The above results indicate that AAA 1111 (*Pseudomonas* sp.) has a new enzyme capable of hydrolyzing acetyl-D-leucinamide to yield acetyl-D-leucine and ammonia.

Recently, we have newly isolated two bacterial strains, AAA 1221 and AAA 1222, which grew in the synthetic medium containing acetyl-D-leucinamide as a sole source of carbon and were different from AAA 1111 in the metabolic activity against benzoic and phenylacetic acids and some D-amino acids. It is of interest that AAA 5120 strain, which could metabolize acetyl-L-leucinamide, but not acetyl-D-leucinamide, and AAA 2472 strain, which metabolized acetyl-D-tryptophanamide, were isolated from the other soil samples.

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Structure of Pteroside Z and D, Glycosides of *Pteridium aquilinum* var. *latiusculum*

From the Japanese bracken, *Pteridium aquilinum* KUNH var. *latiusculum* UNDERWOOD (Pteridaceae), we have isolated three new glycosides pteroside A, B, and C.[1,2] Continuation of our survey has led to the isolation of further two new glycosides which are designated as pteroside Z and D. We now wish to report the results of our investigation which indicate that pteroside Z and D have the stereostructures I and II, respectively.

Pteroside Z on acetylation gave the tetraacetate (III). Enzymatic hydrolysis of pteroside Z afforded glucose and the aglycone (IV), $C_{15}H_{20}O_2$, whose ultraviolet and infrared spectra show it to be a 1-indanone derivative (λ_{max}^{EtOH} 219, 259, 303 nm, ν_{max}^{KBr} 3450, 1670, 1600 cm^{-1}, $\nu_{max}^{CCl_4}$ 3630, 3450, 1700, 1600 cm^{-1}). IV was indicated by nuclear magnetic resonance (NMR) evidence to have two tertiary methyls (δ 1.19, 1.19 ppm), two aromatic methyls (δ 2.42, 2.67 ppm, the location of the latter at C-7 being concluded from the deshielded position), an isolated methylene (δ 2.83 ppm), a hydroxyethyl on the benzene ring (δ 3.00, 3.75 ppm in an A_2X_2 system, the latter signal being shifted to δ 4.12 ppm in the spectrum of its acetate (V)), and an aromatic hydrogen (δ 7.07 ppm). NMDR analysis demonstrated that although the aromatic hydrogen is long-range coupled to both the aromatic methyls, an intramolecular nuclear Overhauser effect (NOE) was observed between the aromatic hydrogen and one of the aromatic methyls (δ 2.42 ppm). Further, a long-range coupling and an NOE were found between the aromatic hydrogen and the isolated methylene. Combined evidence points to the structure VI for the aglycone.

Pteroside D on acetylation gave the pentaacetate (VI). Enzymatic hydrolysis of pteroside D yielded glucose and the aglycone (VII), $C_{15}H_{20}O_3$, mp 193—194°, whose functional groups are very similar to those of IV: 1-indanone moiety (λ_{max}^{EtOH} 219.5, 260, 294 sh, 301.5 nm, ν_{max}^{KBr} 3320, 3200, 1706, 1600 cm^{-1}), two tertiary methyls (δ 1.37, 1.40 ppm), two aromatic methyls at C-5 and C-7 (δ 2.42, 2.84 ppm), a hydroxyethyl at C-6 (δ 3.13, 3.95 ppm in an A_2X_2 system, the latter being displaced to δ 4.20 ppm in the spectrum of its acetate (VIII)).

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1) H. Hikino, T. Takahashi, S. Arihara, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **18**, 1488 (1970).
2) H. Hikino, T. Takahashi, and T. Takemoto, to be published.

