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BRIEF COMMUNICATIONS

SYNTHESIS OF 6-O-MONESTERS OF D-GLUCOSE AND AROMATIC ACIDS

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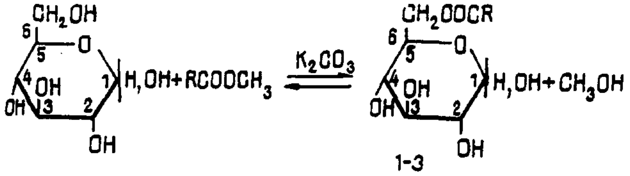
Phenolcarboxylic and cinnamic acids playing an important role in the vital activity of plants are found in nature both in the free state and in the form of glycosides or esters with carbohydrates and alcohol [1].

At the present time the use of natural esters of phenolcarboxylic acids with carbohydrates is limited by their poor accessibility because of the difficulty of isolating them from plants and the complexity of their synthesis (necessity of using protective groups) – the formation of by-products when using acid chlorides and anhydrides [2].

In view of this it appeared of interest to develop a simpler and more accessible method of obtaining water-soluble analogs of natural esters of phenolcarboxylic and cinnamic acids. In the present communication we give information on the synthesis of monoesters of D-glucose with phenolcarboxylic and cinnamic acids.

We obtained monoesters of D-glucose and aromatic acids by the transesterification of the methyl esters of the acids concerned and D-glucose in dimethylformamide in the presence of K_2CO_3.



1-3

R_1–H R_1–OH α; R_2–OH
R_1–OH β; R_2–H
1. R–C_6H_4(*o*-OH); 2. R–C_6H_3—(2.4-OH); 3. R–C_6H_5CH–CH

TABLE 1. Indices of the UV, IR, and PMR spectra of 6-O-Monoesters of D-glucose (1-3)

Compound	UV spectrum, λ_{max}, nm (log ε)	IR spectrum, cm^{-1}	PMR, δ, ppm (0 — HMDS, C_5D_5N)
1. $C_{13}H_{16}O_8$	238(3.87) 307(3.69)	1690(C=O) 1490, 1500, 1585(C=C) 3000—3600(OH)	4—5.9 (7H glue .) 5.3(d, J=8 Гц), H-1 β-anomer) 5.9 (d, J=4 Гц, H-1 α-anomer) 6.5 (4H—OH) 7—7.8 (4H, Ar)
2. $C_{13}H_{16}O_9$	209(4.18) 260(3.93) 299(3.63)	1720(C=O) 1500— 1620(C=C) 3200—3500(OH)	3.4—5.0 (7H gluc.) 5.8 (4H, OH) 6.7—8.3 (3H, Ar)
3. $C_{15}H_{18}O_7$	205(4.33) 216(4.23) 222(4.15) 277(4.19)	1720(C=O) 1500—1620(C=C) 3200—3600(OH)	3.5—5.0 (7H gluc.) 6.1 (4H—OH) 6.4—8.8 (5H arom,) 6.5 d (1H J=15 Hz) 7.25 d (1H J=15 Hz)

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The reaction of D-glucose with methyl salicylate and 2,4-dihydoxybenzoate led to the desired products (1) and (2) with yields of 42 and 7%, respectively. On the interaction of methyl cinnamate with D-glucose the yield of the monoester (3) amounted to 15%. Products (1-3) were isolated chromatographically on a column of silica gel in the chloroform–ethanol (4:1) system.

The 6-O-monoesters of glucose with cinnamic and 2,4-dihydroxybenzoic acids were light brown microcrystalline substances, and the 6-monosalicylate formed colorless hygroscopic crystals. These monesters were readily soluble in water, alcohol, DMFA, and DMSO, and insoluble in benzene and chloroform. Details of the UV, IR and PMR spectra of the compounds synthesized are given in Table 1.

The ^{13}C NMR spectra confirmed that it was mainly the primary hydroxy group of the D-glucose that had been acylated, since the carbon atom in the α-position to the ester group (C-6) was descreened by 3.4-3.8 ppm and that in the β-position (C-5) was screened by 1.5-2.5 ppm as compared with unsubstituted D-glucose.

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