

PHOTOLYSIS OF URONIDE LINKAGE IN SAPONIN

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Recently we reported that ultraviolet irradiation is convenient for hydrolysis of some oleanane triterpenoid saponins resulting in the formation of genuine saponins¹⁾. The subsequent investigation on structure requirement for ready photolysis of glycoside linkage in saponin has revealed that uronic acid is an essential constituent of the carbohydrate portion which is directly connected to the aglycone as shown below.

Mild acid hydrolysis of soyasaponin I isolated from soyabean (Glycine max Merrill) yielded a prosapogenol, $C_{37}H_{60}O_9 \cdot \frac{1}{2} H_2O$, mp. 249-250°, $[\alpha]_D +34.1^\circ$ ($CHCl_3$), which has been determined to be 3-O- β -D-glucuronopyranosyl-soyasapogenol B methyl ester (II) on the basis of chemical and physico-chemical evidences²⁾. $NaBH_4$ reduction of II gave a product, $C_{36}H_{60}O_8$, mp. 254-256°, $[\alpha]_D +38.7^\circ$ (MeOH), whose structure being proved as 3-O- β -D-glucopyranosyl-soyasapogenol B (III) through a standard procedure²⁾.

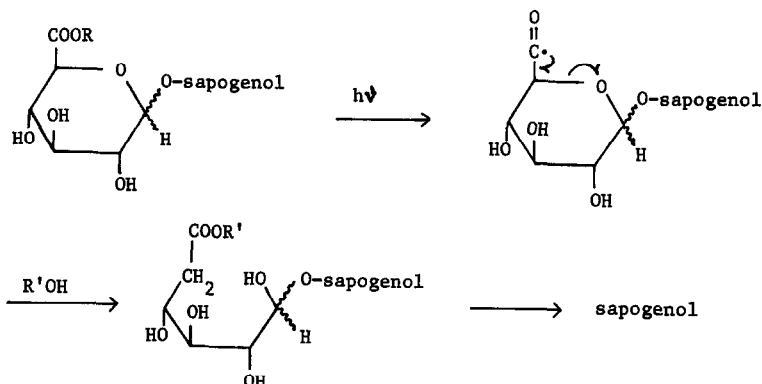
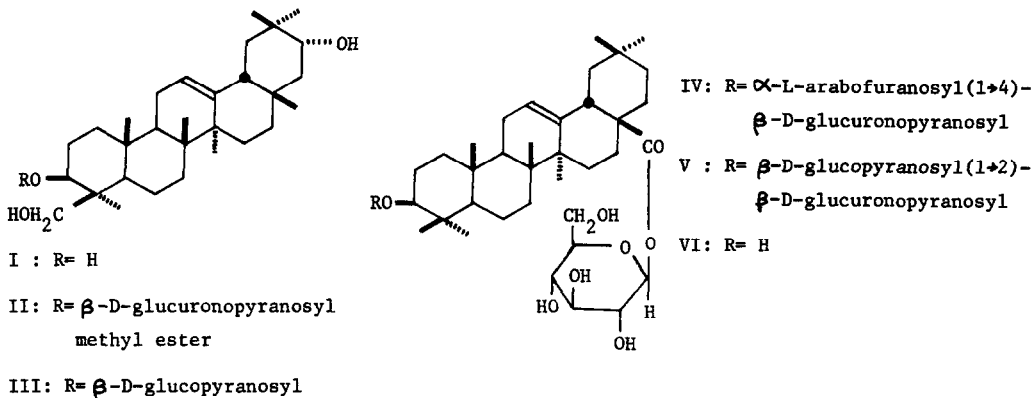
Irradiation of soyasaponin I as reported previously¹⁾ resulted in liberation of soyasapogenol B(I) in a good yield, while irradiation of II in MeOH for 30 min.³⁾ furnished I in a quantitative yield. However, irradiation of III under the same reaction conditions recovered III unchanged, thus showing the glucuronide linkage being attacked photochemically.

In order to obtain an additional evidence, chikusetsusaponin IV(IV) and V(V)⁴⁾ were subjected to photolysis in MeOH and 28-O- β -D-glucopyranosyl-oleanolic acid(VI), which is a genuine prosapogenol (= compound O) obtained previously by the soil bacterial hydrolysis method⁵⁾, was isolated in 60% yield from both saponins as expected. In these cases, photolysis was effected in 25 min. in a quartz tube, while it took 50 min. in a Vycor tube.

As for one of the plausible photochemical paths, a scheme as formally shown below (e.g.,

starting from glucuronide) is attractive and currently under investigation. Since uronic acid often occurs as a constituent in the carbohydrate portion of saponins, the present finding would provide a new degradation method of the carbohydrate portion of saponins.

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References and Footnotes

- 1) I. Kitagawa, M. Yoshikawa, Y. Imakura, and I. Yosioka, *Chem. & Ind.*, 1973, 276.
- 2) Details will be published in our full paper(*Chem. Pharm. Bull.(Tokyo)*).
- 3) For photolysis of saponin, it has been revealed by recent examination that a shorter period of irradiation(e.g., 30 min. in a quartz tube) than that reported previously¹⁾ is enough.
- 4) a) N. Kondo, J. Shoji, N. Nagumo, and N. Komatsu, *Yakugaku Zasshi*, 89, 846 (1969).
b) N. Kondo, Y. Marumoto, and J. Shoji, *Chem. Pharm. Bull.(Tokyo)*, 19, 1103 (1971).
- 5) I. Yosioka, M. Fujio, M. Osamura, and I. Kitagawa, *Tetrahedron Letters*, 1966, 6303.