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ACYLATION OF POLYPRENOLS BY ANHYDRIDES OF DIBASIC ACIDS

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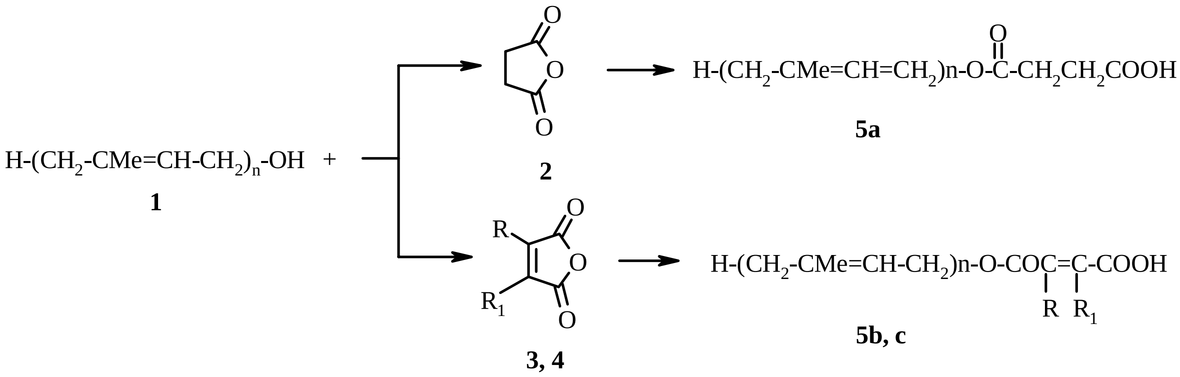
Interest in polyprenol (PP) derivatives is rising because they are mildly toxic and are used in various biologically active preparations [1-3]. Thus, compounds with antiviral, immunotropic, and other properties are based on them [4, 5].

In continuation of research on the chemical transformation of PP (**1**) with 10-13 isoprene units that were isolated from cotton leaves, we reacted **1** with cyclic anhydrides of dibasic acids such as succinic (**2**), maleic (**3**), and phthalic (**3**).

These reactions were expected to form mono- (**5**) and diprenyl esters (**6**) of the dicarboxylic acids. These acid anhydrides were reacted with **1** with stirring and boiling in absolute benzene in the presence of catalytic amounts of dry pyridine. The reactions were complete in 2-6 h depending on the nature of the anhydride. We noted formation of only monoprenyl esters of the dicarboxylic acids (**5a-c**).



3, 5b: $R = R_1 = H$
4, 5c: $R + R_1 = (CH=CH)_2$

The reaction with succinic anhydride was complete in 2 h with formation of **5a** in 82% yield.

The reactions with maleic and phthalic anhydrides proceeded more difficultly, i.e., heating of **1** with the acid anhydrides for 6 h is required. Products **5b** and **5c** were obtained in yields of 52 and 48%, respectively. The purity of the products was monitored using TLC.

IR spectrum (ν, cm^{-1}) of **5a**: 1739 (C=O weak band), 1715 (C=O in CO_2H), 1168 (C–O–C), 1477, 1377 (CH_3–CH_2), 2963 (CH in CH_3), 2927 (CH in CH_2), 1668 (C=C in isoprenoid unit); of **5b**: 1732 (C=O weak band), 1712 (C=O in CO_2H overlaps with C=O weak band), 1166 (C–O–C), 1448, 1377 (CH_3–CH_2), 2962 (CH in CH_3), 2926 (CH in CH_2), 1660 (C=C in isoprenoid unit); of **5c**: 1732 (C=O weak band), 1705 (C=O in CO_2H), 1211 (C–O–C), 1448, 1377 (CH_3–CH_2), 2962 (CH in CH_3), 2926 (CH in CH_2), 1668 (C=C in isoprenoid unit). The IR spectra of **5a-c** lack an absorption band at 3333 cm^{-1} that is characteristic of the hydroxyl in the starting compound. An absorption band for carboxyl OH appears near 3560 cm^{-1}.

The PMR spectra of **5a-c** give signals for $=C\underline{H}CH_2O$, $=C\underline{H}CH_2C$, $=CC\underline{H}_2$, and *trans*- and *cis*-CH_3 groups that are practically identical with those of the starting polyprenol. In contrast with polyprenol, the methylene protons of $=CHC\underline{H}_2O$ shift to weaker field. Thus, they appear for **5a** at 4.58 ppm (d, J = 7 Hz); for **5b**, at 4.76 ppm (d, J = 7 Hz); for **5c**, at 4.87 ppm (d,

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J = 7 Hz). These protons in polyprenols have chemical shifts near 3.97 ppm (d, J = 7 Hz). It should be noted that a similar chemical shift was observed for moraprenol [6]. The =CHC$\underline{H}_2$O protons also shift for polyprenol acetate (4.50 ppm, d, J = 7 Hz). Such a shift is probably explained by the effect of the electron-accepting acyl group.

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