REVISED STRUCTURE OF NOBOTANIN B, A DIMERIC ELLAGITANNIN
OF TIBOUCHINA SEMIDECCANDRA

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Abstract — The structure of nobotanin B, a dimeric ellagitannin
of Tibouchina semidecandra, has been revised to 9 on the basis
of structural analysis of a partial hydrolysate.

Nobotanin B is a dimeric ellagitannin isolated from Tibouchina semidecandra
(Melastomataceae) along with nobotanin A (1) and nobotanin F (2). The structure
3 was proposed for nobotanin B in our previous communication, 1 based on the
following evidence: (i) Nobotanin B is a structural isomer of nobotanin F (2), as
it gave three partial hydrolysates, 4-6, upon the hydrolysis similar to that of
nobotanin F. 1 Each glucose core in nobotanin B was therefore presumed to have a
hexahydroxydiphenoyl (HHDP) group at O-2 〜 O-3 as in nobotanin F. (ii) Methyla-
tion of nobotanin B with dimethyl sulfate and potassium carbonate in acetone gave
a partially degraded product, having eighteen methoxyl groups, and it was
presumed to have the structure 8a which is isomeric to the structure of 7 derived
from 2. However, upon detailed examination by HPLC during the hydrolysos of
nobotanins B and F, we have found that in case of the former, 4 and 5 have been
produced most probably from a dimeric partial hydrolysate of a retention time a
little shorter than that of the starting material, although they can be directly
produced from nobotanin F by the cleavage illustrated by a dotted line in the
structure (2). The observation of this difference prompted us to reinvestigate
the structure of nobotanin B.

A dimeric partial hydrolysate (10), C_{68}H_{50}O_{44}.7H_{2}O, [a]_{D} +37^\circ (MeOH), from
nobotanin B, was isolated as the main product after the treatment with boiling
Table I. $^1$H-NMR Data of the Glucose Moieties of Nobotanin B (9), Partial Hydrolysate (10), Casuarictin (11) and Roxbin B (12) (400 MHz, acetone-d$_6$)

<table>
<thead>
<tr>
<th></th>
<th>H-1</th>
<th>H-2</th>
<th>H-3</th>
<th>H-4</th>
<th>H-5</th>
<th>H-6</th>
<th>H-6'</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>Gluc-A 6.20 d 5.10 dd</td>
<td>5.82 dd 5.17 t</td>
<td>4.67 dd 5.33 dd</td>
<td>3.92 d</td>
<td>Gluc-B 6.02 d 5.18 dd</td>
<td>5.41 t 5.83 t</td>
<td>3.45 dd 4.92 d</td>
</tr>
<tr>
<td></td>
<td>(J=8.5) (J=8.5,9)</td>
<td>(J=9,10)</td>
<td>(J=10)</td>
<td>(J=6,10)</td>
<td>(J=6,13.5)</td>
<td>(J=13.5)</td>
<td>(J=9,10)</td>
</tr>
<tr>
<td>10</td>
<td>Gluc-A 6.30 d 4.91 dd</td>
<td>5.50 dd 3.90 t</td>
<td>4.10 dd 3.81 dd</td>
<td>3.94 d</td>
<td>Gluc-B 5.96 d 5.14 dd</td>
<td>5.33 t 5.80 t</td>
<td>3.49 br.d 4.84 dd</td>
</tr>
<tr>
<td></td>
<td>(J=5.5) (J=8.5,10)</td>
<td>(J=10)</td>
<td>(J=10)</td>
<td>(J=2,13)</td>
<td>(J=13)</td>
<td>(J=9)</td>
<td>(J=9,10)</td>
</tr>
<tr>
<td>11</td>
<td>Gluc-B 6.22 d 5.18 t</td>
<td>5.45 dd 5.17 t</td>
<td>4.50 dd 5.37 dd</td>
<td>3.88 d</td>
<td>(J=9)</td>
<td>(J=9)</td>
<td>(J=9,10)</td>
</tr>
<tr>
<td>12</td>
<td>Gluc-B 6.08 d 4.90 dd</td>
<td>5.21 t 4.89 dd</td>
<td>4.40 br.dd 5.30 dd</td>
<td>3.80 dd</td>
<td>(J=8.5) (J=8.5,9,7)</td>
<td>(J=9.7)</td>
<td>(J=9.7,10)</td>
</tr>
</tbody>
</table>

