J = 11 and 4 Hz); 4.89 (1 H, d, J = 7.5 Hz, anomeric proton at C-1'); 5.35 (1 H, d, J = 7.5 Hz, anomeric proton at C-1''); 5.41 (1 Hz, pseudotriplet, >C=C—H);); 6.30 (1 H, d, J = 7.5 Hz, anomeric proton at C-1'''). On TLC in system 2 silphioside E was identified.

SUMMARY

From the epigeal part of Silphium perfoliatum L a new triterpene glycoside C, has been isolated which is 28-β-D-glucopyranosyl 3-O-[O-β-glucopyranosyl-(1→2) -(6'-O-acetyl-β-D-glucopyranosyl)]oleanolate.

LITERATURE CITED

1. E. S. Davidyants, Zh. M. Putieva, V. A. Bandyukova, and N. K. Abubakirov, Khim. Prir. Soedin., 120 (1984); 666 (1984); 750 (1984).
2. A. S. Shashkov and O. S. Chizhov, Bioorg. Khim., 2, 437 (1976).

PHYTOECDYSTEROIDS OF Silene nutans.

III. NUSILSTERONE

U. Baltaev, Ya. V. Rashkes and N. K. Abubakirov

UDC 547.926:541.69

A new ecdysteroid — nusilsterone — has been insolated from the whole plant Silene nutans L. It has been shown that it is 1β,2β,3β,14α,20R,22R,24ξ,25-octahydroxy-5-β-cholest-7-en-6-one.

We have previously [1, 2] reported the isolation from Silene nutans L. (family Caryophyllaceae) by high-pressure liquid chromatograpy of ecdysterone, polypodin B and 22-deoxyecdysterone. In the present paper we have given experimental details of the finding in this plant of another pytoecdysteroid which we have called nusilsterone (I).

The UV spectrum of the new ecdysteroid had a storng maximum at 244 nm (log ε 4.09), which is characteristic for 6-keto-7-ene steroids, and in the IR spectrum, in addition to the absorption of hydroxy groups (3350-3450 cm^{-1}) there was a band at 1660 cm^{-1} corresponding to a keto group conjugated with a double bond.

The mass spectrum of nusilsterone (I) lacked the molecular ion, but in the region of high mass numbers the leaks of ions with m/z 494 ($M - H_2O^+$), 476, 458, and 440 ($C_{27}H_{36}O_5$) were observed. In the region of the PMR spectrum where olefinic protons usually resonate the new compound had a single broadened one-proton singlet at 6.12 ppm which is characteristic for the protons at C-7 ecdysteroids. It followed from the facts given that the substance that we had isolated belonged to the series of ecdysteroids containing eight OH groups in the molecule, and its molecular weight was 512.

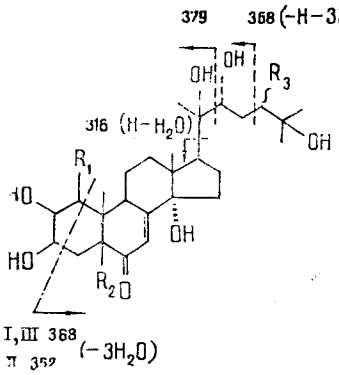
The key fragments formed on the cleavage of the C-20—C-22 contained 379, 361, 343, and 325 m.u., and in this compound an ion with m/z 316 ($C_{19}H_{24}O_4$) characterized the breakdown at the C-17—C-20 bond. These facts showed on the one hand, the presence of an OH group at C-20 and, on the other hand, the presence of four hydroxyls in the steroid nucleus.

The PMR spectrum of nusilsterone (I) had a broadened singlet at 4.10 ppm recalling in its nature the signal of the three protons of integristerone A (II) [3] located geminally to secondary hydroxy groups at C-1, C-2, and C-3. By analogy with integristerone A, we were justified in assuming that in the new ecdysteroid, as well, secondary hydroxy groups were present at C-1, C-2, and C-3 of the steroid nucleus and had the β orientation. One of the two-proton multiplets at 3.69-3.74 ppm had to be assigned to a proton at C-22, and the other to one at C-24.

