UDC 615.711.5

CARDENOLIDE NICOTINATES

I. F. Makarevich

Khimiya Prirodnykh Soedinenii, Vol. 4, No. 4, pp. 255–256, 1968

Nicotinic acid and its derivatives are used in medical practice in several diseases, including disturbances of the coronary blood circulation. Consequently, it appeared of definite interest to introduce it as a component part of cardiac glycosides and aglycones and also to study its influence on the biological action of the latter.

Substance	Empirical formula	Mp, °C	$[\alpha]_D$, deg	Coloration with conc H_2SO_4
Strophanthidin 3-mononicotinate	$C_{30}H_{35}O_7N$	255—257	+39.9 ± 3 (in methanol)	Red (0'), yellow (5')
Digoxigenin 3,12-dinicotinate	$C_{35}H_{40}O_7N$	248—250	+27.4 ± 3 (in pyridine)	Yellow (0'), orange (80')
Cymarin 4'-mononicotinate	—	Amorphous	+31.1 ± 4 (in methanol)	Yellow (0''), green (5''), dark brown (3')

We have obtained in the form of esters the mononicotinates of strophanthidin and cymarin and the 3, 12-dinicotinate of digoxigenin. Their synthesis was effected in the following way. The cardenolide was dissolved in pyridine and nicotinoyl chloride was added at 0° C. The completeness of the reaction was checked by paper chromatography. After the end of the reaction, ice and a mixture of ethanol and chloroform (1:4) were added to the flask. The alcoholic-chloroformic layer was separated off and treated with sodium carbonate solution and with water, dried with anhydrous sodium sulfate, and evaporated in vacuum. The substances were crystallized from methanol. Their properties are given in the table.

UV spectra of the compounds obtained have a maximum at 263 mμ (log ε 3.22) and two sugars at 257 and 269 mμ which are characteristic for bound nicotinic acid, and also a maximum at 217 mμ (log ε 4.16) corresponding to the butenolide ring of a cardenolide.

The results of biological tests carried out by M. A. Angarskaya and Zh. A. Lyubetskaya unfortunately proved to be negative; the substances synthesized possessed no cardiotonic activity. In view of the fact that the benzoylation of the cardiac glycosides also causes a considerable reduction of their cardiotonic activity (compare the fact that the acetylation of the aglycones raises the activity), it may be assumed that the main cause of this phenomenon is the negative influence of the conjugation of an aromatic system. Attention is drawn to the fact that even a considerable distance of the nicotinic acid residue from the aglycone (the bearer of the action of the cardiac glycosides), as was the case in cymarin nicotinate, did not prevent the loss of cardiotonic activity from the glycoside. It is possible that a cardenolide and nicotinic or benzoic acid bound to it exert opposite biochemical effects.

26 February 1968

Khar'kov Chemical and Pharmaceutical Scientific-Research Institute

UDC 547.918

CARDENOLIDES OF CONVALLARIA KEISKEI

N. F. Komissarenko

Khimiya Prirodnykh Soedinenii, Vol. 4, No. 4, p. 256, 1968

It has previously been reported that desglucocheirotoxin, convallatoxin [1], convallatoxol, convallaside [2], and locundeside [3] have been isolated from C. keiskei Miq. In the present communication we give the results of a study of periplogenin rhamnoside (substance I of [1]) and its identification.