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

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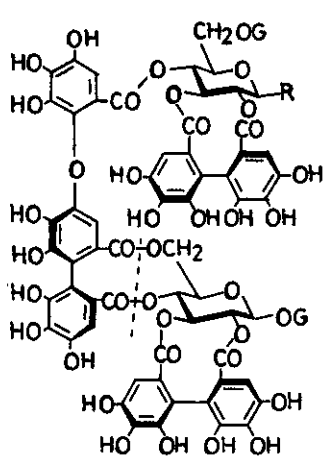
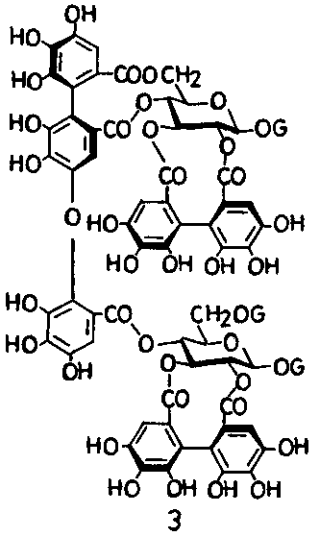
Abstract — The structure of nobotanin B, a dimeric ellagitannin of Tibouchina semidecandra, has been revised to **9** on the basis of structural analysis of a partial hydrolysate.

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 liitle 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



1 R = OH (α, β)
2 R = OG



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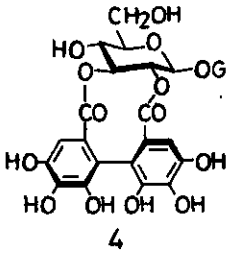

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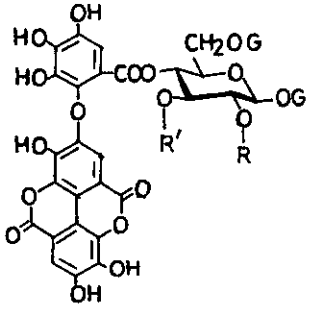
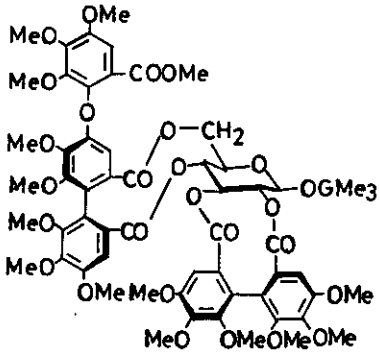


5 R~R′ = (S)-HHDP
6 R = R′ = H



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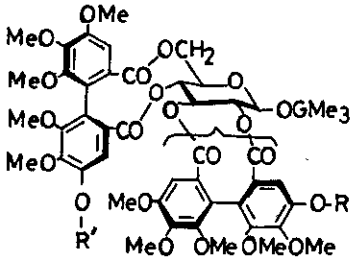
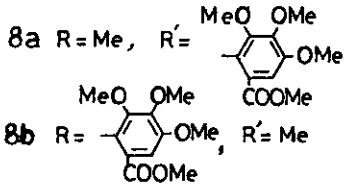
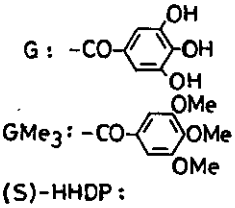




8a R = Me, R′ =

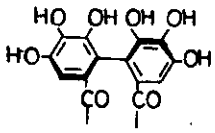
8b R =

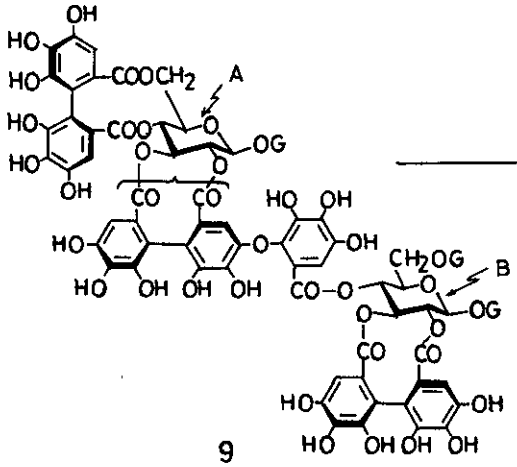


G : -CO-

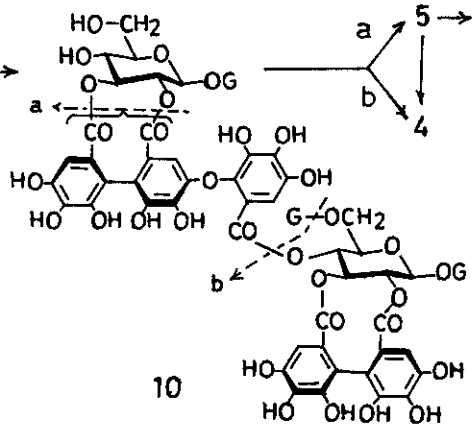
GMe3 : -CO-

(S)-HHDP :





9



10

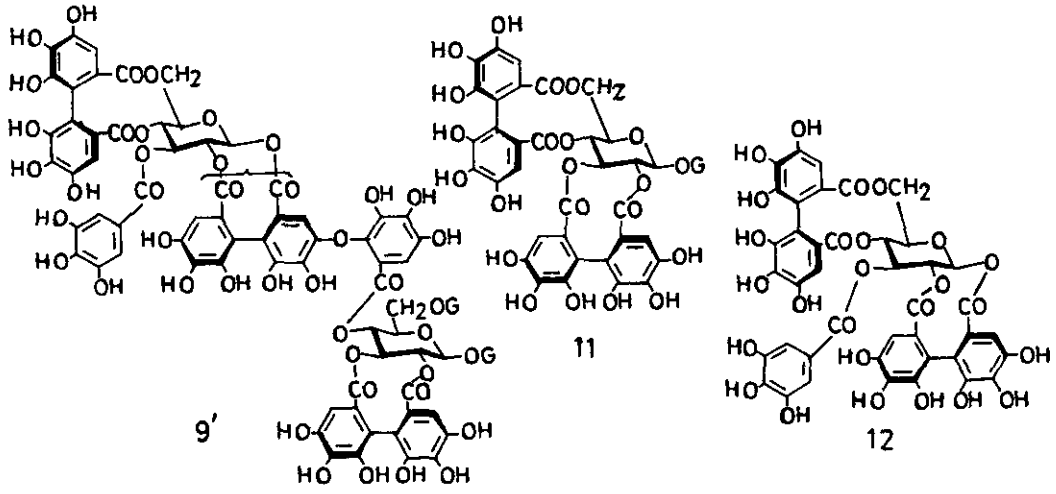


Table I. ^{1}H-Nmr Data of the Glucose Moieties of Nobotanin B (**9**), Partial Hydrolysate (**10**), Casuarictin (**11**) and Roxbin B (**12**) (400 MHz, acetone-d_6)

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

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)

	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}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 (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 ^{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 O-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 valoneoyl group at O-2 and O-3 may be reversed) and **8b**, respectively.

REFERENCES AND NOTES

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4) T. Yoshida, T. Hatano, Xin-Min Chen, M. Fukushima, and T. Okuda, Chem. Pharm. Bull., **35**, 1817 (1987).
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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