

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

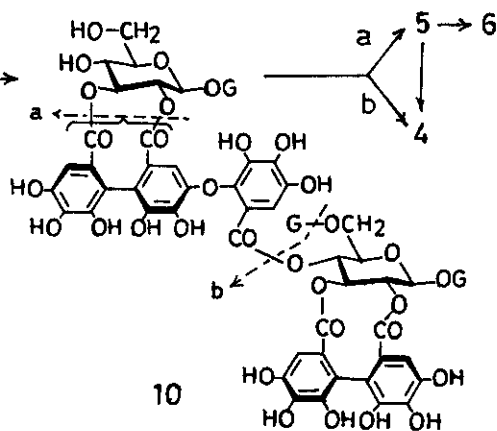
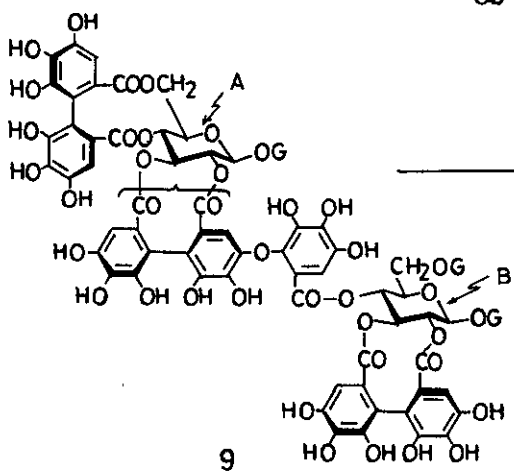
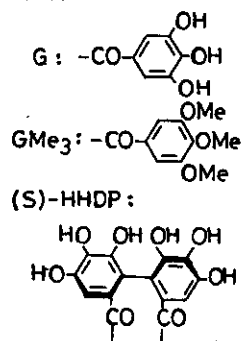
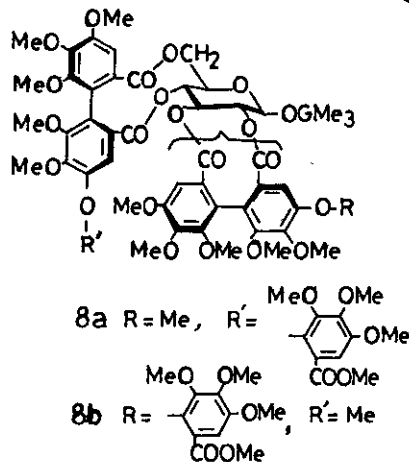
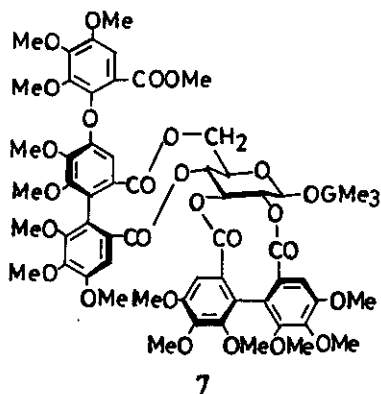
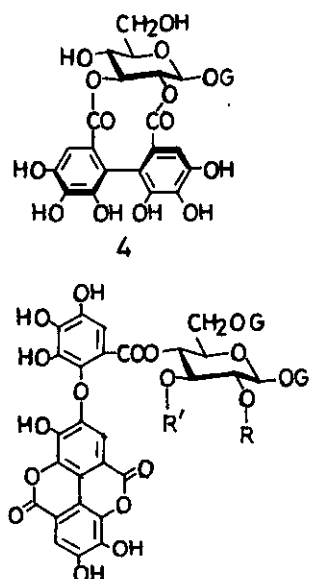
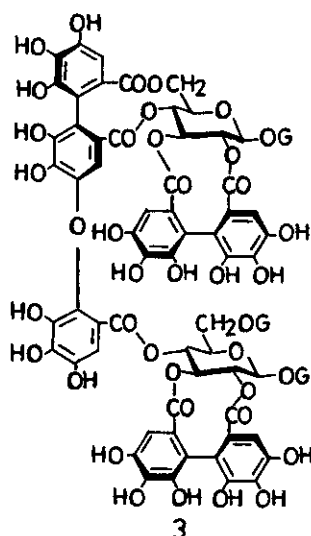
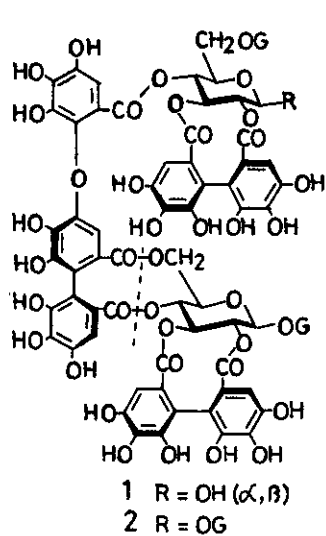
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Abstract — The structure of nobotanin B, a dimeric ellagitannin of Tibouchina semidecandra, has been revised to **9** on the basis of structural analysis of a partial hydrolysate.

