A NEW FLAVONOID FROM SOME SPECIES OF TOADFLAX

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Khimiya Prirodnykh Soedinenii, Vol. 6, No. 1, pp. 128–129, 1970

UDC 547.972

From the herbs of four species of toadflax Linaria vulgaris, L. kurdica, L. Popovii, and L. vulgariformis, we have isolated the total flavonoids with a yield of about 0.6%—pectolinarin and a new crystalline flavonoid glycoside. This flavonoid was obtained by crystallizing the combined material from methanol and ethanol. It has mp 242.5–244° C, $[\alpha]_D^{20}$ −95.9° (c 1; pyridine). Its IR spectrum has absorption bands at, cm^{-1}: 3520, 3290 (phenolic and alcoholic hydroxyls), 1660 (carbonyl of a γ-pyrone ring), 1730 (ester grouping), 1610 and 1580 (vibrations of aromatic systems), and 838 (para substitution in a lateral phenyl group) [1].

Acid hydrolysis yielded the aglycone, $C_{17}H_{14}O_6$, with mp 218–219° C, yield 47.3%; diacetate $C_{21}H_{18}O_8$ with mp 154.5–155° C. From its IR spectrum and to the constants mentioned, we identified the aglycone as pectolinarigenin [2–4]. The acid hydrolysate contained one molecular portion each of glycose and rhamnose, which were identified by paper chromatography and also from the melting points of the ozazones, 204 and 181° C, respectively [2].

To determine the position of attachment of the sugars, the UV spectra of the glycoside and the aglycone were recorded in various media [5–7]. In absolute ethanol, the glycoside exhibited absorption maxima at 328–329 and 277 mμ. A free hydroxy group in position 5 of the glycoside and the aglycone was detected from the bathochromic shift of the maxima in the presence of $AlCl_3$—band I by 18–19 mμ and band II by 19–23 mμ. This was confirmed by the zirconyl/citric acid test [8] and also by the absence of fluorescence of a solution of the glycoside in acetic anhydride [9]. Under the influence of sodium acetate, band I of the spectrum of the aglycone underwent a bathochromic shift of 30 mμ, which shows the presence of a free 7-hydroxy group. This shift was not observed in the glycoside.

Consequently, the pectolinarigenin is glycosidated with the biose in position 7. Fractional hydrolysis with 2% H_2SO_4 in aqueous acetonic solution showed that the terminal sugar is the rhamnose, and the glucose is attached directly to the aglycone.

The glycoside consists of the same structural units and has the same position of attachments of the sugars as pectolinarin [4], but differs from it in respect of its melting point and the presence in the IR spectrum of a band at 1730 cm^{-1}, which is characteristic for the carbonyl of an ester. Saponification under mild conditions led to the formation of acetic acid and a glycoside with mp 257.5–258° C, the IR spectrum of which coincided with that of pectolinarin [4]. The acetic acid was identified by paper chromatography with the diethylamine salt [10] and also by gas-liquid chromatography. A microanalytical determination showed that the substance contained one acetyl group. Thus, the glycoside is monoacetylpectolinarin, the acetyl group being present in the carbohydrate moiety of the molecule.

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18 August 1969