On continuing elution, the same system gave 10 mg of the 1,2:20,22-diacetonide (VII), $C_{33}H_{52}O_9$, with mp 115-118°C (~~chloroform~~-methanol), $[\alpha]_D^{20}$ + 96.0±2° (c 0.46; methanol). Mass spectrum, m/e: 592 M^+, 577, 574, 559, 556, 516, 498, 483, 480, 458, 440, 432, 417, 400, 382, 372, 354, 342, 314, 296, 228, 201, 143, 125, 102, 98, 81.

SUMMARY

From the flower heads of *Rhaponticum integrifolium* we have isolated a new phytoecdysone — integristerone B. It has been shown that it is 1β,2β,3β,5β,14α,20R,22R,25-octahydroxy-5β-cholest-7-en-6-one.

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PHYTOECDYSONES OF *Rhaponticum integrifolium*

IV. 24(28)-DEHYDROMAKISTERONE A

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UDC 547.926+581.192

We have previously reported the isolation from the flower heads of *Rhaponticum integrifolium* C. Winkl. of ecdysterone, integristerone A, and integristerone B [1-3]. Subsequently, from the mother liquors remaining after the separation of these compounds, we have isolated a new phytoecdysone (I) with a molecular weight of 492 and the composition $C_{28}H_{44}O_7$.

In the region of high mass numbers of the mass spectrum of the phytoecdysone (I) there are the peaks of dehydration ions with m/e 474 $(M - H_2O)^+$, 456 $(M - 2H_2O)^+$, and 438 $(M - 3H_2O)^+$, and also ions with m/e 363 (II), 345, and 327, which are characteristic of ecdysones with a 20,22-diol grouping and the steroid nucleus of ecdysterone [4, 5].

The ion with m/e 99 that is characteristic for the mass spectrum of ecdysterone [5] and is formed from the elements of the side chain as the result of the cleavage of the C-20—C-22 bond and the elimination of a molecule of water is shifted by 12 m.u. in the spectrum of (I) (m/e 111, $C_7H_{11}O$). The absence of an isotopic shift for the ion with m/e 111 in the spectrum of the DO analog of the ecdysone (I) is evidence that it has the cyclic structure (III) [3]. The decomposition of the ion (III) taking place with the elimination of a C═O molecule leads to the strong peak of a fragment with m/e 83 (IV, C_6H_{11}). The increase in density of the latter can be explained by its high stability.

The formation of ions with m/e 111 and 83 shows the presence of a hydroxy function at C-25 and, at the same time, the presence in the side chain of the phytoecdysone (I) of an additional carbon atom as compared with ecdysterone.

Thus, the results of mass-spectrometric fragmentation lead us to the conclusion that the substance isolated belongs to the ecdysones of the C-28 series.

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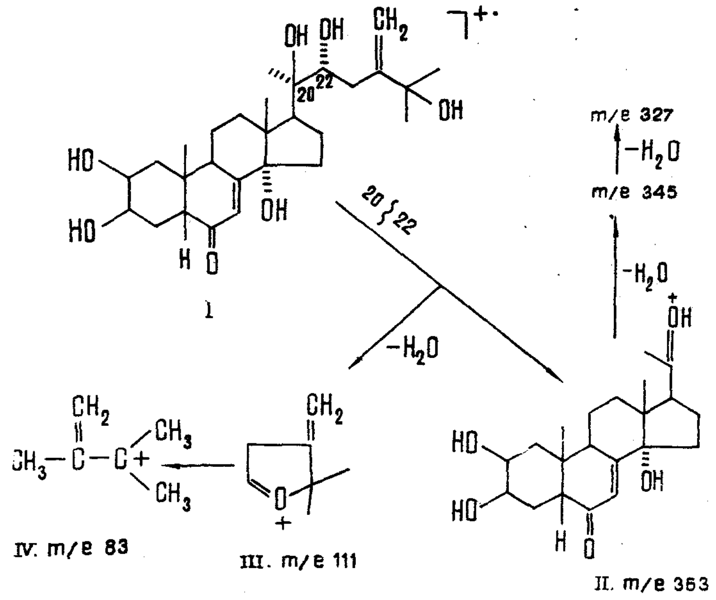

The circular dichroism curve of the compound described is characterized by a negative Cotton effect with $\Delta = -4.3$ ($\pi \to \pi^*$ transition, 248 nm) and a positive Cotton effect with $\Delta = +1.7$ ($n \to \pi^*$ transition, 334 nm), which shows the presence in the ecdysone (I) of a 5β(H)-Δ^7-6-keto-14-hydroxy grouping [6].

The practical coincidence of the values of the chemical shifts of the C-18, C-19, and C-21 methyl groups of the new phytoecdysone with those for ecdysterone [2] permits us to consider that in the steroid nucleus of the compound under investigation hydroxy groups are present in the 2β, 3β, and 14α positions; the hydroxy group at C-20 has the same configuration as in ecdysterone (20R).

