evaporated. This gave 0.45 g of amorphous 10-cyano-3β,5,14-trihydroxy-5β,14β-card-20(22)-enolide, which was recrystallized from methanol, mp 236-240°C; $[\alpha]_{20}^{D}$ +51.1 ± 2° (c 1.0; methanol). Similarly, convallatoxin 19-aldoxime gave 10-cyanoconvallatoxin with mp 263-269°C.

The IR spectra of the 10-cyanocardenolides each have an absorption band in the 2220 cm^{-1} region that is characteristic for a CN group. The elementary analyses of the compounds obtained agreed with those calculated for the compositions $C_{23}H_{31}O_5N$ and $C_{29}H_{41}O_9N$, respectively. The kinetic measurements were carried out by a quantitative analysis of the samples using paper chromatography by a known method [3, 4].

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TRITERPENE GLYCOSIDES OF THE LEAVES OF *Fatsia japonica*. STRUCTURE OF FATSIOSIDES D, E, AND F

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We have characterized the weakly polar glycosides of fresh leaves of *Fatsia japonica* (Thunb.) Deche et Planch (family Araliaceae) [1]. One of the polar glycosides present in the air-dry leaves, fatsioside G, was identified as leontoside D [2]. Below we give information on the determination of the structures of the remaining polar glycosides — fatsiosides D, E, and F.

The glycosides were isolated by extracting the air-dry leaves with aqueous methanol followed by purification of the total material by repeated chromatography on a silica gel column in the chloroform—methanol—water (26:14:3) system.

Complete acid hydrolysis showed that fatsiosides D with mp 181-183°C, $[\alpha]_D^{20}$ +3.1° (c 1.1; MeOH), and F with mp 179-181°C, $[\alpha]_D^{20}$ +29.8° (c 2.1; MeOH) were hederagenin derivatives, and fatsioside E with mp 187-191°C, $[\alpha]_D^{20}$ +37.8° (c 3.1; MeOH) was an oleanolic acid derivative. In the carbohydrate moieties of the glycosides L-rhamnose, L-arabinose, and D-glucose were detected by PC and TLC. After reduction of the hydrolysates with sodium tetrahydroborate followed by acetylation, the acetates of rhamnitol, arabitol, and sorbitol were identified by the GLC method in a ratio of 1:1:2 for fatsioside D and a ratio of 1:1:3 for fatsiosides E and F.

Analysis of the IR spectra of the fatsiosides permitted us to assume that they contained ester bonds. As a result of the alkaline hydrolysis of the glycosides followed by acid hydrolysis of the oligosaccharide split out, and using GLC, we identified rhmanose and glucose in the form of the acetates of the corresponding polyols in a ratio of 1:2. Acid hydrolysis of the modified glycosides led to the identification of arabitol acetate for fatsioside D and of arabitol and sorbitol acetates in a ratio of 1:1 for fatsiosides E and F. After methylation by Hakomori's method [3] followed by methanolysis of the glycosides, methyl 2,3,4-tri-O-methylarabinopyranoside (1), methyl 2,3,4-tri-O-methylrhamnopyranoside (2), and methyl 2,3,6-tri-O-methylglucopyranoside (3) were identified by GLC for fatsioside D, and methyl 2,3,4,6-tetra-O-methylglucopyranoside (4) and methyl 3,4-di-O-methylarabinopyranoside (5) and also the methyl glycosides (2) and (3) for fatsiosides E and F. The results obtained were confirmed by analysis using the chromato-mass spectrometry of the acetates of the partially

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methylated polyols corresponding to the methyl glycosides given above. As a result of the hydrolysis of the methyl ethers of the fatsiosides with reduction and subsequent acetylation, 1,5-di-O-acetyl-2,3,4-tri-O-methylarabitol (6), 1,5-di-O-acetyl-2,3,4-tri-O-methylrhamnitol (7) and 1,4,5-tri-O-acetyl-2,3,6-tri-O-methylsorbitol (8) were identified for fatsioside D, and 1,5-di-O-acetyl-2,3,4,6-tetra-O-methylsorbitol (9) and 1,2,5-tri-O-acetyl-3,4-di-O-methylarabitol (10), and also the polyols (7) and (8), for fatsiosides E and F [4].

On the basis of the facts given above, the polar glycosides from the leaves of *Fatsia japonica* can be assigned the following structures: fatsioside D — hederagenin 3-O-L-Ara$_p$ 28-O-L-Rha$_p$-(1 → 4)-D-Glc$_p$-(1 → 4)-D-Glc$_p$; fatsioside E — oleanolic acid 3-O-D-Glc$_p$-(1 → 2)-L-Ara$_p$ 28-O-L-Rha$_p$-(1 → 4)-D-Glc$_p$-(1 → 4)-D-Glc$_p$; and fatsioside F — hederagenin 3-O-D-Glc$_p$-(1 → 2)-L-Ara$_p$ 28-O-L-Rha$_p$-(1 → 4)-D-Glc$_p$-(1 → 4)-D-Glc$_p$.

Glycosides of similar structure have been isolated by Japanese scientists from the fruit of *Fatsia japonica* [5].

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CASEINIC ACID DERIVATIVES OF CYTISINE AND SALSOLIDINE

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It is possible to prolong the action of drugs by adding physiologically active substances to proteins [1]. Berberine caseinate has been obtained previously [2] with the aim of lowering toxicity and creating a prolonging effect. The basis for such reactions was that casein can be considered as a polybasic acid because of the presence of a large number of carboxy groups belonging to aspartic and glutamic acid residues in the molecule. For the synthesis we took casein obtained in the form of caseinic acid [3]. We condensed the alkaloids cytisine and salsolidine with the caseinic acid. The amine groups of the caseinic acid were blocked by benzyloxycarbonyl groups [4], as was shown by the absence of amine nitrogen determined by the Van Slyke method [5].

The benzyloxycarbonyl protection was subsequently eliminated with a 40% solution of HBr in glacial acetic acid. The carboxy groups of the protein were converted with ethyl chloroformate into reactive mixed anhydrides which were then used in the condensation reaction with the alkaloids. The reaction took place by the following scheme:

$$m\,C_6H_5CH_2OCOCl + (NH_2)_m\text{—Protein mol.}\text{—}(COOH)_n \xrightarrow[\text{pH 8,5}]{0^\circ} (CbO\text{—}NH)_m\text{—}$$

$$\text{—Protein mol.}\text{—}(COOH)_n \quad (I)$$

$$(I) + NH[\text{Alkaloid}] \xrightarrow[\text{pH 7,5};(C_2H_5)_3N;\,ClOCOC_2H_5]{0^\circ} (CbO)\text{—}NH)_m\text{—Protein mol.}\text{—}$$

$$(CO\text{—}N[\text{Alkaloid}])_n \quad (II)$$

$$(II) + \xrightarrow[CH_3COOH]{HBr} (HBrNH_2)_m\text{—Protein mol.}\text{—}(CO\text{—}N[\text{Alkaloid}]) \quad (III)$$

The purity of the products was checked by thin-layer chromatography on silica gel fixed with gypsum in the following systems: 1) butanol—water—acetic acid (4:1:1), and 2) benzene—ethanol (85:15). The revealing agent for the alkaloids was the Dragendorff reagent. The

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