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MODIFICATION OF POLYPRENOLS FROM COTTON LEAVES. ACYLATION BY MONOBASIC ACID ANHYDRIDES

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Polyprenols (PP) are potential biologically active compounds. Syntheses of long-chain PP require many steps [1, 2]. Therefore, it seemed advisable to find available natural sources for their preparation. From this viewpoint, cotton leaves (*Gossypium hirsutum*, Malvaceae), which contain PP (**1**) in the free state [3], are of interest in Uzbekistan.

PP from cotton are isoprene homologs with 10-13 isoprene units, undecaprenol (n = 11) being the dominant one. Depending on the cotton variety and line, the PP content varies from 1 to 4% of the air-dried plant mass. The fraction of undecaprenol in the PP fraction reaches 80%. Tridecaprenol is present in trace quantities [4]. The accumulation of PP is maximum during ripening. This makes them accessible.

PP fractions were isolated from *G. hirsutum* leaves by extracting dry leaves with ethanol, carrying out alkaline hydrolysis, and re-extracting with hexane to obtain the neutral part. The extract was separated further using column chromatography to obtain PP [3, 4]. Development of this method using accessible raw material enabled PP to be isolated in quantities sufficient to study their modification.

Despite many publications on the isolation and synthesis of PP [1, 2, 5, 6], little has been published on their chemical transformations [7, 8]. Transformation is usually carried out to establish the PP structure or to prepare their derivatives as potential biologically active substances. In particular, the geranyl ester of farnesylacetic acid and solanesylacetic and decaprenylacetic acids are known to possess antiulcer activity [9].

We studied previously the reaction of cotton PP with anhydrides of dibasic acids [10].

In this communication, we report results from the acylation of PP from cotton leaves by anhydrides of monobasic acids (acetic, propionic, butyric, and benzoic anhydrides).

The reaction with acetic anhydride was carried out in pyridine at room temperature with stirring. The reaction proceeded rather quickly, producing PP acetate (**2**) in 69% yield.

$$\text{H-(CH}_2\text{-CMe=CH-CH}_2\text{)n-OH+(RCO)}_2\text{O} \rightarrow \text{H-(CH}_2\text{-C=CH-CH}_2\text{)n-O-COR+ROOH}$$

$$n = 10\text{-}13;\ R = \text{CH}_3,\ (\mathbf{2})\ \text{CH}_3\text{-CH}_2\ (\mathbf{3});\ \text{CH}_3\text{-(CH}_2)_2\ (\mathbf{4});\ \text{C}_6\text{H}_5\ (\mathbf{5}).$$

The reactions with propionic and butyric anhydrides were less favorable, i.e., heating of PP with the acid anhydrides for 2 h in benzene was required. The products **3** and **4** were obtained in 52 and 40% yield, respectively. The reaction with benzoic anhydride proceeded analogously to that described above at the boiling point of benzene. However, heating for 4 h was required to complete it. Further separation over a silica-gel column gave PP benzoate in 58% yield. The course of the reaction and the purity of the products were monitored by TLC. The structures of the resulting compounds were proved by IR and mass spectra.

IR and PMR spectra of **2** agree with those of PP acetates with 7-9 PP units that were isolated from birch leaves [8].

IR spectrum (KBr, ν, cm^{-1}): **2**: 1740 (CO), 1240 (–C–O–C–), 1450, 1380 (CH_3–CH_2), 1666 (isoprenol C=C); **3**: 1739 (CO), 1272 (–C–O–C–), 1451, 1380 (CH_3–CH_2), 1668 (isoprenol C=C); **4**: 1733 (CO), 1270 (–C–O–C–), 1450, 1382 (CH_3–CH_2), 1668 (isoprenol C=C); **5**: 1726 (CO), 1270 (–C–O–C–), 1451, 1380 (CH_3–CH_2), 1666 (isoprenol C=C).

The mass spectra of the synthesized compounds contained peaks for the corresponding molecular ions $[M]^+$ 740 (40.2), 808 (65.0), 876 (42.4), and 944 (12.1) and characteristic ions $[M - Ac]^+$ 698 (19.6), 766 (23.3), 834 (18.0), 902 (9.6);

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$[M - AcOH]^+$ 680 (98.0), 748 (100), 816 (36.5), 884 (13.3), etc. (**2**); $[M]^+$ 754 (36.2), 822 (53.2), 890 (32.2), 958 (10.8) and characteristic ions $[M - Ac]^+$ 698 (17.2), 766 (22.8), 834 (19.1), 902 (9.8); $[M - AcOH]^+$ 680 (82.8), 748 (100), 816 (34.5), 884 (10.3), etc. (**3**); $[M]^+$ 768 (28.8), 836 (60.5), 904 (34.8), 972 (8.8) and characteristic ions $[M - Ac]^+$ 698 (14.3), 766 (26.8), 834 (22.9), 902 (9.2); $[M - AcOH]^+$ 680 (90.8), 748 (100), 816 (30.1), 884 (12.3), etc. (**4**); $[M]^+$ 802 (29.8), 870 (56.8), 938 (33.7), 1006 (10.8) and characteristic ions $[M - Ac]^+$ 698 (16.4), 766 (34.2), 834 (24.4), 902 (10.6); $[M - AcOH]^+$ 680 (85.8), 748 (100), 816 (37.5), 884 (12.3), etc. (**5**).

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