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PHYTOECDYSTEROIDS OF Rhaponticum carthamoides

III. RHAPISTERONE C

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A new ecdysteroid, rhapisterone C, has been isolated from seeds of the plant Rhaponticum carthamoides (Willd) Iljin (family Compositae). It has been shown that rhapisterone C is 23ξ-ethylecdysterone.

In studying phytoecdysteroids from Rhaponticum carthamoides seeds [1, 2], we have isolated a new phytoecdysteroid (I) belonging to the ecdysteroids of the C-29 series. The new phytoecdysteroid, which we have called rhapisterone C, was isolated from the moderately polar fraction of a butanolic extract containing the phytoecdysteroids. The amount of rhapisterone C in the plant is very small. For this reason, in separation we used column chromatography and rechromatography on SiO_2 with elution by chloroform–methanol systems [(9:1) and (4:1)].

The IR spectrum of (I) contained bands of hydroxy groups at 3340 and 3500 cm^{-1}, while at 1655 cm^{-1} there was absorption corresponding to a keto group conjugated with a double bond.

The peak of the molecular ion was absent from the mass spectrum of (I). The region of high masses was characterized by the peaks of ions with m/z 472 ($M^+ - 2H_2O$), 454, 439, 436, and 421. The cleavage of the C-20–C-22 bond formed fragments with m/z 363, 345, and 327. An ion with m/z 300 corresponded to breakdown at the C-17–C-20 bond. The above-mentioned fragments of the steroid part of compound (I) were analogous to the mass-spectrometric fragmentation of the steroid part of ecdysterone. In the mass spectra of ecdysteroids with side chains similar to that of ecdysterone, the cleavage of the C-20–C-22 bond after dehydration gives rise to a cyclic fragment with m/z 99. In the mass spectrum of (I), this fragment was displaced by 28 m.u., which means the presence of an additional C_2H_4 group. An ion with m/z 109, formed by the dehydration of the ion with m/z 127, also appeared.

The positions of the substituents in the steroid part and the side chain of (I) were shown with the aid of ^1H and ^{13}C NMR spectra using 2D correlation spectroscopy of ^1H–^1H and ^1H–^{13}C chemical shifts.

The ^{13}C NMR spectrum of compound (I) (Table 1) included at 72.57 ppm the signal of the C-25 carbon atom. When the method of ^1H–^{13}C 2D correlation spectroscopy (2D COSY) was employed, the signal at 72.57 ppm did not appear. This fact is a proof that the C-25 carbon atom did not interact with a proton. Consequently, an OH group and two methyl groups are attached to C-25.

In the PMR spectrum of rhapisterone C, the signal of a proton in the geminal position to a secondary hydroxy group at C-22 appeared in the form of a doublet at 3.87 ppm. This fact is evidence in favor of the assumption that the C_2H_4 residue is attached at C-23, and H-22 interacts with only one proton, in contrast to makisterone C [3, 4], where H-22 inter-

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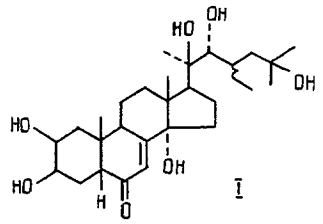
TABLE 1. Chemical Shifts in the ^{13}C NMR Spectrum of Rhapisterone C (δ, ppm)

Atom No.	Chemical shift	Atom No.	Chemical shift	Atom No.	Chemical shift
1	38,01	11	21,59	21	21,53
2	68,05	12	31,76	22	76 02
3	68,10	13	48,11	23	50,67
4	32,46	14	84,14	24	32.62
5	51,40	15	32,02	25	72,57
6	203,43	16	21,14	26*	29.83
7	121,63	17	49,98	27*	25,72
8	166,14	18	17,87	28	25,58
9	34,48	19	24,46	29	13,82
10	38,67	20	76,92		

*Values of the chemical shifts assigned ambiguously.

acts with two protons at C-23. In the $^{1}H-^{1}H$ correlation of chemical shifts, the proton at C-22 interacted with only one proton, at 1.95 ppm. In the case of the $^{1}H-^{13}C$ 2D spectrum, the proton appearing at 1.95 ppm interacted with a carbon atom giving a signal at 50.67 ppm, and the signal at 50.67 ppm therefore related to the C-23 carbon atom.

The totality of the facts given above showed that rhapisterone C is 23ξ-ethylecdysterone.



I

EXPERIMENTAL

IR spectra were obtained on a UR-20 spectrometer (KBr). The mass spectrum was taken on an Mkh-1310 instrument fitted with a system for the direct introduction of the specimen into the ion source, at an ionizing voltage of 40 V, a collector current of 50 μA, and a temperature of the evaporation ampul and the ionization chamber of 160-180°C, while the PMR spectra were recorded on a Bruker AM-400 instrument: δ scale, 0 – TMS, specimen temperature 22 ± 2°C.

