

NONTRITERPENOID GLYCOSIDES OF *PATRINIA INTERMEDIA*

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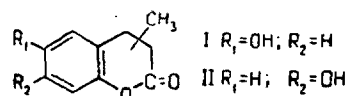
As reported previously, from the roots of *Patrinia intermedia* Roem et Schult we have isolated a glycoside (interoside B) with an unknown aglycone [1]. The IR spectrum of the aglycone clearly showed absorption bands characteristic for aromatic compounds. The fact that the compound was aromatic was also confirmed by its IR and UV spectra (Figs. 1 and 2). The absorption bands at 1735 and 3445 cm^{-1} shows that the aglycone contains a carbonyl and a hydroxy group [2]. The compound does not react with a carbazide or phenylhydrazide, does not reduce Fehling's solution, and readily titrates with alkali, which provided the possibility of determining its molecular weight—180.

The presence of one hydroxy group in the aglycone is shown by the fact that it forms a monoacetyl derivative and a crystalline p-nitrobenzoate. In spite of the fact that the aglycone gives a positive color reaction with tetranitromethane, forms a crystalline dibromide with bromine water, and is readily oxidized by potassium permanganate, it has no double bonds (apart from aromatic ones). Thus, the compound does not titrate with peracetic acid and is not hydrogenated over platinum oxide in acetic acid. The existence of optical activity shows that the aglycone has an asymmetric carbon atom. On the basis of what has been said and the results of elementary analysis, the compound can be given the empirical formula $\text{C}_{10}\text{H}_{10}\text{O}_3$.

To establish the nature of the hydroxy group, the following reactions were carried out. A blue-violet coloration was formed with an aqueous solution of ferric chloride, but the compound did not give such color reactions characteristic for phenols as the phthalein, indophenol, and Lieberman reactions [3]. This can be explained by the fact that these reactions take place only with phenols having an unsubstituted p-position and in this case it may be occupied. The fact that the compound gives a clear reaction with diazotized sulfanilic acid, which can take place with phenols having not only a free p- but also a free o-position, can evidently be explained in the same way.

When the aglycone was treated with an ethereal solution of diazomethane, a liquid monomethyl ether was obtained. However, the acetyl derivative and the p-nitrobenzoate do not react with diazomethane. Consequently, the same hydroxy group takes part in the etherification and acylation reactions. Hence, in the IR spectra of the monomethyl ether and the acetate the same hydroxyl absorption band at 3445 cm^{-1} disappears. Such conditions can be satisfied only by a phenolic hydroxyl. The phenolic nature of the hydroxyl is in agreement with the fact that the aglycone forms a dibromo derivative; the replacement of the two hydrogen atoms in the o-positions take place.

In spite of the marked acidic nature of the compound, the carboxy group in it does not react with diazomethane which is possibly due to the formation of a lactone. Judging from the IR spectrum, this is a δ -lactone (1735 cm^{-1}). On the basis of what had been said above, two possible formulas, (I) or (II), can be put forward for the aglycone.



The choice between these factors was made in the following way. The lithium aluminum hydride reduction of the compound yielded a triol which, in contrast to the initial compound, reduced Fehling's solution, as is characteristic for dihydric phenols, and also gave a positive azo coupling reaction with diazotized sulfanilic acid. Since, according to Griess's rule [3], of dihydric phenols only the meta compounds are capable of undergoing the azo coupling reaction. Formula (2) best explains the properties of the triol obtained.

The position of the methyl group has not yet been determined. It may be present on a tertiary or on a quaternary carbon atom, forming an asymmetric carbon atom in the lactone ring.

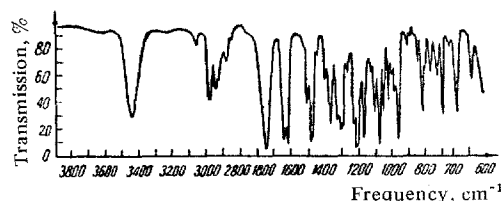


Fig. 1. IR spectrum of the aglycone of interoside B in CCl_4 with compensation.

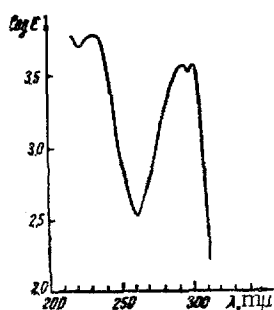


Fig. 2. UV spectrum of the aglycone of interoside B in hexane.

Experimental

The IR spectra were recorded on an IR-10 spectrophotometer in CCl_4 with compensation, and the UV spectra on an SF-4 instrument in hexane.

Hydrolysis of interoside B acetate. [1]. A solution of 0.49 g of the acetate in 20 ml of ethanol and 10 ml of 7% hydrochloric acid was heated in the water bath for 2 hr. The solvent was evaporated off and the solid residue was sublimed in vacuum at 1–2 mm. This gave 0.04 g of the aglycone with mp $78-80^\circ\text{C}$, $[\alpha]_{\text{D}}^{20} -68.5 \pm 3^\circ$ (c 3.94; chloroform). IR spectrum: 3445 cm^{-1} , 3060, 1735, 1640, 1615, 1500, 1480, 1160, 1100, 1080, 960, 805, 730, 685 cm^{-1} ; UV spectrum: λ_{max} 228, 290, 300 m μ (log ϵ 3.78, 3.57, 3.57).

