PHYTOECDYSTEROIDS OF PLANTS OF THE GENUS Lychnis

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In the territory of the USSR the genus Lychnis L., family Caryophyllaceae, is represented by eight species. Of these species, ecdysteroids have previously been detected only in Lychnis chalcedonica L. (Maltese cross campion) [2] and L. fulgens Fisch. et Curt. (briliant campion) [3].

We have investigated the epigeal mass of wild-growing plants of the genus Lychnis and of plants of this genus introduced into the Siberian Botanical Garden (Tomsk University) [4]. In the present communication we give the results of an investigation of two species: the wild-growing L. wilfordii (Regel.) Maxim (Wilford's campion) and the introduced species L. chalcedonica. The substances isolated by selective extraction with butanol of methanolic extracts were shown by preliminary analysis with the aid of TLC to contain five ecdysteroids. By chromatography on columns of alumina and silica gel two ecdysteroids (I and II) were isolated from L. wilfordii, and four (I, II, III, IV) from L. chalcedonica. On the basis of their physicochemical characteristics, and also by direct comparison with authentic samples, they were identified as ecdysterone (I), polypodin B (II) [5], 24(28)-dehydromakisterone A (III) [6] and integristerone A (IV) [7]. The yields of ecdysteroids calculated on the air-dry raw material from L. wilfordii were 0.097 and 0.010%, and from L. chalcedonica 0.045, 0.006, 0.0003, and 0.0002%, respectively.

Substance (I) – $C_{27}H_{44}O_7$, mp 240-242°C (from ethyl acetate–methanol), $[\alpha]_D$ +65.1° (c 1.4; methanol), $\lambda_{max}^{C_2H_5OH}$ 243 nm (log ε 4.05); ν_{max}^{KBr}, cm^{-1}: 3340-3500 (OH); 1660 (Δ^7-6-keto grouping). Mass spectrum, m/z: 480 (M^+), 462, 444, 426 ($M^+ - 4H_2O$), 300, 161, 143, 125, 107, 363, 345, 327, 309 ($M^+ - 117 - 3H_2O$), 99, 81. PMR spectrum (200 MHz, deuteromethanol, δ, ppm) 0.89 (CH_3-18), 0.96 (CH_3-19), 1.20 (CH_3-26/27), 1.20 (CH_3-21), 3.15 (H at C_{22}), 3.30 (H at C_9), 3.81 (H at C_2), 3.87 (H at C_3), 5.81 (H at C_7).

Substance (II) – $C_{27}H_{44}O_8$ mp 248-250°C (fom ethyl acetate–methanol), $[\alpha]_D$ +83.4° (c 0.9; methanol), $\lambda_{max}^{C_2H_3OH}$ 241 nm (log ε 4.01); ν_{max}^{KBr}, cm^{-1}: 3300-3440 (OH), 1685 (Δ^7-6-keto grouping); CD: Δε = +3.2 (330 nm), Δε = –5.6 (253 nm). Mass spectrum, m/z: 497 (M^+ + 1), 478 ($M^+ - H_2O$), 379, 361, 343, 325, 317, 299, 281, 161, 143, 125, 107, 99, 81.

Substance (III) – $C_{28}H_{44}O_7$, mp 246-248°C (from ethyl acetate–methanol), $[\alpha]_D$ +54.2° (c 0.3; methanol), $\lambda_{max}^{C_2H_5OH}$ 245 nm (log ε 4.11); ν_{max}^{KBr}, cm^{-1}: 3300-3500 (OH), 1665 (Δ^7-6-keto grouping). Mass spectrum, m/z: 474 ($M^+ - H_2O$), 456, 438, 363, 345, 327, 309, 300, 173, 113, 111, 97, 95, 93, 83, 71, 69.

Substance (IV) – $C_{27}H_{44}O_8$, mp 246-248°C (from ethyl acetate–methanol), $[\alpha]_D$ +34.2° (c 0.95; methanol), $\lambda_{max}^{C_2H_5OH}$ 245 nm (log ε 4.10); ν_{max}^{KBr}, cm^{-1}: 3300-3450 (OH), 1665 (Δ^7-6-keto grouping). Mass spectrum, m/z: 478, 460, 442, 424, 406, 427, 409, 379, 361, 343, 325, 316, 301, 161, 143, 125, 99, 81. PMR spectrum (100 MHz, deuteropyridine, δ, ppm): 1.12 (CH_3-18), 1.32 (CH_3-19), 1.24 (CH_3-26/27), 1.46 (CH_3-21), 3.42 (H at C_9), 3.74 (H at C_{22}), 4.16 (3H at C_1, C_2, C_3), 6.14 (H at C_7).

