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# BOERAVINONE A AND B, NEW ROTENOID ANALOGUES FROM BOERHAAVIA DIFFUSA LINN

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Two new rotenoid analogues, boeravinone A and B, have been isolated from the roots of Boerhaavia diffusa Linn. (Nyctaginaceae) and their structures have been determined based on the 2-D NMR spectroscopy including INADEQUATE and $^{1}H$-$^{13}C$ long range COSY.

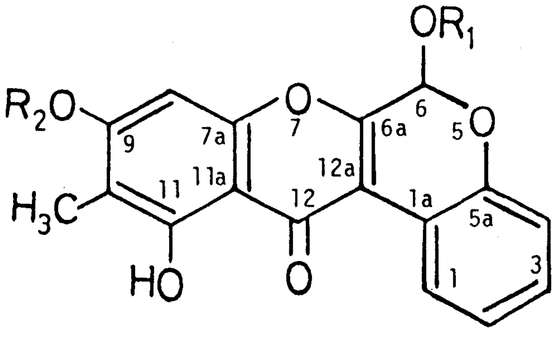
KEYWORDS —— Boerhaavia diffusa; Nyctaginaceae; rotenoid; boeravinone A; boeravinone B

The roots of Boerhaavia diffusa Linn. (Nyctaginaceae) are used as a folk medicine for treatment of asthma and abdominal tumor in India.$^{1)}$ From this plant new rotenoid analogues have been isolated and their structures elucidated.

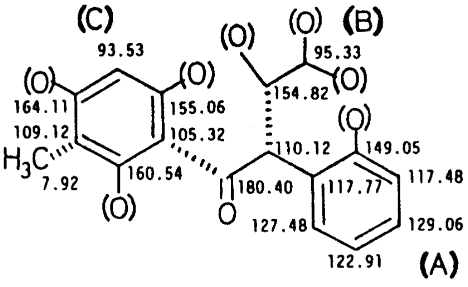
The ether extract from the dried roots (1.2 kg) of B. diffusa, collected in Mannang, Nepal, was separated by silica gel column chromatography followed by repeated preparative TLC to give three new rotenoid analogues, named boeravinone A (125 mg), B (41 mg), and C (129 mg), together with known sterols, sterol glucosides, and fatty acids. This paper deals with the structure elucidation of boeravinone A (1) and B (2).

Boeravinone A (1), mp 215-217°C, yellow needles (from MeOH-$CH_2Cl_2$), $[\alpha]_D$ 0° (acetone), has the molecular formula $C_{18}H_{14}O_6$ and showed IR (KBr) absorption at 3250 (OH), 1650 (conj. CO), and 1620 $cm^{-1}$ and UV (EtOH) bands at 340, 300, 276, and 217 nm (log ε: 3.39, 4.07, 4.37, and 4.39). Its mass spectrum exhibited the $M^+$ peak at m/z 326 and fragment ion peaks at m/z 295 ($M^+$-$OCH_3$) and 267 ($M^+$-$OCH_3$-CO).

The $^{1}H$- and $^{13}C$-NMR spectra of 1 indicated the presence of a carbonyl ($\delta_C$ 180.4), five aromatic CH groups ($\delta_H$ 6.56, 7.16, 7.20, 7.29, 9.10; $\delta_C$ 93.53, 122.91, 117.48, 129.06, 127.48), a hydroxyl ($\delta_H$ 13.44), a methoxy group ($\delta_H$ 3.45; $\delta_C$ 55.73), and a t-methyl group ($\delta_H$ 2.39; $\delta_C$ 7.92) (Table I). Each carbon signal except the quarternary one was assigned based on the $^{1}H$-$^{13}C$ COSY spectral data.$^{2)}$



1: $R_1 = CH_3$, $R_2 = H$
2: $R_1$, $R_2 = H$
3: $R_1$, $R_2 = CH_3$



(—: connectivity was detected; ---: connectivity was not detected)

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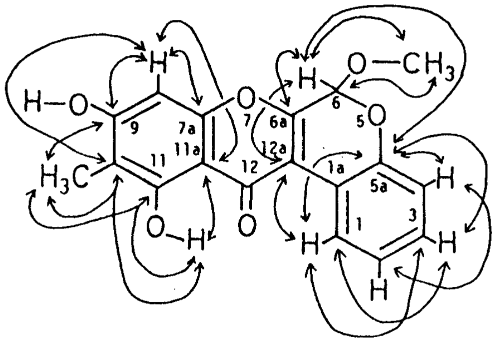

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Methylation of 1 with diazomethane gave a methyl ether (3), $C_{19}H_{16}O_6$ (amorphous powder). The $^1$H-NMR spectrum of 3 showed a singlet due to a newly introduced methoxy group (δ 3.91), together with a one-proton singlet (δ 12.94) which could be ascribed to a phenolic OH, strongly hydrogen-bonded with the 12-ketone group (Table I).

Boeravinone A was found to have a number of quarternary carbons (Table I). So the 2-D INADEQUATE spectrum[2)] of 1 was measured to clarify the sequence of carbon atoms in the molecule. The result indicated the presence of partial structures (A, B, and C) as depicted in 4.

