SUMMARY

From the unsaponifiable fraction of an ethereal extract of the leaves of *Betula ermanii* a new triterpene of the dammarane series — 20,24-epoxydammarane-3β,6α,25-triol (II) — and its 6-O-acetyl derivative (I) have been isolated.

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THE HYDROLYSIS OF THE SAPONINS OF *Aralia manchurica*

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The saponins of *Aralia manchurica* (Manchurian aralia) consist of glycosides of oleanolic acid (aralosides A, B, and C). In addition to a tincture, which is used in medicine as a tonic, the total preparation "Saparal" recommended for the same purposes, is obtained from the Manchurian aralia [1]. The latter includes all three aralosides. Oleanolic acid and its semisynthetic derivatives, which possess physiological activities of various types [2-4], may be widely introduced into the practice of the public health service.

It appeared of interest to study the hydrolysis of the saponin aralosides, since the industrial wastes from the production of "Saparal" may serve as an additional source for the production of oleanolic acid.

Literature information relating to the conditions of the hydrolysis of the saponins of the Manchurian aralia is contradictory: Various hydrolysis mixtures and temperature conditions are proposed [5]. Moreover, the aglycone obtained in the process of hydrolysis requires additional purification from the products of transformation of sugars. To solve the problem posed we have investigated the hydrolysis of samples of the technical preparation "Saparal" kindly provided by the experimental factory of the All-Union Scientific-Research Institute of Medicinal Plants.

Below we give details of hydrolysis in various systems. The analysis of the samples was carried out every 5 min by thin-layer chromatography ["Silufol" plates, solvent system chloroform—methanol—water (61:32:7)]

Hydrolizing Mixture ratio (1:1)	Temperature, °C	Time of Hydrolysis
Water — 10% H_2SO_4	120	More than 4 h
Water — 20% H_2SO_4	"	"
Water — 30% H_2SO_4	"	"
CH_3COOH — 10% H_2SO_4	"	1 h 30 min
CH_3COOH — 20% H_2SO_4	"	30 min
CH_3COOH — 30% H_2SO_4	"	30 min
Acetone — 10% H_2SO_4	80	More than 4 h
Acetone — 20% H_2SO_4	"	"

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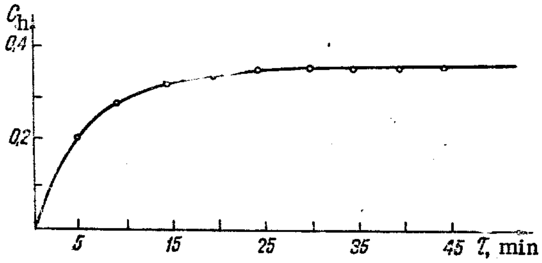

Fig. 1. Graph of the dependence of the hydrolysis yield on the time.

Hydrolyzing Mixture ratio (1:1)	Temperature, °C	Time of Hydrolysis
Acetone — 30% H_2SO_4	80	More than 4 h
Kiliani's mixture ($HCl + CH_3COOH + H_2O$, 10:35:35)	120	More than 4 h

The optimum agents for acid hydrolysis are a 1:1 mixture of 20% sulfuric acid and acetic acid and a 1:1 mixture of 30% sulfuric acid and acetic acid. The results obtained concerning the dependence of the yield of oleanolic acid on the time were used to plot a graph (Fig. 1) and to calculate the hydrolysis constant K from the formula

$$K = -\frac{2{,}303 \cdot \lg \frac{C}{C_0}}{\tau},$$

where C is the amount of aglycone remaining at time τ, and C_0 is the initial amount of aglycone.

The invariability of K shows that the hydrolysis of Saparal is a first-order reaction:

τ, min	C/C_0	$\log C/C_0$	K	Amount of aglycone obtained after hydrolysis	Initial amount of aglycone
5	0.3958	−0.4025	0.1854	0.2050	0.3390
10	0.1562	−0.8063	0.1856	0.2863	0.3390
15	0.0619	−1.2083	0.1855	0.3183	0.3390
20	0.0245	−1.6108	0.1855	0.3310	0.3390
25	0.0097	−2.0132	0.1855	0.3360	0.3390
30	0.0038	−2.4202	0.1856	0.3380	0.3390

The time of hydrolysis calculated from the equation for C = 99.9% is 25 min, as is confirmed by the figures given above.

EXPERIMENTAL

Six identical samples (about 1 g) of "Saparal" powder were placed in round-bottomed flasks and each was dissolved in 100 ml of hydrolyzing mixture; then they were heated at 120°C (air bath) under reflux for 5, 10, 15, 20, 25, and 30 min, respectively. The course of hydrolysis was followed chromatographically. After the mixtures had been cooled, the precipitates were transferred quantitatively to No. 2 glass filters, washed with water to neutrality, and dried to constant weight; mp 301-304°C (from ethanol). Found, %: C 78.50; H 11.2; $C_{30}H_{48}O_3$. Calculated, %: C 78.90; H 10.6.

A further increase in the time of hydrolysis led to the same results as heating for 30 min.

SUMMARY

1. To perform the hydrolysis of the technical preparation "Saparal" the optimum conditions are 30-min heating in a 1:1 mixture of acetic acid and 20% sulfuric acid or a 1:1 mixture of acetic acid and 30% sulfuric acid.

2. It has been established that the hydrolysis of Saparal is a first-order reaction with K_h = 0.1855.

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A COMPARATIVE STUDY OF THE ALKALOIDS OF *Corydalis* SPECIES

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A chemical study has been made of five species of Corydalis: *Corydalis rosea* Leych., introduced into the Botanical Gardens of VILR [All-Union Scientific-Research Institute of Medicinal Plants]; *C. gigantea* Trautv. et Mey, growing in the Far East; *C. vaginans* Royle, introduced into the Botanical Garden of VILR; *C. marschalliana* Pers., growing in the Crimea; and *C. remota* Fisch., growing in the Far East. The results of the investigation are given in Table 1 and below [1-3].

Alkaloid	Source of Isolation
1. Sanguinarine	*C. rosea, C. gigantea, C. marschalliana, C. remota, C. vaginans*
2. Dihydrosanguinarine	*C. gigantea, C. vaginans, C. remota*
3. Cheilanthifoline	*C. vaginans, C. gigantea*
4. Scoulerine	*C. gigantea, C. vaginans, C. marschalliana*
5. Ophiocarpine	*C. gigantea*
6. Isocorypalmine	*C. vaginans*
7. Corydaline	*C. marschalliana*
8. Isocorybulbine	"
9. Tetrahydropalmatine	"
10. Adlumine	*C. gigantea, C. rosea, C. vaginans*
11. d*l*-Adlumine	*C. rosea*
12. Adlumidine	*C. rosea, C. gigantea, C. remota*
13. d*l*-Adlumidine	*C. rosea*
14. Bicuculline	*C. vaginans, C. gigantea, C. remota*
15. Ochotensine	*C. vaginans*
16. Corydaine	"
17. Ochrobirine	"
18. *l*-O-Methylcorpaine	"
19. Bulbocapnine	*C. vaginans, C. marschalliana*
20. Protopine	*C. vaginans, C. rosea, C. gigantea, C. remota, C. marschalliana*
21. Corycavine	*C. marschalliana*
22. α-Allocryptopine	*C. remota*

Analysis of the results obtained shows that the species studied differ fairly greatly in their chemical composition. The alkaloids of the benzophenanthridine and protopine groups

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