THE STRUCTURE OF PRANFERIN – A NEW COUMARIN FROM THE ROOTS OF Prangos ferulaceae

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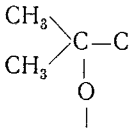
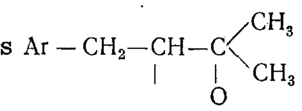
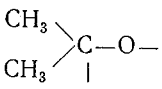
As recently reported [1], a new coumarin $C_{18}H_{22}O_5$, mp 167.5-169°C, which has been called pranferin, has been isolated from the roots of Prangos ferulaceae (L.) Lindl. On the basis of spectral and chemical characteristics structure I was proposed for it. No substance of a similar type has been found in plants previously.

The correctness of the proposed structure caused us doubt for the following reasons. On the one hand, it was in contradiction to biogenetic considerations and, in particular, to the isoprene rule (gem-trimethyl group, two chains of four carbon atoms); and on the other hand an unusually low value of the protons of the CH_3CO group was found in the NMR spectrum of pranferin (δ 1.43 ppm).

In its elementary composition, pranferin differs from the coumarin closest biogenetically – meranzin $C_{15}H_{16}O_4$, which contains an isopentenyl chain and is present in this plant – by a C_3H_6O group. Probably the signal with δ 1.43 ppm (3 H) in the NMR spectrum of pranferin is due to the methyl protons not in a $CH_3C=O$ group but in a CH_3-C-O- group. Thus, in the molecule of the substance there are four C-methyl groups, of which at least two are present in the fragment  $\mathrm{(CH_3)_2\underset{\underset{\underset{|}{O}}{|}}{C}-C}$ (δ 1.43 and 1.29 ppm). The signals of methyl groups in the form of singlets show that they are present on quaternary carbon atoms. This permits the assumption that pranferin contains the groupings  $\mathrm{Ar-CH_2-\underset{|}{CH}-\underset{\underset{O}{|}}{C}(CH_3)_2}$ and  $\mathrm{(CH_3)_2\underset{|}{C}-O-}$ and is, apparently, an acetonide of meranzin hydrate (V). The chemical shifts of the methyl groups of pranferin are close to those of the acetonide of foliosidine [2].

To check this hypothesis, we have performed the synthesis of pranferin starting from osthole, which we isolated from the roots of Prangos pabularia Lindl. Osthole (II) was oxidized with peracetic acid, as a result of which we obtained its oxide with mp 105-105.5°C (III), which was then subjected to hydration by a known method [3]. We isolated a substance with mp 118-119°C identified by its IR spectrum as meranzin hydrate (IV), which has been described in the literature [3, 4]. When an acetone solution of the substance was acidified with sulfuric acid (at room temperature), the acetonide (V) $C_{18}H_{22}O_5$, with mp 167.5-169°C (from acetone), mol. wt. 318 (mass spectrometrically), was obtained.

A comparison of the IR, UV, NMR, and mass spectra of pranferin and the acetonide of meranzin hydrate showed that they were identical. The acid hydrolysis of the acetonide formed the coumarin (VI) with the composition $C_{15}H_{16}O_4$, mp 65-66°C (from petroleum ether), shown to be identical by its IR spectrum and a mixed melting point with isomeranzin (VI), and the volatile fraction of the hydrolysate yielded acetone (2,4-dinitrophenylhydrazone with mp 123-124°C). The reduction of the acetonide with sodium tetrahydroborate gave a product with mp 100-102°C (from petroleum ether).

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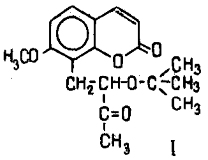
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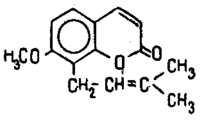
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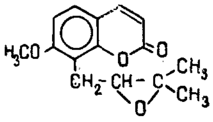
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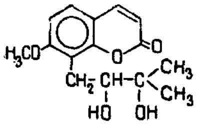
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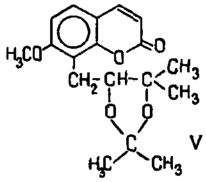
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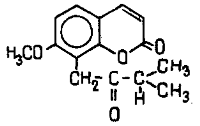
VI

Thus, the structure of pranferin and the products of its conversion proposed previously are not in agreement with the facts. Pranferin must be considered as the acetonide of meranzin hydrate (V). Unfortunately, the authors who isolated pranferin do not give the R_f values of the initial mixture of coumarins, and therefore it does not appear possible to answer the question of whether the substance is a native product or an artifact.

EXPERIMENTAL

The IR spectra were taken on a UR-10 spectrophotometer (paraffin oil), the UV spectra on a Hitachi spectrophotometer, the NMR spectra on a JNM-4H-100/100 MHz instrument (with HMDS as internal standard) in $CDCl_3$, and the mass spectra on an MKh-1303 mass spectrometer fitted with a system for the direct introduction of the substance into the ion source at an ionizing potential of 40 eV.

Osthole oxide and osthole oxide hydrate (meranzin hydrate) were obtained by published procedures [3, 4].

Preparation of the Acetonide of Meranzin Hydrate. A solution of 0.1 g of meranzin hydrate in 10 ml of acetone was treated with 1 ml of conc. sulfuric acid, and the mixture was left for a day. Then it was diluted with water (1 : 2) and treated with ether. After drying with sodium sulfate, the ethereal solution was distilled. Crystals deposited with mp 167.5-169°C (from acetone).

Hydrolysis of the Acetonide. A. Preparation of Acetone 2,4-DNPH. A mixture of 0.12 g of the acetonide and 20 ml of 10% sulfuric acid was heated on the sand bath for 6 h. The volatile fraction was trapped in a 0.1% ethanolic solution of 2,4-dinitrophenylhydrazine. After recrystallization from ethanol, the crystals that separated out had mp 123-124°C and gave no depression in admixture with acetone 2,4-dinitrophenylhydrazone.

B. Preparation of Isomeranzin. The acid solution after hydrolysis was diluted with water (1 : 1) and shaken with ether. The ethereal extract was concentrated, and a substance with mp 65-66°C (petroleum ether) was isolated.

Reduction of the Acetonide. A solution of 0.1 g of the acetonide in 30 ml of methanol was treated with 0.15 g of sodium tetrahydroborate, and the mixture was left for three days. Then it was acidified with 10% sulfuric acid and treated with ether. After evaporation of the solvent, crystallization of the residue from petroleum ether yielded a substance with mp 100-102°C.

SUMMARY

The structure proposed previously for the coumarin pranferin has been corrected on the basis of synthesis, spectral studies, and conversion products. It has been established that pranferin is meranzin hydrate acetonide.

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