Next, we measured the $^1$H-$^{13}$C long range COSY[3)] of 1 in order to confirm the connectivities of the partial structures and substituent groups. As shown in the formula 5, the carbon signal at δ 110.12 (C-12a) is correlated with the protons at δ 5.89 (6-H) and 9.10 (1-H), and the signal at δ 95.33 (C-6) is correlated with the proton at δ 3.45 ($OCH_3$). Also, the carbon signals at δ 109.12 (C-10), 149.05 (C-5a), and 160.54 (C-11) are correlated with the proton signals at δ 2.39 ($CH_3$), 6.56 (8-H), and 13.44 (11-OH), at δ 5.89 (6-H), 7.20 (4-H), 7.29 (3-H), and 9.10 (1-H), and at δ 2.39 ($CH_3$), and 13.44 (11-OH), respectively. Some of the other significant long range correlations observed are also shown by arrows.

Although connectivity could not be detected between carbons 12 and 11a (each quarternary carbon), there must be a chemical bonding between them since the 11-OH is internally hydrogen-bonded with the 12-ketone group. Also, in view of the composition, an ether linkage should exist between quarternary carbons 6a and 7a.

On the basis of the above results, the structure of boeravinone A was determined to be 1.

Boeravinone B (2) was obtained as an amorphous yellow powder, $[\alpha]_D$ 0° (acetone), and has the molecular formula $C_{17}H_{12}O_6$. Its $^1$H-NMR spectrum showed a pattern very similar to that of 1, except for the absence of a singlet due to the methoxy group (Table I), indicating that the structure is 2.

Treatment of boeravinone B (2) with p-TsOH in MeOH gave a methyl acetal, mp 207-209°C, which was found to be identical with boeravinone A (1) by IR and $^1$H-NMR comparisons. Therefore, the structure of boeravinone B was established to be 2.

The biological activities of 1 and 2 are currently under investigation.

Rotenoids,[4)] which are shown to possess an insecticidal activity and other interresting biological activities,[5)] have so far been isolated only from the Leguminosae and Stemonaceae plants. Our present result provided the first example of the isolation of rotenoid analogues from a plant of the Nyctaginaceae family. Distribution of rotenoid analogues in other Nyctaginaceae plants and their biological activities would be a problem of particular interest.

Table I. $^{1}$H (400 MHz) and $^{13}$C (100 MHz) NMR Spectra of Boeravinone A (1), B (2), and the Dimethyl Ether Derivative (3)

| Position | Boeravinone A (1) (pyridine $d_5$) |  | Boeravinone B (2) (pyridine $d_5$) |  | Dimethyl ether (3) ($CDCl_3$) |  |
|---|---|---|---|---|---|---|
|  | δ H[a,b] | δ C[c,d] | δ H[a,b] | δ C[c,d] | δ H[a] | δ C[e] |
| 1 | 9.10 dd<br>(8.0,1.3) | 127.48 d | 9.14 dd<br>(8.0,1.2) | 127.44 d | 8.85 dd<br>(8.0,1.5) | 127.23 |
| 1a | ——— | 117.77 s | ——— | 118.00 s | ——— | 117.10 |
| 2 | 7.16 ddd<br>(8.0,7.6,1.3) | 122.91 d | 7.16 ddd<br>(8.0,6.0,3.0) | 122.53 d | 7.17 ddd<br>(8.0,7.5,1.5) | 122.98 |
| 3 | 7.29 ddd<br>(8.0,7.6,1.3) | 129.06 d | 7.30 m | 128.96 d | 7.30 ddd<br>(8.0,7.5,1.5) | 128.96 |
| 4 | 7.20 dd<br>(8.0,1.3) | 117.48 d | 7.30 m | 118.00 d | 7.12 dd<br>(8.0,1.5) | 116.97 |
| 5a | ——— | 149.05 s | ——— | 150.06 s | ——— | 148.37 |
| 6 | 5.89 s | 95.33 d | 6.52 s | 89.53 d | 5.80 s | 95.06 |
| 6-OMe | 3.45 s | 55.73 q | ——— | ——— | 3.60 s | 55.95 |
| 6a | ——— | 154.82 s | ——— | 155.19 s | ——— | 154.40 |
| 7a | ——— | 155.06 s | ——— | 155.77 s | ——— | 155.00 |
| 8 | 6.56 s | 93.53 d | 6.65 s | 93.58 d | 6.45 s | 89.35 |
| 9 | ——— | 164.11 s | ——— | 164.08 s | ——— | 163.64 |
| 9-OMe | ——— | ——— | ——— | ——— | 3.91 s | 56.04 |
| 10 | ——— | 109.12 s | ——— | 109.00 s | ——— | 109.73 |
| 10-Me | 2.39 s | 7.92 q | 2.42 s | 8.08 q | 2.12 s | 7.37 |
| 11 | ——— | 160.54 s | ——— | 160.59 s | ——— | 159.21 |
| 11a | ——— | 105.32 s | ——— | 105.28 s | ——— | 106.16 |
| 11-OH | 13.44 s | ——— | 13.67 s | ——— | 12.94 s | ——— |
| 12 | ——— | 180.40 s | ——— | 180.69 s | ——— | 180.28 |
| 12a | ——— | 110.12 s | ——— | 109.47 s | ——— | 110.54 |

δ values in ppm. a) Coupling constants in Hz. b) $^{1}$H-$^{1}$H Correlation spectra were measured. c) The multiplicities of carbon signals were determined by means of the DEPT method, and are indicated as s, d, t, and q. d) $^{1}$H-$^{13}$C Correlation spectra were measured. e) Only the complete decoupling spectrum was measured.

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