

Melting points were determined with a Kofler-type apparatus and are uncorrected. Optical rotations were measured in acetone or methanol solutions on a JASCO DIP-140 digital polarimeter at 28 °C and an ORD

spectrum on a JASCO J-20 spectropolarimeter in dioxane. UV spectra were taken with a Shimadzu 202 UV spectrometer in EtOH solutions and IR spectra with a JASCO IRA-2 or a Nicolet DX FT-IR spectrometer in chloroform solutions unless otherwise noted. ^{1}H- and ^{13}C-NMR spectra were taken on a JEOL JNM-GX 400 spectrometer with tetramethylsilane as an internal standard, and chemical shifts are recorded in δ values. ^{1}H–^{1}H COSY, ^{1}H–^{13}C COSY, ^{1}H–^{13}C long-range COSY, and 2D INADEQUATE spectra were obtained with the JEOL standard pulse sequences and data processing was performed with the JEOL standard software. MS and high-resolution MS were obtained with a JEOL JMS-D 300 spectrometer (ionization voltage, 70 eV; accelerating voltage, 3 kV) using a direct inlet system. Column chromatography was done with Mallinkrodt silica gel. Preparative thin layer chromatography (TLC) was carried out on Merck Kieselgel GF_{254} plates and the plates were examined under UV light. Extraction of substances from silica gel was done with MeOH–CH_2Cl_2 (1:9 or 3:7) and solutions were concentrated *in vacuo*. TLC analyses were done on Merck Kieselgel GF_{254} plates and spots were detected by the use of 1% $Ce(SO_4)_2$–aqueous H_2SO_4 (10%) reagent. For drying organic solutions, anhydrous $MgSO_4$ was used.

Isolation of Boeravinone C (1a) Details of the extraction and isolation of boeravinone C from the roots of *Boerhaavia diffusa* were reported in the preceding paper.[1] Fraction 4 (1.1 g), obtained from the silica gel column chromatography of the neutral fraction of the ether extract, was separated by repeated preparative TLC with MeOH–$CHCl_3$ to give two compounds. The less polar compound was identified as boeravinone A (**2**). The more polar compound was recrystallized from $CHCl_3$ to yield boeravinone C (**1a**) (129 mg), pale yellow needles (chloroform), mp 248—249 °C. $[\alpha]_D$ −459.9° (c=0.15, acetone). IR ν_{max}^{KBr} cm^{-1}: 3550, 3440 (OH), 1630 (conj. CO), 1580, 1510, 1480 (phenyl). UV λ_{max} nm (log ε): 207.4 (4.03), 212sh (4.01), 293.5 (3.94), 331sh (3.05); UV λ_{max} (2 drops of 3 N NaOH added) nm (log ε): 219.5 (4.38), 240.5 (3.95), 295.5 (3.85), 370 (2.93). ORD ($c=1.31\times10^{-4}$, dioxane) [M] (nm): 7.22 $\times10^6$ (325), −1.01 $\times10^7$ (355). ^{1}H- and ^{13}C-NMR: Tables I and II. MS m/z: 344 (M^+), 326 (M^+-H_2O), 299 (a, $M^+-CO-OH$), 181 (b, base peak), 163 (c). High-resolution MS m/z: Found 344.0914, Calcd for $C_{18}H_{16}O_7$ (M^+) 344.0896; Found 326.0807, Calcd for $C_{18}H_{14}O_6$ 326.0790; Found 299.0837, Calcd for $C_{17}H_{15}O_5$ 299.0919; Found 181.0504, Calcd for $C_9H_9O_4$ 181.0500; Found 163.0368, Calcd for $C_9H_7O_3$ 163.0394.

Acetylation of Boeravinone C (1a) A mixture of **1a** (10 mg), acetic anhydride (0.2 ml) and pyridine (0.2 ml) was left to stand at room temperature for 17 h. After decomposition of the excess reagent with water, the reaction mixture was extracted with chloroform. The chloroform layer was washed with brine, dried, and concentrated *in vacuo*. The residue was separated by preparative TLC with MeOH–$CHCl_3$ (2:98) into two fractions. The less polar fraction gave a triacetate (**1c**) (5.5 mg), amorphous. IR ν_{max} cm^{-1}: 1760, 1745, 1710 (CO), 1620, 1480 (phenyl). UV λ_{max} nm (log ε): 220 (4.26), 230sh (4.17), 277.5 (4.17), 309.3 (3.83). ^{1}H- and ^{13}C-NMR: Tables I and II. MS m/z: 470 (M^+), 428, 426, 386, 384, 342, 340, 298 (base peak), 223, 181. High-resolution MS m/z: Found 470.1203, Calcd for $C_{24}H_{22}O_{10}$ (M^+) 470.1213; Found 428.1150, Calcd for $C_{22}H_{20}O_9$ 428.1108; Found 426.1305, Calcd for $C_{23}H_{22}O_8$ 426.1314; Found 386.0966, Calcd for $C_{20}H_{18}O_8$ 386.1000; Found 384.1203, Calcd for $C_{21}H_{20}O_7$ 384.1209; Found 342.1103, Calcd for $C_{19}H_{18}O_6$ 342.1103; Found 340.0932, Calcd for $C_{19}H_{16}O_6$ 340.0946; Found 298.0831, Calcd for $C_{17}H_{14}O_5$ 298.0841; Found 223.0595, Calcd for $C_{11}H_{11}O_5$ 223.0606; Found 181.0484; Calcd for $C_9H_9O_4$ 181.0500.

