A Synthesis of Cinnamoyloxyisoflavones

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Abstract—Interaction of 7-hydroxyisoflavonones with cinnamoyl chloride results in cinnamoyloxyisoflavonones.

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INTRODUCTION

Among natural flavonoids, including isoflavonoids, compounds with a complex structure occur, whose molecules have residues of cinnamic acids. Natural flavonoids were found to contain three common hydroxy-cinnamic acids and sinapic (3,5-dimethoxy-4-hydroxy-cinnamic) acid are attached to antocyanidins, whereas three of them, to carbohydrate fragments of antocyans.

Flavolignans belong to a large class of phenolic natural compounds classified under a common term lignoids. They are flavanoid derivatives containing residues of cinnamic alcohol or other similar fragments attached to phenol hydroxy groups in ring A or B. Medicines on their basis exert beneficial effect on cardiovascular and central nervous systems, have P-vitamin, hepatoprotective, cholagogue, antiatherosclerotic, and other kinds of activity [1-3].

The same wide spectrum of biological activities is intrinsic of the isoflavanoids with cinnamoyl residues attached to phenol hydroxyl groups. Therefore, the synthesis of isoflavones esterified at phenol hydroxyls and close in structure to natural isoflavones is of a particular interest.

RESULTS AND DISCUSSION

We studied the interaction of 7-hydroxyisoflavones (I) and (II) [4, 5] with cinnamoyl chloride in order to obtain 7-cinnamoylisoflavones. As a result, 7-cinnamoyloxyisoflavones (III) and (IV) were formed as shown in scheme.



The structures of the compounds were confirmed by elemental analyses and ¹H NMR spectra. In the spectra, the olefin protons of 7-cinnamoyl substituent appeared as doublets with spin-coupling constant of 15.5 Hz.

Thus, the easy obtaining of isoflavonoid acyl derivatives at their hydroxyl groups allows the synthesis of new interesting compounds.

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EXPERIMENTAL

2-Alkyl-3-(1,4-benzodioxan-6-yl)-7-cinnamoyloxychromones (III) and (IV). A mixture of cinnamic acid (2.96 g, 20 mmol) and phosphorus pentachloride (4.99 g, 240 mmol) was heated in dry toluene for 30 min, phosphorus oxychloride was distilled off, and a solution of the corresponding 7-hydroxyisoflavone (I) or (II) (10 mmol) in pyridine (20 ml) was added. The reaction mixture was kept for 4 h at 100–110°C and poured in 2% aqueous solution of hydrochloric acid (200 ml). The precipitated crystals were filtered, dried, and recrystallized from DMF.

(III); yield 53%; mp 202–203°C; ¹H NMR (DMSOd₆, δ , ppm, J, Hz): chromanone protons: 2.30 (3 H, s, 2-Me), 8.10 (1 H, d, J 8.5, H5), 7.35 (1 H, dd, J 8.5 and 2.5, H6), 7.60 (1 H, d, J 2.5, H8); cinnamoyl protons: 7.96 (1 H, d, J 15.5, α -CH), 6.93 (1 H, d, J 15.5, β -CH), 7.49–7.84 (5 H, m, H2 + H3 + H4 + H5 + H6); protons of 1.4-benzodioxane: 6.80 (1 H, d, J 2.0, H5), 6.75 (1 H, dd, J 7.5 and 2.0, H7), 6.94 (1 H, d, J 7.5, H8), 4.29 (4 H, s, OCH₂CH₂O. Found, %: C 73.60, H 4.6. C₂₇H₂₀O₆. Calc., %: C 73.65, H 4.54.

(**IV**); yield 60%; mp 182–183°C; ¹H NMR (DMSOd₆, δ, ppm, J, Hz): chromanone protons: 1.20 (3 H, t, C**H**₃CH₂), 2.57 (2H, quintet, CH₃C**H**₂), 8.10 (1 H, d, J 8.5, H5), 7.34 (1 H, dd, J 8.5 and 2.5, H6), 7.63 (1 H, d, J 2.5, H8); cinnamoyl protons: 7.95 (1 H, d, J 15.5, α-CH), 6.83 (1 H, d, J 15.5, β-CH), 7.50–7.84 (5 H, m, H2 + H3 + H4 + H5 + H6); protons of 1.4-benzodioxane: 6.78 (1 H, d, *J* 2.0, H5), 6.72 (1 H, dd, *J* 7.5 and 2.0, H7), 6.93 (1 H, d, *J* 7.5, H8), 4.29 (4 H, s, OCH₂CH₂O. Found, %: C 74.05, H 4.8. $C_{28}H_{22}O_6$. Calc., %: C 74.02, H 4.84.

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