ν_{max}^{KBr} 3370 cm^{-1} (OH), 1645 cm^{-1} (Δ^7-6-keto grouping). Mass spectrum, m/e (%): 464 (M^+; 1), 446 (3), 428 (10), 413 (8), 410 (14), 395 (6), 392 (6), 377 (5), 347 (35), 329 (90), 312 (33), 311 (28), 303 (9), 302 (11), 297 (13), 295 (14), 285 (30), 284 (35), 234 (15), 233 (15), 99 (100), 81 (73).

Literature information [2, 3]: mp 250-252°C, $\lambda_{max}^{C_2H_5OH}$ 243 nm (ε 12,100), ν_{max}^{KBr} 3450, 1645 cm^{-1}; M^+ 464.

3,22-Diacetyl-2-deoxyecdysterone. The ecdysterone (IV) (0.38 g) was acetylated with acetic anhydride under the same conditions as were given for the preparation of the diacetate of the preceding compound. The column with the crude product was eluted with chloroform–methanol (100:1). This gave 0.31 g of the diacetyl derivatives $C_{31}H_{48}O_8$, mp 185-186°C (from methanol), $[\alpha]_D^{24}$ +79.3 ± 3° (c 0.50; CH_3OH); $\lambda_{max}^{C_2H_5OH}$ 243 nm (log ε 4.10); ν_{max}^{KBr} (cm^{-1}) 3460 (OH), 1740 (C=O), 1665 (Δ^7-6-keto grouping), 1265 (C–O–C). Mass spectrum, m/e (%): 548 (M^+; 0,2), 530 (0,5), 515 (1), 512 (0,5), 497 (2), 488 (2), 470 (15), 460 (5), 455 (10), 452 (33), 442 (6), 437 (22), 389 (80), 371 (45), 346 (13), 341 (11), 329 (80), 327 (23), 326 (18), 311 (100), 276 (32), 275 (11), 216 (36), 215 (27), 99 (48), 81 (84).

SUMMARY

Five phytoecdysones have been isolated from Silene praemixta M. Pop. (family Caryophyllaceae), among them the known 2-deoxy-α-ecdysone and 2-deoxyecdysterone and the new silenosterone and premixisterone.

Silenosterone has the structure of 14α,22R,25-trihydroxy-5β-cholest-7-ene-3,6-dione. This is the first time that a native ecdysterone has been found with a ketone group at C-3.

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PHYTOECDYSONES OF Silene praemixta.

II. Premixisterone

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The structure of premixisterone (I) — a new ecdysteroid from S. praemixta M. Pop. (Caryophyllaceae) — has been established. Compound (I) has the composition $C_{27}H_{44}O_5$, mp 110-112°C (from $C_2H_5OH + H_2O$), $[\alpha]_D^{24}$ 0 ± 4° (c 0.85; MeOH), $\lambda_{max}^{C_2H_5OH}$ 202 nm (log ε 3.35), ν_{max}^{KBr} 3415 cm^{-1} (OH), 1710 cm^{-1} (C=O), and does not contain the Δ^7-6-keto grouping that is characteristic of natural ecdysteroids. The acetylation of (I) with $(CH_3CO)_2$ in Py gave the amorphous 3,22-diacetylpremixisterone (II), $C_{21}H_{48}O_7$. Compound (I) has the structure of 3β,14α,22R,25-tetrahydroxy-5β-cholest-8-en-6-one. The IR, PMR, and mass spectra of (I) and (II) are given.

We have previously [1] reported that five phytoecdysones have been found in Silene praemixta M. Pop., family Caryophyllaceae, including two new ones — silenosterone and premixi-

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sterone. The present publication is devoted to determining the structure of premixisterone (I).

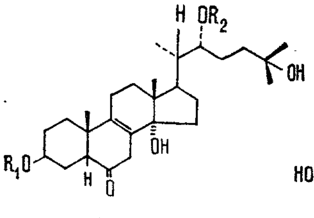
The UV spectrum of the new phytoecdysterone lacks the absorption maximum at 242-244 nm that is customary for the overwhelming majority of ecdysteroids. In place of this it is possible to see a weaker maximum at 202 nm which must obviously be ascribed to an isolated tri- or tetrasubstituted double bond in a polycyclic nucleus. In full agreement with the UV spectrum, in the IR spectrum of premixisterone there is no absorption band at 1640-1670 cm^{-1} that is characteristic for a Δ^7-6-keto grouping, but there is a maximum at 1710 cm^{-1} corresponding to the single carbonyl group.

In its main outlines, the mass spectrum of premixisterone (I) resembles that of 2-deoxy-α-ecdysone (III), which is found in the same plane [1]. Characteristic for each compound is the presence of a molecular peak with the same m/e value (M^+ 448). The elementary compositions of the steroids being compared are also the same — $C_{27}H_{44}O_5$. Fragments with high masses formed by the splitting out of the elements of water or of a methyl group (with m/e 430, 415, 412, 397, 379) are either identical in intensity or have only slight differences.

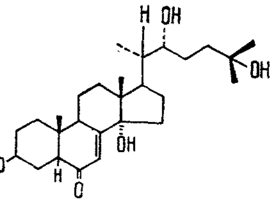
The fragmentation of the side chain of premixisterone (I), like the decomposition of the corresponding section of the molecule of 2-deoxy-α-ecdysone (III), is characterized by high-intensity peaks with m/e 99 and 81. This shows that the side chains of the two ecdysones have the same structure and do not contain a diol grouping, as is the case with ecdysterone.

