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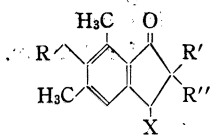
Further Characterization of 1-Indanone Derivatives from Bracken, *Pteridium aquilinum* var. *latiusculum*

In the previous communication[1] structures (I—VI) of six sesquiterpenoids having 1-indanone nucleus from methanol extract of air-dried young leaves of *Pteridium aquilinum* KUHN var. *latiusculum* UNDERWOOD (Pteridaceae) (Japanese name, warabi) were reported. This communication concerns further characterization of four derivatives from more polar fractions of the extract.

TABLE I



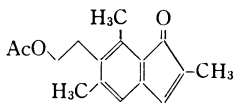
		R	R′	R″	X	Trivial name[2]
I	BI-2[1]	CH_2OH	CH_3	H	H	petrosin B
II	BH-4[1]	COOH	CH_3	H	H	pterosin E
III	HJ-5[1]	CH_2Cl	CH_3	H	H	pterosin F
IV	HQ-2[1] (hypolepin B[3])	CH_2OH	CH_3	CH_3	H	pterosin Z
V	BJ-4[1]	CH_2OH	CH_3	CH_3	OH	pterosin D
VI	BK-3[1]	CH_2OH	CH_3	CH_2OH	H	pterosin A
VII	Ac-3	CH_2OH	CH_3	H	OH	pterosin C
VIII	BM-5	CH_2OH	CH_2OH	H	H	pterosin G
X	pteroside C[4,5]	CH_2O-gl	CH_3	H	OH	
XI	pteroside B[6]	CH_2O-gl	CH_3	H	H	
XII	pteroside A[4,5]	CH_2O-gl	CH_3	CH_2OH	H	
XIII	pteroside D[5]	CH_2O-gl	CH_3	CH_3	OH	
XIV	pteroside Z[5]	CH_2O-gl	CH_3	CH_3	H	
XV	hypolepin A[3]	CH_2Cl	CH_3	CH_3	H	pterosin H
XVI	hypolepin C[3]	CH_2OCH_3	CH_3	CH_3	H	pterosin I

(gl=β-D-glucopyranose)

1) K. Yoshihira, M. Fukuoka, M. Kuroyanagi, and S. Natori, *Chem. Pharm. Bull.* (Tokyo), **19**, 1491 (1971).
2) The decision was made by the agreement by Professor T. Takemoto and Dr. H. Hikino, Tohoku University, Dr. Y. Hayashi, Osaka City University, and the authors at Nagoya, October 18, 1971.
3) Dr. Y. Hayashi, Osaka City University, private commuication; *cf.* M. Nishizawa, Y. Hayashi, and T. Sakan, The paper presented at the 15th Symposium on the Chemistry of Terpenes, Essential Oils, and Aromatics, Osaka, November 1971, Abstracts of Papers, p. 141.
4) H. Hikino, T. Takahashi, and T. Takemoto, The paper presented at the Annual Meeting of Pharmaceutical Society of Japan, Fukuoka, April 1971, Abstracts of Papers, p. 777.
5) H. Hikino, T. Takahashi, and T. Takemoto, The paper presented at the 40th Meeting of Tohoku Branch, Pharmaceutical Society of Japan, Sendai, July 1971.
6) H. Hikino, T. Takahashi, S. Arihara, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **18** 1488 (1970).

Two of them tentatively named Ac-3 and BM-5 are assigned again as 1-indanone derivatives (VII and VIII) from the following evidences:

