STRUCTURE OF THE COUMARIN SECHULIN

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One of us has previously reported the isolation from the roots of Seseli seseliflorum Schrenk of new sulfur-containing coumarins and chromones [1]. On studying the chemical composition of a representative of the same genus, from the roots of Seseli tschuense E. Nik, sp. novo, growing in the high mountain regions of Khirgizia, we isolated another sulfur-containing coumarin which we have called sechulin. Sechulin, $C_{18}H_{16}O_5S$, mp 245-246.5°C (from methanol), $[\alpha]_D^{20} + 833.3°$ (c 0.6; chloroform), possesses a neutral nature, is readily soluble in chloroform and carbon tetrachloride, sparingly in ethanol and ether, and insoluble in petroleum ether, water, and acids. On being heated with aqueous alkali, it passes into solution and on subsequent acidification separates out unchanged, which shows that it is a lactone. On titration with alkali, it consumes 2 moles of the latter. Consequently, there are two lactone rings in its molecule. With diazotized sulfanilamide, the substance forms a bright red coloration, but it does not react with carbonyl reagents.

The UV spectrum has λ_{max} 310 nm (log ε 4.2), which is characteristic for 7-hydroxycoumarin derivatives [2]. The IR spectrum shows two absorption bands (1720 and 1730 cm^{-1}) due to carbonyl groups, one of which is present in an α-pyrone ring of a coumarin and the other in an unsaturated lactone ring. These results show that sechulin is a dilactone.

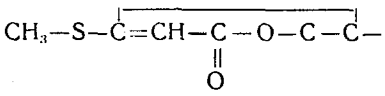
The NMR spectrum of sechulin (Fig. 1) contains the signals of four aromatic protons, showing that it belongs to the 7,8-disubstituted coumarins – doublets at 7.60 and 6.17 ppm, J = 10 Hz, and at 7.22 and 6.70 ppm, J = 8.5 Hz, corresponding to the H_4, H_3, H_5, and H_6 protons, respectively [3].

A singlet at 4.43 ppm (2H) is due to methylene protons at a benzyl carbon atom attached to C_8 and forming part of the pyran ring. The absence of splitting of this signal shows that there is a quaternary carbon atom in the vicinal position. In the strong-field region there are two singlets at 1.57 and 1.18 ppm (3H) corresponding to the protons of two nonequivalent methyl groups. Such a position of the signals is characteristic for the coumarins with a 2,3-dimethylchroman ring that have been found in recent years (inophyllolide, etc.) [4].

This permits the conclusion that sechulin is based on a 2,3-dimethyldihydropyranocoumarin nucleus, to which a residue with the composition $C_4H_4O_2S$ is attached at $C_{2'}$ and $C_{3'}$. The oxygen atoms of this residue form part of a lactone ring.

A three-proton singlet at 2.43 ppm corresponds to the protons of a methyl group attached to sulfur, $CH_3{-}S$, and the absence of a band of the stretching vibrations of a thionyl group shows that the sulfur is present in a $CH_3{-}S{-}C$ grouping. In view of the presence in the phylogenetically close species Seseli seseliflorum Schrenk and in the species under investigation, Seseli tschuense [5], of esters of methylthioacrylic acid, it may be assumed that the residue of this acid is included in the structure of sechulin, i.e., the thiomethyl grouping is in the β position to the carbonyl group. In this case, the one-proton singlet at 7.90 ppm is due to the α-olefinic proton of the methylthioacrylic acid residue. This residue is attached to the dihydropyran ring through a C–C bond in the β position to the oxygen atom of the lactone ring.

The absorption band of the carbonyl group in the IR spectrum at 1720 cm^{-1} shows that it is part of a conjugated δ-lactone, i.e., of the



$$\mathrm{CH_3{-}S{-}\overset{|}{C}{=}CH{-}\underset{\underset{O}{\|}}{C}{-}O{-}C{-}\overset{|}{C}{-}}$$

grouping. In this case, sechulin most probably has one of the two alternative structures (I and II).

