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BALANOPHONIN, A NEW NEO-LIGNAN FROM BALANOPHORA JAPONICA MAKINO

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Balanophonin, a new neo-lignan was isolated from Balanophora japonica Makino and its structure was discussed. Structure and stereochemistry were determined by a combination of chemical method and extensive use of ^{1}H and ^{13}C-NMR spectrometry.

KEYWORDS —— Balanophora japonica Makino; Balanophoraceae; parasitic plant; balanophonin; new neo-lignan; lignans; lignan glucoside; phenylpropanoids; phenylpropanoid glucoside; ^{13}C-NMR

In the continuing research on the constituents of the Balanophoraceae,[2] we have examined the fresh whole plant of Balanophora japonica Makino (Japanese name: Tsuchitorimochi). Balanophora japonica Makino is a parasitic plant growing on the terminal roots of host plants, such as Symplocos lucida Sieb. et Zucc. (Japanese name: Kuroki), S. prunifolia Sieb. et Zucc. (Japanese name: Hainoki), and S. lancifolia Sieb. et Zucc. (Japanese name: Shirobai; Symplocaceae), and is distributed throughout Southern Japan.[3]

In 1956, Yagishita reported the isolation of two triterpenes, taraxasterol and β-amyrin, and palmitic acid from this plant.[4]

The fresh plants collected at Bounotsu of Kagoshima prefecture were separated into the above- and under-ground parts and extracted with methanol at room temperature. The ether-soluble fraction of the aboveground parts contained four known phenylpropanoids, ferulyl aldehyde (2), methyl p-cumarate (3), caffeic acid (4), and caffeic acid methyl ester (5); the lignan (-)-pinoresinol (6); and the polyphenol methyl gallate (7). Compounds of 2, 3, 5, 6, (-)-lariciresinol (8), and a new neo-lignan, balanophonin (1)[5] were isolated from the same fraction of the underground parts. From the water-soluble fraction of the methanol extract, coniferin (9), ferulyl aldehyde β-D-glucoside (10) and (-)-pinoresinol β-D-glucoside (11) were obtained.

Balanophonin (1) [a pale yellow oil; $[\alpha]_D$ -115.1° (c=1.3, $CHCl_3$)] showed the mass molecular ion at m/z 356, in agreement with the molecular formula $C_{20}H_{20}O_6$. The presence of a ferulyl aldehyde moiety was confirmed by the UV absorption [λ_{max}^{MeOH} (ε): 258 (22,200) and 285sh (7,230) nm], IR bands [$\nu_{max}^{CHCl_3}$: 1670, 1620 and 1595 cm^{-1}], and also by the ^{1}H-NMR spectrum of a characteristic peak at δ9.55 (1H, d, J=7.8Hz, 9'-H), δ7.38 (1H, d, J=15.6Hz, 7'-H), δ6.56 (1H, dd, J=7.8,15.6Hz, 8'-

H) and broad meta-coupling aromatic protons at δ7.12 and δ7.02. These signals were also identified by single-frequency off resonance decoupling experiments in the ^{13}C-NMR spectrum (Table 1).

The remaining part of balanophonin (1) except for the above moiety was determined to be dihydroconiferyl alcohol as follows. In the IR spectrum of 1, a hydroxy band appeared at 3560 cm^{-1}, and three overlapped aromatic protons (δ6.86) and dihydrobenzofuran-type signals were observed at δ5.62 (1H, d, *J*=7.1Hz, 7-H), δ3.50-4.00 (3H, m, 8,9-H), along with a methoxy signal (δ3.89) on the ^{1}H-NMR spectrum. These data were in good agreement with the results obtained from the ^{13}C-NMR spectral data (Table 1).

Treatment of (1) with acetic anhydride and pyridine afforded the diacetate (1a) [a colorless oil; $\nu_{max}^{CHCl_3}$: 1760, 1740, 1670, 1620, and 1595 cm^{-1}; *m/z*: 440 (M^+), 380, 339, 323, and 316].
The ^{1}H-NMR spectrum of the diacetate (1a) revealed signals due to two acetyl groups (δ2.30 and 2.06), and methylene protons (δ4.40, 2H, dd, *J*=2.9,6.6Hz) at C_9.
From the above experiment, physical data, and the biogenetic point of view, the structure of balanophonin, which incorporates ferulyl aldehyde and the dihydroconiferyl alcohol residues, should be (1) exclusive of its stereochemistry.

The stereochemistry of the dihydrofuran ring in balanophonin (1) was determined to be *trans* by the observation of 7.8% NOE enhancement between H-7 and 9-methylene protons in the acetate (1a).