The most important difference between the spectra of the compounds under comparison is found in the contribution of the ion with m/e 277. Its elementary composition is $C_{18}H_{29}O_2$. In the spectrum of premixisterone, in the range from M^+ to 200 m/e the peak of this ion is the maximum peak. In the case of 2-deoxy-α-ecdysone in the same interval a fragment with m/e 234 is more pronounced, and relative to the intensity of this peak, that of the ion with m/e 277 amounts to only 5%. The ion with m/e 234 is also fairly prominent in the spectrum of compound (I).

The acetylation of premixisterone (I) with acetic anhydride gave a diacetate (II). In the high-mass region of the spectrum of this compound the maximum peak is that of an ion with m/e 454 which was apparently formed as the result of the elimination of the elements of water and of acetic acid ($M^+ - 18 - 60$). In the spectrum of 3,22-diacetyl-2-deoxy-α-ecdysone the fragment with m/e 454 is less pronounced. The mass spectrum of the diacetate (II) contains the peak of an ion with m/e 319 which is an analog of the ion with m/e 277 in the spectrum of premixisterone, but its intensity is comparatively low.



I. $R_1 = R_2 = H$
II. $R_1 = R_2 = Ac$



III

In the PMR spectrum of the new compound, attention is attracted primarily by the absence of the signal of the H-7 olefinic proton. In this region of the spectrum there are only highly broadened signals of hydroxy groups (4.6-6.2 ppm). There is no signal of the proton at C-9. In 2-deoxy-α-ecdysone (III) this proton resonates at 3.42 ppm. Of other differences in the spectra of the compounds being compared it must be mentioned that in premixisterone the signal of the C-18 methyl is shifted downfield by 0.20 ppm. This is in harmony with the fact that in cheilanthone A — an ecdysteroid from Cheilanthes tenuifolia [2] — which differs from α-ecdysone only by the absence of a double bond at C-7, the signal of this angular methyl group also suffers a paramagnetic shift by 0.13 ppm. The values of the chemical shifts of the other signals in the PMR spectra of compounds (I) and (III) are completely comparable:

	3-H	*7-H*	*9-H*	*18-H₃*	*19-H₃*	*21-H₃*	*22-H*	*26/27-H₆*
Premixisterone	4,09	—	—	0,81	0,98	1,09	3,72	1,30
2-Deoxy-α-ecdysone	4,00	6,13	3,42	0,61	0,95	1,17	4,00	1,26

On analyzing the combined information obtained by various methods, we came to the conclusion that, unlike other ecdysone-like compounds, premixisterone contains not a Δ^7 but a Δ^8 double bond. In the remainder of the molecule, the structure of the new phytoecdysone is identical with that of 2-deoxy-α-ecdysone.

Of the ecdysteroids described in the literature, podecdysone B, found in *Podacarpus elatus* [3], is close to premixisterone in structure. Podecdysone contains two double bonds: Δ^8 and Δ^{14}. In the spectral characteristics of podecdysone B the most striking fact is that the presence of a double bond between C-8 and C-9 has no effect on the chemical shift of the protons of the methyl group at C-19 (the PMR spectra of podecdysone B and of ecdysterone were compared), while the protons of the methyl group at C-18 undergo an appreciable paramagnetic shift (by 0.13 ppm in deuteropyridine). This fact can be used as another explanation of the reason for the shift in the signal of the C-18 methyl protons in premixisterone, with the stipulation that in podecdysone B the downfield shift is caused not by a single double bond but by conjugated double bonds.

As a working formula for premixisterone we propose the structure of 3β,14α,22R,25-tetrahydroxy-5β-cholest-8-en-6-one (I).

EXPERIMENTAL

For the method of isolation, the instruments, and the chromatographic conditions, see the preceding paper [1].

Premixisterone (I). $C_{27}H_{44}O_5$, mp 110-112°C (from dilute aqueous ethanol), $[\alpha]_D^{24}$ 0 ± 4° (c 0.86; CH_3OH), R_f ~ 0.43 (chloroform–ethanol (9:1), TLC on silica gel); $\lambda_{max}^{C_2H_5OH}$ 202 nm (log ε 3.35); ν_{max}^{KBr} 3415 cm^{-1} (OH), 1710 cm^{-1} (C=O). Mass spectrum, m/e (%): 448 (M^+; 1), 430 (11), 415 (4), 412 (7), 397 (5), 394 (3), 379 (2), 361 (10), 343 (6), 332 (5), 314 (5), 303 (4), 299 (4), 285 (7), 284 (4), 277 (33), 234 (18), 233 (14), 215 (16), 99 (100), 81 (37).

The substance is readily soluble in ethanol, acetone, and chloroform and sparingly soluble in benzene and water.

3,22-Diacetylpremixisterone (II). At room temperature, 36 mg of premixisterone in 5 ml of pyridine was acetylated with 2.5 ml of acetic anhydride for 16 h. After the reagents had been distilled off in vacuum, the residue was chromatographed on silica gel (15 g). Elution of the column with chloroform gave 28 mg of the amorphous diacetate (II), $C_{31}H_{48}O_2$, ν_{max}^{KBr} (cm^{-1}) 3440 (OH), 1730, 1710 (C=O), 1250 (C–O–C). Mass spectrum, m/e (%): 532 (M^+; 2), 517 (1), 514 (4), 496 (1), 472 (18), 457 (11), 454 (40), 439 (4), 436 (6), 412 (10), 394 (38), 379 (11), 374 (12), 373 (12), 345 (18), 327 (8), 326 (9), 319 (6), 314 (20), 313 (12), 285 (18), 276 (8), 275 (9), 267 (10), 259 (15), 228 (16), 216 (26), 215 (40), 186 (25), 161 (30), 99 (100), 81 (80).

SUMMARY

Premixisterone — a new ecdysterone from *Silene praemixta* M. Pop. (family Caryophyllaceae) — has the structure of 3β,14α,22R,25-tetrahydroxy-5β-cholest-8-en-6-one.

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