PHLOROGLUCIDES OF Dryopteris mediterranea

L. M. Molodozhnikova and A. I. Ban'kovskii

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Dryopteris mediterranea Fom. is a perennial evergreen herbaceous plant growing in the mountain regions of the Caucasus. It has not previously been studied chemically. We have investigated the rhizomes collected in 1965 in the Adjar ASSR.

The finely ground rhizomes of the fern (1 kg) were extracted with ethanol (1 : 8) for a day (three times). The ethanol was distilled off in vacuum, and the resulting extract was treated repeatedly with aqueous barium hydroxide; the aqueous extracts were combined and acidified with conc. hydrochloric acid. The flocculent precipitate that deposited was filtered off and washed with water until chloride ions were absent. This gave about 15 g of "crude filicin" in the form of a light brown powder. Of this, 10 g was chromatographed on a column of 300 g of anhydrous silica. Elution with petroleum ether gave fractions 1-3, a mixture of petroleum ether and benzene (4 : 1) gave fractions 5-12, a mixture of petroleum ether and benzene (1 : 1) fractions 13-44, and benzene alone fractions 45-62. The volume of each fraction was 100-150 ml.

Fractions 1-3 gave 0.8 g of a substance with the composition $C_{25}H_{32}O_8$, mp 140-142°C (from acetone); it was readily soluble in chloroform and benzene, sparingly soluble in acetone and methanol, and insoluble in water; R_f 0.95 [in the petroleum ether–chloroform (1 : 1) system].

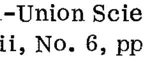
Its IR spectrum had no clear band corresponding to hydroxy groups, which may be due to intramolecular hydrogen bonds; there were bands at 1651 cm^{-1} (C = O) and 1560 cm^{-1} (aromatic ring).

UV spectrum: λ_{max} 224 and 338 nm (log ε 4.46 and 4.33, respectively). In composition, melting point, and UV and IR spectra, this compound is identical with albaspidin [1]. A mixture with an authentic sample gave no depression of the melting point.

Fractions 4-12 which contained a single substance were combined; distillation of the solvent gave 0.3 g of a lemon-yellow crystalline product with the composition $C_{24}H_{30}O_8$ which had a double mp, 87 and 152°C (methanol). The IR spectra had absorption bands at 3500 and 3230 cm^{-1} (OH), 1635 cm^{-1} (C =O), and 1590 cm^{-1} (aromatic ring). The acetyl derivative had the composition $C_{32}H_{38}O_{12}$, mp 72-75°C (aqueous ethanol). In its composition, melting point, and UV and IR spectra, and also the composition and melting point of the acetate, the substance corresponds to flavaspidic acid [2]. A mixture with an authentic sample showed no depression of the melting point.

Fractions 13-17, consisting of albaspidin, flavaspidic acid, and a substance with R_f 0.3, were not investigated.

Fractions 18-62 with R_f 0.3 were combined. After the solvent had been distilled off, 0.5 g of yellow crystals of a substance (I) with the composition $C_{22}H_{26}O_8$, mp 206-208°C (ethanol) deposited; they were readily soluble in pyridine, acetone, and alkalis, less readily in chloroform and benzene, and insoluble in water. The IR spectra showed absorption bands at 3200, 3525, and 2680 cm^{-1} (OH), 1640 and 1619 cm^{-1} (C = O) and 1580 cm^{-1} (aromatic ring); the UV spectrum had λ_{max} 292 nm (log ε 4.40).

The NMR spectrum contained three multiplets: 3.1 ppm (α-CH_2–), 1.75 ppm (β-CH_2–), and 0.8 ppm (CH_3 of an acyl residue) and four singlets, at 2.2 ppm (Ar–CH_3), 1.4 ppm (signal of a gem-dimethyl group), 2.5 ppm  $\left(-\underset{\diagdown CH_3}{C}=O\right)$, and 3.8 ppm (–$CH_2$–).

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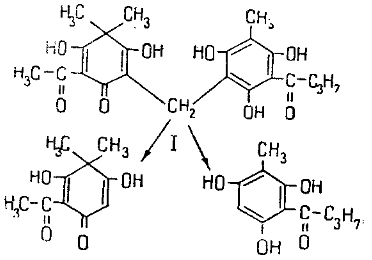

II III

This compound gave a benzoate, $C_{36}H_{34}O_{10}$, mp 105-106.5°C (ethanol). The hydrolysis of (I) with 5% aqueous alkali yielded two products: $C_{10}H_{12}O_4$, mp 170-172°C (petroleum ether–acetate) and $C_{11}H_{14}O_4$, mp 162-164°C (chloroform–ethanol), which were identified on the basis of their compositions, melting points, and UV and IR spectra as acetylfilicinic acid (II) and 3-methylbutyrylphloroglucinol (III) [the flavaspidic and acetylfilicinic acids and the 3-methylbutyrylphloroglucinol were kindly given to us by A. Pentilla (Finland)].

Mixtures of these substances with authentic samples gave no depression of the melting points. In addition to this, the hydrolysis of I gave butyric and acetic acids, as shown chromatographically [3].

The facts presented permit the conclusion that compound I is acetylflavaspidic acid, which has been synthesized previously by Pentilla and Sundman [4]; this is the first time it has been isolated from a plant.

LITERATURE CITED

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