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THE COUMARIN DIVERSIN FROM THE ROOTS OF FERULA DIVERSIVITTATA

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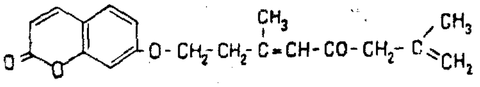
On prolonged storage of the resin isolated from the roots of F. diversivittata uniform slightly yellowish crystals appear with mp 97–98.5° C (from aqueous ethanol), R_f 0.53 (Al_2O_3, activity grade II, $CHCl_3$), composition $C_{19}H_{20}O_4$, mol. wt. 312 (mass spectrometrically). Yield 10%.

UV and IR spectra show that this substance is a coumarin derivative. When it was dissolved in caustic potash or sulfuric acid, a stable blue fluorescence appeared and when it was heated (0.2 g) in 2 ml of acetic acid and 0.5 ml of sulfuric acid umbelliferone with mp 233° C was obtained. The substance is apparently new and has been called diversin. The fourth oxygen atom of diversin is probably located in an aliphatic chain in the form of a CO group (IR spectrum – band at 1670 cm^{-1}). This was established by hydrogenating diversin with platinum oxide in ethanol. On hydrogenation, the hydrogen corresponding to approximately two double bonds was taken up: tetrahydrodiversin $C_{19}H_{24}O_4$ was obtained with mp 37–38.5° C (from aqueous ethanol), $[\alpha]_D$ $-8°$ (c 7.1; chloroform). The IR spectrum has a maximum at 1710 cm^{-1} (CO group of a ketone).

These results permit the assumption that the maximum in the IR spectrum of diversin at 1670 cm^{-1} corresponds to a conjugated keto group. In actual fact, when tetrahydrodiversin was cleaved with sulfuric acid (20 minutes heating to 60° C in acetic acid solution), a mixture of products readily soluble in ether was formed. Umbelliferone was extracted from the ethereal solution by shaking it with alkali; the products insoluble in the alkali proved to be a mixture of two substances. One of them with R_f 0.65 (Al_2O_3, activity grade II, ether) n_D 1.4470 is apparently a ketol; in the UV spectrum there is a maximum at 286 mμ (log ε 1.2) and in the IR spectrum peaks at 1716 and 3400 cm^{-1}. Peaks corresponding to the coumarin nucleus are not shown.

We assumed that the aliphatic chain of diversin has a structure of the myrcene type. However, the exhaustive hydrogenation of diversin in the presence of platinum oxide in acetic acid did not give 2,6-dimethyloctane as the end-product, although the substances formed contained an isopropyl group (bands at 1170 and 1380 cm^{-1}). The hydrogenation of diversin formed umbelliferone (traces), and the side chain was represented by mixtures of small amounts of a diol, a ketol, an alcohol, and a ketone possessing a strong unpleasant odor.

At the same time, the NMR spectrum of diversin, taken on a spectrometer with a working frequency of 60 MHz, has two singlet signals of tertiary vinyl-methyl groups with τ 8.1 (3H) and 7.82 (3H) and a doublet signal with τ 7.97 (2H). Moreover, in the τ 3.8 ppm region there is a signal with a total area of somewhat less than three protons superposed on the proton at C_3 of the coumarin nucleus. These features of the NMR spectra agree well with structure (I) proposed for diversin. The CH_2O group is possibly responsible for the signal at τ 5.8 (2H) and the CH_2 group adjacent to it appears in the form of two triplets (each 1H) at τ 6.9 and 7.35. It is not excluded that diversin contains a small amount of the isomer (II) without a terminal methylene group:



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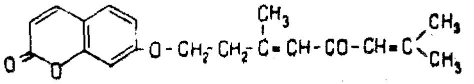

II

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