Institute of Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent.

Translated from Khimiya Prirodnykh Soedinenii. No. 4, pp. 522-525, July-August, 1985. Original article submitted September 18, 1984.

0009-3130/85/2104-0489$09.50



I. R_1, R_3=OH; R_2=H. M 512

II. R_1=OH; R_2, R_3=H. M 496

III. R_1, R_3=H; R_2=OH. M 496

The circular dichroism (CD) curve of nusilsterone (I) exhibited positive and negative Cotton effects with $\Delta\varepsilon$ = +1.59 ($\pi\rightarrow\pi^*$ transition, 331 nm) and $\Delta\varepsilon$ = −3.38 ($n\rightarrow\pi^*$ transition, 251 nm), which showed the presence of a 6-keto-14-hydroxy-7-ene-15β(H) grouping in the ecdysteroid.

In the mass spectra of edcysteroids, the simultaneous presence of OH groups at C-22 and C-25 usually leads after their dehydration and the cleavage of the C-20–C22 bond to a cyclic fragment with m/z 99 [4]. In the spectrum of nusilsterone (I), this fragment was displaced by 16 m.u. and contained an additional oxygen atom ($C_6H_{11}O_2$, m/z 115). Its dehydration led to an ion with m/z 97 (C_9H_9O), which was the maximum ion in this spectrum. This meant that one of the OH group was present at C-23 or C-24. The choice between the alternative positions was made on the basis of the results of a study of the mass numbers and elementary compositions of the ions arising on the cleavage of the C-23–C-24 bond. The existence of an ion with m/z 368 ($C_{23}H_{28}O_4$) in the spectra of nusilsterone (I), as in that of integristerone A (II) [3] and that and polypodin B (III) showed the existence of an equal number of OH groups in the C-1–C-23 chain. It was most likely that the additional hydroxyl in nusilsterone was located at C-24.

According to Pinheiro et al. [5], the mass spectrum of abutasterone with an OH group at C-24 also contains peaks with m/z 115 and 97.

In the process of determining the accurate masses of the ions of nusilsterone (I) we turned our attention to the presence of a component of the ion with m/z 368 [6] corresponding to the composition $C_{24}H_{22}O_3$ (about 1/3 of the sum of the heights of the ions of this mass). A check on the compositions of the ions with m/z 367 and 369 also revealed considerable proportions of components including 24 carbon atoms. Ions of such a composition cannot arise as a result of C-24–C-25 cleavage. We assumed that they appeared as a consequence of the cleavage of the bonds of ring A due to the presence of a triol chain. Measurement of the compositions of the corresponding ions with m/z 351 and 353 in the spectrum of integristerone A (II) confirmed the presence of a C_{24} component.

It must be assumed that these ions were formed by the cleavage of the C-1–C-10 and C-3–C-4 bonds with the migration of hydrogen in one or the other direction and the loss of three molecules of water. A similar experiment with the m/z 367-369 ions of polypodin B, which does not contain a triol chain, gave rise to practical none of a component including 24 carbon atoms.

The combination of facts given shows that nusilsterone (I) has the structure of 1β,2β, 3β,14α,20R, 22R,24ξ,25-octahydroxy-5β-cholest-7-en-6-one.

EXPERIMENTAL

IR spectra were obtained on a UR-20 spectrometer (KBr). Circular dichroism was determined on a I-20 spectropolarimeter. Mass spectra were recorded on a MKh-1310 instrument fitted with a system for the direct introduction of the smaple into the ion source, at an ionizing voltage of 50 V, a collector current of 30 μA, and a temperature of the evaporator bulb and of the ionization chamber of 130-150°C.

The accuracy of the mass determinations at R = 10,000 was $5\cdot10^{-6}$. The reference substance was perfluorokerosine. The PMR spectra were recorded on a JNM-4H-100 instrument, δ scale, 0 – HMDS, temperature of the sample 22 ± 2°C.

