THE STEREOCHEMISTRY OF FEROPOLOL, FEROPOLIN, FEROPOLONE, AND FEROPOLIDIN

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We have previously isolated feropolin (I), feropolol (II), feropolone (III), and feropolidin (IV) from *Ferula polyantha* Eug. Kor. (synonym *Peucedanum polyanthum*) and have shown their structures [1]. The last-mentioned compound is the natural product of the cyclization of feropolol, as was shown by the cyclization of (II) with sulfuric acid in ethanol. Under these conditions, in addition to (IV) we obtained a very small yield of gummosin (V), a substance with an established absolute configuration [2-6]. In view of this, the study of the absolute configurations of (I-IV) is of definite interest. The formation of only two bicyclic cyclization products with an angular methyl group from feropolol shows that the primary process is probably the dehydration of the hydroxy group at $C_{9'}$ (II) with the formation of a double bond at $C_{9'}$-$C_{10'}$. Consequently, the hydroxy group at $C_{9'}$ in (II) has the axial orientation [7, 8]. In the following stage of the reaction cis addition takes place at $C_{9'}$—$C_{10'}$ double bond with the formation of two cyclization products — feropolidin (IV) and gummosin (V). The configuration with the nonsteroid trans linkage of the decalin ring and with the substituent ($-CH_2OAr$) at $C_{1'}$ in the axial position has been suggested [2-6].

Since the $C_{1'}$, $C_{9'}$, and $C_{10'}$ asymmetric centers may be involved in the cyclization reaction the substance with the endocyclic double bond (IV) may have eight isomers. In view of cis addition with respect to the double bond, it may be concluded that the four isomers with the cis linkage of the decalin rings are excluded, and feropolidin, like gummosin, has the trans linkage of the iresane ring.

The hydrogenation of ferropolidin and gummosin over a platinum catalyst in ethanol led to two dihydro derivatives with the composition $C_{24}H_{32}O_4$. The PMR spectrum of dihydroferopolidin lack the signals of the C_3—H and C_4—H protons of the coumarin nucleus but the signal of the olefinic proton is retained, and in the spectrum of dihydrogummosin the signals of the protons of the exomethylene group have disappeared and the signals of the protons of the umbelliferone residue have remained unchanged. These facts unambiguously show that feropolidin is not an isomer of gummosin in relation to the position of the double bond.

Of the other four possible configurations (a-d), the last two are unacceptable: feropolidin gives a depression of the melting point with conferol (d), and feropolidin acetate differs in its physicochemical constants from the acetate of "c" — anhydrokellerin.

On the basis of these signs of the specific rotations of terpenoid coumarins of the iresane series, by analogy with other iresane derivatives [9] we have recently put forward absolute configurations for a number of coumarins [10]. According to the laws that we have established, from the sign of its specific rotation (+154°, c 1.0; chloroform), feropolidin should possess a steroid trans linkage. This is confirmed by the following facts: the PMR sepctrum of feropolidin shows signals at (ppm) 0.85, 0.88, 0.90 (s, 3 H each, $C_{5'}$—$2CH_3$, $C_{9'}$—CH_3), 1.68 (br. s, 3 H, $C_{2'}$—CH_3), 3.43 (br. s, 1 H, $\Sigma_{1/2}J = 6$ Hz, C_6—H), 3.80 (q, 1 H, $J_{gem} = 10.5$ Hz, $J_{vic} = 1.5$ Hz), and 4.12 ppm (q, H, $J_{gem} = 10.5$ Hz, $J^2_{vic} = 6.0$ Hz, $C_{1'}$—CH_2—O—). In addition, in the 6.12-7.56 ppm region there are the signals of five protons of the coumarin nucleus. A comparison of the PMR spectra of feropolidin and anhydrokellerin* show that the CSs and SSCCs of the signals of the $C_{1'}$—CH_2OAr groups are similar, and consequently they have the same configuration at $C_{1'}$, $C_{9'}$, and $C_{10'}$.

