between the aromatic hydrogen and one of the aromatic methyls (δ 2.39 ppm), 2) a long range coupling was observed between the aromatic hydrogen and the carbinyl hydrogen, and 3) the aromatic hydrogen is fairly deshielded (−0.58 ppm in comparison with that of the aglycone (VI)) by the secondary hydroxyl. The findings that an NOE was observed between the C-2 methyl hydrogens and the C-3 hydrogen, and the CD curves of the acetates (VIII and X) show negative n-π* Cotton effects ($[\theta]_{325}^{-68°}$ −5200, $[\theta]_{327}^{-65°}$ −11000, respectively),[4] indicate the 2(*R*),3(*R*)-configuration.

Examination of the NMR spectra of the glycoside acetates (III and VIII) and the aglycone acetates (V and X) reveals that the signals for the carbinyl hydrogens in the C-6 hydroxyethyl groups of the latter suffered from downfield shift (−0.32 and −0.45 ppm) as compared with those of the former, demonstrating that glucose is linked to the C-6 hydroxyethyl group in each glycoside. Further, the glucose residue of each glycoside is concluded to be present as a β-D-glucopyranoside moiety by evidence similar to that for pteroside B.[1]

Whereupon it follows that pteroside A and C are represented by formulae I and II, respectively.

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4) *cf.* M.-J. Brinne, G. Ouannes, and J. Jaques, *Bull. Soc. Chim. France*, **1967**, 613.

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Hōnokiol, a New Phenolic Compound isolated from the Bark of *Magnolia obovata* THUNB.

Previously, a biphenyl derivative, magnolol (I), was isolated from the bark of *Magnolia officinalis* REHD. et WILS. (a Chinese drug "Houpo, 厚朴") and *M. obovata* THUNB. (a Japanese drug "Wakōboku, 和厚朴"), (Magnoliaceae).[1] From the biogenetical point of view, we have investigated about the MeOH-extract of the bark of the latter species and isolated a new biphenyl derivative (II). It was named as hōnokiol after "Hōnoki", Japanese name of *M. obovata*.

In this communication, we wish to report the establishment of the structure of II.

Hōnokiol (II), mp 87.5°,[2] $C_{18}H_{18}O_2$ (*Anal.* Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 80.68; H, 6.77. molecular ion peak: *m/e* 266), soluble in usual organic solvents and caustic alkali, $[\alpha]_D^{15°}$ ±0°, gave a bluish color by $FeCl_3$ test in $CHCl_3$, but did not react with Emerson reagent, Gibbs reagent or Echtblau Salz B. These tests suggested that II was a phenolic compound which had substituents at *para* positions to hydroxyl groups. Infrared absorption (IR) spectrum (ν_{max}^{KBr} cm^{-1}) of II showed the presence of hydroxyl at 3280, phenyl at 1610, 1500, 882 and 826 and vinyl groups at 1645, 1410, 987 and 907. The nuclear magnetic

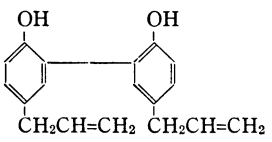
1) Y. Sugii, *Yakugaku Zasshi*, **50**, 709 (1930).
2) All melting points are uncorrected.

resonance (NMR) spectrum (δ in $CDCl_3$) showed the following signals: 3.32 (2H, doublet, aryl-C<u>H</u>$_2$-CH=), 3.43 (2H, doublet, aryl-C<u>H</u>$_2$-CH=), 5.1 (4H, multiplet, two -CH=C<u>H</u>$_2$), 5.5—6.0 (2H, broad singlet, two OH), 6.0 (2H, multiplet, two -C<u>H</u>=CH$_2$) and 6.8—7.3 (6H, multiplet, aromatic H). Ultraviolet absorption (UV) spectrum gave a maximum absorption at 294 mμ (ε=8200) in EtOH and the maximum shifted to 312 mμ (ε=12800) by addition of NaOH.

Acetylation of II with acetic anhydride and sodium acetate afforded a diacetate (III), bp 180—200° (2 mmHg), $C_{22}H_{22}O_4$ (*Anal.* Calcd. for $C_{22}H_{22}O_4$: C, 75.41; H, 6.33. Found: C, 74.87; H, 6.02. molecular ion peak: *m/e* 270). IR spectrum of III indicated the presence of acetyl groups ($\nu_{max}^{CHCl_3}$ cm^{-1}: 1762, 1377) and NMR spectrum (δ in $CDCl_3$) showed the presence of two acetyl groups at 2.08 (3H, singlet) and 2.32 (3H, singlet), respectively.

The phenylurethane derivative (IV) which was obtained from II, mp 150—152°, had a formula $C_{32}H_{28}O_4N_2$ (*Anal.* Calcd. for $C_{32}H_{28}O_4N_2$: C, 76.17; H, 5.59; N, 5.55. Found: C, 76.14; H, 5.62; N, 5.49.).

II absorbed two mōles of hydrogen by catalytic hydrogenation over 5% Pd-C and was derived to tetrahydrohōnokiol (V), mp 118°, $C_{18}H_{22}O_2$ (*Anal.* Calcd. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 80.29; H, 8.38. molecular ion peak: *m/e* 270). NMR spectrum (δ in $CDCl_3$) of V, indicated the presence of propyl groups at 0.94 (3H, triplet), 0.98 (3H, triplet), 1.64 (4H, multiplet), 2.54 (2H, triplet) and 2.62 (2H, triplet). Hydroxyl groups were also found at 4.86 (1H, broad singlet) and 5.09 (1H, broad singlet), respectively.



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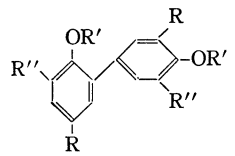

	R	R′	R″
II:	$CH_2CH=CH_2$	H	H
III:	$CH_2CH=CH_2$	$COCH_3$	H
IV:	$CH_2CH=CH_2$	CONH-aryl	H
V:	$CH_2CH_2CH_3$	H	H
VI:	$CH_2CH_2CH_3$	H	Br

Bromination of V in CS_2 gave dibromo derivative (VI), $C_{18}H_{20}O_2Br_2$ (molecular ion peak: *m/e* 430). NMR spectrum (δ in DMSO-d_6) of VI showed four isolated aromatic hydrogens at 7.03 (1H, doublet, J=2), 7.22 (1H, doublet, J=2), 7.30 (1H, doublet, J=2) and 7.48 (1H, doublet, J=2). These spin-spin coupling constants were due to *meta* coupling. Formation of VI suggested that two *ortho* positions to hydroxyl groups of V were substituted.

The above data showed that hōnokiol (II) was a position isomer of I. V was identified with the authentic sample (4,2′-dihydroxy-3,5′-dipropylbiphenyl) prepared by demethylation of the Ullmann reaction product syntesized from 2-iodo-4-propylanisole and 4-iodo-2-propylanisole. The structure of (II) was thus established to be 3,5′-diallyl-4,2′-dihydroxybiphenyl.

Further studies about *M. obovata* are in progress and the details will be reported in near further.

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