

spot with the R_f value of its methyl ester appeared. On GLC, peaks with relative retention time (RRTs) corresponding to methyl oleanolate and to β -sitosterol arose. On TLC, the presence of additional spots was observed but it has not been possible to determine their nature by GLC.

GLC analysis was performed on a Tsvet-100 instrument with a flame-ionization detector under the following conditions: carrier gas helium (60 ml/min), glass columns (0.4×150 cm) filled with Chromaton N-AW (0.200-0.250 mm) impregnated with 65% of SE-30 (174-300°C at 4°C/min).

Thus, the extract of a suspension culture of the cells of *Panax ginseng* C. A. Mey that was studied contained as the main components β -sitosterol β -D-glucoside and an oleanolic acid glycoside and must be studied in more detail.

LITERATURE CITED

1. T. Furuya, H. Kojima, K. Syono, and T. Ishii, Chem. Pharm. Bull., **18**, 2371 (1970).
2. T. Furuya, H. Kojima, K. Syono, and T. Ishii, K. Uotni, and M. Nishio, Chem. Pharm. Bull., **21**, 98 (1973).
3. R. I. Vysotskaya and L. I. Slepyan, Rast. Resur., **16**, No. 1, 123 (1980).

THERMAL TRANSFORMATIONS OF CARDIAC GLYCOSIDES AND AGLYCONS

I. F. Makarevich, A. I. Maslennikov, A. I. Pavlii,
V. S. Kulagina, D. V. Ol'khovik, S. G. Kislichenko,
and Yu. A. Chernyaev

UDC 547.911+547.926

The transformation of cardenolides under the action of dry heat has been investigated using a derivatograph on the Paulik-Paulik-Erdy system with photorecording. The transformed cardenolides formed in the first stages of the process were isolated preparatively in the pure form and were identified by a direct comparison with authentic samples. Strophanthidin, erysimin, gitoxin, gitoxigenin, strophanthidin oxime, and convallatoxin oxide (for their structures, see [1, 2]), were investigated.

On slow heating from room temperature to 230°C (2 h), strophanthidin formed a mixture of 17 α -strophanthidin (mp 245-247°C, $[\alpha]_D^{20} + 35.1 \pm 2^\circ$ (s 0.8; methanol), strophanthidin and anhydrocardenolides. The anhydrocardenolides were the main products; their presence was shown by the IR-spectrum, which had absorption bands in the 1650-1670 cm^{-1} region belonging to isolated C=C bonds.

Erysimin, on slow heating to 230°C (2 h) formed a mixture of cardenolides identical in their chromatographic characteristics with the mixture obtained in the experiments with strophanthidin. This unexpected result indicates, in the first place, the complete thermal hydrolysis of the glycoside.

A second, preparative, experiment with comparatively rapid heating (8-9°C/min) to a temperature of 185°C led to the formation of a mixture of cardenolides the main representative of which proved to be strophanthidin (mp 227-241°C); in addition, 17 α -strophanthidin (mp 245-248°C), erysimin, and 17 α -erysimin $[\alpha]_D^{21} + 22.0 \pm 3^\circ$ (c 1.0; methanol) were isolated. The capacity of erysimin for undergoing hydrolysis on dry heating is perhaps the main characteristic of this glycoside. Gitoxin, in spite of the presence of the same D-digitoxose residue in it, does not have the tendency to such ready hydrolysis (see below).

At 220°C, gitoxigenin and gitoxin were completely converted in 7 min into 16-anhydro- and 14,16-dianhydro- derivatives: 16-anhydrogitoxigen $[\alpha]_D^{20} + 88.0 \pm 5^\circ$ (s 0.4; methanol) λ_{max} ethanol 215 and 270 nm (in the UV region, 16-anhydrogitoxin has λ_{max} methanol 222 and

Khar'kov State Pharmaceutical Institute. All-Union Scientific-Research Institute of Drug Chemistry and Technology, Khar'kov. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 462-463, May-June, 1987. Original article submitted October 10, 1986; revision submitted January 10, 1987.

297); 14,16-dianhydrogitoxigenin $[\alpha]_D^{23} + 510 \pm 20^\circ$ (s 0.3; chloroform) (14,16-dianhydrogitoxin has λ_{\max} methanol 219 and 338 nm).

