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Structure of Pteroside B, Glycoside of *Pteridium aquilinum* var. *latiusculum*

From the Japanese bracken, *Pteridium aquilinum* KUHN var. *latiusculum* UNDERWOOD (Pteridaceae), a novel glycoside has been isolated and named pteroside B. In the present communication, we wish to report that pteroside B has the stereostructure I.

Pteroside B, $C_{20}H_{28}O_7 \cdot H_2O$, mp 119—121°, on acetylation gave the tetraacetate (II), mp 141—141.5°. Enzymatic hydrolysis of pteroside B yielded glucose and the aglycone (III), $C_{14}H_{18}O_2$, mp 104°, whose ultraviolet (UV) and infrared (IR) spectra indicated it to be a 1-indanone derivative (λ_{max} 217, 260, 304 nm, ν_{max} 1700, 1670, 1595 cm^{-1}). The nuclear magnetic resonance (NMR) spectrum of the aglycone (III) showed the presence of a secondary methyl (δ 1.24 ppm), two aromatic methyls (δ 2.41, 2.64 ppm, the location of the latter at C-7 being deduced from its deshielded line position and the $\Delta\delta_{CDCl_3-C_6H_6} = -0.11$ ppm[1]), a hydroxyethyl on the benzene ring (δ 2.78, 3.72 ppm in an A_2X_2 system, the latter signal being displaced to δ 4.10 ppm in the spectrum of its acetate (IV)) and an aromatic hydrogen (δ 7.03 ppm). Since double resonance experiments revealed that the aromatic hydrogen is adjacent to both the aromatic methyls, the substitution pattern of the benzene ring was thus established. The situation of the secondary methyl at C-2 was deduced from the facts that, in the NMR spectrum of the diacetate (V) derived from the aglycone (III) by borohydride reduction followed by acetylation, the newly formed C-1 carbinyl hydrogen appeared as a single peak (δ 5.87 ppm) and that, in the NMR spectrum of the indene (VI) formed by acid treatment of the acetate (V), the methyl doublet observed in the spectrum of the acetate (V) disappeared and instead a vinyl methyl signal (δ 2.14 ppm) and a vinyl hydrogen signal (δ 6.53 ppm) occurred.

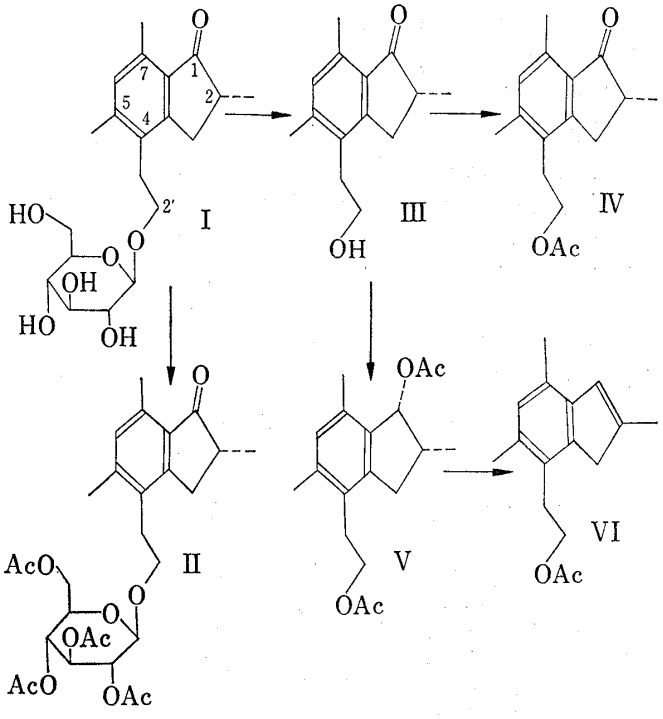

Chart 1

The absolute configuration at C-2 was concluded to be *R* on the basis that the CD curve of the aglycone (III) showed the positive Cotton effect for n-π^* transition ($[\theta]_{324}^{190°}$ +4280).[2]

The size of the ring and the stereochemistry of the glucose residue were clarified as follows. In the NMR spectrum of the tetraacetate (II), saturation of the C-6′ methylene signals did not alter the signals associated with the hydrogens on the acetoxyl-bearing carbons, demonstrating that it possesses the 1,5-(pyranose) ring structure. The C-1′ anomeric hydrogen signals in the NMR spectra of pteroside B and its acetate (II)

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occurred as doublets with the large coupling constants (8 Hz), a fact which indicated it to be a β-anomer. The rotation contribution of the glucose component in pteroside B ($[M]_D$ of pteroside B$-[M]_D$ of the aglycone (III)$=-107$) showed that the glucose involved is of the D series.[3]

On the basis of the above evidence, pteroside B is concluded to be 2(*R*), 5,7-trimethyl-4-(2′-hydroxyethyl)-indan-1-one 2′-β-D-glucopyranoside (I).

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C-13 Resonance Chemical Shift for Substituted Ethyl and Isopropyl Derivatives

Recently, the C-13 resonance chemical shifts for organic compounds have become of interest from the physical, chemical, and biological view point.[1] Numerous C-13 chemical shifts for liquid ethyl and isopropyl derivatives are presented in Tables I and II.

TABLE I. C-13 Chemical Shifts for C_2H_5R Derivatives Ref. CS_2 (ppm)

R	α-C	β-C	
NEt_2	145.8	180.5	
NHEt	148.9	177.6	
OH	135.5	175.1	
OEt	127.4	178.3	
OCOMe	133.1	179.1	173.0 ($OCO^{13}Me$)
Ph	163.8	177.3	
Cl	153.2	174.0	
Br	165.1	173.1	
CO_2H	165.6	184.6	
CO_2Me	166.1	184.4	142.3 ($CO_2{}^{13}Me$)
CHO	156.0	187.1	
COMe	156.8	185.7	164.4 ($CO^{13}Me$)
COEt	158.0	185.6	
CN	71.2	182.4	
NO_2	122.4	181.6	
H[a)]	188.0	188.0	
Me[b)]	177.8	178.3	

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b) D.M. Grant and E.D. Paul, *J. Am. Chem. Soc.*, **86**, 2984 (1964)

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