## HYDROXYCINNAMIC ACIDS AND FLAVONOIDS

OF Antitoxicum scandens. I

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We have investigated the epigeal part of Antitoxicum (Vincetoxicum) scandens Pobed, family Asclepiadaceae [1] collected in June, 1974, in the Crimean oblast. The air-dry raw material was extracted with methanol three times. The methanolic extracts were combined, evaporated, diluted with water, and filtered.

By two-dimensional chromatography on paper in the solvent systems BAW (4:1:2) (first direction) and 15% CH<sub>3</sub>COOH (second direction) we detected in the extract obtained no less than 15 substances of phenolic nature consisting of flavonoids and phenolic carboxylic acids. The extract was treated with ethyl acetate. Fractions containing only a few components were combined, evaporated, and separated by paper chromatography in 2% CH<sub>3</sub>COOH and on a column of cellulose powder using aqueous solutions of CH<sub>3</sub>COOH.

Six substances (I-VI) were isolated in the individual state. According to qualitative reactions, substances (I-IV) were assigned to the phenolic carboxylic acids, and (V) and (VI) to flavonoid aglycones. On the basis of physicochemical investigations [2, 3] substance (I) was identified as sinapic acid ( $C_{11}H_{12}O_5$ , mp 199-200°C), (II) as ferulic acid ( $C_{10}H_{10}O_4$ , mp 168-171°C), (III) as caffeic acid ( $C_{9}H_{8}O_4$ , mp 197-200°C), (IV) as chlorogenic acid ( $C_{16}H_{18}O_9$ , mp 200-204°C), (V) as quercetin ( $C_{15}H_{10}O_7$ , mp 310-313°C), and (VI) as kaempferol ( $C_{15}H_{10}O_6$ , mp 274-276°C).

The glycosides of the aqueous extract were separated on a column of Kapron powder. Water and mixtures of water and ethanol were used as eluents. This gave a substance (VII) consisting of a diglycoside ( $C_{27}H_{30}O_{16}$ •  $H_{2}O$ , mp 227-230°C, [ $\alpha$ ]<sub>D</sub>-110°C, in methanol), which was cleaved, according to paper chromatography into quercetin, D-glucose, and L-rhamnose. The enzymatic hydrolysis of substance (VII) with an enzyme preparation of the fungus Aspergillus oryzae formed quercetin 7- $\alpha$ -L-rhamnoside and D-glucose, an alkaline hydrolysis [4] formed quercetin 3- $\beta$ -D-glucoside and L-rhamnose. Stepwise acid hydrolysis with a 0.04 N solution of hydrochloric acid in 50% ethanol in the boiling water bath led to the formation of considerable amounts of the intermediate substances mentioned above in 35-40 minutes.

Thus, substance (VII) can be characterized as quercetin  $3-\beta-D$ -glucosido- $7-\alpha-L$ -rhamnoside [5, 6]. We have isolated a similar substance previously from the epigeal part of clasping pepperweed [7].

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