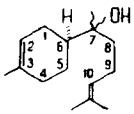

from the oleoresins of the spruce and three species of fir two signals of methyl groups attached to carbinol carbon atoms (1.12 and 1.0 ppm) were observed in a ratio of 4:1 with the predominance of the weak-field signal. Consequently, in the four oleoresins the main isomer is (+)-6S,7R-α-bisabolol and the minor isomer is the 6S,7S- compound. Only the oleoresins of the Siberial stone pine and the Korean pine contained a single diastereoisomer of (+)-α-bisabolol, which had the 6S,7R- configuration. Apart from the PMR spectra, the two diasteromers have small differences in the ^{13}C NMR spectra. For 6S,7R-α-bisabolol the following signals are characteristic ($CDCl_3$; ppm from TMS; internal standard $CDCl_3$, δ 76.9 ppm); 133.71 s, 131.58 s, 124.49 d, 120.67 d, 74.21 s, 43.24 d, 39.26 t, 30.97 t, 25.98 t, 25.58 q, 23.86 t, 23.89 q, 23.20 q, 22.19 t, 17.55 q; for 6S,7S-α-bisabolol – 134.00 s, 131.58 s, 124.50 d, 120.45 d, 74.19 s, 42.90 d, 40.01 t, 30.96 t, 26.82 t, 25.57 q, 23.85 t, 23.85 q, 23.19 q, 21.97 t, 17.55 q.

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STEROLS OF THE FAR EASTERN RED ALGA *Ahnfeltsia tobuchiensis*

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Red algae which are widely distributed in the Far Eastern zone, form one of the possible sources of the production of new and unusual sterols [1, 2]. It has been established previously that among the sterols of algae of the family *Rhodophycea* cholest-5-en-3β-ol predominates and there are considerable amounts of cholesta-5,24-dien-3β-ol and cholesta-5,22-dien-3β-ol [3, 4]. Among the sterols with more alkylated side chains from red algae have been isolated 24-ethylcholest-5-en-3β-ol ergosta-5,24(28)-dien-3β-ol, and (24E)stigmasta-5, 24(28)-dien-3β-ol.

Continuing an investigation of Far Eastern algae [5], we have studied the sterol composition of the industrially harvested alga *Ahnfeltsia tobuchiensis*.

The dry and comminuted alga collected in November in Troits inlet, Peter the Great Bay, Sea of Japan, was extracted with chloroform–ethanol (1:1). After the saponification of the evaporated extract, the combined sterols, amounting to 0.0115% of the weight of the dry algal sample, were obtained by the usual working up procedure and chromatographic separation on silica gel. According to GLC and chromato-mass spectrometry, the main components of the fraction were cholest-5-en-3β-ol (59%) and 24-ethylcholest-5-en-3β-ol (32%). Fractions containing cholestadiene and cholestatriene made up 7% of the weight of the sterol fraction.

After the acetylation of the sterol fraction and chromatographic separation of the combined acetates on silica gel impregnated with $AgNO_3$, the acetates of 24-methylcholest-5-en-3β-ol (M – 60, 384; M – 75, 369; 260; 255; 247; 213) and of 5α-cholestan-3β-ol (M – 60, 370; M – 75, 355; 276; 275; 257; 230; 215) were characterized.

Thus, we have established that the sterol fraction of *Ahnfeltsia tobuchiensis* contains a set of Δ^5-sterols among which cholest-5-en-3β-ol and 24-ethylcholest-5-en-3β-ol predominate. An interesting fact is the considerable amount of di- and triunsaturated sterols.

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CARDIAC GLYCOSIDES FROM THE SEEDS OF *Digitalis ciliata*

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As has been shown previously, the seeds of *Digitalis ciliata* Trautv. contain a considerable amount of cardiac glycosides and steroid saponins [1, 2]. An original method has been developed for obtaining the steroid saponin digitonin from the seeds of this plant, and its production has been set up.

The aqueous liquid remaining after the seperation of the digitonin contained the cardiac glycosides of the initial raw material. For their isolation, the aqueous liquid was extracted successively with benzene–chloroform and with ethanol–chloroform. The first extract yielded combined glycosides containing two main cardenolides, and the second yielded seven.

Thw combined benzene–chloroform glycosides were separated on a column of silica gel of type L40/100 with elution by benzene containing increasing concentrations of ethanol. This gave the individual cardenolides (1) and (2).

Cardenolide (3) was isolated by the partition chromatography of the combined ethanol–chloroform glycosides on a column of type KSA silica gel saturated with water, using ethyl acetate–water as the mobile phase. The adsorption chromatography of the same combined material on a column of silica gel of type L60/100 with ethyl acetate–ethanol yielded cardenolide (4),

Cardenolide (1) – $C_{43}H_{66}O_{14}$, mp 218-222°C; $[\alpha]_D^{20}$ +25,2° (*c* 1,0 ; ethanol); $[\alpha]_D^{20}$ +4,9° (*c* 1,0 ; pyridine). UV spectrum, λ_{max}: 218 nm (log ε 4.19); in PC and TLC, it appeared in the region of acetyldigitoxin-α. The Legal, Raymond, Kedde, Pesez and Keller–Kiliani reactions for cardiac glycosides were positive. The Svendsen–Jensen and Keller–Kiliani reactions gave the colorations specific for glycosides of the digitoxigenin series and digitoxose. The reaction for an acetyl group was positive [3]. Alkaline saponification formed digitoxin. Acid hydrolysis gave an aglycone with mp 245-247°C, $[\alpha]_D^{20}$ +18,5° (*c* 1,22 ; ethanol) which was identified as digitoxigenin, and the sugar digitoxose.

On the basis of the results obtained, cardenolide (1) was characterized as digitoxigenin 3-O-bisdigitoxosidoacetodigitoxoside or acetyldigitoxin-α [2, 4].

Cardenolide (2) – $C_{41}H_{64}O_{13}$, mp 244-246°C, $[\alpha]_D^{20}$ +18,0° (*c* 0,1 ; chloroform + 1% ethanol). UV spectrum, λ_{max}: 220 nm (log ε 4.065). It gave all the reactions characteristic for glycosides of the digitoxigenin series and for digitoxose. It was not saponified by alkali Acid hydrolysis formed the aglycone digitoxigenin and the sugar digitoxose. Thus, cardenolide (2) was digitoxigenin 3-O-tridigitoxoside or digitoxin [5].

Cardenolide (3)– $C_{49}H_{76}O_{19}$, mp 244-246°C, $[\alpha]_D^{20}$ +31,0° (*c* 1,0 ; ethanol). UV spectrum, λ_{max}: 220 nm (log ε 4.2). Alkaline saponification formed a glycoside with the R_f value of deacetyllanatoside A. The Frerjacque reaction for an acetyl group was positive. After enzymatic hydrolysis, digitoxin and D-glucose were obtained. Acid hydrolysis yielded digitoxigenin, while digitoxose, digilanidobiose and glucose were detected in the carbohydrate fraction.

Cardenolide (3) was identiefied as digitoxigenin 3-O-bisdigitoxosideacetyldigilanidobio-

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