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PHYTOECDYSTEROIDS OF PLANTS OF THE GENUS *Rhaponticum*

II. CARTHAMOSTERONE B FROM *Rh. carthamoides*

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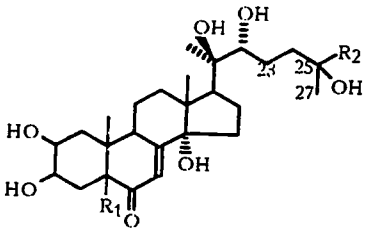
The structure of a new ecdysteroid — carthamosterone B, isolated from the seeds of Rhaponticum carthamoides *— has been established from an investigation of its spectral characteristics.*

We have previously [1] reported the presence in the seeds of *Rhaponticum carthamoides* (fam. Compositae) of various known ecdysteroids and also a new one — carthamosterone A (**3**), the structure of which has been established. On continuing the study of the total extractive substances, we have isolated another new ecdysteroid — carthamosterone B (**1**).

In addition to an absorption band at 3400 cm^{-1} due to hydroxy groups and another due to a keto group conjugated with a double bond (1670 cm^{-1}), the IR spectrum of (**1**) contained a band at 1710 cm^{-1} corresponding to the carbonyl group of a simple ester residue. In its UV spectrum there was an absorption maximum at 245 nm (log ε 4.00). The mass spectrum of carthamosterone B lacked a peak of the molecular ion, and the main peaks of fragmentary ions that were observed had *m/z* 460 (71), 363 (75), 345 (82), 327 (85), 301 (42), and 300 (100) (for the complete characteristics of the mass spectrum of (**1**), see the Experimental section). The first fragment peak was formed through the splitting out from the molecular ion of two water molecules and carbon monoxide, while the others were characteristic for the breakdown of the steroid part of the ecdysterone (**2**) molecule [2].



1. R_1=H,R_2=$COOCH_3$;
2. R_1=H,R_2=CH_3;
3. R_1=OH,R_2=$COOCH_3$;
4. R_1=H,R_2=COOH

In the region of the resonance of methyl groups in the PMR spectrum of carthamosterone B, unlike that of ecdysterone, there were singlet signals of the protons of only four methyl groups: at (ppm) 1.07 (CH_3-19), 1.20 (CH_3-18), 1.49 (CH_3-27), and 1.59 (CH_3-21). At 3.88 ppm there was a singlet of the methyl of a methoxycarbonyl group. The chemical shifts of the other isolated protons were identical with those in the spectrum of ecdysterone (Table 1).

Attention is attracted by the fact that on passing from the PMR spectrum of ecdysterone (**2**) to that of (**1**) there is a paramagnetic shift of the CH_3-27 signal by 0.13 ppm, as is observed in a comparison of the spectral characteristics of (**2**) and ecdysonic acid (**4**) [3].

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TABLE 1. Chemical Shifts of the Protons in the PMR Spectrum of Carthamosterone B (**1**) and Ecdysterone (**2**) (δ, ppm C_5D_5N, 0 — TMS)*

Compound	Positions of the protons				
	H-2,3	H-7	H-9	H-22	CH_3-18
1	4.0–4.3	6.24	3.58	3.88	1.20
2	4.0–4.3	6.26	3.58	3.88	1.21
	CH_3-19	CH_3-21	CH_3-26	CH_3-27	$COOCH_3$
1	1.07	1.59	–	1.49	3.88
2	1.06	1.58	1.36	1.36	–

*The signals of the protons of the methyl groups were singlets; the H-7 proton appeared in the form of a broadened singlet, and the others as broadened multiplets.

The facts given above permitted the unambiguous statement that the molecule of (**1**) is based on that of ecdysterone, with only one difference in the side-chain of carthamosterone B due to the fact that a methoxycarbonyl group has been formed from one of the methyl groups, at C-25.

Thus, carthamosterone is natural methyl ecdysonate.

EXPERIMENTAL

For methods of isolation, instruments, and chromatographic conditions, see [1].

Isolation of Carthamosterone B (1). The rechromatography of the mixture of three ecdysteroids led to the isolation of ecdysterone (**2**) and carthamosterone A (**3**) [1]. Further elution with the chloroform–methanol (4:1) system led to the additional isolation of 12 mg (0.0008%, yield calculated on the air-dry raw material) of carthamosterone B (**1**), which had the composition $C_{28}H_{44}O_9$, mp 179-182°C (methanol–ethyl acetate). UV spectrum (C_2H_5OH, λ_{max}, nm): 245 (log ε 4.00). IR spectrum (KBr, ν, cm^{-1}): 3400 (OH), 1670 (7-ene-6-keto grouping), 1710 (ester group), 1204, 1140 (C–O–C; ester bond). Mass spectrum, *m/z* (%): 460 (M^+-$2H_2O$-CO; 7.1), 458 (4), 442 (71), 429 (22), 427 (34), 425 (28), 424 (28), 411 (22), 409 (22), 391 (20), 363 (75), 345 (82), 344 (69), 328 (84), 327 (85), 301 (42), 300 (100), 285 (42), 267 (47), 159 (85), 143 (88), 141 (99), 123 (85), 114 (95), 105 (88).

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