Furthermore, the comparison of CD $[[\theta]_{255}$ $-7,470]$⁶⁾ and ORD curve $[[\phi]_{358}^{T}$ -52.8×10^4, $[\phi]_{330}$ 0, $[\phi]_{280}^{P}$ $+97.6\times10^4$, $[\phi]_{259}^{T}$ $+56\times10^4$, $[\phi]_{239}^{P}$ $147.2\times10^4]$ with the published data ⁷⁾ on like compounds indicates that the absolute stereochemistry must be that shown in 1.

Table 1. ^{13}C-NMR Spectral Data of Balanophonin (1) and Derivatives$^{a)}$

Carbon No.	(1)	(2)	coniferyl alcohol⁹⁾
1	129.1 s		129.4 s
2	108.6 d		108.8 d
3	146.5 s		146.9 s
4	145.6 s		145.7 s
5	114.3 d		114.7 d
6	119.1 d		120.3 d
7	88.8 d		131.3 d
8	52.9 d		126.2 d
9	63.7 t		63.6 t
1'	127.8 s	126.6 s	
2'	112.3 d	109.8 d	
3'	144.4 s	147.1 s	
4'	151.2 s	149.2 s	
5'	132.0 s	124.0 s	
6'	118.0 d	115.1 d	
7'	152.9 d	153.2 d	
8'	126.0 d	126.2 d	
9'	193.2 d	193.6 d	
3-OMe	55.9 q		55.9 q
3'-OMe	56.0 q	56.0 q	

a) Run in $CDCl_3$ at 25.05 MHz on a JEOL FX-100 spectrometer with Me_4Si as an internal standard. s: singlet; d: doublet; t: triplet; q: quartet. Peak assignments were based on comparison with related compounds and by single-frequency irradiation of known proton resonances.

This study indicates that a close phytochemical relationship exists between the host plant and the parasitic plant. In fact, (-)-pinoresinol β-D-glucoside (11) was also obtained from S. lucida Sieb. et Zucc..$^{8)}$

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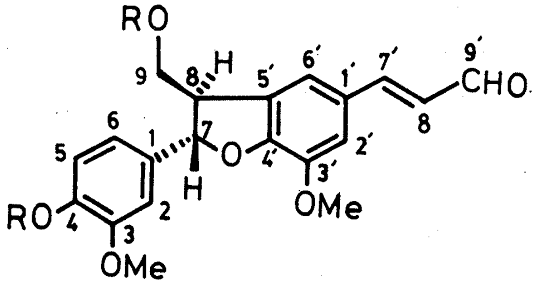
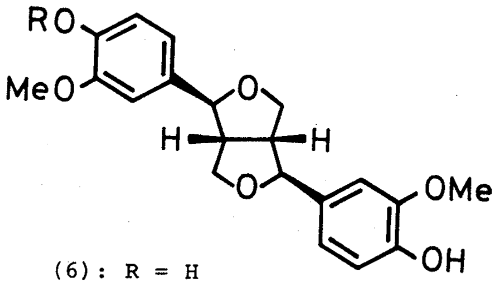
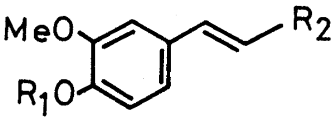


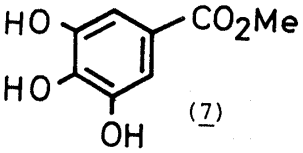
(1): R = H (7*S*,8*R*)
(1a): R = Ac



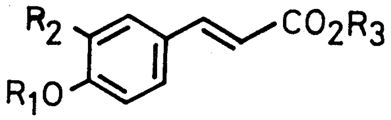
(6): R = H
(11): R = β-D-glucosyl



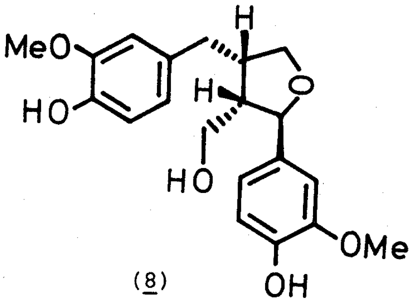
(2): R_1 = H, R_2 = CHO
(9): R_1 = β-D-glucosyl, R_2 = CHO
(10): R_1 = β-D-glucosyl, R_2 = CH_2OH



(7)



(3): R_1 = R_2 = H, R_3 = Me
(4): R_1 = R_3 = H, R_2 = OH
(5): R_1 = H, R_2 = OH, R_3 = Me



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