Substances (III) and (IV) were shown to be identical with authentic samples of 24(28)-dehydromakisterone A and integristerone A, which were first detected in the flower heads of Rhaponticum integrifolium C. Winkl [6, 7].

LITERATURE CITED

1. S. G. Gorshkov, Flora of the USSR [in Russian], Nauka, Moscow–Leningrad (1936), p. 698.
2. S. Imai, T. Toyosato, M. Sakai, J. Sato, S. Fujioka, E. Murata, and M. Goto, Chem. Pharm. Bull., 17, 340 (1969).
3. U. A. Baltaev, P. G. Gorovoi, and N. K. Abubakirov, Khim. Prir. Soedin., 794 (1986).

Siberian Botanical Garden, Tomsk. Institute of Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 584-585, July-August, 1991. Original article submitted October 17, 1990.

0009-3130/91/2704-0513$12.50

4. L. N. Zibareva and T. P. Sviridova, Rast. Res., 25, No. 4, 561 (1989).
5. J. Jizba, V. Herout, and F. Šorm, Tetrahedron Lett., No. 51, 5139 (1967).
6. U. A. Baltaev, M. B. Gorovits, Ya. V. Rashkes, and N. K. Abubakirov, Khim. Prir. Soedin., 463 (1978).
7. U. A. Baltaev, M. B. Gorovits, N. D. Abdullaev, M. R. Yagudaev, and N. K. Abubakirov, Khim. Prir. Soedin., 813 (1977).

STACHYSTERONE D, VITICOSTERONE E AND α-ECDYSONE FROM Lychnis chalcedonica

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We have previously reported the isolation from the epigeal part of Maltese cross campion Lychnis chalcedonica L., family Caryophyllaceae, of ecdysterone, polypodin B, 24(28)-dihydromakisterone, and integristerone A [1].

On rechromatography of the fractions of weakly polar compounds [SiO_2, chloroform–methanol: 1) (15:1); 2) (9:1)] three ecdysteroids were isolated. Their yields, calculated on the air-dry raw material were: for (I) – 0.0004; (II) – 0.0001; (III) – 0.0005%.

Substance (I), $C_{27}H_{42}O_6$, mp 255-257°C (ethyl acetate–methanol).

PMR spectrum (C_5D_5N, 0 – HMDS, δ, ppm): 0.95 (CH_3-18/19, s), 1.10 (CH_3-26/27, s), 1.28 (CH_3-21, s); 3.92-4.10 (H-2, 3 and H-22, m), 3.42 (H-9, t), 6.06 (H-7, br.s).

Mass spectrum, m/z: 462 (M^+), 444, 426, 406, 363, 345, 327, 309, 301, 279, 161, 125, 99, 81, 55.

Compound (I) was identified from its spectral characteristics as stachysterone D [2-4].

Substance (II), $C_{29}H_{46}O_8$, mp 196-198°C (acetone), $[\alpha]_D^{20}$ +58.9 ± 2° (c 0.72; methanol), ν_{max}^{KBr}, cm^{-1}: 3430 (OH), 1670 (Δ^7-6-keto grouping), 1730, 1275 (ester grouping).

PMR spectrum (C_5D_5N, 0 – HMDS, δ, ppm): 0.94 (CH_3-19, s), 1.08 (CH_3-18, s), 1.30, 1.36 (CH_3-26/27, s), 1.48 (CH_3-21, s), 1.80 (OAc), 3.46 (H-9, m), 3.68 (H-22, m), 4.08 (H-2, 3, m), 6.06 (H-7, br.s).

Mass spectrum, m/z: 522 (M^+), 462, 444, 426, 408, 411, 393, 375, 363, 301, 99, 81.

Compound (II) was identified from its spectral indices and by a direct TLC comparison (system 2) with an authentic sample as viticosterone E [5, 6].

Substance (III), $C_{27}H_{44}O_6$, mp 236-238°C (ethyl acetate–methanol), $[\alpha]_D^{20}$ +63.0 ± 2° (c 0.65; methanol).

PMR spectrum (C_5D_5N, 0 – HMDS, δ, ppm): 0.59 (CH_3-18, s), 0.94 (CH_3-19, s), 1.14 (CH_3-21, d, ^3J = 6 Hz), 1.24 (CH_3-26/27, s), 3.36 (H-9, m), 3.82 (H-2, 22, m), 4.06 (H-3, m), 6.02 (H-7, br.s).

Mass spectrum, m/z: 464 (M^+), 446, 431, 428, 413, 410, 395, 377, 348, 330, 315, 300, 126, 117, 109, 99, 81.

From its spectral characteristics and also by a direct comparison with an authentic sample, compound (III) was identified as α-ecdysone [7, 8].

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