SUMMARY

Partial syntheses have been performed of glycosides of oleanolic acid at the C-3 hydroxyl and at the C-28 carboxy group: the 3-O-β-D-xylopyranoside (songoroside A), the 3,28-bis-O-β-D-xylopyranoside, and the 28-O-β-gentiobioside 3-O-β-D-xyloside of oleanolic acid.

The possibility has been shown of the formation of oleanolic acid 13,28-lactone 3-O-β-D-xylopyranoside in the glycosylation of oleanolic acid with acetobromoxylose.

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POLAROGRAPHIC DETERMINATION OF ALKALOIDS OF THE PYRROLIZIDINE SERIES IN PLANT RAW MATERIAL

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A polarographic method has been developed for the determination of platiphylline, sarracine, and seneciphylline in the epigeal part of the groundsel *Senecio platyphylloides* at a dropping mercury electrode in 0.5 M tetraethylammonium iodide solution.

Methods are known for the quantitative determination of platyphylline hydrogen tartrate in medicinal preparations which are based on processes of nonaqueous titration or of extraction followed by colorimetry or spectrophotometry [1], and also known are methods for the quantitative determination of platyphylline and seneciphylline in plant raw material which consist in repeated extraction of the alkaloids with ether from an alkaline medium followed by repeated extraction with a solution of hydrochloric acid and fractional titration [2] and a method for the quantitative determination of the alkaloids using extraction, chromatography, and photocolorimetry [3].

The disadvantages of these methods for the quantitative determination of alkaloids is the necessity for separating the combined alkaloids, the use of toxic and expensive organic solvents, the long times of analysis, and the unavoidable losses of alkaloids at all stages of the process.

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We have developed a polarographic method for the quantitative determination of alkaloids of the pyrrolizidine series which is based on the fact that the alkaloids (platyphylline, sarracine, and seneciphylline), and also their N-oxides, which are present in the plant raw material, are polarographically active. Platyphylline and sarracine give catalytic waves at the same potential, namely, —2.0 V, which permits the polarographic determination only of the sum of these two alkaloids. For platyphylline the height of the wave is proportional to its concentration in the range from 0.06 to 2.5 mg per 10 ml of solution, and for sarracine in the range from 5 to 0.1 mg per 10 ml of solution. Seneciphylline gives a wave at a more negative potential, —2.25 V, and the proportionality of the height of the wave to the concentration is in the range of from 0.001 to 0.1 mg per 10 ml of solution.

For investigation we used extracts of the epigeal part of *Senecio platyphylloides*, family Compositae. The results of thin-layer chromatography showed the presence of two distinct spots corresponding to platyphylline and seneciphylline.

To determine the optimum concentrations of platyphylline and seneciphylline when they were present together under the conditions of polarography we first investigated artificial mixtures of model systems. The limiting amounts of platyphylline and seneciphylline in the polarography of artificial mixtures were as follows:

Amount of platyphylline, mg per 10 ml of solution	*Permissible limits of the change in the concentration of seneciphylline*	*Amount of seneciphylline, mg per 10 ml of solution*	*Permissible limits of the change in the concentration of platyphylline*
2,50	0,06—0,02	0,10	1,50—0,25
2,00	0,07—0,02	0,08	1,80—0,15
1,00	0,09—0,015	0,05	2,50—0,05
0,50	0,10—0,006	0,03	1,20—0,05
0,25	0,07—0,002	0,01	0, —0,02
0,10	0,05—0,002	0,005	0,25—0,02
0,05	0,02—0,001	0,001	0,10—0,002

At approximately equal amounts of platyphylline and seneciphylline in the plant raw material [4], it was first necessary to carry out polarography with the aim of determining the platyphylline quantitatively and then, after 10-fold dilution and repeated polarography to determine the seneciphylline quantitatively. Under these conditions a polarogram of the extract showed two waves (Fig. 1) the potentials of which coincided with those given for platyphylline and seneciphylline. As we have shown previously [5], the N-oxide forms of the alkaloids present in the solution are reduced simultaneously with the basic forms.

EXPERIMENTAL

The work was carried out with a PA-3 polarograph and a dropping mercury electrode (m = 1.2 mg/sec, t = 3 sec). As the auxiliary electrode we used a saturated calomel electrode. Polarography was performed in a thermostated cell (25 ± 0.02°C) without the elimination of oxygen from the solution and the extract. The supporting solution was a 0.5 M aqueous solution of tetraethylammonium iodide. We used a 0.1% solution of gelatin to eliminate polarographic maxima. Polarography was carried out in the negative range of potentials from —0.6 to —2.6 V.

Construction of Calibration Graphs. In separate 500-ml measuring flasks, 0.125 g of platyphylline hydrogen tartrate, 0.25 g of sarracine, and 0.005 g of seneciphylline were dissolved and made up to the mark with a 0.5 M solution of tetraethylammonium iodide. From each of the solutions obtained, portions of 80, 60, 40, 20, 10, 5, and 1 ml were transferred to seven 100-ml measuring flasks and were made up to the marks with the supporting solution.

To construct the calibration graphs, 5-ml portions of each solution were taken and were chromatographed in the range of potentials given above. Calibration graphs were plotted in the coordinates current (μA) vs concentration (mg/10 ml of solution). The numerical coefficient for platyphylline hydrogen tartrate was 0.727.

Analysis of the Plant Raw Materials. The air-dry raw material comminuted to a size of particles passing through a sieve with apertures having a diameter of 1 mm (GOST 214-77) (1 g) was exhaustively extracted with 70% ethanol (1:10), the extract was evaporated in vacuum to dryness, and the residue was dissolved in 5 ml of water. To determine the platyphylline,

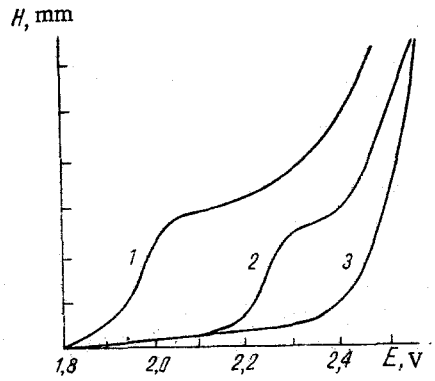

Fig. 1. Polarograms of a groundsel extract: 1) 0.5 ml of extract in 5 ml of supporting electrolyte; 2) after 10-fold dilution; 3) 0.05 M $(C_2H_5)_4NI$.

1 ml of the solution was transferred to a 25-ml measuring flask and was made up to the mark with the 0.5 M solution of tetraethylammonium iodide, and 5 ml of the resulting solution was polarographed. The amount of platyphylline in the extract (in grams) was determined from the calibration graph and was then recalculated to its percentage content in the dry raw material, which came to 0.215%.

To determine seneciphylline, 1 ml of extract was transferred to a 250-ml measuring flask and was made up to the mark with the 0.5 M supporting solution, and 0.5 ml of the resulting solution was used for polarography. The amount of seneciphylline in the extract was determined from the calibration graph as 0.165%. The total amount of alkaloids in the groundsel extract was 0.38%.

SUMMARY

A polarographic method has been developed for determining alkaloids of the pyrrolizidine series (platyphylline, sarracine, seneciphylline) in the epigeal part of *Senecio platyphylloides*.

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