3-O-METHYLKAEMPFEROL FROM THE FLOWERS OF Cirsium arvense

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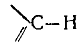
Continuing a study of the flavonoid composition of the flowers of Cirsium arvense L. (Canada thistle) [1], we have isolated from the ethereal fraction an individual substance C with the composition $C_{16}H_{12}O_6$, mp 290-292°C (ethanol) in the form of yellow acicular crystals soluble in ethyl ether and in methanol and ethanol.

In the Bryant flavonoid reaction [2], the colored pigment passed into the octanol, which shows the aglycone nature of this compound. This was also confirmed by the value of $D_{1\%}^{1\,\mathrm{cm}}$ of 537.

On paper in UV light a brown spot appeared, which permits the assumption that the substance has the nature of a flavone or a 3-substituted flavonol.

The UV spectrum of the substance studied showed absorption maxima at 351 and 268 nm. In the presence of sodium acetate a bathochromic shift of the maximum of the long-wave band by 17 nm was observed, which shows the presence of a free hydroxy group in position 7. With sodium acetate and boric acid there were no bathochromic shifts, which confirms the absence of an o-dihydroxy grouping in the 3',4' position. Sodium methoxide produced a bathochromic shift of the long-wave maximum by 49 nm and of the short-wave band by 8 nm. The latter is characteristic for a hydroxy group in position 4'. Zirconium nitrate gave a bathochromic shift of the maximum of the long-wave band by 55 nm and one of the short-wave band by 12 nm which disappeared on the addition of citric acid. This circumstance shows the presence of a hydroxy group in position 5.

Thus, substance C, according to UV spectroscopy, has free hydroxy groups in the 4', 5, and 7 positions. This is in harmony with the fact that the products of alkaline degradation contain phloroglucinol and p-hydroxybenzoic acid.

The IR spectrum of substance C had the following absorption bands (cm^{-1}): 3150, 2940, 2870 (stretching vibrations of OH groups), 1650 (stretching vibrations of a carbonyl group), 1570, 1610 (stretching vibrations of =C=C groups), and 845, 855, 870 (nonplanar deformation vibrations of the  groups of a benzene ring) [3, 4].

In the NMR spectrum of substance C a doublet at 7.88 ppm (2 H), J = 8 Hz, corresponds to the 2',6' protons, a doublet at 6.80 ppm (2 H), J = 8 Hz, to the protons in the 3'5' position, and doublets at 6.26 and 6.14 ppm each with an intensity of 1 H, J = 2.5 Hz, are due to the signals of the protons in positions 8 and 6, respectively. A singlet at 3.87 ppm with an intensity of 3 H corresponds to a methoxy group. The absence of the signal of the proton in position 3 confirms the presence of a methoxy group in this position.

On the basis of its IR, UV, and NMR spectra, the product of the demethylation of substance C was identified as kaempferol, which was one more proof of its identity as 3-O-methylkaempferol [5].

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