FEKRYNOL AND ITS ACETATE FROM *Ferula krylovii*

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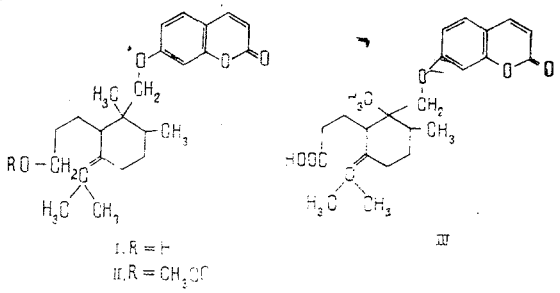
Together with other terpenoid coumarins [1, 2], from an acetone extract of the roots of *Ferula krylovii* Korov. by chromatograph on alumina (activity grade II) in petroleum ether–ethyl acetate we have isolated two new substances: (I) – $C_{24}H_{32}O_4$, M^+ 384, liquid, $[\alpha]_D^{16}$ +18° (c 1.0; ethanol), which has been called fekrynol, and (II) – $C_{26}H_{34}O_5$, M^+ 426, mp 80-82°C (ethyl acetate–petroleum ether), $[\alpha]_D^{22}$ –26.8° (c 1.0; ethanol). On alkaline hydrolysis, (II) was converted into (I), and the acetylation of (I) gave substance (II) identical with the natural compound according to its IR and PMR spectra and melting point. Consequently, (II) is the acetate of fekrynol.

The UV spectrum of (II) in ethanol (λ_{max} 325 nm, log ε 4.19; λ_{min} 260 nm, log ε 3.1) is characteristic for a 7-O-substituted coumarin, and the IR spectrum contains carbonyl bands at 1730, 1720, and 1710 cm^{-1}. In the PMR spectrum of (II) (Varian HA-100D, δ, ppm, CCl_4; 0 – TMS), in addition to the signals of umbelliferone (H_3, 6.11, d, J = 9.5 Hz; H_4, 7.51 d, J = 9.5 Hz; H_5, 7.26, d, J = 9.0 Hz; H_6 and H_8, 6.73, m), the signals of the protons of the following functional groups are observed: $CH_3COO-CH_2-$ (1.98, s, 3 H; 3.96, t, ΣJ = 12.0 Hz, 2 H); CH_2OAr (3.64 and 3.87, d, J = 8 Hz, 1 H each), $-CH_2-CH-C\equiv C-$ (2.94, t, ΣJ = 14 Hz, 1 H); $-CH_2-C\equiv C-$ (2.4, m), $(CH_3)_2C=C$ (1.61 and 1.44, s, 3 H each); CH_3-C- (1.09, s, 3 H); CH_3-CH- (0.91, d, J = 7.0 Hz, 3 H).

These facts permit the assumption that structures (I) and (II) correspond to fekrynol and its acetate. Thus, these substances are close in structure to galbanic acid (III) [3]. It can be seen from a comparison of the PMR spectra of (I) and (III) [3] that they differ practically only by the presence of a two-proton triplet at 3.52 ppm in the spectrum of fekrynol (I) which is due to the presence in its molecule of a CH_2-OH group in place of the COOH group of galbanic acid.



The reduction of (II) with $LiAlH_4$ in anhydrous ether gave an oily product identical, according to its PMR spectrum, with the product of the reduction of methyl galbanate obtained under the same conditions. In this process, not only is the methoxycarbonyl group reduced but so also is the carbonyl of the α-pyrone ring and the double bond in positions 3, 4.

The identity of the products of the reduction of (II) and (III) is evidence in favor of the structures (I) and (II) put forward for fekrynol and its acetate.

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FLAVONOIDS OF THE NEEDLES OF *Juniperus sabina*

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We have previously reported the finding in *Juniperus sabina* L. of eight flavone substances, in addition to ten flavans [1, 2].

The flavonoids were extracted by steeping the comminuted needles with methanol. The combined flavonoids were separated by fractional extraction using ether, ethyl acetate, and butan-1-ol successively. Having used absorption chromatography on polyamide and partition chromatography on silica gel, we have isolated four compounds (I-IV).

Compound (I) formed yellow crystals with mp 350-353°C, R_f 0.92 in the butan-1-ol—acetic acid—water (4:1:5) system (1) and 0.00 in 2% acetic acid (2); λ_{max} 272, 333 nm (methanol). Under the action of alkali it was cleaved to phloroglucinol and p-hydroxybenzoic acid. The compound corresponded to an authentic sample of apigenin, i.e., 4',5,7-trihydroxyflavone.

Compound (II) formed light yellow needles with mp 183-185°C $[\alpha]_D^{20}$ −172° (c 1.0; ethanol), R_f 0.73 (1) and 0.32 (2), λ_{max} 256, 350 nm (methanol). Alkaline cleavage led to the formation of phloroglucinol and protocatecbuic acid. Acid hydrolysis (0.1 N HCl, 2 h) gave the aglycone, with R_f 0.71 (1), λ_{max} 255, 370 nm, which was identified as quercetin. L-Rhamnose with R_f 0.52 (1) was detected in the hydrolysate. On the basis of the results of acid and alkaline cleavage, its IR spectrum (840, 1010, 1050 cm^{-1}) and UV spectra with diagnostic additives together with polarimetric analysis (M_DK_f = −416°), compound (II) was characterized as quercetin 3-α-L-rhamnofuranoside.

Compound (III) formed yellow crystals with mp 208-210°C, $[\alpha]_D^{20}$ −35° (c 1.0; ethanol), R_f 0.66 (1) and 0.18 (2), λ_{max} 258, 356 nm (methanol). Under the action of acid (0.1 N HCl, 2 h), glucose with R_f 0.21 (1) was split out; the aglycone was identified as quercetin. From the results of UV spectroscopy with diagnostic additives and a polarimetric calculation (M_DK_f = −127.6), compound (III) was identified as 3-α-D-glucopyranosyloxy-3',4',5,7-tetrahydroxyflavone (isoquercitrin).

Compound (IV) formed light yellow crystals with mp 190-192°C $[\alpha]_D^{20}$ +9.3° (c 0.9; ethanol), R_f 0.49 (1) and 0.38 (2), λ_{max} 255, 370 nm (methanol). The products of acid hydrolysis were found to contain the aglycone quercetin and the biose rutinose, which was then cleaved into glucose and rhamnose. Hydrolysis by the method of Fox et al. [3] permitted the detection of an intermediate monoglycoside which was identified as quercetin 3-O-β-D-glucopyranoside. It was established by a polarimetric analysis that the rhamnose was present in the β-furanose form. The PMR spectrum of substance (IV) corresponded to the given structure. The anomeric proton of the glucose was recorded at 5.11 ppm in the form of a doublet with $J_{1,2}$ = 6 Hz, confirming the β form of the bond, and the anomeric proton of the rhamnose at 4.22 ppm in the form of a singlet (cis-C_1-H and C_2-H), which corresponds to the β form of the bond in a L-rhamnofuranoside. The splitting out of rutin on enzymatic hydrolysis with α-rhamnodiastase showed the 1 → 6 arrangement of the bond between the sugar residues and confirmed the β form of the anomeric center of the rhamnose.

Thus, compound (IV) is quercetin 3-O-(6-O-β-rhamosyl-β-D-glucopyranoside). The steric form of rutinoside in junipers has not previously been established.

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