SESELIFLORIN, A NEW COUMARIN FROM Seseli sessiliflorum

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From a methanolic extract of the roots of Seseli sessiliflorum Schrenk. by chromatography on KSK silica gel we have isolated a new coumarin with the composition $C_{18}H_{18}O_5S$, mp 142-144°C, $[\alpha]_D^{19} - 58.4°$ (c 0.85, chloroform) which we have called "seseliflorin" (I). The fact that it belongs to the class of coumarins is in accordance with its UV spectrum (λ_{max}, nm: 224, 249, 260; 292; 296, and 334; log ε 4.10, 3.77, 3.84, 4.26, 4.26, 4.27) and its IR spectrum [1730 cm^{-1} (C=O of an α-pyrone) and 1635 and 1565 cm^{-1} (−C=C− bond of a coumarin nucleus)] (Fig. 1). A strong absorption band at 1700 cm^{-1} shows that seseliflorin is an ester, which is confirmed by its capacity for hydrolysis.

Acid methanolysis of I gave a hydroxylactone $C_{14}H_{14}O_4$ (II) with mp 187-189°C, $[\alpha]_D^{19} + 12°$ (c 0.8, chloroform), whose NMR spectrum was identical with that of marmesin [1]: H_3, doublet (1H), δ 6.19, J = 10.0 Hz; H_4, doublet (1H), δ 7.59 J = 10.0 Hz; H_5, singlet (1H), δ 7.23; H_8, singlet (1H), δ 6.71; $2H_4'$, doublet (2H), δ 3.22, J = 9.0 Hz; H_5, triplet (1H), δ 4.75, J = 9.0 Hz; OH, broadened singlet (1H), δ 1.98; and gem-dimethyl group, singlets at 1.39 and 1.26 ppm (3H each).

When the IR spectra of II and of marmesin taken in the form of mulls in paraffin oil are compared, complete coincidence of the absorption bands in the region of characteristic frequencies (3500-1500 cm^{-1}) is observed, with some difference in the long-wave part of the spectra. This fact, and also the different values of $[\alpha]_D$ for marmesin (+26.8°, chloroform) [2] and II (+12°, chloroform) show that II is a mixture of optical isomers of 5'-(1-hydroxy-1-methylethyl)-4',5'-dihydrofuro-2',3':7,6-coumarin. This hypothesis is confirmed by the identity of the IR spectra of chloroform solutions of II and marmesin.

The dehydration of II by heating it with P_2O_5 in benzene led to the formation of anhydromarmesin, which also confirms the structure of the coumarin part of the molecule I.

The composition of the acid residue of I, C_4H_5OS, is derived from a comparison of the empirical formulas of I and II, and its structure from a comparison of the IR and NMR spectra of I and II (Fig. 2a and 2b). In the IR spectrum of II the absorption band at 1700 cm^{-1} disappears, and in its NMR spectrum the singlet at 2.36 ppm (3H) and the doublets with δ 5.71 and 7.00 ppm (1H each), J = 10.0 Hz, disappear, which shows that these spectral features are due to the acid residue and unambiguously that its structure is that of 3-methylthioacryloyl, $CH_3-S-CH=CH-CO-$.

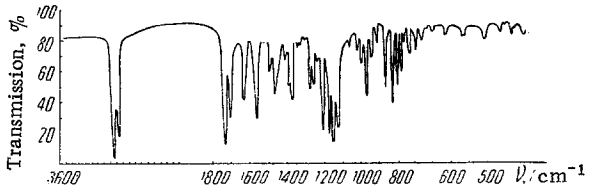

Fig. 1. IR spectrum of seseliflorin (mull in paraffin oil).

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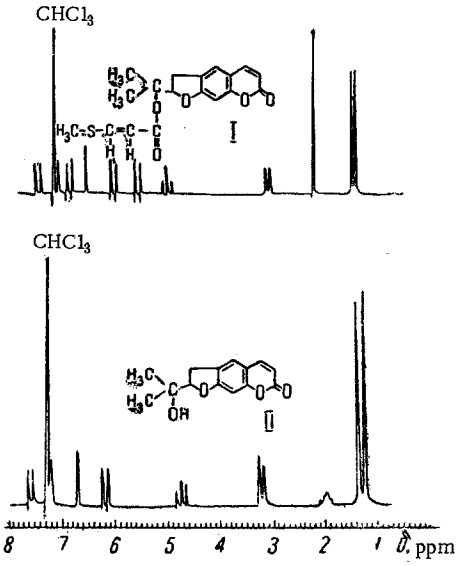

Fig. 2. NMR spectrum of seseliflorin (I) and its hydrolysis product (II).

