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STEREOCHEMISTRY OF PTAQUILOSIDE, A NOVEL NORSESQUITERPENE GLUCOSIDE FROM BRACKEN, PTERIDIUM AQUILINUM VAR. LATIUSCULUM

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Abstract. The absolute stereostructure of ptaquiloside (1), a novel norsesquiterpene glucoside isolated from bracken, Pteridium aquilinum var. latiusculum has been elucidated by the ^{1}H NMR spectral method and an X-ray crystallographic analysis of ptaquiloside tetraacetate (2).

In connection with the carcinogenic property[1,2,3] of bracken, Pteridium aquilinum var. latiusculum, we have examined the constituents of this plant, isolated an unstable norsesquiterpene glucoside named ptaquiloside (1) from the fraction exhibiting carcinogenicity, and elucidated the planar structure.[4]

In this paper the complete stereostructure of ptaquiloside (1) is described.

The configuration of the glycosidic linkage in 1 was already determined to be β.[4] The cis relationship between H-14 and H-9 in ptaquiloside (1) was revealed by the observation of the NOE between them in the ^{1}H NMR spectrum (CD_3OD, 270 MHz) of 1: on irradiation of H-14 (δ 1.29, s) the intensity of the H-9 signal (δ 2.64, d, J = 1.3 Hz) was increased.

In order to establish the whole stereostructure including absolute stereochemistry of ptaquiloside (1), an X-ray crystallographic analysis of ptaquiloside tetraacetate (2) [mp 173 - 174 °C (dec.) (MeOH)][4] was performed as follows.

CRYSTAL DATA: $C_{28}H_{38}O_{12}$, MW 566.6, orthorhombic, $P2_12_12_1$, a = 15.900(2), b = 18.158(3), c = 10.252(2) Å, V = 2960.0(8) Å^3, Z = 4, D_x = 1.27 g·cm^{-3}, μ(Mo Kα) = 0.093 mm^{-1}.

The intensity measurements were performed for $2\theta \leq 55°$ on a Rigaku automated four-circle diffractometer with graphite-monochromated Mo Kα radiation, a θ-2θ scan technique, and a crystal of dimensions 0.55 x 0.55 x 0.60 mm. The structure was solved by direct methods. Refinement was carried out by block-diagonal least squares based on F with weights $w^{-1} = \sigma^2(|F_o|) + (0.015\ |F_o|)^2$. All the H atoms were found on the difference Fourier maps. Non-H atoms were treated anisotropically, and H atoms were refined isotropically.[5] Convergence was achieved with R = 0.044, wR = 0.049 and S = 1.95 for 2520 observed unique reflections.[6] The absolute structure of 2 was determined based on the known absolute configuration of D-(+)-glucose,[7] since the aromatization reaction of ptaquiloside (1) was found to provide D-(+)-glucose and pterosin B (3).[4,8] An ORTEP drawing is shown in Fig. 1, indicating that the absolute stereostructure of ptaquiloside tetraacetate must be represented by 2.[9,10] The absolute stereostructure of ptaquiloside was thus determined to be 1.

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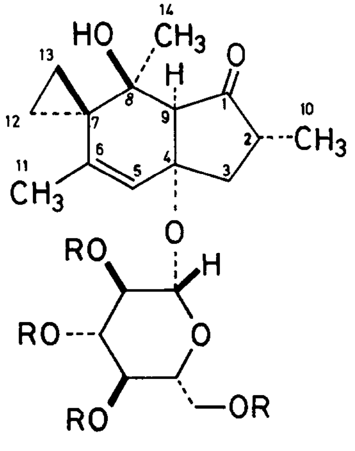

1 R = H

2 R = COCH3

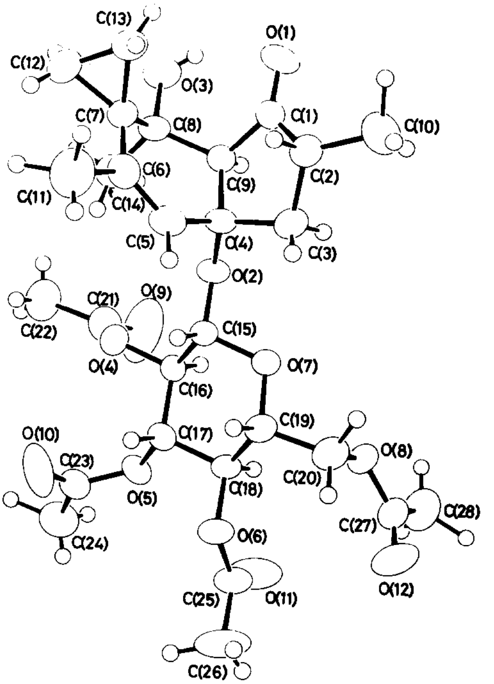

Fig. 1. A computer generated ORTEP drawing of the molecule 2.

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5. All computations were carried out using the Universal Crystallographic Computation Program System UNICS III: T. Sakurai and K. Kobayashi, Rikagaku Kenkyusho Hokoku, 55, 69 (1979).
6. Full details of all X-ray crystal structure determination will be published separately.
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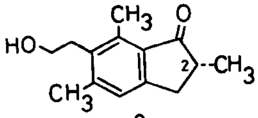
8. Pterosin B (3) obtained from ptaquiloside (1) was levorotatory [mp 109 - 109.5 °C, $[\alpha]_D^{25}$ -44° (c 1.0, MeOH)]. The absolute configuration at C-2 of (-)-3 was proved to be R: see M. Kuroyanagi, M. Fukuoka, K. Yoshihira, and S. Natori, Chem. Pharm. Bull., 22, 723 (1974); M. Fukuoka, M. Kuroyanagi, K. Yoshihira, and S. Natori, Chem. Pharm. Bull., 26, 2365 (1978). The absolute configuration at C-2 of 1 determined by the present study is identical with that of (-)-3 previously reported.



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10. Tables of atomic parameters, bond lengths, and bond angles have been deposited with the Cambridge Crystallographic Data Centre.

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