O-ACYLATED FLAVONOID GLYCOSIDES OF THE NEEDLES OF *Pinus sylvestris*

IV. DI-p-COUMAROYLISOQUERCITRIN

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From ethereal extracts of an evaporated methanolic extract of the needles of the Scotch pine (*Pinus sylvestris* L.) by chromatography on polyamide we have isolated a new diacylated flavonol glycoside (I).

Compound (I) has the composition $C_{39}H_{32}O_{16}$, mp 182-186°C, $[\alpha]_D^{20}$ −44.6° (c 0.6; methanol), ν_{CO} 1695, 1685, 1655 cm^{-1}, λ_{max}, nm (log ε), MeOH: 270 (4.45), 302 sh. (4.70), 3.15 (4.75), 360 sh. (4.30); NaOMe: 274, 368; NaOAc: 277, 302 sh., 315, 380; NaOAc + H_3BO_3: 265, 302 sh., 313, 380; $AlCl_3$: 273, 302 sh., 313, 444; $AlCl_3$ + HCl: 278, 302 sh., 313, 410.

On the basis of the PMR spectrum (Fig. 1) and the products of alkaline and acid hydrolysis it was established that compound (I) contains quercetin, glucose, and p-coumaric acid in a molar ratio of 1:1:2. The UV spectrum included a broad band at 315 nm characteristic for cinnamic acid derivatives, while the spectra with diagnostic additives showed the presence of free 7-OH and 3',4'-OH groups, and a free 5-OH group was detected from the PMR spectrum.

The conclusion concerning the attachment of the glucose to the 3-OH group of quercetin was also confirmed by the UV spectra of the deacylated product (II), which was identical with that of isoquercitrin (quercetin 3-O-β-D-glucopyranoside).

Stepwise alkaline hydrolysis gave p-coumaric acid, isoquercitrin (II), and two isoquercitrin monocoumaroates. When compound (I) was subjected to acid hydrolysis, no flavonoid compounds other than quercetin were found.

The PMR spectrum of (I) in deuteroacetone contained the signals of 13 aromatic protons, which were assigned to the quercetin and to two trans-p-coumaric acid residues ($J_{\alpha,\beta}$ = 16 Hz). The positions of attachment of the acyl residues were determined from the chemical shifts and multiplicities of the signals of the carbohydrate protons. Three glucose protons formed a

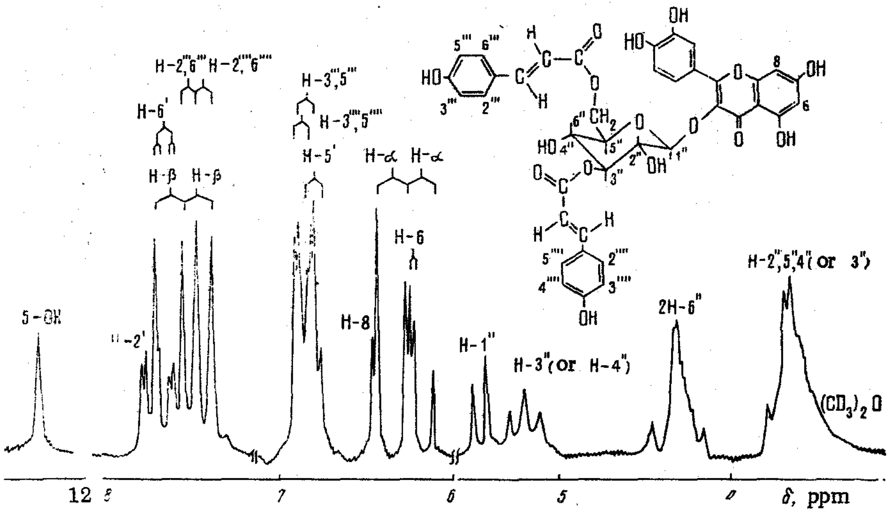

Fig. 1. PMR spectrum of di-O-p-coumaroylisoquercitrin (I) in deuteroacetone.

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group of overlapping signals in the 3.3-3.8-ppm region. The other four protons resonate in a weaker field. The greatest paramagnetic shift was undergone by the signal of the anomeric proton (doublet at 5.45 ppm with J = 8 Hz) corresponding to H-1" of β-D-glucopyranose. A two-proton multiplet with its center at 4.32 ppm belongs to a geminal methylene group (2H-6"). Consequently, one of the p-coumaric acid residues esterifies the 6"-OH group. The position of the second residue can be deduced from the presence of a triplet ($J_1 = J_2 = 9.5$ Hz) at δ 5.2 ppm, the appearance of which is explained by the acylation of the 3"-OH or the 4"-OH group of the glucose. An unambiguous choice between these two positions is impossible on the basis of the available spectral information. However, it may be assumed that structure (I) (see Fig. 1) with the acyl residues in positions 3" and 6" is preferable on the basis of the analogy with the reliably determined structure of other 3",6"-acylated compounds that we have found in the needles of this species of pine.

FLAVONOIDS FROM THE FLOWERS OF *Cirsium oleraceum*

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3-O-Methylkaempferol, apigenin, and luteolin have been isolated previously from the flowers of *Cirsium oleraceum* (L.) Scop. [1]. Continuing a study of the flavonoid composition of this plant, we have isolated and identified another four substances (IV-VII).

Substance (IV), $C_{28}H_{32}O_{14}$, mp 267-260°C, $[\alpha]_D^{20}$ −120° (c 0.65; formamide). From the products of acid hydrolysis we obtained glucose, rhamnose, and an aglycone $C_{16}H_{12}O_5$ with mp 261-263°C (mp of the acetate 202-204°C) which was identified as acacetin.

Substance (V), $C_{29}H_{34}O_{15}$, mp 247-250°C, $[\alpha]_D^{20}$ 92.8° (c 0.6; formamide). From the productes of hydrolysis by sulfuric acid we isolated glucose, rhamnose, and an aglycone $C_{17}H_{14}O_6$ with mp 219-222°C (mp of the acetate 155-156°C), identified as pectolinarigenin.

Substance (VI), $C_{15}H_{10}O_7$, mp 308-310°C (mp of the acetate 199-200°C), was identified as quercetin [2].

Substance (VII), $C_{16}H_{12}O_7$, mp 255-261°C, was identified as 3-O-methylquercetin [3].

From their elementary composition and the products of acid hydrolysis and of alkaline degradation and their UV, IR, and NMR spectra, substances (IV) and (V) were identified as linarin and pectolinarin, respectively.

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