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CARDIAC GLYCOSIDES FROM THE SEEDS OF *Digitalis ciliata*

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As has been shown previously, the seeds of *Digitalis ciliata* Trautv. contain a considerable amount of cardiac glycosides and steroid saponins [1, 2]. An original method has been developed for obtaining the steroid saponin digitonin from the seeds of this plant, and its production has been set up.

The aqueous liquid remaining after the seperation of the digitonin contained the cardiac glycosides of the initial raw material. For their isolation, the aqueous liquid was extracted successively with benzene–chloroform and with ethanol–chloroform. The first extract yielded combined glycosides containing two main cardenolides, and the second yielded seven.

Thw combined benzene–chloroform glycosides were separated on a column of silica gel of type L40/100 with elution by benzene containing increasing concentrations of ethanol. This gave the individual cardenolides (1) and (2).

Cardenolide (3) was isolated by the partition chromatography of the combined ethanol–chloroform glycosides on a column of type KSA silica gel saturated with water, using ethyl acetate–water as the mobile phase. The adsorption chromatography of the same combined material on a column of silica gel of type L60/100 with ethyl acetate–ethanol yielded cardenolide (4),

Cardenolide (1) – $C_{43}H_{66}O_{14}$, mp 218-222°C; $[\alpha]_D^{20}$ +25,2° (*c* 1,0 ; ethanol); $[\alpha]_D^{20}$ +4,9° (*c* 1,0 ; pyridine). UV spectrum, λ_{max}: 218 nm (log ε 4.19); in PC and TLC, it appeared in the region of acetyldigitoxin-α. The Legal, Raymond, Kedde, Pesez and Keller–Kiliani reactions for cardiac glycosides were positive. The Svendsen–Jensen and Keller–Kiliani reactions gave the colorations specific for glycosides of the digitoxigenin series and digitoxose. The reaction for an acetyl group was positive [3]. Alkaline saponification formed digitoxin. Acid hydrolysis gave an aglycone with mp 245-247°C, $[\alpha]_D^{20}$ +18,5° (*c* 1,22 ; ethanol) which was identified as digitoxigenin, and the sugar digitoxose.

On the basis of the results obtained, cardenolide (1) was characterized as digitoxigenin 3-O-bisdigitoxosidoacetodigitoxoside or acetyldigitoxin-α [2, 4].

Cardenolide (2) – $C_{41}H_{64}O_{13}$, mp 244-246°C, $[\alpha]_D^{20}$ +18,0° (*c* 0,1 ; chloroform + 1% ethanol). UV spectrum, λ_{max}: 220 nm (log ε 4.065). It gave all the reactions characteristic for glycosides of the digitoxigenin series and for digitoxose. It was not saponified by alkali Acid hydrolysis formed the aglycone digitoxigenin and the sugar digitoxose. Thus, cardenolide (2) was digitoxigenin 3-O-tridigitoxoside or digitoxin [5].

Cardenolide (3)– $C_{49}H_{76}O_{19}$, mp 244-246°C, $[\alpha]_D^{20}$ +31,0° (*c* 1,0 ; ethanol). UV spectrum, λ_{max}: 220 nm (log ε 4.2). Alkaline saponification formed a glycoside with the R_f value of deacetyllanatoside A. The Frerjacque reaction for an acetyl group was positive. After enzymatic hydrolysis, digitoxin and D-glucose were obtained. Acid hydrolysis yielded digitoxigenin, while digitoxose, digilanidobiose and glucose were detected in the carbohydrate fraction.

Cardenolide (3) was identiefied as digitoxigenin 3-O-bisdigitoxosideacetyldigilanidobio-

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side or lanatoside A [2, 6].

Cardenolide (4) – mp 239-241°C, $[\alpha]_D^{20}$ +3.0° (*c* 0.5 ; methanol). On PC and TLC it appeared at the level of an authentic sample of digitalinum verum, and a mixture gave no depression of of the melting point. With the Svendsen–Jensen reagent it fluoresced blue, which is characteristic for the glycosides of the gitoxigenin series. In the Keller–Kiliani reaction the layer of sulfuric acid acquired a carmine-red color and did not change under the action of acetic acid. The Pesez reaction was also negative, which also showed the absence of a 2,6-deoxysugar. It contained no acetyl or formyl groups. Acid hydrolysis gave the aglycone gitoxigenin and a sugar component consisting of glucose and digitalose. It underwent enzymatic hydrolysis with the enzyme of the grape snail with extreme difficulty, being split partially into strospeside and glucose.

The facts given above gave us grounds for concluding that cardenolide (4) was gitoxigenin 3-O-monodigitalosideglucoside or digitalinum verum [2, 7].

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PYRROLE DERIVATIVES FROM THE MARINE SPONGE Axinellidae Gen sp.

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Continuing a study of the secondary nitrogen-containing metabolites of marine sponges [1, 2] we have investigated the composition of an ethanolic extract from a marine sponge of the family Axinellidae (Tanzania, Mange reef) from the collections of the 12th voyage of the Scientific Research Ship "Professor Bogorov."

Repeated chromatography on silica gel and Sephadex LH-20 of a crude extract led to the isolation of five compounds each containing a pyrrole grouping in its structure.

The melting point and spectral characteristics of compound (I) coincided completely with those given in the literature for 4,5-dibromopyrrole-2-carboxylic acid [3, 4]. The structures of compounds (II), (III), and (IV) were established on the basis of a comparison of their spectral characteristics with literature information for 1,2,3,4-tetrahydropyrrolo[2,3-c]-5H-azepine-1,5-diol [5], debromohymenialdisine hydrochloride [5, 7], and hymenialdisine [6, 7], and also by a direct comparison with authentic samples of the substances isolated from the marine sponge Acanthella carteri [2].

From a fraction giving a qualitative reaction with diazotized benzidine and with the reagent for a guanidine group (sodium nitroprusside–potassium ferricanide in an alkaline medium), we isolated compound (V) with the composition $C_{11}H_{11}N_5OBr_2 \cdot HCl$, mp 222-223°C (MeOH–$H_2O$), $[\alpha]_D^{22}$ –204°. The mass spectrum showed the presence of two bromine atoms – M^+ 391, 389, 387 (1:2:1) – and of a guanidine fragment – 374, 372, 370 (M – NH_3), 363, 361, 359 (M – CHNH), 349, 347, 345 (M – NH_2CN) – in compound (V). These facts coincided with those given in the literature for dibromophakellin hydrochloride [8]. The ^{13}C NMR spectrum [(DMSO-d_6), δ: 156.5 (s, C-15); 153.3 (s, C-8); 124.8 (s, C-5); 114.5 (d, C-3); 105.8 (s, C-4); 101.5 (s, C-2); 82.0 (s, C-10); 68.1 (s, C-6), 44.6 (t, C-13); 38.6 (t, C-11); 19.0

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