THE STRUCTURE OF THEASAPONIN

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The triterpene glycoside theasaponin isolated from the seeds of Thea sinensis L. (tea) has been investigated repeatedly [1-3, 5-8]. Udea [1] found that the aglycone is a hexahydroxy- or pentahydroxy-β-amyrin, esterified with 1 mole of angelic acid, and the carbohydrate part consists of glucuronic acid (GA), galactose (Gal), arabinose (Ara), and xylose (Xyl). According to Mizuno [2], theasaponin is a multimonosaccharide glycoside (GA, Gal, Ara, Xyl) esterified by angelic acid. According to Tscheshe et al. [3], theasaponin consists of a mixture (unseparated) of glycosides of very similar structure with the same carbohydrate chain α-Xyl-[1→2]-α-Ara-[1→2]-β-GA-[1— attached to position 3 of the aglycones (theasa-

$$\beta\text{-Gal-[1}\rightarrow\text{3]}$$

pogenols A, B, and E and camelliagenins A and D). The aglycones are esterified with acetic, angelic, and tiglic acids in a ratio of 3:1:4. The structures of theasapogenols A, B, and E and of camelliagenins A and D from raw material of Japanese origin have been established [5-8].

From the seeds of tea growing in the Adjar ASSR we have isolated a crystalline chromatographically homogeneous glycoside with the composition $C_{59}H_{90}O_{27} \cdot 2H_2O$ (from aqueous ethanol), mp 223-224°C, $[\alpha]_D^{19}$ +10° (c 2.7; 70% ethanol). Acetate, $C_{87}H_{118}O_{41}$, mp 167-170°C.

On acid and subsequent alkaline hydrolysis of the glycoside, by chromatography in a thin layer of silica gel we identified aglycones similar to those described previously [5-8]. In the acid hydrolysate GA, Gal, Ara, and Xyl were found by paper and thin-layer (silica gel) chromatography. In the products of the acid hydrolysis of the glycoside fully methylated by Hakomori's method [4] by thin-layer and gas-liquid chromatography in the presence of markers we identified 2,3,4,6-tetra-O-methyl-D-galactose, 2,3,4-tri-O-methyl-D-xylose, and 3,4-di-O-methyl-L-arabinose (1:1:1). Reduction of the glycoside with $LiAlH_4$ gave a deacyl glycoside with composition $C_{52}H_{86}O_{24} \cdot 2H_2O$, mp 249-252°C, $[\alpha]_D^{20}$ +18.8° (c 0.46; methanol/water, 1:1), which was then subjected to exhaustive methylation and acid hydrolysis. Gas-liquid and thin-layer chromatography of the acid hydrolysate showed the presence of, in addition to the monosaccharide derivatives mentioned, 4,6-di-O-methyl-D-glucose (1:1:1:1). Consequently, the branched carbohydrate chain of this glycoside has the same structure as that described by Tscheshe et al. [3].

The fatty acids obtained after the alkaline hydrolysis of the glycoside were determined by gas-liquid chromatography both in the free state and as the methyl esters; acetic, angelic, and tiglic acids were found in a ratio of 2:1:1, i.e., a similar qualitative composition to but a different quantitative composition from that given in the literature [3].

Thus, the glycoside that we have isolated, according to its empirical formula, the qualitative composition of the degradation products, and the structure of the carbohydrate chain, is similar to the theasaponin described previously [3]. However, it gives a depression of the melting point with a mixture of the theasaponin isolated by Tscheshe et al. [3] and kindly supplied to us, and the reduced deacyl glycoside has a melting point (~110°C) different from that described by Tscheshe et al. [3].

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