Two broadened one-proton singlets in the PMR spectrum of the phytoecdysone (I) at 5.14 and 4.97 ppm, in combination with the mass-spectral characteristics given above, show the presence of a vinylidene link in the side chain of this phytoecdysterone.

The position of attachment of the $=CH_2$ group is obviously the C-24 atom. It is just this position which explains the shift in the resonance lines of the C-26 and C-27 methyl groups downfield by 0.18-0.24 ppm as compared with the corresponding signals of the PMR spectrum of ecdysterone [2].

Thus, the ecdysone (I) is a 24(28)-unsaturated derivative of the known phytoecdysone makisterone A [4, 7]. We have called the new phytoecdysone 24(28)-dehydromakisterone A. The R configuration of the 22-hydroxy group in 24(28)-dehydromakisterone A is given by analogy with known ecdysones [8].

EXPERIMENTAL

For general details, see [2].

The elementary compositions of the ions were measured on an MKh-1310 instrument.

24(28)-Dehydromakisterone A (I). In the preceding paper [3] we described the isolation from 25 kg of flower heads of *Rh. integrifolium* of ecdysterone, integristerone A, and integristerone B. From the mother solutions remaining after the isolation of these ecdysones, by repeated rechromatography on silica gel [with elution by chloroform–methanol (15:1)] we obtained 60 mg (0.00024%, calculated on the air-dry raw material) of 24(28)-dehydromakisterone A, $C_{28}H_{44}O_7$, mp 244-246°C (methanol); $[\alpha]_D^{20}$ +54.4±2° (c 0.37; methanol); $\lambda_{max}^{C_2H_5OH}$ 245 nm (log ε 4.15); ν_{max}^{KBr}, cm^{-1}: 3300-3500 (OH), 1665 (conjugated ketone). CD (c 0.08; methanol): $\Delta\varepsilon = -4.3$ (248 nm); $\Delta\varepsilon = +1.7$ (338 nm). PMR spectrum (C_5D_5N, 100 MHz, HMDS, δ, ppm): 0.95 (3 H at C-19, s); 1.08 (3 H at C-18, s); 1.40, 1.46 (6 H at C-26 and C-27, s); 1.46 (3 H at C-21, s); 3.45 (H at C-9, m); 3.75-4.20 (3 H at C-2, C-3, and C-22, m); 4.97, 5.14 (2 H at C-28, broadened singlets); 6.08 (H at C-7, broadened singlet).

Mass spectrum, m/e (%): 474 (3), 456 (11), 438 (15), 363 (66), 345 (100), 327 (47), 309 (13), 300 (26), 173 (17), 113 (37), 111 (55), 97 (52), 95 (63), 93 (35), 83

(91), 71 (62), 69 (62). Measurement of the masses of the ions with m/e 111 and 83. Found: 111.0813, 83.0869. Calculated: 111.0810, 83.0861. Composition: 111 ($C_7H_{11}O$), 83 (C_6H_{11}).

SUMMARY

A new phytoecdysone has been isolated from the flower heads of *Rhaponticum integrifolium*, and for it the structure of 24(28)-dehydromakisterone A has been established.

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INFLUENCE OF SOLVENTS ON THE PARAMETERS OF THE PMR SPECTRA OF THE PHTHALIDE-ISOQUINOLINE ALKALOIDS. VI

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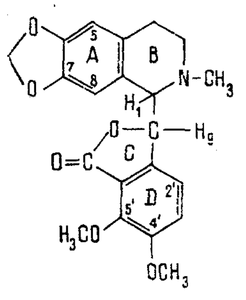
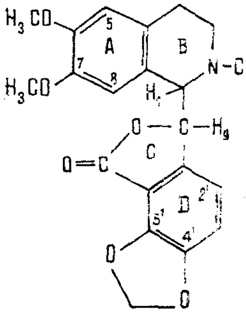
In the present work, which is a continuation of our investigations of the influence of solvents on the parameters (CSs and SSCCs) of the NMR spectra of alkaloids [1], we give the results of d-β- and d-α-hydrastines (I) and (II), respectively, corlumine (III), and adlumine (IV). The structures of these bases have been established previously [2-5]. The determination of the absolute configurations and stereochemical features of the phthalide-isoquinoline alkaloids has been considered by Znatzke et al. [6] and by Sate and Moir [7]. Later, summarizing the available information and basing his considerations on the results of his own NMR investigations, Shamma [8] suggested that the erythro (I, III) and threo (II, IV) conformations were the most likely for the bases of this series. We have studied the influence of solvents on the parameters of the NMR spectra of alkaloids (I-IV) in the following 10 solvents: $CDCl_3$, CCl_4, CD_3CN, CD_3OD, $(CD_3)_2CO$, DMF, DMSO, TFA, C_5D_5N, and C_6D_6. The results for four solvents are given in Tables 1 and 2.



I. 1R,9S II. 1S,9S



III. 1S,9R IV. 1R, 9R

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