Isolation of Nusilsterone (I). The air-dry whole plant Silene nutans (10 kg) collected in 1983 in the environs of Ryazan' was extracted with a mixture of ethanol and methanol in a ratio of 2:1. The sum of the extractive substances so obtained was concentrated to 300 ml and diluted with two volumes of water. To free it from hydrophobic compounds, the aqueous alcoholic extract was treated with hexane (4 × 500 ml), and then the ecdysteroids were extracted with butanol (3 × 400 ml). After the solvent had been distilled off, 49.2 g of combined pytoecdysteroids was obtained.

The combined material obtained in this way was tranfereed to a column of silica gel, and elution was performed with chloroform–ethanol–water (65:50:6).

Unknown ecdysteroids of low polarity, 22-deoxyecdysterone, ecdysterone, and polypodin B were eluted from the column in succession. The following fractions 18-20 contained the new pytoecdysteroid, and these fractions were combined. The rechromatography of the combined fraction (5 g) yielded 1050 mg of two phytoecdysteroids, one of which was apparently integristerone A [3]. Additional separation of the mixture gave 200 mg (0.002% on the weight of the raw material of nusilsterone, $C_{27}H_{44}O_9$, mp 218-219°C (from a mixture of methanol and acetone), $[\alpha]_D^{20}$ + 111.2 ± 2° (*c* 0,3[illegible]; methanol); $\lambda_{max}^{C_2H_5OH}$, nm: 244 (log ε 4.09). ν_{max}^{KBr}, cm^{-1}: 3350-3450 (OH); 1660 (Δ^7-6-keto group). CD (c 0.06; dioxane): $\Delta\varepsilon$ = +1.59 (331 nm); $\Delta\varepsilon$ = −3.38 (251 nm). Mass spectrum, m/z (%): 512 (M^+, 0); 495 (1), 476 (2), 458 (10), 440 (4), 425 (6), 422 (3), 391 (3), 379 (4), 369 (2), 368 (5), 367 (2), 361 (15), 360 (11), 344 (25), 343 (24), 326 (35), 325 (27), 316 (25), 301 (17), 300 (23), 299 (15), 283 (21), 281 (21), 115 (60), 97 (100). PMR spectrum (C_5D_5N, 100 MHz, δ, 0 − HMDS, ppm): 0.91 (3 H at C-18, s); 1.32 (3 H at C-19, s); 0.98 and 1.04 (2 × 3 H at C-26 and C-27, s); 1.42 (3 H at C-21, s); 3.51 (H at C-9, m); 3.69-3.74 (2 H at C-22 and C-24, m); 4.10 (3 H at C-1, C-2, and C-3, m); 6.12 (H at C-7, br. s).

SUMMARY

From the whole plant Silene nutans L. a new ecdysteroid − nusilsterone − has been isolated. It has been shown that it is 1β,2β,3β,14β,20R,22R,24ξ,25-octahydroxy-5β-cholest-7-en-6-one.

LITERATURE CITED

1. U. Baltaev, Yu. P. Belov, M. N. Chumachenko, and N. K. Abubakirov, Khim. Prir. Soedin., 322 (1984).
2. U. Baltaev, Ya. V. Rashkes, V. N. Darmograi, Yu. P. Belov, and N. K. Abubakirov, Khim. Prir. Soedin., 62 (1985).
3. U. Baltaev, M. B. Gorovits, N. D. Abdullaev, M. R. Yagudaev, and N. K. Abubakirov, Khim. Prir. Soedin., 813 (1977).
4. U. Baltaev, M. B. Gorovits, N. D. Abdullaev, Ya. V. Rashkes, M. R. Yagudaev, and N. K. Abubakirov, Khim. Prir. Soedin., 457 (1978).
5. M. L. B. Pinheiro, W. W. Filho, A. I. da Rocha, and B. P. E. Wenkert, Phytochemistry, 22, 2320 (1983).
6. Ya. V. Rashkes and N. K. Abubakirov, Khim. Prir. Soedin., 518 (1980).