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A STUDY OF THE CHEMICAL COMPOSITION OF SAUSSUREA FROLOVII

II. Taraxasterol

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In a further study of saussurol [1] it was established that its acetate undergoes partial isomerization during chromatography on alumina (pH 7.5-8, activity grade I). Gradient elution of the column with benzene—ether gave 1-lupenyl acetate, from which 1-lupenol was obtained. Further elution led to the formation of a mixture of 1-lupenyl acetate and then the initial acetate. In view of this behavior of saussurol acetate, the constants given in the preceding communication [1] were incorrect.

The method developed later for purifying saussurol by crystallization of the residue from a petroleum ether extract of the plant from 95% ethanol with subsequent chromatography on alumina (pH 7.5-8, activity grade I) made it possible to isolate saussurol with mp 220-222° C (from ethanol), $[\alpha]_D^{20}$ +96 ± 2° (c 1.15). Its acetate has mp 243-245° C (from chloroform—methanol), $[\alpha]_D^{20}$ +103 ± 1° (c 1.14). These constants are very close to those for taraxasterol [2, 3]. Since in the IR spectrum of saussurol there are absorption bands at 890 and 3060 cm^{-1}, which are characteristic for a $=C=CH_2$ group, the hydrocarbon saussurene [1] and then saussurol acetate were ozonized in carbon tetrachloride at -25° C by the passage of a current of ozonized oxygen (5%) for 90 min. After the usual working up, the formaldehyde was identified as the di-β-naphthylmethane derivative [4] with a yield of 28% of the theoretical. Chromatography of the water-insoluble residue on silica gel [elution with benzene—ether (9 : 1)] gave 30-nor-20-taraxastenone [2].

The IR spectrum of this compound lacked absorption bands due to a $>C=CH_2$ group and exhibited a strong band at 1704-1706 cm^{-1} (carbonyl group in a six-membered ring) [5]. Similarly, ozonolysis of saussurol acetate led to the formation of formaldehyde with a 34% yield and the corresponding nor-ketone with mp 262-264° C (from ethyl acetate), $[\alpha]_D^{20}$ +64 ± 3° (c 1.20). IR spectrum: 1250 and 1730 cm^{-1} (acetate), 1706-1707 cm^{-1} (ketone) [5].

Found, %: C 79.6, 79.7; H 10.7, 10.8. Calculated for $C_{31}H_{50}O_3$, %: C 79.1; H 10.7.

Oxime (amorphous):

Found, %: N 2.9, 2.8. Calculated for $C_{31}H_{51}O_3N$, %: N 2.9.

On the basis of the above data it may be concluded that saussurol is identical with taraxasterol.

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A STUDY OF THE SAPONINS OF HEDERA COLCHICA

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We have studied the saponins of the leaves of Hedera colchica C. Koch. (Colchis ivy), family Araliaceae, collected in the regions of southern Georgia.

From this point we have isolated the total (about 15% on the air-dry raw material) triterpene saponins and in these we have established by thin-layer chromatography, in silica gel in systems with different pH values [1], the presence of three glycosides—A, B, and C—with similar *Rf* values. The main component is the most polar saponin C.

By acid hydrolysis of the saponins we obtained a mixture of two aglycones. By chromatography in a thin layer of silica gel in the chloroform–ethanol (25:1) system, the aglycones were identified as oleanolic acid and hederagenin. Samples of the sapogenins were given to us by N. K. Abubakirov.

The main genin was isolated in the pure crystalline state with mp 303–307° C; its IR spectrum: 3360 cm^{-1} (hydroxyl); 1683 cm^{-1} (carbonyl of a carboxy group), which was identical with the IR spectrum of oleanolic acid.

Tschesche et al. [2], in studying another species of ivy—Hedera helix L.—found glycosides of the same sapogenins. We are continuing the study of the sapogenins of Hedera colchica.

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COMPOSITION OF THE GLYCOSIDIC FRACTION FROM STYCHOPUS JAPONICUS

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In 1952, R. Nigrelli [1] showed that the holothuria Actinopyga agassizi contained a substance that was toxic for fishes and higher animals. He called it holothurin. On biological tests, the toxin was detected [2] in 30 species of holothuria belonging to four out of the five orders forming this class, including St. japonicus Selenka [3].

The results of a study of the chemical structure and biological properties of holothurin from A. agassizi have been given in the literature [1, 2, 4–6].

From Holothuria vagabunda, Japanese workers [7] isolated a glycoside which they also called holothurin.

We have studied the glycosides from a methanolic extract of the far eastern trepang (St. japonicus). "Sea ginseng," as the trepang is called, has long been used as a medicinal substance in eastern medicine. However, nothing has been known about the chemical properties of its active principles.

The chromatography of the methanolic extract in a thin layer of silica gel showed the presence of 10–12 substances in it.

As a result of the preparative purification of a methanolic extract obtained from 4.5 kg of raw trepangs by partition chromatography on alumina in the butanol—toluene—water system, 1.4 g (2.8%) of a glycosidic fraction was isolated, the hydrolysis of which was shown chromatographically to give the same mixture of monosaccharides as was obtained in the hydrolysis of holothurin from A. agassizi.

After partition chromatography of the total glycosides on silica gel, two chromatographically pure glycosides were isolated: stychoposide A and stychoposide C. Stychoposide A was purified twice on silica gel. A white amphorous substance with mp 215–217° C, $[\alpha]_D^{25}$ −62.3 ± 5° (c 5.01; pyridine) was obtained. IR spectrum: 3400–1745 cm^{-1}.

Found, %: C 58.87, 58.84; H 8.59, 8.60; S 2.08, 2.09.

Both glycosides differed from holothurin in their behavior on thin-layer chromatography in silica gel in the chloroform—methanol (2:1)/water system (revealing agent sulfuric acid). On hydrolysis, stychoposides A and C gave identical mixtures of products of the change of the aglycone which differed, however, from the analogous mixtures isolated in the hydrolysis of holothurin [chromatography in a thin layer on silica gel in the ethyl acetate—chloroform (3:2) system, revealing agent sulfuric acid]. The thin-layer chromatography of the mixture of monosaccharides [butanol—acetone—water (4:5:1) system] obtained in the hydrolysis of stychoposides A and C and of holothurin showed that stychoposide A and holothurin have an identical set of monosaccharides, among which it was possible to identify glucose, xylose, and 3-O-methylglucose, while stychoposide C also contained galactose.