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PHYTOECDYSTEROIDS OF PLANTS OF THE GENUS *Rhaponticum*
I. CARTHAMOSTERONE A FROM *Rh. carthamoides*

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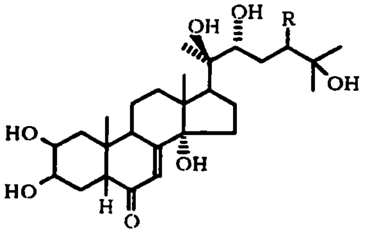
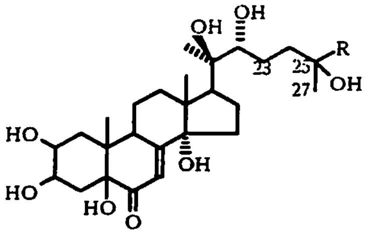
A new ecdysteroid — carthamosterone A — has been isolated from the seeds of Rhaponticum carthamoides. *Its structure has been established from the results of spectral investigations.*

We have continued a study of plants of the genus *Rhaponticum* (fam. Compositae) [1-3]. From the seeds of *Rh. carthamoides*, in addition to the known 24(28)-dehydromakisterone A (1) and ecdysterone (2) [4-6], we have isolated the new ecdysteroid carthamosterone A (4).

The UV spectrum of carthamosterone A had an absorption maximum at 245 nm (log ε 4.01), and in the IR spectrum a broad absorption band was observed at 3405 cm^{-1} (OH group). At 1674 cm^{-1} there was absorption corresponding to a keto group conjugated with a double bond. In addition, at 1710 cm^{-1} a band was seen in the form of an inflection that corresponded to the carbonyl group of an ester function. This was also shown by the presence of a three-proton singlet of a methoxycarbonyl group in the PMR spectrum of carthamosterone A at 3.75 ppm.



1. R=CH_2
2. R=H



3. R=CH_3
4. R=$COOCH_3$
5. R=COOH

The mass spectrum of carthamosterone A lacked the peak of the molecular ion. At the same time there were peaks of ions with *m/z* 379, 361, 343, 325, 317, and 316 witnessing the presence of four hydroxy groups in the molecule [7-9].

The PMR spectrum of (4) revealed singlet signals of the protons of four methyl groups at 1.15, 1.20, 1.49, and 1.59 ppm and also the resonance lines of isolated protons at (ppm) 3.58 (H-9), 3.88 (H-22), 4.0-4.3 (H-2,3), and 6.26 (H-7). The assignment of these signals is given in Table 1.

A comparison of the characteristics of these signals with those of ecdysteroids known in the literature showed closeness of the chemical shifts of the majority of protons of (4) and of polypodin B (3), with the exception of CH_3-27.

The facts given above permitted the assumption that compound (4) was a natural derivative of polypodin B containing a methoxycarbonyl ester grouping in the side-chain. As can be seen from Table 1, on passing from (3) to (4) the chemical shifts of H-22 and CH_3-18 do not change and, moreover, the PMR spectrum of compound (4) contains the signals of only four methyl groups. Furthermore, one of the singlet signals of methyl groups has undergone a paramagnetic shift by 0.12

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TABLE 1. Chemical Shifts of the Protons in the PMR Spectra of Polypodin B (**3**) and Carthamosterone A (**4**) (δ, ppm, C_5D_5N, 0 — TMS)

Compound	Positions of the protons				
	H-2,3	H-7	H-9	H-22	CH_3-18
3	4.0–4.3	6.23	3.59	3.85	1.20
4	4.0–4.3	6.26	3.58	3.88	1.20
	CH_3-19	CH_3-21	CH_3-26	CH_3-27	$COOCH_3$
3	1.15	1.58	1.37	1.37	–
4	1.15	1.59	–	1.49	3.75

ppm. An analogous change has been found in the literature [10] for ecdysonic acid (**5**). These facts unambiguously show the formation of a methoxycarbonyl group in (**4**) from one of the methyl groups at C-25.

Thus, carthamosterone A is a natural derivative of polypodin containing a methoxycarbonyl group at C-25.

EXPERIMENTAL

For eluting columns we used the chloroform–methanol (9:1) (1) and (4:1) (2) systems.

IR spectra were obtained in KBr on a Perkin-Elmer System 2000 FT-IR spectrometer.

PMR spectra were taken on a Tesla BS-567 A (100 MHz) spectrometer in C_5D_5N relative to TMS. For other information, see [4].

Isolation of the Phytoecdysteroids. The air-dry comminuted seeds *Rh. carthamoide*s (1.5 kg) were extracted with methanol (5 liters). The extract was concentrated, the residue was diluted with water, and the resulting precipitate was removed. The methanol was evaporated off, and the aqueous residue was extracted first with chloroform and then with butanol. The dark resinous mass obtained after the distillation of the butanol was chromatographed on a column of silica gel. Elution with system 1 gave 22 mg (0.001%) (here and below, the yields are calculated on the air-dry raw material) of 24(28)-dehydromakisterone A (**1**) with mp 245-246°C (methanol), $[\alpha]_D^{22}$ +55.2 ± 2°C (c 0.25 methanol) [5].

Eluting the column with system 2 led to the isolation of ecdysterone with mp 243-244°C (from ethyl acetate) and $[\alpha]_D^{22}$ +60.7 ± 2° (methanol) [4, 6].

The continued washing of the column with the same system gave a fraction containing a mixture of three phytoecdysteroids, including ecdysterone (**2**) and carthamosterone A (**4**). The rechromatography of these eluates using system 2 gave 10 mg (0.0007%) of carthamosterone A.

Carthamosterone A (4) has the composition $C_{28}H_{44}O_{10}$, mp 170-172°C (methanol–ethyl acetate). UV spectrum (C_2H_5OH, λ_{max}, nm): 245 (log ε 4.01). IR spectrum (KBr, ν,cm^{-1}): 3405 (OH), 1674 (7-ene-6-keto grouping), 1710 (ester group), 1202, 1138 (C–O–C; ester band).

Mass spectrum, *m/z* (%): 494 (0.2), 478 (0.2), 477 (0.6), 459 (40), 446 (1), 441 (1), 425 (11), 422 (11), 409 (13), 379 (37), 361 (60), 343 (60), 326 (100), 325 (80), 317 (37), 316 (60), 99 (82), 81 (60).

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