Strophanthidin 19-aldoxime formed as the primary transformation products 10-cyanostrophanthidin (mp 236-240°C), $[\alpha]_D^{20} + 51.0 \pm 2^\circ$ (s 0.7; methanol) and 10-cyano-17 α -strophanthidin. Assuming that this simple method of obtaining cardenolide nitriles may have independent value, we performed a kinetic investigation under various temperature conditions with the aim of selecting the optimum variant. It was established that at 250°C the maximum amount of 10-cyanostrophanthidin reached 45% after 15 min, and that of 10-cyano-17 α -strophanthidin 36% after 26 min. The activation energy of the process is 106 kJ/mole.

Convallatoxin oxime also formed nitriles as the primary products of thermal transformations.

The results obtained indicate the fairly high lability of cardiac glycosides and aglycons under the action of heat, which must be considered in laboratory practice and, particularly, under production conditions.

LITERATURE CITED

1. I. F. Makarevich, E. P. Kemertelidze, S. G. Kislichenko, et al., Cardenolides and Bufadienolides [in Russian], Metsniereba, Tbilisi (1975).
2. I. F. Makarevich, E. P. Kemertelidze, Transformed Cardiac Glycosides and Aglycons and their Biological Activity [in Russian], Metsniereba, Tbilisi (1984).

AN INVESTIGATION OF THE ALKALOID CONTENT OF SOME CENTRAL ASIAN PLANTS

M. V. Telezhenetskaya, A. D. Matkarimov,
S. N. Khadzhibekov, and S. Yu. Yunusov

UDC 547.944/945

We have investigated several plants of the family Boraginaceae. There is no information in the literature on the presence of alkaloids in *Suchtelenia calycina* DC., *Tournefortia sogdiana* M. Pop., and *Caccina crassifolia* C. Koch. The epigeal part of *S. calycina* collected in the Ust Urt plateau in the flowering stage contained 1.1% of total alkaloids, the bulk of which consisted of echinatine [1], which was identified by a direct comparison with an authentic sample. In view of the hepatotoxic properties of echinatine [2], it is undesirable to use the plant as a fodder plant. *T. sogdiana* was gathered in the environs of Peski, Turkmenia. The epigeal part contained a total of 3.5% of alkaloids, from which a substance was isolated with mp 145-147°C, $[\alpha]_D - 16.1^\circ$ (s 3.1; ethanol).

Mass spectrum, m/z: 283 (M^+ , 268, 240, 229, 238, 140, 138, 120, 94, 93, 80. PMR (CDCl₃): 0.98 (3 H, d); 0.90 (3 H, d); 1.19 (3 H, d). These facts characterized the base as supinine [1]. The epigeal part of *C. crassifolia*, gathered in the flowering stage in the gorge of the R. Fandar'ya in Tadzhikistan yielded 0.08% of a mixture of bases, the separation of which on a column of silica gel led to the isolation of a compound with 137°C (M^+ 299). According to the results of mass and PMR spectra, it was probably a new isomer of heliotridine retronecine trachelanthates, since its melting point did not agree with any of the five known pyroolizidine esters with mol. wt. 299 [3].

The epigeal part of *Rindera austroechinata* M. Pop. was collected in Kirkkuduk in Tadzhikistan in the budding stage. Echinatine and its N-oxide have been isolated from this plant previously [1]. In our sample, likewise, echinatine was the main alkaloid. The mother liquor after its separation was transferred to a column of alumina. Elution was performed with benzene and with ether. On elution with benzene-ethanol-chloroform, a base was isolated with mp 116-117°C $[\alpha]_D^{20} + 88.0 \pm 5^\circ$ (s 0.4; ethanol), -16.5° (c 1.4; chloroform); picrate with 164°C; M^+ 237. From these characteristics it was identified as 7-angeloylheliotridine [4]. This is the first time that it has been isolated from the genus *Rindera*. The ethereal eluates were rechromatographed on a column of silica gel. Rinderine [1] was isolated by elution with benzene-chloroform (1:1).

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnikh Soedinenii, No. 3, pp. 463-464, May-June, 1987. Original article submitted January 23, 1987.