FLAVONOIDS OF Apocynum lancifolium AND A. pictum

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We have previously [1] reported the presence of cardiac glycosides in the roots of A. lancifolium Russan and A. pictum Schrenk. We have found no information on the flavonoid composition of plants of the genus Apocynum in the literature available to us.

To isolate the flavonoids, the comminuted foliage of the above-mentioned plants, which had previously been treated with dry chloroform, was extracted with ethanol. The flavonoids were separated on a column filled with polyamide sorbent. From the foliage of A. lancifolium we isolated a flavonoid glycoside $C_{27}H_{30}O_{16}$ with mp 186-188°C, $[\alpha]_D$ +20° (c 0.1; methanol), $\lambda_{max}^{CH_3OH}$ 360, 265, 258 nm; with CH_3COONa $\Delta\lambda$−+40 nm, with $H_3BO_3 + CH_3COONa$ $\Delta\lambda$−+40 nm; with C_2H_5ONa $\Delta\lambda$−+55 nm; with $ZrOCl_2$ $\Delta\lambda$−+65 nm (the shifts of the first band are shown in all cases). The glycoside was hydrolyzed with 2% sulfuric acid; quercetin ($C_{15}H_{10}O_7$), mp 308-310°C, D-glucose, and L-rhamnose were formed. On stepwise cleavage with 0.1% hydrochloric acid (reaction temperature 80-90°C, time 2 h, check after each 5-10 min) it was possible to obtain the intermediate quercetin β-D-glucoside, $C_{21}H_{20}O_{12}$, with mp 215-217°C. These results show that the substance that we isolated is quercetin 3-L-rhamnosyl-D-glucoside, i.e., possibly, rutin. In actual fact, on paper chromatography in the n-butanol−acetic acid−water (4:1:5) system and in 15% acetic acid, the flavonoid from A. lancifolium migrated at the same level as a sample of rutin from the inflorescences of Sophora japonica L. However, the specific rotation of the compound that we had isolated was positive. Consequently, we consider that the substance is one of the 16 possible isomers of rutin [2], namely neoisorutin recently found in Physochlaina physaloides (family Solonaceae) and having the structure of quercetin 3-O-β-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside [4].

For the flavonoid from A. pictum, $C_{21}H_{20}O_{12}$, mp 220-222°C $[\alpha]_D$ +40° (c 0.1; methanol) $\lambda_{max}^{CH_3OH}$ 360, 267, 260 nm. On the addition of ionizing additives, the 360 nm maximum shifted as follows ($\Delta\lambda$): with CH_3COONa by +35 nm, with $CH_3COONa + H_3BO_3$ by +35 nm, with C_2H_5ONa by +55 nm, and with $ZrOCl_2$ by 55 nm. On hydrolysis with 2% sulfuric acid, the flavonoid split into D-glucose and quercetin. On a paper chromatogram in the n-butanol−acetic acid−water (4:1:5) system, the glycoside from A. pictum appeared at the same level as isoquercitrin. At the same time, the compound that we had obtained differed from isoquercitrin by its strong positive rotation. This is possible only if the D-glucose is attached to the quercetin not by a β but by an α linkage. To determine the size of the oxide ring of the D-glucose, we used the modified method of comparing molecular rotations developed for flavonoids [3]. For the quercetin 3-D-glucoside from A. pictum, $[M]_D \cdot K_P$ is +102°. $[M]_D$ for phenyl α-D-glucofuranosyl is +155° and for phenyl α-D-glucopyranoside +402°. From this it may be suggested that the substance that we isolated had the structure of quercetin 3-α-D-glucofuranoside. The quercetin glycosides found in A. lancifolium and A. pictum attract attention by the unusual nature of their structure and deserve a more detailed study.

LITERATURE CITED

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