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) Methylation 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 hydrolyses 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**), $C_{68}H_{50}O_{44} \cdot 7H_2O$, $[\alpha]_D^{+31} (MeOH)$, from nobotanin B, was isolated as the main product after the treatment with boiling



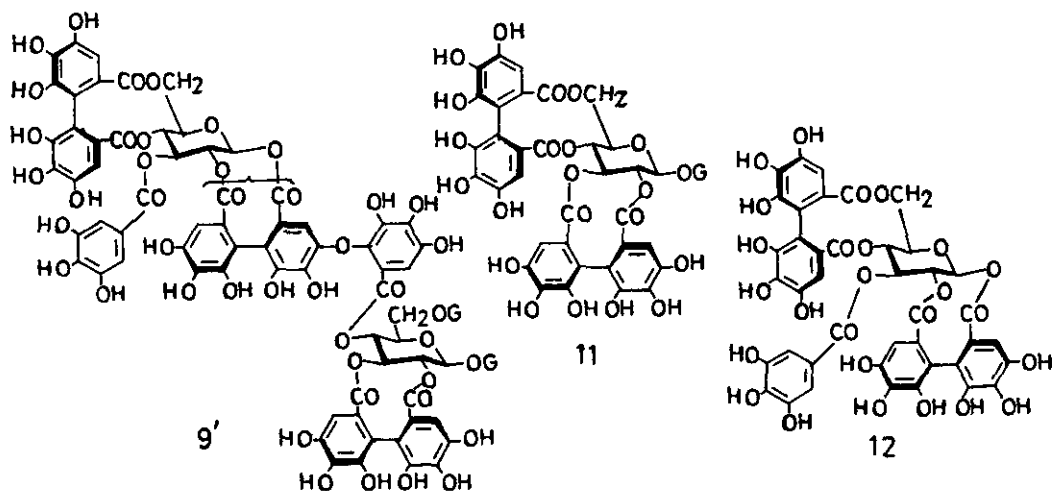


Table I. $^1\text{H-Nmr}$ Data of the Glucose Moieties of Nobotanin B (9), Partial Hydrolysate (10), Casuarictin (11) and Roxbin B (12) (400 MHz, acetone- d_6)

		H-1	H-2	H-3	H-4	H-5	H-6	H-6'
9	Gluc-A	6.20 d (J=8.5)	5.10 dd (J=8.5, 9)	5.82 dd (J=9, 10)	5.17 t (J=10)	4.67 dd (J=6, 10)	5.33 dd (J=6, 13.5)	3.92 d (J=13.5)
	Gluc-B	6.02 d (J=8.5)	5.18 dd (J=8.5, 10)	5.41 t (J=10)	5.83 t (J=10)	3.45 dd (J=2, 10)	4.92 d (J=13)	3.91 dd (J=2, 13)
10	Gluc-A	6.30 d (J=8.5)	4.91 dd (J=8.5, 9)	5.50 dd (J=9, 10)	3.90 t (J=10)	4.10 dd (J=6, 10)	3.81 dd (J=6, 13)	3.94 d (J=13)
	Gluc-B	5.96 d (J=8.5)	5.14 dd (J=8.5, 10)	5.33 t (J=10)	5.80 t (J=10)	3.49 br.d (J=10)	4.84 dd (J=2, 13)	3.97 d (J=13)
11		6.22 d (J=9)	5.18 t (J=9)	5.45 dd (J=9, 10)	5.17 t (J=10)	4.50 dd (J=7, 10)	5.37 dd (J=7, 13)	3.88 d (J=13)
12		6.08 d (J=8.5)	4.90 dd (J=8.5, 9.7)	5.21 t (J=9.7)	4.89 dd (J=9.7, 10)	4.40 br.dd (J=6.5, 10)	5.30 dd (J=6.5, 13)	3.80 dd (J=1.5, 13)

Table II. $^{13}\text{C-Nmr}$ Data of the Glucose Moieties of Nobotanin B (9), Casuarictin (11) and Roxbin B (12) (100 MHz, acetone- d_6)

	C-1	C-2	C-3	C-4	C-5	C-6
9 ^{a)} Gluc-A	92.34	76.77	76.98	69.61	73.37	63.37
Gluc-B	92.34	75.38	78.07	66.89	73.92	63.57
11 ^{b)}	92.4	76.0	77.3	69.3	73.5	63.1
12	92.51	77.24	78.22	69.62	73.24	63.03

a) Assigned by $^1\text{H-}^{13}\text{C}$ shift correlation spectrum.

b) Data from Reference 2.

water for 7 h. The ^1H -nmr spectrum (400 MHz, acetone- d_6) of 10 indicates the presence of three galloyl groups (δ 7.27, 7.09 and 6.95), a valoneoyl and an HHDP group (δ 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 (δ 5.17 \rightarrow 3.90) and a part of C-6 methylene proton signals (δ 5.33 \rightarrow 3.81) of the glucose core A, from those of nobotanin B (Table I), to indicate that the elimination of HHDP group occurred at O-4~O-6. This evidence, and production of 4 and 5 upon prolonged hydrolysis of 10, led to a conclusion that a galloyl and a valoneoyl group are located at O-1, O-2 and O-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 ^1H - 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 O-1 of each glucose core in nobotanin B was obtained by a reversed-phase HPLC analysis⁵ 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 valoneoyl group at O-2 and O-3 may be reversed) and 8b, respectively.

REFERENCES AND NOTES

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- 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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