THE DEHYDRATION OF MARMESIN WITH PHOSPHORUS PENTOXIDE

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The dehydration of marmesin (I) and its optical isomer nodakenetin with phosphorus pentoxide to form anhydromarmesin has been described as a characteristic reaction for the compounds mentioned [1-3]. We have used this reaction to show the structure of the carbon skeleton of the molecule of seseliflorin as 5'-[1-methyl-1-(trans-3-methylthioacryloyloxy)ethyl]-4',5'-dihydrofuro-2',3':7,6-coumarin [4].

It was observed that, in addition to anhydromarmesin, during the reaction an intermediate compound (II) was formed which disappeared completely with an increase in the reaction time, and the sole final product was anhydromarmesin. Compound (II) was isolated from the reaction mixture formed by heating 1.0 g of marmesin with 5.0 g of P_2O_5 in 50 ml of chloroform in the water bath for 1 h, this mixture containing the starting material, anhydromarmesin, and substance (II). The elementary analysis of (II) indicated the composition $C_{14}H_{12}O_3$ (corresponding to the loss of one molecule of water), mp 117-118°C. The IR spectrum lacked the absorption band of a hydroxyl. The nature of the UV spectrum of (II) (λ_{max}, nm: 205, 224, 248.5, 259, 301 (inflection), 335; log ε 4.57, 4.07, 3.67, 3.58, 3.81, 4.24) shows the retention of the structure of the dihydrofuran ring. The structure of (II) was established definitively by an analysis of its NMR spectrum (Fig. 1). In the region of aromatic protons the pattern characteristic of 6,7-disubstituted coumarins was observed (H_3 and H_4: δ 6.02 and 7.41, doublet, $J = 9.7$ Hz; H_5 and H_8: δ 7.09 and 6.63, singlet). In addition, the spectrum contained the signals of protons forming an ABX system (δ_A 3.01, δ_B 3.35, δ_X 5.52; $J_{AB} = 15.4$ Hz, $J_{AX} = 7.8$ Hz, $J_{BX} = 9.2$ Hz), the signals of two protons of a $>C = CH_2$ group (δ_1 4.90, δ_2 5.06, broadened signals appearing in the form of singlets), and the signal of a methyl group on

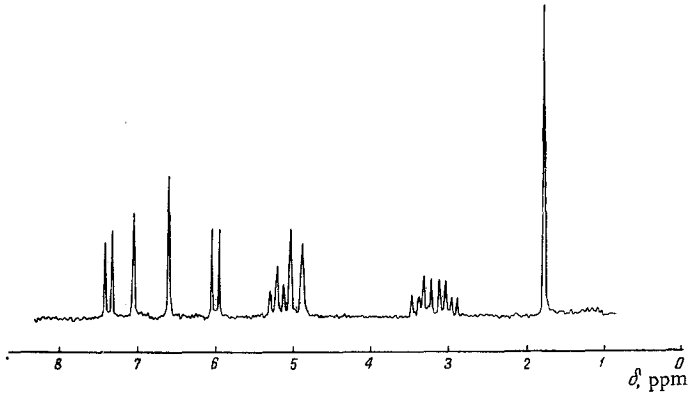

Fig. 1. NMR spectrum of the intermediate product of the dehydration of marmesin (II) in CCl_4 (HA-100D instrument, 100 MHz, 0 – TMS).

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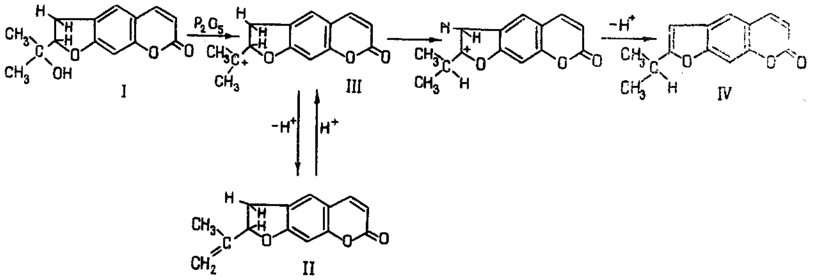
a double bond (1.77 ppm, 3H). Between the protons of the methyl and methylene groups long-range spin-spin coupling with a constant of ~1 Hz was observed, and this was confirmed by the double-resonance method, the signal at 4.90 ppm being split to the greater extent. This enables it to be assigned to a proton in the transposition to a CH_3 group. The existence of long-range spin-spin coupling (≈1.2 Hz) between the A and B protons of the ABX system, on the one hand, and H_5, on the other hand, was established similarly. Long-range coupling between the X proton and the protons of the methyl group was also found qualitatively by double resonance. The results obtained suggest for (II) the structure of 5'-isopropenyl-4',5'-dihydrofuro-2',3':7,6-coumarin. On being heated with a tenfold amount of phosphorus pentoxide in benzene for 2 h at the boil, substance (II) was converted quantitatively into anhydromarmesin (IV).

Thus, the formation of anhydromarmesin may take place both directly from marmesin and also from substance (II) through an intermediate carbonium ion (III) according to the well-known mechanism for the dehydration of alcohols [5] in the following way:



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