PHYTOECDYSTEROIDS OF Rhaponticum carthamoides.

II. Rhapisterone B.

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A new ecdysteroid (rhapisterone B) has been isolated from the seeds of Rhaponticum cathamoides (Willd.) Iljin. (family Compositae). It has been shown that it is 2β,3β,11α,14α,20R,24ξ-hexahydroxy-5β-cholest-7-en-6-one.

We have previously reported the isolation of phytoecdysteroids from the roots with rhizomes of Rhaponticum carthamoides. In the present paper we give the results of an investigation of the seeds of R. cathamoides for the presence of phytoecdysteroids.

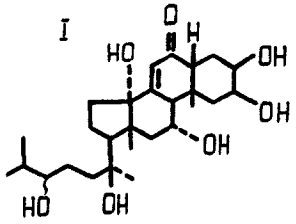
The air-dry seeds of R. cathamoides were extracted with methanol. After the appropriate working up with the aid of column chromatography on silica gel, in addition to known ecdysteroids we succeeded in isolating an ecdysteroid (I) with a previously undescribed structure. The structure of the new ecdysteroid which we have called rhapisterone B has been shown on the basis of spectral characteristics.

The mass spectrum of compound (I) did not contain the molecular peak. The high-mass region was characterized by the peaks of ions with m/z 462. 444, 426, 411, and 408. Cleavage of the C-20–C-22 bond formed ions with m/z 379, 361, 343, and 325. An ion with m/z 301 corresponded to breakdown at the C-17–C-20 bond. The fragments mentioned were analogous to the fragments of the mass-spectrometric breakdown of ajugasterone C [2]. In ajugasterone C the breakdown of the side chain is characterized by the peaks of ions formed on the cleavage of the C-17–C-20 bond, with m/z 145, 127, and 109, and on the cleavage of the C-20–C-22 bond, giving ions with m/z 101 and 83.

In ecdysteroid (I), cleavage of the side chain was marked by ions with m/z 145 and 109. In contrast to ajugasterone C and 22-deoxyecdysterone [3], in the compound (I) under investigation no ion with m/z 127 appeared. However, in the spectrum of rhapisterone B there was the peak of an ion with m/z 55, formed, in all probability, by the cleavage of the C-23–C-24 bond followed by dehydration. The above facts mean that one of the two hydroxy groups present in the side chain of the new ecysteroid is located at C-24. This conclusion was confirmed by the PMR spectrum. A three-proton singlet of the C-21 methyl group appearing at 1.42 ppm showed the presence of an OH group at C-20.

The signals of the C-26 and C-27 methyl groups were highly screened and appeared in the form of a doublet at 0.67 ppm, which showed the presence of H at C-25. The spectrum of ecdysteroid (I) lacked a signal where that of a proton at C-22 usually appears. However, in the strong field, in the 3.61-3.72 ppm region, there was a two-proton signal of protons at C-9 and C-24. The signals of the protons at C-11 and C-2 were shifted downfield and appeared at 4.45 ppm [2]. Consequently, ecdysteroid (I) is 2β,3β,11α,14α,20R,24ξ-hexahydroxy-5β-cholest-7-en-6-one.

I



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EXPERIMENTAL

IR spectra were obtained on a UR-20 spectrophotometer (KBr). Mass spectra were taken on a MKh-1310 instrument fitted with a system for the direct introduction of the substance into the ion source, at an ionizing voltage of 80 V a collector current of 60 μA, and a temperature of the evaporator bulb and the ionization chamber of 190-200°C, and PMR spectra were taken on a Bruker AC-200 instrument, δ scale, 0 – TMS; temperature of the sample 22 ± 2°C.

Isolation of Rhapisterone B (I). The air-dried comminuted seeds of R. carthamoides (1.2 kg) were extracted with methanol. The methanol was evaporated to a volume of 250 ml and was diluted with 375 ml of water. After the extraction of the hydrophobic compounds with hexane, the phytoecdysteroids were extracted from the aqueous methanolic fraction with butanol. The butanol was distilled off in vacuum, giving 30.41 g of total extractive substances. After the separation of the known phytoecysteroids, the fractions with the unknown ecdysteroid (20 mg) were transferred to a column of SiO_2. Elution with the chloroform–methanol (9:1) system yielded 6 mg of pure rhapisterone B. The yield was 0.00005% on the weight of the air-dry raw material.

Rhapisterone B (I) – $C_{27}H_{44}O_7$, amorphous ν_{max}^{KBr}, cm^{-1}: 3350-3500 (OH), 1655 (Δ^7 keto group). Mass spectrum (m/z, %): 462 ($M^+ - H_2O$) (3), 444 (4), 426 (6), 408 (6), 393 (3), 379 (12), 361 (30), 343 (100), 325 (75), 301 (60), 267 (45), 145 (21), 109 (15), 83 (12), and 55 (25). PMR spectrum (C_5D_5N, ppm): 0.67 (6H, d, H-26, 27), 1.10 (3H, s, H-18), 1.15 (3H, s, H-19), 1.42 (3H, s, H-21), 3.61-3.72 (2H, m, H-9 and H-24), 4.12 (1H, m, H-3), 4.45 (2H, m, H-2 and H-11), 6.11 (1H, broadened singlet, H-7).

LITERATURE CITED

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