Table II. $^{13}$C-NMR Data of the Glucose Moieties of Nobotanin B (9), Casuarictin (11) and Roxbin B (12) (100 MHz, acetone-d$_6$)

<table>
<thead>
<tr>
<th></th>
<th>C-1</th>
<th>C-2</th>
<th>C-3</th>
<th>C-4</th>
<th>C-5</th>
<th>C-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>9a)</td>
<td>Gluc-A 92.34</td>
<td>76.77</td>
<td>76.98</td>
<td>69.61</td>
<td>73.37</td>
<td>63.37</td>
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<tr>
<td>Gluc-B</td>
<td>92.34</td>
<td>75.38</td>
<td>78.07</td>
<td>66.89</td>
<td>73.92</td>
<td>63.57</td>
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<tr>
<td>11b)</td>
<td>92.4</td>
<td>76.0</td>
<td>77.3</td>
<td>69.3</td>
<td>73.5</td>
<td>63.1</td>
</tr>
<tr>
<td>12</td>
<td>92.51</td>
<td>77.24</td>
<td>78.22</td>
<td>69.62</td>
<td>73.24</td>
<td>63.03</td>
</tr>
</tbody>
</table>

a) Assigned by $^1$H-$^{13}$C Shift correlation spectrum.
b) Data from Reference 2.
water for 7 h. The $^1$H-nmr spectrum (400 MHz, acetone-d$_6$) of 10 indicates the presence of three galloyl groups ($\delta$ 7.27, 7.09 and 6.95), a valoneayl and an HHDP group ($\delta$ 7.12, 6.72, 6.47, 6.45 and 6.08), suggesting that 10 lacks one of the HHDP groups in nobotanin B. Extensive spin-spin decoupling experiments for the glucose proton signals of 10 revealed significant upfield shifts of H-4 ($\delta$ 5.17 → 3.90) and a part of C-6 methylene proton signals ($\delta$ 5.33 → 3.81) of the glucose core A, from those of nobotanin B (Table I), to indicate that the elimination of HHDP group occurred at 0-4→0-6. This evidence, and production of 4 and 5 upon prolonged hydrolysis of 10, led to a conclusion that a galloyl and a valoneayl group are located at 0-1, 0-2 and 0-3 in the glucose core A of 10, and of nobotanin B. Between the assignable structures 9 and 9' of nobotanin B, the former is supported by comparison of its $^1$H- and $^{13}$C-nmr data with those of casuarictin (11)$^2,3$ and roxbin B (12)$^4$; As in Tables I and II, the proton and $^{13}$C signals, particularly C-1 and C-3 signals, of glucose core A in nobotanin B, coincide with those of 11. Further evidence for the presence of a galloyl group at 0-1 of each glucose core in nobotanin B was obtained by a reversed-phase HPLC analysis$^5$ of the reaction mixture of degalloylation with tannase: A peak of gallic acid and four peaks due to anomers were shown. The latter four peaks were replaced by a single peak of different retention time after treatment of the reaction mixture with NaBH$_4$.$^6$ The structures of nobotanin B and the octadecamethyl derivative obtained on the methylation are therefore revised to 9 (orientation of the valoneayl group at 0-2 and 0-3 may be reversed) and 8b, respectively.

REFERENCES AND NOTES
5) HPLC: column, YMC A312 (ODS)(150 mm x 6 mm); eluent, 0.01M phosphate buffer- EtOH (100:5); detection, A$_{280}$

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