1-Methylhypoxanthine: mp>300°, UV λ_{max}^{pH1}: 250 mμ (ε=8700), λ_{max}^{pH7}: 251 mμ (ε=8400), λ_{max}^{pH11}: 261 mμ (ε=8900) (lit.,[1] UV λ_{max}^{pH1}: 249 mμ, $\lambda_{max}^{pH5.12}$: 251 mμ, λ_{max}^{pH11}: 260 mμ). 1-Benzylhypoxanthine: mp 268—269° (lit.,[2] mp 268—270°). UV λ_{max}^{pH1}: 251 mμ (ε=10300), λ_{max}^{pH7}: 252 mμ (ε=9500), λ_{max}^{pH11}: 262 mμ (ε=10200) (lit.,[3] UV $\lambda_{max}^{neutral\ molecular}$: 251 mμ, λ_{max}^{anion}: 261 mμ).

Thus a convenient synthetic method for preparation of 1-alkyl-substituted hypoxanthine is also provided.

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2) E. Shaw, *J. Am. Chem. Soc.*, **80**, 3899 (1958).
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Structure of Pteroside A and C, Glycosides of *Pteridium aquilinum* var. *latiusculum*

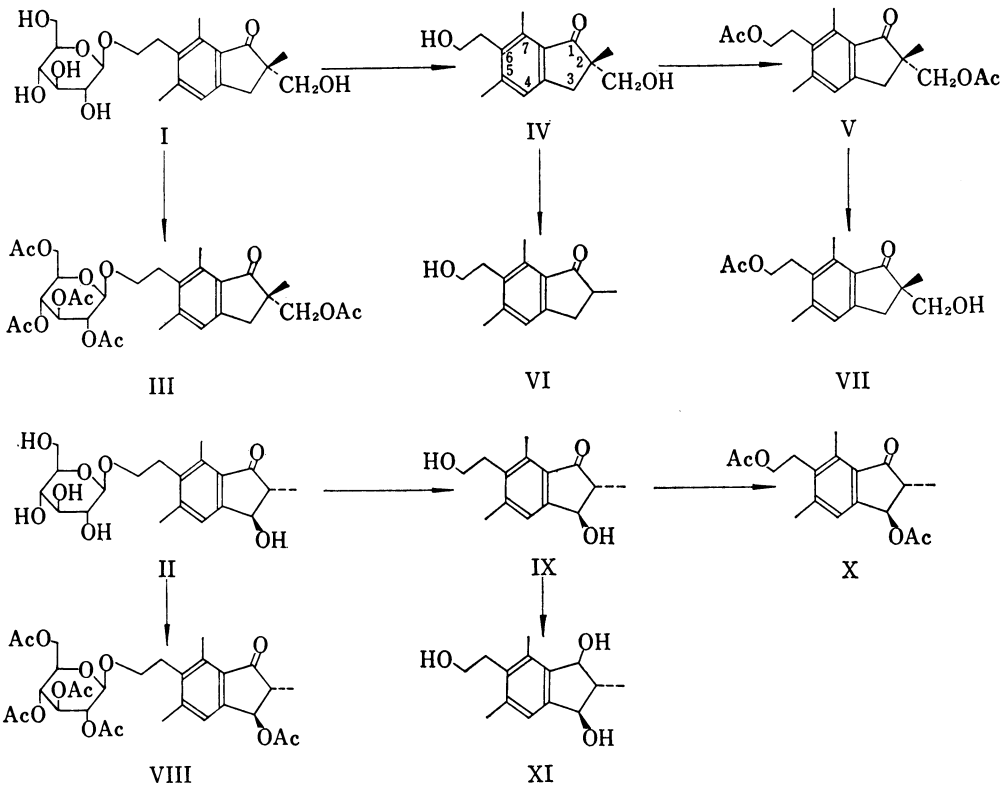
We have previously isolated a new glycoside pteroside B from the Japanese bracken, *Pteridium aquilinum* KUHN var. *latiusculum* UNDERWOOD (Pteridaceae).[1] Further survey has resulted in the isolation of other new glycosides pteroside A and C whose stereostructures I and II, respectively, are reported in this communication.