In 3'-angeloyloxy-2',2'-dimethyl-4'-(trans-3-methylthioacryloyloxy)-3',4'-dihydropyrano-5',6':8,7-coumarin, floroselin [3], the identical acyloxy group has the trans configuration. The equality of the coupling constants of the olefinic protons in the 3-methylthioacryloyloxy group of seseliflorin, floroselin, and the chromone seselirin, which we have isolated from the roots of the same plant Seseli sessiliflorum Schrenk. [4], leads to the conclusion that the configuration of the acid residue is the same in all three compounds.

Thus, I is 5'-[1-methyl-1-(trans-3-methylthioacryloyloxy)ethyl]-4',5'-dihydrofuro-2',3':7,6-coumarin.

EXPERIMENTAL

The UV spectrum was taken on an SF-4A spectrophotometer, the IR spectrum on a UR-10 instrument (mulls in paraffin oil and solutions in chloroform), and the NMR spectra on a HA-100D (100 MHz) instrument in $CDCl_3$ (internal standard, TMS). The mass-spectrometric determination of the molecular weight was carried out by P. I. Zakharov, the NMR spectra were taken by O. G. Rud, the IR and UV spectra by A. A. Kir'yanov, and the microanalyses were performed by E. A. Nikonova. The elementary analyses of all the compounds corresponded to the calculated figures.

Isolation of Seseliflorin. A 1.2-kg sample of the dried and comminuted roots of Seseli sessiliflorum Schrenk. was extracted with methanol (3 × 5 liters). The combined extracts (10.8 liters) were evaporated to 220 ml, diluted with a double volume of water, and treated with ether (10 × 250 ml). The ethereal extracts were washed with 5% sodium carbonate solution (5 × 100 ml), and then with water (3 × 100 ml), and dried over Na_2SO_4, and the solvent was evaporated off in vacuo. The oily residue (67.0 g) after the separation of the floroselin [3] was chromatographed on a column filled with KSK silica gel (d = 7.5 cm, h = 34 cm). The eluent was a mixture of petroleum ether and ethyl acetate with a gradually increasing concentration of the latter. The 25th-29th fractions [eluent, ethyl acetate–petroleum ether (15 : 85)] yielded 0.5 g of a crystalline substance with mp 142-144°C (from ethanol), $[\alpha]_D^9$ − 58.4°,(c 0.85, chloroform). Found %: C 62.66, 62.77; H 5.38, 5.30; S 8.93, 9.03. mol. wt. 346 (mass spectrometry). $C_{18}H_{18}O_5S$. Calculated %: C 62.42; H 5.24; S 9.25. mol. wt. 346.32.

Acid Methanolysis of I. A mixture of 0.1 g of seseliflorin and 30 ml of 2N HCl in methanol was heated in a water bath for 10 h. The reaction was monitored by paper chromatography. After the methanolysis ended, the reaction mixture was diluted with a double volume of water, and the methanol was distilled off in vacuo. Crystals deposited in the form of fine colorless needles, $C_{14}H_{14}O_4$, mp 187-189°C (after vacuum sublimation on heating in a bath of Wood's metal at 160-165°C), $[\alpha]_D^{19}$ + 12° (c 0.8, chloroform). The IR spectra of II and of an authentic sample of marmesin in the form of solutions in chloroform were identical. On paper chromatography in a system of butan-1-ol saturated with 1.5 N NH_3 followed by treatment with a 0.2% ethanolic solution of bromphenol blue, an acid with R_f 0.24 which was identical with the trans-2-methylthioacrylic acid isolated by us previously from floraselin was found among the reaction products.

Dehydration of II. A solution of 0.02 g of II in 10 ml of benzene was treated with 0.2 g of P_2O_5 and heated in a water bath for 3 h. Then the P_2O_5 was filtered off,and the solvent was distilled off in vacuo. This gave 0.01 g of a crystalline substance with mp 135-137°C (from methanol). A mixture with an authentic sample of anhydromarmesin gave no depression of the melting point. The IR spectrum of the dehydration production of II was identical with that of anhydromarmesin.

CONCLUSIONS

From the roots of Seseli sessiliflorum Schrenk. we have isolated a new dihydrofurocoumarin $C_{18}H_{18}O_5S$ for which the structure 5'-[1-methyl-1-(trans-3-methylthioacryloyloxy)ethyl]-4',5'-dihydrofuro-2',3':7,6-coumarin is proposed.

LITERATURE CITED

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