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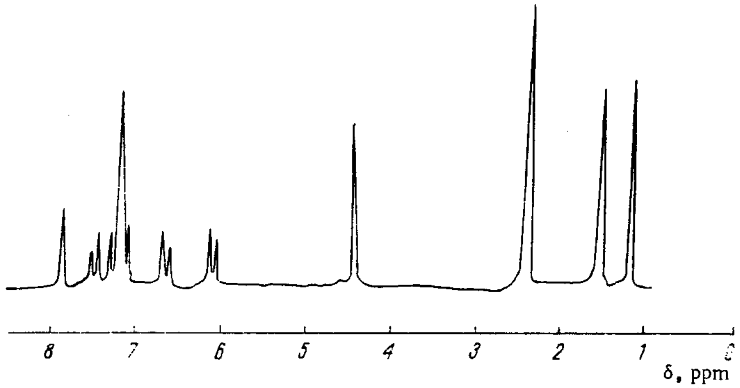
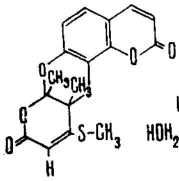
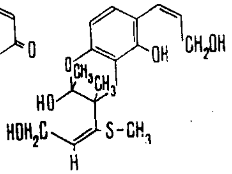


Fig. 1. NMR spectra of sechulin.

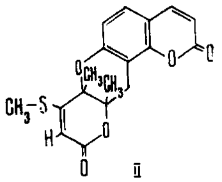
On the reduction of sechulin with sodium tetrahydroborate, both lactone carbonyls were reduced, forming a tetrol with M^+ 352, R_f 0.1, in the IR spectrum of which the bands of the carbonyls had disappeared and there was intense absorption in the 3200-3400 cm^{-1} region. The tetrol was not dehydrated by reaction with phosphorus pentoxide. Consequently, the third hydroxy group is present at $C_{2'}$, and sechulin must have structure (I).



I



III



II

EXPERIMENTAL

The IR spectra were taken on a UR-10 spectrometer (KBr), the NMR spectra on a JNM-4H-100/100 MHz instrument ($CDCl_3$, chemical shifts given on the δ scale from the signal of HMDS taken as 0), and the mass spectra on a MKh-1303 instrument. The purities of the substances were checked by chromatography in the petroleum ether–ethyl acetate (2 : 1) system on "Silufol" plates and on paper impregnated with a 10% solution of formamide in methanol using the hexane–benzene–methanol (5 : 4 : 1) system with diazotized sulfanilamide as the chromogenic agent.

Isolation of Sechulin. The dried and comminuted roots of Seseli tschuense E. Nik., sp. novo (3 kg) were steeped with methanol (3 × 10 liters). The combined extracts were concentrated to 2 liters, diluted with 2 volumes of water, and extracted with diethyl ether (3 × 0.5 liter). The solvent was distilled off in vacuum to dryness. The oily residue (40 g) was chromatographed on a column (h = 40 cm, d = 9 cm) filled with KSK silica gel.

Fractions 29-38 (the eluent was 15% of ethyl acetate in petroleum ether) yielded 1.0 g of a crystalline substance with mp 245-246.5°C (from methanol), $[\alpha]_D^{20}+833.3°$ (c 0.6; chloroform).

Found, %: C 63.00; 63.10; H 4.96; 5.08; S 8.38; 8.39 M^+ 344 (mass spectrometry). $C_{18}H_{16}O_5S$. Calculated, %: C 62.79; H 4.65; S 9.20; Mol. wt. 344.

Reduction of Sechulin. With stirring, 0.6 g of sodium tetrahydroborate was added to a solution of 0.3 g of sechulin in 30 ml of methanol, and the reaction mixture was left for 24 h. Then the solution was acidified with 20% H_2SO_4, diluted with water, and treated with ether (3 × 30 ml). The ethereal extracts were combined, and the solvent was evaporated off to give 0.15 g of an oily liquid with R_f 0.1, M^+ 352 (mass spectrometry).

Attempted Dehydration of the Tetrol. To a solution of 0.05 g of the product of the reduction of sechulin in 10 ml of anhydrous benzene was added 0.05 g of phosphorus pentoxide, and the mixture was boiled on the sand bath for 1 h. No change was observed in the substance.

CONCLUSIONS

From the roots of Seseli tschuense E.Nik. sp. novo a new sulfur-containing coumarin has been isolated with the composition $C_{18}H_{16}O_5S$, mp 245-246.5°C, and it has been called sechulin. Its most probable structure has been established on the basis of its NMR, IR, UV, and mass spectra and also reduction and titration reactions. This is the first sulfur-containing dilactone that has been found in the coumarin series.

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