NEW FLAVONOID GLYCOSIDES OF Phelodendron lavallei AND Ph. amurense

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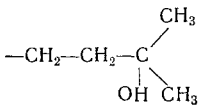
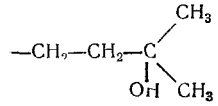
From the leaves of Phellodendron lavelli Dode (Lavalle cork-tree) and Ph. amurense R. (Amur cork-tree) we have isolated two flavonoid glycosides differing in structure from those studied previously: phellamuran, phellodendroside, dihydrophelloside, amurensin, noricariside, and phelloside [1-4]. We have named the substances phellavin and phellatin.

Phellavin (I), $C_{26}H_{32}O_{12}$, mol. wt. 550 (ebullioscopically, "Hitachi 115" instrument), mp 151-153°C $[\alpha]_D$ − 43° (c 0.61; methanol), λ_{max} 345, 290 nm, R_f 0.86 in 15% acetic acid, acetate $C_{40}H_{46}O_{19}$ with mp 187-189°C.

Phellatin (II), $C_{26}H_{30}O_{12} \cdot 1/2\ H_2O$, mp 262-265°C, $[\alpha]_D$ − 30° (c 0.3; dimethylformamide), R_f 0.24 in 15% acetic acid.

The hydrolysis of phellavin with 10% sulfuric acid gave the aglycone IV, $C_{20}H_{20}O_6$, mp 217-218°C, mol. wt. 356 (mass spectrometrically), λ_{max} 297 nm, acetate with mp 189-191°C. D-Glucose (III) was found in the hydrolysate by thin-layer chromatography in silica gel.

The NMR spectrum of the silylated aglycone [5] had the signals of H-2',6' protons (7.25 ppm), H-3', 5' protons (6.74 ppm), the singlet (5.80 ppm) of H-8, two doublets (4.90 and 4.08 ppm, J = 11 Hz) ascribed to the H-2 and H-3 protons of a trans-flavanonol, two triplets (2.58 and 1.72 ppm) with an intensity of two proton units, each corresponding to an $Ar-CH_2-CH_2-$ grouping, and a signal (1.34 ppm) assigned to a gem-dimethyl grouping. The NMR spectrum of silylated phellavin exhibited the signals of the protons of glucose (6 H in the 3.4-3.8 ppm region) and the signal of the anomeric proton of β-glucose (5.04 ppm). The NMR spectrum of the full acetate of phellavin showed the signals of two aromatic acetyl groups (2.30 and 2.25 ppm) and five aliphatic acetyl groups (~2.00 ppm), four of which are those of acetylated glucose and one is at C-3 of a flavanonol. The hydroxy groups in positions 3, 4', and 5 of the nucleus of phellavin are free (established by UV and NMR spectroscopy).

To answer the question of the positions of the carbohydrate substituent and the  substituent, phellavin was oxidized with hydrogen peroxide in an alkaline medium and the UV and NMR spectra of this compound were studied. The product of the oxidation of phellavin with mp 262-265°C proved to be identical with phellatin (II), and the product of the oxidation of the aglycone of phellavin (I) with the glycone of phellatin (V). The NMR spectrum of phellatin has the signals of the H-2',6' protons (7.85 ppm) and the H-3',5' protons (6.76 ppm), and a singlet (6.36 ppm) assigned to a proton in position 8, which shows that the  residue is in position 6. In addition, the spectrum of phellatin has the signal of the anomeric proton of β-glucose (5.06 ppm) and of the protons of glucose (6H in the 3.40-3.80 ppm region).

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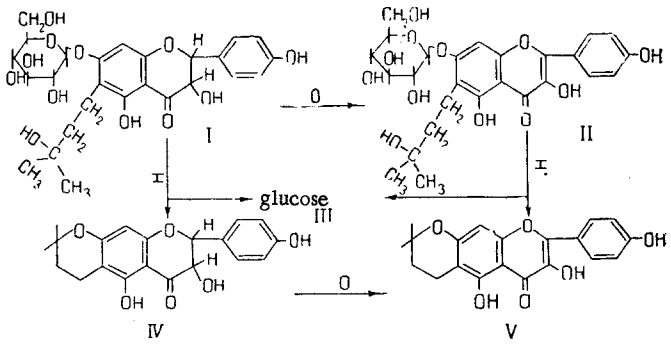

In phellatin (II) and phellavin (I) the glucose is present in position 7 and there is no bathochromic shift of the absorption maximum in the presence of sodium acetate. No shift is found, either, in the spectra of their aglycones, which may be due to the formation of a pyran ring between the γ-hydroxyisopentyl radical and the hydroxyl in position 7 of the flavonoid nucleus.

When the molecular rotations of phellatin and of known flavonol 3- and 7-glucosides were compared, it was found that the glucose in phellatin, and consequently in phellavin, also, is present in the pyranose form.

Thus, phellavin is 7-β-D-glucopyranosyl-4',5-dihydroxy-6-(γ-hydroxyisopentyl)flavanonol, and phellatin is 7-β-D-glucopyranosyl-4',5-dihydroxy-6-(γ-hydroxyisopentyl)flavonol.

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