Pteroside A on acetylation gave the pentaacetate (III). Enzymatic hydrolysis of pteroside A yielded glucose and the aglycone (IV), $C_{15}H_{20}O_3$, mp 129—130°, whose ultraviolet (UV) and infrared (IR) spectra showed that it is a 1-indanone derivative (λ_{max}^{MeOH}: 219, 261, 300 sh, 306 nm, ν_{max}^{KBr}: 1700, 1603 cm^{-1}). The nuclear magnetic resonance (NMR) spectrum of the aglycone (IV) indicated the presence of a tertiary methyl (δ 1.26 ppm), two aromatic methyls (δ 2.38, 2.80 ppm, the location of the latter at C-7 being concluded from the deshielded position), an isolated methylene (δ 2.75, 3.57 ppm in an AB system), a hydroxyethyl on the benzene ring (δ 3.08, 3.91 ppm in an A_2X_2 system, the latter signal being displaced to δ 4.12 ppm in the spectrum of its diacetate (V)), a hydroxymethyl (δ 3.78, 4.17 ppm in an AB system), and an aromatic hydrogen (δ 7.04 ppm). Analysis of the spectrum revealed that although the aromatic hydrogen is long range coupled to both the aromatic methyls, an intramolecular nuclear overhauser effect (NOE) was observed only between the aromatic hydrogen and one of the aromatic methyls (δ 2.38 ppm) but not between the aromatic hydrogen and the other aromatic methyl (δ 2.80 ppm). Further, long range couplings were found between the aromatic hydrogen and the isolated methylene hydrogens. The accumulated data point to the gross structure of the aglycone (IV). This assumption was confirmed by the transformation of the aglycone (IV) to the aglycone (VI) of pteroside B by alkali treatment.[2] The IR spectrum of the monoacetate (VII), obtained by partial hydrolysis of the

1) H. Hikino, T. Takahashi, S. Arihara, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **18**, 1488 (1970).
2) In this connection, the structure of the aglycone of pteroside B, whose substitutions in the benzene ring has been previously allotted by the presence of long-range couplings between the aromatic hydrogen and the two aromatic methyls in its NMR spectrum,[1] should be revised.

diacetate (V), indicated the presence of an intramolecularly hydrogen-bonded hydroxyl ($\nu_{max}^{CCl_4}$: 3500 cm^{-1}) and a free hydroxyl ($\nu_{max}^{CCl_4}$: 3620 cm^{-1}), and the proportion of the former relative to the latter increased by going from high to low temperature. While the rotational strength of the negative circular dichroism (CD) band (n-π^*) of the diacetate (V) increased upon lowering the temperature. Combined evidence shows the absolute configuration at C-2 to be *S*.[3] Thus, the stereostructure of the aglycone (IV) has been deduced.

Pteroside C on acetylation furnished the pentaacetate (VIII). When pteroside C was subjected to enzymatic hydrolysis, formed glucose and the aglycone (IX), $C_{14}H_{18}O_3$, mp 168—170°, whose functional groups are very similar to those of the aglycone (VI): 1-indanone moiety (λ_{max}^{MeOH}: 218, 260, 297.5 sh, 303.5 nm, ν_{max}^{KBr}: 1680, 1600 cm^{-1}), a secondary methyl (δ 1.47 ppm), two aromatic methyls at C-5 and C-7 (δ 2.39, 2.74 ppm), a hydroxyethyl at C-6 (δ 3.12, 3.90 ppm in an A_2X_2 system, the latter being shifted at δ 4.06 ppm in the spectrum of its diacetate (X)) and an aromatic hydrogen at C-4 (δ 7.61 ppm). Significant feature is the presence of a hydrogen on a hydroxy-carrying carbon (δ 5.02 ppm) which was revealed to couple to the hydrogen on the methyl-bearing carbon (δ 2.88 ppm) and the aromatic hydrogen. Further, sodium borohydride reduction of the aglycone (IX) gave the triol (XI). In the NMR spectrum of the triol (XI) the methine hydrogen (δ 2.59 ppm) is coupled with the newly formed carbinyl hydrogen (δ 4.87 ppm), with the secondary methyl hydrogens (δ 1.53 ppm) and with the carbinyl hydrogen (δ 4.77 ppm), functional groups in the cyclopentanone moiety being thus accommodated. The substitution pattern of the benzene ring in the aglycone (IX) was corroborated by the facts that although long range couplings were again found between the aromatic hydrogen and the two aromatic methyls, 1) an NOE was found only



3) H.E. Smith, R.T. Gray, T.J. Shaffner, and P.G. Lenhert, *J. Org. Chem.*, **34**, 136 (1969).

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.