STRUCTURE OF THE COUMARIN SACHALININ

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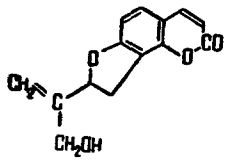
We have previously reported the isolation from the roots of Angelica sachalinensis Maxim (Sakhalinian angelica) of a new coumarin, which we called sachalinin [1]. Continuing a study of this lactone by spectral methods, we have found that its molecular weight, determined mass spectrometrically, is 244 proton units. This has enabled us to refine the empirical formula of the lactone, $C_{14}H_{12}O_4$. Sachalinin is an optically active compound, with $[\alpha]_D^{25}$ −187.1° (c 0.75, ethanol).

The NMR spectrum of sachalinin has doublets at 7.51 and 7.12 ppm, J = 10 Hz, and 7.15 and 6.25 ppm, J = 9 Hz, due, respectively, to the H-4 and H-3 and the H-5 and H-6 interacting protons, which made it possible to assign the lactone to the group of 7,8-disubstituted coumarins. A signal of eight lines with a center at 3.25 ppm (2H) and a triplet at 5.47 ppm (1H), forming a typical pattern of an ABX system, shows the presence of an $Ar-CH_2-CH$ grouping forming part of a dihydrofuran ring. Two singlets at 5.24 and 5.38 ppm (1H each) are produced by the protons of a methylene group on a quaternary carbon atom and a singlet at 4.38 ppm (2H) by the protons in an $-OCH_2-C=C$ grouping. A broadened signal at 6.49 ppm (1H) is due to a hydroxyl proton. On the basis of these facts, and also of biogenetic considerations, sachalinin is 2'-(1'-hydroxymethylvinyl)-2',3'-dihydrofuro-4',5':8,7-coumarin, and its structure is as follows:



A substance with this structure but dextrorotary, $[\alpha]_D^{20}$ +20.4° (ethanol), called discophoridin, has been isolated from the Australian plant Velleia discophora F. Muell [2]. We are the first to have isolated the levorotatory isomer (sachalinin).

The NMR spectrum was recorded on a JNM-4H-100 (100 MHz) instrument in pyridine. The positions of the signals were determined relative to tetramethylsilane as internal standard, taken as 0.

LITERATURE CITED

1. G. K. Nikonov and M. G. Pimenov, KhPS [Chemistry of Natural Compounds], 73 (1965).
2. G. Bottomley, Austr. J. Chem., 16, 163 (1963).

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