PHYTOECDYSONES OF Serratula

IV. SOGDYSTERONE

I. L. Novosel'skaya,
M. B. Gorovits,
and N. K. Abubakirov

UDC 547.926:591.147

Previously, from S. sogdiana Bge. family Compositae we isolated ecdysterone [1] and viticosterone E [2]. Subsequently, by repeated rechromatography on silica gel and alumina of a methanolic extract from the flowers of the plant we have obtained a new phytoecdysone which we have called sogdysterone. Yield 0.003%.

Sogdysterone (I), $C_{27}H_{44}O_8$, is an amorphous substance, $[\alpha]_D^{20}$ + 43.9° (c 0.41; methanol); $\lambda_{max}^{C_2H_5OH}$ 242 nm (log ε 3.98); γ_{max}^{KBr} 3300-3500 (OH), 1665 cm^{-1} (C=C−C=O). It is a more polar compound than the other phytoecdysones isolated from S. sogdiana − R_f 0.16 [SiO_2/gypsum; chloroform−methanol (4 : 1)]. The optical rotatory dispersion curve of (I) (dioxane) showed positive ($[M]_{358}$ + 3520°; $[M]_{315}$ − 622°; a = +41°) and negative ($[M]_{260}$ − 3800°; $[M]_{233}$ + 14,300°; a = −181°) Cotton effects. This nature of the curve showed the presence of a 5β-Δ^7-6-oxo-14-hydroxy grouping in sogdysterone [3].

In the high-mass region of the mass spectrum of (I) there are peaks of ions with m/e 478 (M−H_2O), 460 (M−$2H_2O$), 442 (M−$3H_2O$), 424 (M−$4H_2O$), 409 (M−$4H_2O$−CH_3) and 406 (M−$5H_2O$), due to processes involving dehydration and the splitting off of one of the methyl groups. The peaks of ions with m/e 379, 361, 343, and 325 show the presence of four hydroxy groups in the steroid skeleton of the new phytoecdysone [4-6].

The fragmentation of the side chain of (I) is similar to the decomposition of the side of ecdysterone and is characterized by ions with m/e 99, 81, and 69 [7, 8].

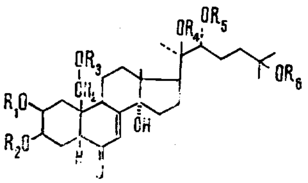
NMR spectrum of (I) (C_5H_5N, 100 MHz; HMDS, δ, ppm): 1.06 (3 H at C_{18}, s), 1.25 (6 H at C_{26} and C_{27}, s), 1.46 (3 H at C_{21}, s), 3.50 (H at C_9, m), 3.75 (H at C_{22}, m), and 6.15 (H at C_7). A broad four-proton multiplet in the 4.07-4.40 ppm region shows the presence of protons at C_2, C_3, and C_{19}. The absence from the NMR spectrum of I of the absorption of a C_{19}-methyl group permits the assumption that one of the hydroxy groups is located at C_{19}.

The acetylation of sogdysterone gave a mixture of the amorphic 2,3,19,22-tetraacetate (II), $C_{35}H_{52}O_{12}$ (M^+ − AcOH − H_2O; m/e 586); $[\alpha]_D^{20}$ + 56.4° (c 0.39; methanol) and the amorphous 2,3,19,22,25-pentaacetate (III), $C_{37}H_{54}O_{13}$ (M^+ − AcOH − $2H_2O$; m/e 610). NMR spectrum of (II) ($CDCl_3$): 0.80 (3 H at C_{18}, s), 1.18 and 1.15 (6 H at C_{26} and C_{27}, s), 1.22 (3 H at C_{21}, s).

In solution in dry acetone under the action of phosphotungstic acid, phytoecdysone (I) forms an amorphous diacetonide (IV), $C_{33}H_{52}O_8$ (M^+ 576), $[\alpha]_D^{20}$ + 50.0° (c 0.48; methanol). The production of the diacetonide (IV) shows the cis orientation of the hydroxy groups at C_2 and C_3. Bearing in mind the fact that the same plant contains ecdysterone and viticosterone E, the glycol grouping in sogdysterone can be assigned the 2β,3β-configuration.

The results of a comparison of the chemical shifts of the C_{18}, C_{21}, C_{25}, and C_{27} methyl groups of the new phytoecdysone with ecdysterone and of the tetraacetate of (II) with the triacetate of ecdysterone [1, 2, 7], and also the facts given above on mass-spectrometric fragmentation and optical rotatory dispersion permit the structure of 19,20R-dihydroxyecdysone to be proposed for sogdysterone:

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 429-430, May-June, 1975. Original article submitted February 20, 1975.



	R$_1$	R$_2$	R$_3$	R$_4$	R$_5$	R$_6$
I.	H	H	H	H	H	H
II.	Ac	Ac	Ac	H	Ac	H
III.	Ac	Ac	Ac	H	Ac	Ac
IV.	>CMe$_2$H			>CMe$_2$H		

LITERATURE CITED

1. I. L. Zatsny, M. B. Gorovits, and N. K. Abubakirov, Khim. Prirodn. Soedin., 840 (1971).
2. I. L. Zatsny, M. B. Gorovits, and N. K. Abubakirov, Khim. Prirodn. Soedin., 175 (1973).
3. H. Scherrer, Helv. Chim. Acta, 52, 2428 (1969).
4. J. Jizba, V. Herout, and F. Šorm, Tetrahedron Lett., 5139 (1967).
5. K. Nakanishi, Pure Appl. Chem., 25, 167 (1971).
6. B. Z. Usmanov, M. B. Gorovits, and N. K. Abubakirov, Khim. Prirodn. Soedin., 125 (1973).
7. N. N. Galbraith and D. H. S. Horn, Aust. J. Chem., 22, 1045 (1969).
8. I. L. Zatsny, M. B. Gorovits, Ya. V. Rashkes, and N. K. Abubakirov, Khim. Prirodn. Soedin., 155 (1975).