BIOACTIVE COMPOUNDS OF THE FLORA OF BELARUS.
4. PTEROSINS A AND B FROM *Pteridium aquilinum*

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*Sesquiterpenoids pterosins A (**1**) and B (**2**) and the flavonol glycoside astragalin were isolated from the aerial part of the bracken-fern* Pteridium aquilinum.

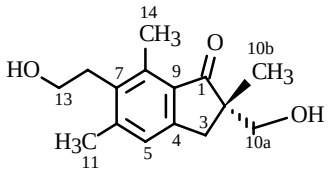
Key words: pterosins A and B, astragalin, bracken-fern *Pteridium aquilinum*, Hypolepidaceae.

The content of biologically active compounds in most representatives of the flora of Belarus has been insufficiently studied. These plants include, in particular, the common bracken-fern *Pteridium aquilinum* L. (Hypolepidaceae), which is commonly found in Belarussian forests, is widely distributed, and varies considerably in form, for which reason it is sometimes divided into several subspecies. Several studies [1-5] of the isolation from *P. aquilinum* of various biologically active compounds such as flavonoids, terpenoids, and steroids have been published. However, the content of these compounds depends significantly on the habitat.

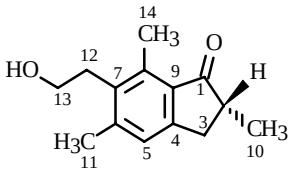
Our goal was to determine if bracken-fern growing in Belarus can be used as raw material for isolating boilogically active compounds.

We previously used a method that is usually applied to the isolation of phytoecdysteroids to isolate astragalin from tripinnate oak fern [6]. We used this method to investigate the composition of the ethanol extract of the aerial part of bracken-fern. Three pure compounds were isolated. Their structures were determined using spectral data.

Thus, IR and UV spectra of the first molecule indicated the presence of hydroxyls, ketones, and aromatic rings that were probably adjacent and conjugated. The PMR spectrum of this compound contained several signals (Table 1) due to three methyls in its structure. Judging from the magnitude of the chemical shifts and the multiplicity of the signals, one of these methyls was tertiary; the two others, bonded to an aromatic ring. PMR spectral data reliably prove that this compound contains two primary hydroxyls. Comparision of the PMR spectral data with the literature [2-4] enabled us to establish the structure of the first compound as pterosin A (**1**), the chemical structure of which is derived from 1-indanone and belongs to the sesquiterpenoid illudoids.



1



2

The second compound (**2**) isolated by us from bracken-fern has a structure similar to that of **1**. According to IR and UV spectra, its structure, like that of **1**, contains the 1-indanone system and a hydroxyl. The PMR spectrum confirms the presence in **2** of an aromatic ring, a primary hydroxyl, and three methyls. Two of the methyls are bonded to the aromatic ring; the third is secondary. Based on a comparison of IR, UV, and PMR spectral data with those in the literature [2-4], we established that **2** is pterosin B, which, like **1**, has a chemical structure belonging to the sesquiterpenoid illudoids.

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TABLE 1. PMR Spectra (δ, ppm, $CDCl_3$, J/Hz) of **1** and **2**

Proton	Pterosin A (**1**)	Pterosin B (**2**)
H-2		3.24 dd (J_1 = 17, J_2 = 8)
2H-3	2.75 d (J = 17)	2.55-2.65 m
	3.06 d (J = 17)	
H-5	7.14 s	7.11 s
3H-10		1.27 d (J = 6)
2H-10a	3.76 d (J = 10)	
3H-10b	1.21 s	
3H-11	2.43 s	2.44 s
2H-12	3.01 t (J = 7)	3.03 t (J = 7)
2H-13	3.75 t (J = 7)	3.76 t (J = 7)
3H-14	2.67 s	2.68 s

The third compound (**3**) isolated pure by us from the aerial part of bracken-fern was the flavonol glycoside astragalin, the structure of which was proved by direct comparison with a specimen of astragalin isolated previously from tripinnate oak fern *Gymnocarpium dryopteris* [6].

The isolation of biologically active compounds from bracken-fern is continuing.

EXPERIMENTAL

Melting points were determined on a Kofler block. IR spectra were recorded in KBr disks on a UR-20 instrument in the range 700-3600 cm^{-1}. UV spectra of ethanol solutions were recorded on a Specord M-400 instrument. PMR spectra were obtained on an AC-200 NMR spectrometer (Bruker) at working frequency 200 MHz. Chemical shifts are given relative to TMS as an internal standard.

Isolation of Pterosins A and B. Dried and finely ground fronds of *P. aquilinum* (78.8 g) collected in July 2003 near Lyubasheva village of Gantsevich region of Brest district were extracted with ethanol (3 × 500 mL) at room temperature. Solvent was removed in vacuum. The solid was dissolved in aqueous ethanol (200 mL, 30%). The aqueous ethanol solution was washed with hexane (200 mL). The ethanol was evaporated in vacuum. The solid was extracted twice with *n*-butanol (50 and 25 mL). The butanol extract was evaporated in vacuum to afford a solid (0.63 g) that was chromatographed over a silica-gel column with elution by ethanol:chloroform of increasing polarity (1:10, 1:8, 1:4) and then pure ethanol to give 18 fractions.

Fractions 1 and 2 were combined to give the total compounds (62.8 mg). Then these were separated by preparative TLC on silica-gel plates with elution by ethylacetate:petroleum ether (1:1) to afford pterosin B (**2**, 28.4 mg) in overall yield 0.036% calculated per air-dried raw material, mp 98-102°C (CH_2Cl_2), lit. mp 109-110°C [4, 5], 107-109°C [6]. IR spectrum (ν, cm^{-1}): 3450 (OH), 1715 (C=O), 1615 ($C=C_{arom}$). UV spectrum (λ_{max}, nm): 217 (33,600), 259 (14,460), 301 (3350).

Chromatography of fraction 4 (147.4 mg) on silica-gel plates with elution by ethylacetate:petroleum ether (1:1) with subsequent recrystallization from $CHCl_3$:hexane isolated pterosin A (**1**, 32.1 mg) in overall yield 0.02% calculated per air-dried raw material, mp 123-126°C, lit mp 125-127°C [4-6]. IR spectrum (ν, cm^{-1}): 3400 (OH), 1705 (C=O), 1610 ($C=C_{arom}$). UV spectrum (ν_{max}, nm): 217 (28,950), 260 (13,610), 303 (2380).

Fractions 14-16 were combined to afford total compounds (0.128 g) that were further separated by preparative TLC on silica-gel plates with elution by $CHCl_3$:2-propanol:water (6.25:2.0:0.15). The main compound was recrystallized from CH_3OH to afford astragalin (0.0167 g) in overall yield 0.02% calculated per air-dried raw material, mp 172-175°C (CH_3OH), lit mp 173-176°C (CH_3OH) [1]. The PMR spectrum of this compound was identical to that of astragalin isolated previously from tripinnate oak fern [6].

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