Isolation of Rhapisterone C (I). Air-dry comminuted seeds of Rh. carthamoides (1.2 kg) were extracted with methanol. The methanol was evaporated off in a rotary evaporator under reduced pressure at 40-45°C to a volume of 250 ml and was then diluted with 375 ml of water. After the elimination of hydrophobic compounds with hexane, the phytoecdysteroids were extracted from the aqueous methanolic fraction with butanol, and the butanol was distilled off under reduced pressure, to give a total of 30.41 g of extractive substances. After the separation of the known ecdysteroids, the fractions containing rhapisterone C were combined. The combined fractions were chromatographed repeatedly on a column of SiO_2 with elution by chloroform–methanol systems (9:1 and 4:1). This gave 20 mg of rhapisterone C in the individual form. The yield on the weight of the air-dry raw material was 0.00016%.

Rhapisterone C – $C_{29}H_{48}O_7$, mp 249-250°C (ethyl acetate–methanol). ν_{max}^{KBr}, cm^{-1}: 3340-3500 (OH), 1655 (Δ^7-6-keto group). Mass spectrum (m/z, %) 472 ($M^+ - 2H_2O$) (4), 454(28), 439(16), 436(4), 421(4), 363(16), 345(40), 327(24), 300(32), 171(20), 154(16), 127(100), 109(40), 83(16), and 69(9). PMR spectrum (C_5D_5N, 400 MHz, ppm): 1.01 (CH_3-29, t), 1.08 (CH_3-19, s), 1.22 (CH_3-18, s), 1.25 and 1.38 (CH_3-26 and CH_3-27, s), 1.56 (CH_3-21, s), 3.00-3.02 (2H, H-5 and H-17, m), 3.60 (H-9, m), 3.87 (H-22, d, J = 10 Hz), 4.16 (H-2, m), 4.22 (H-3, m), 6.26 (H-7, br. s).

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SYNTHETIC ANALOGUES OF Peganum ALKALOIDS

VII. BROMINE-SUBSTITUTED QUINAZOLINE ALKALOIDS AND THEIR ANALOGUES

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The quinazoline bases pentamethylenequinazoline and peganol react with bromosuccinimide in glacial acetic acid to form the corresponding 6-bromoquinazoline derivatives. Some by-products of the bromination reaction have been isolated and characterized. 6-Bromopeganol has been subjected to x-ray structural analysis.

We have previously found that the quinazoline alkaloids peganine (I) and deoxypeganine (DOP, II) form the corresponding 6-bromo derivatives (III) and (IV) on interaction with bromosuccinimide (BSI) in glacial acetic acid [1]. We have continued a study of this reaction on homologues of DOP and have also determined the structures of some minor products.

On the reaction of pentamethylenequinazoline (V) with BSI in acetic acid, 6-bromopentamethylenequinazoline (VI) and a base (VII) with mp 95-96°C were isolated as the main products. The structures of these compounds were shown in a way similar to that for the corresponding compounds in [1]. However, the PMR spectrum of (VII) contained, in addition to signals of the protons of the aromatic and azepine rings, a four-proton singlet at 2.70 ppm. The presence of peaks with m/z 292/294 and 99 in the mass spectrum of (VII) led us to the conclusion that the substance under consideration was a molecular complex of 6-bromopentamethylenequinazolone (VIII) with succinimide (SI) in a ratio of 1:1 (PMR spectrum). For a definitive proof, we synthesized this complex by another method. We first obtained 6-bromopentamethylenequinazolone (VIII) [2], the PMR spectrum of which practically coincided with that of compound (VII), with the exception of the signal at 2.70 ppm. In addition, the R_f values and melting points of compounds (VII) and (VIII) proved to be different. A mixed melting point showed a clear depression. Then the 6-bromopentamethylenequinazolone was heated in glacial acetic acid in the presence of an equimolar amount of succinimide. The product isolated was identical with complex (VII) (PMR spectrum). On HPLC analysis it was found that 6-bromopentamethylenequinazolone (VIII), the molecular complex (VII), and succinimide gave individual peaks (Fig. 2). Although the retention times of the latter two substances differed only slightly, the results obtained permitted an unambiguous conclusion in favor of the individuality of compound (VII).

2,3-Polymethylenequinazolones do not form 6-bromo derivatives under the conditions of this reaction, and therefore 6-bromovasicinone (IX), 6-bromodeoxyvasicinone (X), and the complex of 6-bromopentamethylenequinazolone with SI (VII) could be formed only by oxidation from the corresponding 6-bromoquinazolines during the reaction and in the isolation of the products. The ease of oxidation of 6-bromopeganine was confirmed by its conversion into 6-bromoacetylvasicinone (XI) on acetylation. The structures of (IX) and (X) were confirmed by the formation of identical substances on the potassium permanganate oxidation of 6-bromopeganine (III) and 6-bromo-DOP (IV), respectively.

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