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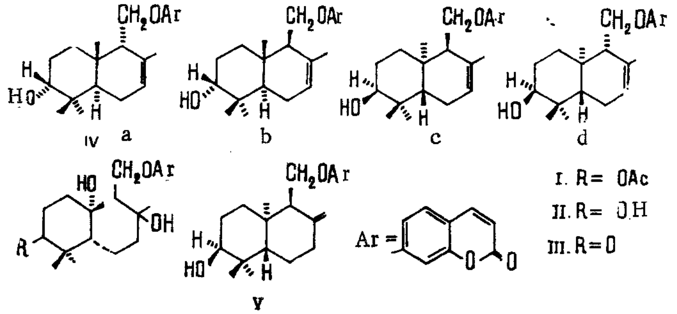

Thus, feropolidin (IV) is the mirror isomer of deacetylanhydrokellerin (c) with the axial $-CH_2OAr$ substituent at C_1' and for this we propose the absolute configuration "a." On the basis of the results obtained, it may be concluded that feropolin (I), feropolol (II), and feropolone (III) have the absolute configurations (I-III).

LITERATURE CITED

1. T. Kh. Khasanov, A. I. Saidkhodzhaev, and G. K. Nikonov, Khim. Prirodn. Soedin., 91 (1976).
2. N. P. Kir'yalov and S. D. Movchan, Khim. Prirodn. Soedin., 383 (1966).
3. V. Yu. Bagirov, N. P. Kir'yalov, V. I. Sheichenko, and V. N. Bochkarev, Khim. Prirodn. Soedin., 466 (1970).
4. M. E. Perel'son, N. P. Kir'yalov, and A. I. Ban'kovskii, Khim. Prirodn. Soedin., 244 (1975).
5. M. E. Perel'son, A. A. Kir'yanov, A. I. Ban'kovskii, N. P. Kir'yalov, and T. V. Bukreeva, Khim. Prirodn. Soedin., 442 (1976).
6. S.-M. Nasyrov, V. T. Andrianov, Yu. T. Struchkov, T. Kh. Khasanov, A. I. Saidkhodzhaev, and G. K. Nikonov, Khim. Prirodn. Soedin., 657 (1976).
7. H. Silver, J. R. Sherer, and K. L. Stevens, J. Org. Chem., 36, No. 17, 2422 (1971).
8. D. H. Barton, A. da Campos-Neves, R. S. Cookson, J. Chem. Soc., 3500 (1956).
9. G. Cimino, S. de Stefano, W. Fenical, L. Minale, and J. J. Sims, Exper., 31, 1250 (1975).
10. A. I. Saidkhodzhaev and V. M. Malikov, Khim. Prirodn. Soedin., 707 (1978)[in this issue].

CHEMICAL COMPOSITION OF THE STEMS OF *Ferula diversivittata*

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Continuing a study of the chemical composition of *Ferula diversivittata* Rgl. et Schmalh. [1-3] we have investigated the stems of the plant collected in the municipality of Daudan, Ashkhabad Oblast.

The combined substances were extracted from the stems of the plant with hydrolysis alcohol. The concentrated alcoholic extract was diluted with water (1:2) and treated with ether. From the ether-soluble fraction of the resin, chromatography on a column of KSK silica gel with petroleum ether–benzene yielded five individual substances: (I) – $C_9H_6O_3$, mp 228°C; (II) – $C_{19}H_{20}O_4$, mp 98°C; (III) – $C_{19}H_{20}O_4$, mp 55-57°C; (IV) – $C_{25}H_{30}O_7$, mp 179-180°C, $[\alpha]_D$ –36°C (c 0.1; chloroform); (V) – $C_{29}H_{32}O_9$, mp 185-186°C, $[\alpha]_D$ –284° (c 0.5; benzene).

The water-soluble fraction of the extract was treated with butanol. The concentrated butanol extract was deposited on a column of KSK silica gel and was eluted with chloroform–ethanol. This gave substance (VI) $C_{25}H_{34}O_{10}$, mp 154-155°C, $[\alpha]_D$ + 10° (c 1.0; ethanol).

From their physicochemical constants, elementary compositions, IR and NMR spectra, and mixed melting points with authentic samples, the substances were identified, respectively,

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