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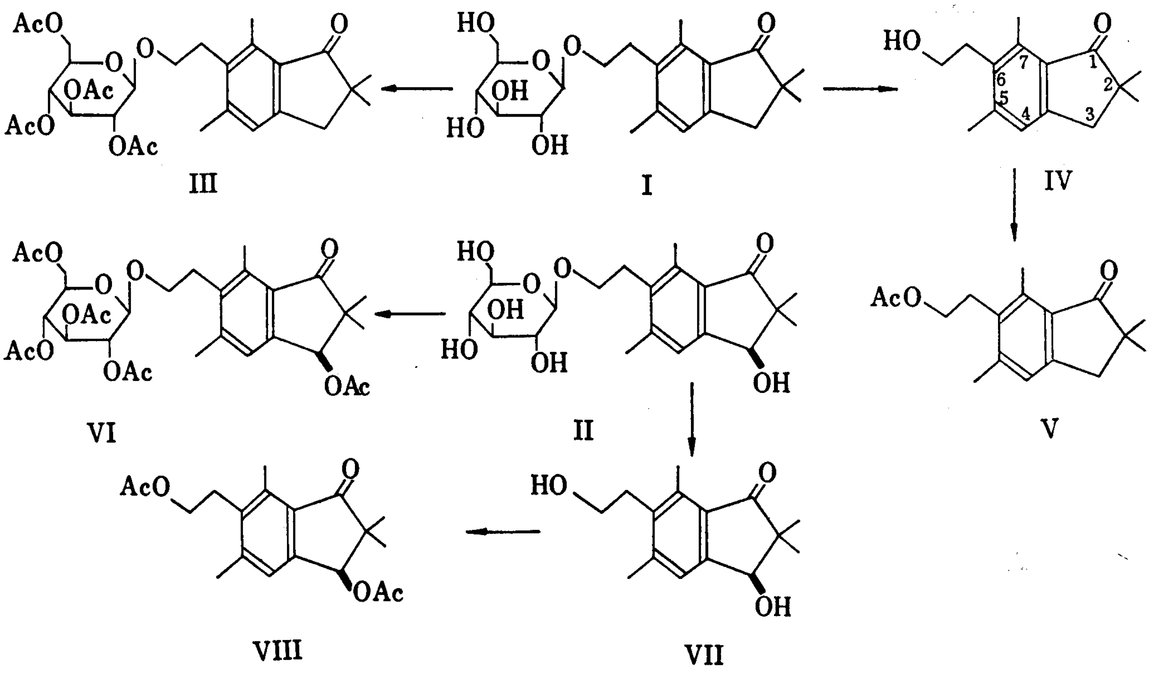
Further, a carbinyl hydrogen (δ 5.12 ppm), and an aromatic hydrogen at C-4 (δ 7.61 ppm), a long-range coupling and an NOE were observed between the carbinyl hydrogen and the aromatic hydrogen and an NOE was found between the aromatic hydrogen and one of the aromatic methyls (δ 2.42 ppm). VII differs from IV in having one extra oxygen atom which is thus deduced to participate in a secondary hydroxyl group at C-3. Since the circular dichroism (CD) curves of the acetates (VI and VIII) show negative n-π* Cotton effects ($[\theta]_{327}^{-68°}$ -7750, $[\theta]_{325}^{-68°}$ -2300, respectively), the configuration at C-3 is concluded to be S.[3]



The NMR spectra of the glycoside acetates (III and VI) and the corresponding aglycone acetates (V and VIII) show that the signals for the carbinyl hydrogens in the hydroxyethyls in the latter shifted downfield (−0.50 and −0.58 ppm) in comparison with those of the former, indicating glucose to be linked to the hydroxyethyl group in each glycoside. Further, glucose residue of each glycoside was deduced to be present as a β-D-glucopyranoside moiety by data similar to those for pteroside B.[1]

On the basis of the above evidence, it is concluded that pteroside Z and D have the stereostructures I and II, respectively.

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[3] *cf.* M.-J. Brinne, G. Ouannes, and J. Jaques, *Bull. Soc. Chim. France*, **1967**, 613.