FLAVONOIDS OF Aconitum orientale

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We have previously reported the presence of lespedin and of kaempferol 7-rhamnoside in the leaves of Aconitum orientale Mill (Caucasian monkshood) [1, 2].

By fractional extraction on acidic and alkaline polyamide [3] we have isolated another two flavonoid glycosides with the following compositions: (II, $C_{27}H_{30}O_{15}$), and (III, $C_{27}H_{30}O_{16}$). After recrystallization from aqueous acetone, the glycoside (II) had mp 194-196°C, $[\alpha]_D^{20}$ −46.2° (c 0.5; ethanol), $[M]_D$ −274°C; UV spectrum: λ_{max} 320, 268 nm; and the glycoside (III) had mp 184-185°C, $[\alpha]_D^{20}$ −46.8° (c 0.52; ethanol), $[M]_D$ −285°C; UV spectrum: λ_{max} 340, 255 nm.

Quantitative acid hydrolysis showed that for each mole of aglycone, both in (II) and in (III) there were one mole each of rhamnose and glucose (yield of aglycone 48%). The aglycone of (II) had mp 273-275°C, and its acetate had mp 180-182°C. UV spectrum: λ_{max} 367, 266 nm. The aglycone of (III) had mp 310-313°C and its acetate had mp 199-201°C; UV spectrum: λ_{max} 373, 255 nm.

From its physicochemical properties and the absence of a depression of the melting point of a mixed sample, the aglycone (II) was identified as kaempferol and the aglycone (III) as quercetin.

The UV spectrum of each aglycone showed a bathochromic shift by 10-15 nm in the presence of sodium acetate, with no bathochromy in the glycosides, and also a bathochromic shift with $AlCl_3$ which disappeared in the glycosides and was stabilized in the case of the aglycones under the action of HCl, which showed glycosidation at C_3 and C_7 of the flavone nucleus.

In a hydrolyzate after neutralization for both glycosides glucose (R_f 0.17) and rhamnose (R_f 0.41) were found by chromatography in the presence of authentic samples [Partridge's system – BAW (4:1:5)].

The differential IR spectroscopy of the glycosides showed the absorption band of the carbohydrate components: in the glycoside II – 1070 and 1030 cm^{-1} (C−O), 1000 cm^{-1} (−O−C−O of a glycosidic unit), 980 cm^{-1} (ring CH_3 groups), 920 cm^{-1} (asym. vibrations), 880 (β anomer), and 835 cm^{-1} (α anomer); in the glycoside (III) the bands were present at 1070, 1025, 1000, 980, 920, 898, 820, and 730 cm^{-1}. The presence of two absorption bands in the 1100-1010 cm^{-1} region may show that the carbohydrate components have furanose rings [4].

In the stepwise acid hydrolysis of the glycosides (II) and (III) with 1% H_2SO_4 solution, 7-monosides were isolated, and their hydrolysis gave the corresponding aglycone and rhamnose. On their hydrolysis with a 1% solution of KOH [5], 3-glycosides were formed. The UV spectroscopy of the intermediate products, in comparison with the glycosides and aglycones, confirmed the results of glycosidation at C_7 and C_3.

The facts given above permit the conclusion that glycoside (II) is kaempferol 3,7-glucorhamnoside and glycoside (III) is quercetin 3,7-glucorhamnoside. The presence of α- and β-glycosidic links, and also of furanose rings of the sugars may be assumed for both glycosides.

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