The more polar fraction afforded a diacetate (**1b**) (6 mg), amorphous. IR ν_{max} cm^{-1}: 3550 (OH), 1760 (CO), 1690 (conj. CO), 1620, 1480 (phenyl). UV λ_{max} nm (log ε): 222 (4.37), 277.6 (4.32), 312.5 (3.96). ^{1}H- and ^{13}C-NMR: Tables I and II. MS m/z: 428 (M^+), 386 (base peak), 368, 344, 326, 298, 223. High-resolution MS m/z: Found 428.1101, Calcd for $C_{22}H_{20}O_9$ (M^+) 428.1107; Found 386.1006, Calcd for $C_{20}H_{18}O_8$ 386.1002; Found 368.0881, Calcd for $C_{20}H_{16}O_7$ 368.0896; Found 344.0867, Calcd for $C_{18}H_{16}O_7$ 344.0896; Found 326.0793, Calcd for $C_{18}H_{14}O_6$ 326.0790; Found 298.0809, Calcd for $C_{17}H_{14}O_5$ 298.0841; Found 223.0603, Calcd for $C_{11}H_{11}O_5$ 223.0606; Found 205.0469, Calcd for $C_{11}H_9O_4$ 205.0500; Found 190.0650, Calcd for $C_{11}H_{10}O_3$ 190.0670; Found 181.0499, Calcd for $C_9H_9O_4$ 181.0501.

Acetylation of the Diacetate (1b) The diacetate (**1b**) (1.5 mg) was treated with acetic anhydride (0.2 ml) in pyridine (0.2 ml) at room temperature for 7 d. Then, the reaction mixture was worked up in the usual manner. The product was separated in the same manner as above to yield a triacetate (1.6 mg) and a diacetate (0.1 mg), which were identified as **1c** and **1b**, respectively, by ^{1}H-NMR comparisons.

Sodium Borohydride Reduction of Boeravinone C (1a) $NaBH_4$ (20 mg) was added to a solution of **1a** (20 mg) in anhydrous MeOH (10 ml) and the mixture was stirred at room temperature for 2 h. After neutralization by addition of 5% HCl and evaporation of MeOH under reduced pressure, the mixture was diluted with water and extracted with AcOEt. The AcOEt extract was washed with brine, dried, and concentrated. The residue was purified by preparative TLC with MeOH–benzene (1:9) to afford an alcohol (**4**), which was recrystallized from $CHCl_3$ to give pale yellow needles (14 mg) (70% yield), mp 208—209 °C. $[\alpha]_D$ −15° (c=0.95, MeOH). IR ν_{max} cm^{-1}: 3550—3400 (OH), 1600, 1485 (phenyl). UV λ_{max} nm (log ε): 211 (4.79), 212sh (4.41), 280.5 (3.78). ^{1}H- and ^{13}C-NMR: Tables I and II. MS m/z: 346 (M^+), 328 (M^+-H_2O), 299 (base peak), and 181. High-resolution MS m/z: Found 346.1038, Calcd for $C_{18}H_{18}O_7$ (M^+) 346.1052; Found 328.0954, Calcd for $C_{18}H_{16}O_6$ 328.0947; Found 299.0918, Calcd for $C_{17}H_{15}O_5$ 299.0918; Found 181.0534, Calcd for $C_9H_9O_4$ 181.0502; Found 147.0471, Calcd for $C_9H_7O_2$ 147.0446.

Lithium Borohydride Reduction of Boeravinone C (1a) $LiBH_4$ (20 mg) was added to a solution of **1a** (10 mg) in anhydrous Et_2O (10 ml), and the mixture was stirred at room temperature for 1 h. After neutralization by addition of 5% HCl, the mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with brine, dried, and concentrated. The residue was separated by preparative TLC with MeOH–benzene (1:9) into two fractions. The less polar fraction gave **4** (1.5 mg).

The more polar fraction afforded an alcohol (**5**) (4.8 mg), yellow needles from MeOH–$CHCl_3$, mp 203—205 °C. $[\alpha]_D$ −64.5° (c=0.11, acetone), ^{1}H-NMR: Table I. MS m/z: 346 (M^+), 328 (M^+-H_2O), 299 (base peak), and 181. High-resolution MS m/z: Found 346.1056, Calcd for $C_{18}H_{18}O_7$ (M^+) 346.1052; Found 328.0964, Calcd for $C_{18}H_{16}O_6$ 328.0948; Found 299.0913, Calcd for $C_{17}H_{15}O_5$ 299.0919; Found 181.0514, Calcd for $C_9H_9O_4$ 181.0501; Found 147.0453, Calcd for $C_9H_7O_2$ 147.0447.

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References and Notes

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