PHLOROGLUCIDES OF *DRYOPTERIS PHEGOPTERIS*

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Dryopteris phegopteris (L.) C. Chr. (narrow beechfern) is a perennial herbaceous plant of the family Polypodiaceae growing in the Caucasus and in Siberia which has not previously been studied chemically.

We have studied the rhizomes of this species of fern collected in the summer of 1968 (Gomis-Mta, Adjar ASSR).

An ethanolic extract of the raw material was evaporated and treated with an aqueous solution of barium hydroxide with subsequent acidification with HCl. This gave about 1% of "crude filicin." Chromatography on paper impregnated with a 30% solution of formamide in acetone in the petroleum ether–chloroform (1 : 1) system showed that the "crude filicin" consisted of three substances of the phloroglucinol type, which were then separated on a column of silica gel. Two individual compounds were obtained.

The first substance had the composition $C_{25}H_{32}O_8$, mp 122–123° C (from ethanol). The IR spectrum had bands at (cm^{-1}): 3200, 2740, 2660 (OH), 1650 and 1610 ($C{=}O$), and 1570 (aromatic ring); the UV spectra had two maxima at λ_{max} 230 and 292 mμ (log ε 4.51 and 4.39; the NMR spectra showed three multiplets: 3.1 ppm ($CO{-}CH_2{-}$), 1.8 ppm ($CO{-}CH_2{-}CH_2{-}$), 1.1 ppm ($CO{-}CH_2{-}CH_2{-}CH_3$), and 4 singlets at 3.7 ppm ($Ar{-}OCH_3$); 2.1 ppm ($Ar{-}CH_3$); 1.5 ppm (broadened signal of a gem-dimethyl group); and 3.6 ppm ($-CH_2-$).

The anilide of the substance, with the composition $C_{31}H_{37}NO_7$, mp 130–132° C (absolute ethanol) was obtained by Boehm's method [1]. Hydrolysis of the compound obtained from the plant with 5% aqueous alkali gave three products, with mp 140–142° C (ethanol), 69–71° C (hexane), and 95–97° C (petroleum ether–acetone).

By comparing our results with literature data [2-4] the substance obtained was found to be identical with aspidin, and the products of its hydrolysis with Ψ-aspidin, Ψ-aspidinol, and butyrylfilicinic acid, respectively. The identities were confirmed by mixed melting points.

The other substance, with the composition $C_{12}H_{16}O_4$, had mp 143–144° C (from benzene). The IR spectrum had absorption bands at (cm^{-1}): 3300 (OH), 1645 ($C{=}O$), and 1590 (aromatic ring), and the UV spectrum had λ_{max} 225, 330, and 287 mμ (log ε 3.52, 4.09, and 4.26); mol. wt. 224 (mass spectrometry). The NMR spectrum had three multiplets, at 3.0 ppm ($CO{-}CH_2{-}$), 1.7 ppm ($CO{-}CH_2{-}CH_2{-}$), and 1.0 ppm ($CO{-}CH_2{-}CH_2{-}CH_3$), and three singlets, at 3.8 ppm ($Ar{-}OCH_3$), 2.0 ppm ($Ar{-}CH_3$), and 5.95 ppm ($Ar{-}CH$). The diacetate, $C_{16}H_{20}O_6$, had mp 64–66° C (from aqueous ethanol).

On comparison of the above information with literature data [2, 5], the second substance was identified as aspidinol.

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