



RAPISTERONE D, A PHYTOECDYSTEROID FROM *RHAPONTICUM CARTHAMOIDES*

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Abstract—From *Rhaponticum carthamoides* seeds, a new phytoecdysteroid rapisterone D has been isolated and characterized. The structure of the new phytoecdysteroid has been proved using physical-chemical methods.

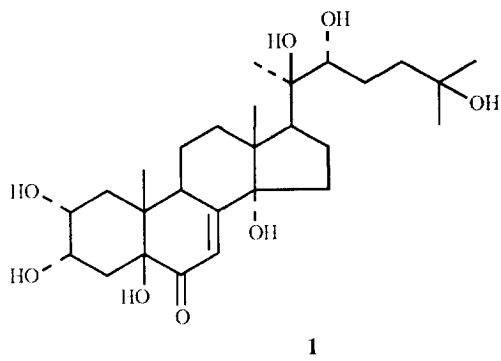
INTRODUCTION

While proceeding with systematic study of *Rhaponticum carthamoides* phytoecdysteroids, we investigated the seeds for phytoecdysteroid content [1, 2]. This led us to the isolation of a new phytoecdysteroid, which we name rapisterone D (**1**).

RESULTS AND DISCUSSION

In the EI-mass spectrum of ecdysteroid **1** the molecular peak is absent. The ions with m/z 478 [$M - H_2O$]⁺, 463 [$M - H_2O - Me_3$]⁺, 445 [$M - 2H_2O - Me$]⁺, 427 [$M - 3H_2O - Me$]⁺, 409 [$M - 4H_2O - Me$]⁺ and 391 [$M - 5H_2O - Me$]⁺ characterize the high mass region. On cleavage of the C-20–C-22 bond, the ions with m/z 379 [$M - 117$]⁺, 361 [$M - 117 - H_2O$]⁺ and 325 [$M - 117 - 3H_2O$]⁺ are formed. The ion with m/z 301 [$C_{19}H_{25}O_3$]⁺ corresponds to the break of the bond of C-17–C-20. The mass spectral fragmentation of the side chain is shown by ions with m/z 99 [$C_6H_{11}O$]⁺ and 81 [C_6H_9]⁺. These data are analogous to the mass spectral fragmentation of polypodine B [3].

With the help of ¹H and ¹³C NMR spectra and using 2D correlation spectroscopy (2D Cosy), the different positions of the substituents in ring A of ecdysteroid **1** compared to polypodine B have been proved. In the ¹³C NMR spectrum of **1** (Table 1) at 79.8 ppm the signal of C-5 is evident. In using the 2D method of ¹H–¹³C correlation, the signal at 79.8 ppm is not seen. This proves the presence of a hydroxyl group at C-5. In the NMR spectrum of rapisterone D at 4.25 ppm as the triplet of doublets with the constants $J = 12$ and 4 Hz, there is seen the signal of an axial proton with the half-width of $W_{1/2} = 22$ Hz, geminal to the secondary hydroxyl group. At 4.14 ppm as a quartet with the constant of $J = 3.5$ Hz with the half-width of $W_{1/2} = 8.5$ Hz, there is a signal of an equatorial proton, geminal to the secondary hydroxyl group. By using the method of 2D correlation spectro-



scopy (2D Cosy), ¹H–¹³C, we have shown that the signals of protons at 4.25 and 4.14 ppm are connected correspondingly to the C-3 and C-2 carbon atoms.

Upon ¹H–¹H 2D of the correlation spectroscopy, the C-3 axial proton at 4.25 ppm interacts, except for the proton at C-2 (4.14 ppm), with the protons at 2.08 and 2.15 ppm; these protons at ¹H–¹³C correlation interact with the signal of the C-4 carbon at 34.8 ppm.

In the case of ¹H–¹H 2D of the correlation spectroscopy, the C-2 equatorial proton at 4.14 ppm, except the proton at C-3 (4.25 ppm), interacts with the proton at 2.09 and 1.95 ppm; the latter on ¹H–¹³C correlation interacts with the signal C-1 of the carbon at 36.0 ppm. Thus, the hydroxyl groups at C-3 and C-2 possess α -orientation. This is evident from the ¹³C NMR spectra, where the signal C-9 of the carbon atom is shifted into the weak field compared to the polypodine B and is seen at 38.2 ppm [4].

The shift of the weak field by 0.1 ppm of the signal C-19 of the methyl in the NMR spectrum compared with that of polypodine B also confirms the α -orientation of hydroxyl groups at C-3 and C-2 [5]. Thus, the new ecdysteroid has the structure of 5 β -cholest-7-en-2 α ,3 α ,5,14 α ,20R,22R,25-heptaoxy-6-one.

Table 1. Chemical shifts of the ^{13}C NMR spectra of rapisterone D (δ , ppm)

| Atom no. | Chemical shift | Atom no. | Chemical shift | Atom no. | Chemical shift |
|----------|----------------|----------|----------------|----------|----------------|
| 1 | 36.0 | 11 | 21.3 | 21 | 21.6 |
| 2 | 69.8 | 12 | 31.6 | 22 | 77.5 |
| 3 | 67.9 | 13 | 48.1 | 23 | 27.4 |
| 4 | 34.8 | 14 | 84.0 | 24 | 42.6 |
| 5 | 79.8 | 15 | 32.0 | 25 | 69.6 |
| 6 | 200.9 | 16 | 22.0 | 26 | 29.9 |
| 7 | 119.8 | 17 | 50.0 | 27 | 30.1 |
| 8 | 116.8 | 18 | 17.1 | | |
| 9 | 38.2 | 19 | 17.8 | | |
| 10 | 44.7 | 20 | 76.8 | | |

EXPERIMENTAL

The mass spectrum has been taken on MX-1310 supplied with the system of the direct introduction of the substance into the ion resource at the ionizing current of 60 V, the collector current of 50 nA, the temp. of the evaporating ampule and the ionization chamber 100–180°.

Rapisterone D isolation. The air-dried-milled seeds of *Rhaponticum carthamoides* (1.2 kg) were extracted with MeOH. The MeOH was evapd in vacuum at 40–45° to a vol. of 250 ml and this was diluted with 375 ml of H₂O. After the extraction of the hydrophobic compounds from the H₂O–MeOH fr., the phytoecdysteroid was extracted into BuOH. The BuOH was removed in vacuum and gave 30.41 g of crude material. After the isolation of known ecdysteroids, the frs (240 mg) containing rapisterone D were chromatographed on a column with SiO₂, eluted with CHCl₃–MeOH (20:1). This gave 12 mg of rapisterone D, a yield of 0.0001%.

Rapisterone D. C₂₇H₄₄O₈, mp 246–248° (EtOAc–MeOH), IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{−1}: 3370–3490 (OH), 1690 (Δ^7 -6-

ketogroup). ¹H NMR spectrum (C₅D₅N, 400 MHz, ppm) 1.12 (3H, s, H-18), 1.18 (3H, s, H-19), 1.35 (6H-26, 27), 1.56 (3H, s, H-21), 3.83 (1H, dd, H-22), 4.14 (1H, k, $J=3.5$ Hz, H-2), 4.25 (1H, dt, $J=12$ and 4 Hz, H-3), 3.61 (1H, m, H-9), 2.95 (1H, t, H-17), 6.24 (1H, broad singlet, H-7).

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