A KETOSAPOGENIN FROM THE LEAVES OF Yucca gloriosa

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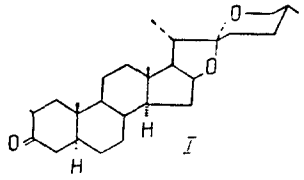
A native ketosapogenin of the spirostane series (25R)-5α-spirostan-3-one) has been isolated from the leaves of mound lily yucca.

In an investigation of the chemical composition of the leaves of mound lily yucca Yucca gloriosa (the plant source of tigogenin, the raw material for the synthesis of steroid hormones [1, 2]) we have isolated a new steroid sapogenin (I), which we have called yuccagenone.



I

Substance (I) was not hydrolyzed by diluted solutions of acids and was not saponified by an aqueous methanolic solution of alkali. The IR spectrum contained absorption bands at 865, 900 > 920, and 995 cm^{-1}, which are characteristic for the spiroketal grouping of spirostanes of the 25R series [3]. The elementary composition ($C_{27}H_{42}O_3$) showed the presence of three oxygen atoms, one of which was, in all probability, in a carbonyl group. A confirmation of this was the absence from the IR spectrum of signals in the 3200-3600 cm^{-1} region and the presence of an intense band at 1710 cm^{-1}. In the mass spectrum, an ion with m/z 300 showed the presence of a carbonyl group in ring A, B, or C [4].

The ^{13}C NMR spectrum contained 26 lines, one of which was of double integtral intensity (Table 1). For the detailed assignment of the signals in the spectrum of compound (I) we made a comparison of the experimental an expected values of the CSs. For the prediction of the CSs in rings A and B we used literature information for 3-ketoandrostane [5], and for rings C, D, E, and F information for tigogenin [6].

The weakest-field absorption line was observed at δ 211.9, which permits its unambiguous assignment to the resonance of a carbonyl carbon nucleus as a component of a six-membered carbocycles [7]. A comparison of CS of the carbonyl nucleus with those in ketoandrostanes or ketocholestanes [8] gave grounds for assuming that the keto group was present at one of the atoms C-2, C-3, C-6, C-7, and C-11. Characteristic CS values for Cp1 and C-12 are more than δ 215.0 [8]. If it is borne in mind that the strongest-field line in the spectrum, δ 11.5, can be assigned to the resonance of the nucleus of the C-19 angular methyl group, the most probable position of the keto group would be C-3 or C-7. Analysis of the set of experimental CSs of the nuclei of rings A and B in comparison with those for 3-ketoandrostane [5, 8] permitted the conclusion that the best correspondence was characteristic for a keto group at the C-3 atom.

Thus, a comparison of the experimental results of IR and ^{13}C NMR spectroscopies and mass spectrometry has enabled us to characterize compound (I) as (25R)-5α-spirostan-3-one.

EXPERIMENTAL

IR spectra were taken on a UR-20 spectrophotometer in KBr tablets; ^{13}C NMR spectra on a BS-567 spectrometer (Tesla, resonance frequency 25.14 MHz for ^{13}C nuclei), $CDCl_3$, calibrated

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TABLE 1. ^{13}C NMR Chemical Shifts of (25R)-5α-Spirostan-3-one

Number of the carbon nucleus	Experimental CS, ppm	Expected CS, ppm: reference to the values for 3-ketoandrostane	Expected CS, ppm: reference to the values for tigogenin	Number of the carbon nucleus	Experimental CS, ppm	Expected CS, ppm: reference to the values for 3-ketoandrostane	Expected CS, ppm: reference to the values for tigogenin
1	38 5	38,7		14	56,1		56,3
2	38,1	38,1		15	31,8		31,8
3	211,9	211,0		16	80,8		80,8
4	44,7	44,6		17	62,3		62,3
5	46 7	46,7		18	16,4	11,4	16,5
6	28,8	29,0		19	11,5		
7	31,8	32,1		20	41,6		41,6
8	35,0	35,7	35,2	21	14,5		14,5
9	53,9	54 1		22	109,2		109,2
10	35,8	35,7		23	31,4		31,4
11	21,3		21,1	24	28,8		28,8
12	39,9		40,1	25	30,3		30,3
13	40,6		40,6	26	66,9		66,8
				27	17,1		17,1

from the central line of the $CDCl_3$ triplet (δ 76.9); and mass spectra on a MAT-112 instrument (Varian). Melting points were determined on a Kofler block, and optical activities on a SU-2 polarimeter.

For purification and the elimination of other steroid aglycons, we used alumina (Brockmann activity grade II) and type L 40/100 silica gel. As the adsorbent for TLC we used Silufol UV-254 plates and the following solvent systems: chloroform–ethanol (25:1 and (20:1) and benzene–ether (6:1).

Isolation. The air-dry comminuted leaves of mound lily yucca (100 kg) were extraced with chloroform–gasoline (2:1). The residue after the solvent had been distilled off was chromatographed on columns, first of alumina and then of silica gel. The columns were washed successively with benzene and with benzene–chloroform. The fractions containing the ketosapogenin (I) were collected and evaporated, and the residue was recrystallized from methanol. The yield of compound (I) amounted to 0.08% in relation to the raw material.

(25R)-5α-Spirostan-3-one (yuccagenone). mp 172-174°C (methanol); $[\alpha]_D^{20}$ −55° (c 1.0; $CHCl_3$). IR spectrum: ν_{max}^{KBr}, cm^{-1}, 865, 890, 900, 920, 940, 960, 980, 995, 1010, 1030, 1050, 1060, 1070, 1100, 1120, 1130, 1150, 1180, 1210, 1710. ^{13}C NMR spectrum – see Table 1. Mass spectrum, m/z (%): 414 (M^+, 18), 399(2.4), 355(7.3), 345(11.7), 341(18), 300(27), 285(27.7), 271(38), 139(100), 126(17.5), 122(35.6), 115(30.7).

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