The compound, Ac-3 (VII), generally appears as chromatographically pure crystals of mp 153—156°, showing M^+ 234.124 *m/e* (Calcd. for $C_{14}H_{18}O_3$, 234.126), λ_{max}^{EtOH} mμ (log ε): 217.5, 259, 301 (4.51, 4.12, 3.23), and ν_{max}^{KBr} cm^{-1}: 3350, 1680, 1600. However the nuclear magnetic resonance (NMR) spectrum revealed that the compound was contaminated with its diastereoisomer (VII') (*ca.* 20%) (*vide infra*). Although the separation of the two has so far been unsuccessful, the diacetate (VII''), oil, $[\alpha]_D^{18}$ −5.6° ($CHCl_3$), was obtained as a single compound. NMR spectrum of VII'' showed the presence of one sec. methyl (δ 1.36 (3H, d, J=7.5 Hz)), two aromatic methyls (δ 2.45 (3H, s), 2.68 (3H, s)). Cone acetoxyethyl (δ 2.04 (3H, s), 4.10 (2H, t, J=7.5 Hz), 3.02 (2H, t, J=7.5 Hz)), one sec. acetoxyl (δ 2.15 (3H, s), 5.79 (1H, d, J=3 Hz)), and one aromatic proton (δ 7.18 (1H, s)). Comparison of these spectral data with those of I—VI and their acetates suggested the structure (VII) for Ac-3. Treatment of VII'' with sodium hydride resulted in the loss of one mole of acetic acid to form 1-indenone derivative (IX), mp 71—72°, λ_{max}^{EtOH} mμ (log ε): 244, 250.5, 335 (4.53, 4.63, 3.42), ν_{max}^{KBr} cm^{-1}: 1740, 1700, 1600, NMR δ ($CDCl_3$): 1.82 (3H, d, J=1.7 Hz), 2.04 (3H, s), 2.30 (3H, s), 2.52 (3H, s), 2.90 (2H, t, J=7.5 Hz), 4.07 (2H, t, J=7.5 Hz), 6.51 (1H, br. s), 6.86 (1H, q, J=1.7 Hz). The structure (IX) suggested by these spectral data was confirmed by the formation of IX from the acetate of BI-2 (I) by selenium dioxide oxidation. Thus the structure (VII) of Ac-3 was unequivocally established. From the structure and the NMR observations (*e.g.* C-3 proton of the acetate of VII' observed in the acetate mixture prepared from VII containing VII', δ 6.18 (1H, d, J=6 Hz)) the contaminant (VII') was assumed to be the epimer at C-2 bearring the methyl *cis* to the hydroxyl at C-3, while in Ac-3 (VII) the methyl and the hydroxyl were *trans*. The compound, Ac-3 (VII), corresponds to the aglycone of pteroside C (X).[4]



IX

The compound, BM-5 (VIII), mp 152—153°, $[\alpha]_D$ ±0° (MeOH), $C_{14}H_{18}O_3$ (M^+ 234.162 *m/e*, Calcd. 234.126), showed also the characteristic UV (λ_{max}^{EtOH} mμ (log ε): 217.5, 261, 305.5 (4.43, 4.14, 3,30)) and infrared (IR) absorptions (ν_{max}^{KBr} cm^{-1}: 3540, 1690, 1600) of 1-indanone. The formation of diacetate (VIII') and the comparison of the NMR data of VIII (δ (CD_3OD): 2.39 (3H, s), 2.60 (3H, s), 2.90 (2H, t, J=8 Hz), 3.53 (2H, t, J=8 Hz), 3.77 (2H, d, J=5.5 Hz), 2.4—3.1 (3H), 7.05 (1H, br. s)) and the acetate (VIII') with other indanone derivatives (I—VII) and their acetates respectively clearly disclosed the presence of two aromatic methyls, one hydroxyethyl, and one hydroxymethyl in VIII and, from the analogy to other compounds from the same source, the structure (VIII) was proposed.

The other two compounds (XI, XII) are glucosides of 1-indanone derivatives and they are respectively identified with pteroside B[6] and A[4] by the comparison of physical data and hydrolysis to BI-2 (I) and BK-3 (VI) respectively. In the former case the direct comparison with the sample was also carried out. The structures of pterosides[4,6] were revised to X-XII from the evidences provided in the previous communication.[1]

Hikino, *et al.*[5] also presented papers concerning about the revision of the structures, the stereochemistry, and further isolation of pteroside D (XIII) and Z (XIV) corresponding to the glucosides of our BJ-4 (V) and HQ-2 (IV).

Quite recently Hayashi, *et al.*[3] isolated three compounds tentatively designated as hypolepins A, B, and C from *Hypolepis punctata* Mett. (Pteridaceae) (Japanese name, iwahimewarabi) and proved the sturctures respectively as XV, IV, and XVI. The identity of hypolepin B with HQ-2 (IV) was confirmed by direct comparison.[3] The compound expressed by the formula (XVI), mp 56—57°, IR ν_{max}^{KBr} cm^{-1}: 1700, 1600, NMR δ ($CDCl_3$): 1.21 (6H, s), 2.40 (3H, s), 2.67 (3H, s), 2.82 (2H, s), 2.98 (2H, br. t), 3.55 (3H, s), 3.41 (2H, br. t), 6.98 (1H, br. s), had already been obtained in our hands as the by-product of methylation of BI-2 (I) with

sodium hydride and methyl iodide to HQ-2 (IV).[1] The identity with the natural product was also confirmed by the direct comparison.[3]

In order to avoid the confusion in literatures 1-indanone derivatives from ferns (I—VIII, XV, XVI) will hereafter be designated as pterosins, while the glucosides (X—XIV) have been named as pterosides,[4-6] the trivial names according to this decision being shown in Table I.[2]

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