Found, %: C 63.97; H 6.17; mol. wt. 182, 183 (potentiometry). Calculated for $\text{C}_{10}\text{H}_{10}\text{O}_3 \cdot 1/2\text{H}_2\text{O}$, %: C 64.01; H 5.92; mol. wt. 186.

Monomethyl ether. The aglycone (0.1657 g) was treated with 15 ml of an ethereal solution of diazomethane. After a day, the ether was evaporated off and the product was distilled from a flanged flask to give the monomethyl ether of the aglycone. Yield 96%. Mp $110-115^\circ\text{C}/1.5-2\text{ mm}$, $[\alpha]_{\text{D}}^{20} -63.7 \pm 3^\circ$ (c 6.6; chloroform). IR spectrum: 1740 cm^{-1} , 1620, 1480, 1240, 1040, 960, 800, 730, 685 cm^{-1} .

Found, %: C 68.95, 68.82; H 6.29, 6.42. Calculated for $\text{C}_{11}\text{H}_{12}\text{O}_3$, %: C 68.75; H 6.25.

Monoacetate. A solution of 0.1522 g of the aglycone in 2 ml of acetyl chloride was boiled in the water bath for 2 hr. The reaction mixture was poured into 50 ml of ice water, and the product was extracted with ether, dried over sodium sulfate, and distilled in vacuum. The yield of monoacetate was 95%; bp $115-117^\circ\text{C}/2\text{ mm}$, $[\alpha]_{\text{D}}^{20} -57 \pm 3^\circ$ (c 5.8; methanol). IR spectrum: 1760 cm^{-1} , 1615, 1600, 1480, 1248, 1040, 960, 805, 755, 670 cm^{-1} .

Found, %: C 65.58, 65.67; H 5.54, 5.61. Calculated for $\text{C}_{12}\text{H}_{12}\text{O}_4$, %: C 65.44; H 5.49.

p-Nitrobenzoate. A solution of 0.15 g of the aglycone in 4 ml of pyridine was treated with 0.155 g of p-nitrobenzoyl chloride and the mixture was heated in the water bath for 2 hr. Then it was poured into 50 ml of ice water, and the crystals that deposited were washed with water, dried, and recrystallized from 90% ethanol. The yield of p-nitrobenzoate was 96%, mp $123-125^\circ\text{C}$; $[\alpha]_{\text{D}}^{20} -14 \pm 3^\circ$ (c 4.2; chloroform).

Found, %: C 62.58, 62.87; H 4.20, 3.99; N 4.02, 4.26. Calculated for $\text{C}_{17}\text{H}_{13}\text{NO}_6$, %: C 62.40; H 3.98; N 4.28.

Bromination. With stirring, bromine water was added dropwise to a solution of 0.0526 g of the aglycone in 5 ml of a mixture of ethanol and water (4 : 1) until a yellow color appeared. The ethanol was evaporated off and the crystalline product was filtered off, washed with water, dried, and sublimed in vacuum (1–2 mm). The yield of dibromo derivative was 95%, mp $84.5-85.5^\circ\text{C}$, $[\alpha]_{\text{D}}^{20} -68.2 \pm 3^\circ$ (c 6.3; ethanol) UV spectrum: λ_{max} 240, 310, 320 m μ (log ϵ 3.85, 3.78, 3.78); IR spectrum: 3395 cm^{-1} , 3055, 1610, 1475, 1180, 965, 1080, 1100 cm^{-1} .

Found, %: C 35.35, 35.54; H 2.94, 2.78; Br 47.20, 48.16. Calculated for $\text{C}_{10}\text{H}_8\text{Br}_2\text{O}_3$, %: C 35.70; H 2.38; Br 47.60.

Reduction. With stirring, a solution of 1.3593 g of the aglycone in 20 ml of absolute diethyl ether was added to 0.7 g of lithium aluminum hydride in 20 ml of absolute ether, and the mixture was boiled for 6 hr and left for 12 hr. The excess of lithium aluminum hydride and the complex were decomposed by the addition of 80% acetic acid. The reaction product was extracted first with ether (3 \times 20 ml) and then with ethyl acetate. The organic extracts were washed with water, dried over calcined sodium sulfate, and evaporated. This gave 1.35 g of a viscous oil. When an attempt was made to distill it, the product polymerized.

The triol (0.2260 g) was treated with 5 ml of dimethyl sulfate in 30 ml of 30% caustic potash and the mixture was boiled and stirred. The reaction product was extracted with benzene (3 \times 20 ml), washed with water to neutrality, and dried over sodium sulfate. The syrupy product was distilled in a flanged flask at $121-122^\circ\text{C}/2\text{ mm}$. Yield 44%, $[\alpha]_{\text{D}}^{20} 0 \pm 3^\circ$ (c 6.5; chloroform).

Found, %: C 69.20; H 8.77. Calculated for $\text{C}_{13}\text{H}_{20}\text{O}_3$, %: C 69.60, H 8.92.

Conclusions

The structure 7-hydroxy-3- (or -4-) -methyl-3,4-dihydrocoumarin has been proposed for the aglycone of a new glycoside-interoside B-isolated from *Patrinia intermedia* Roem et Schult.

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