# SAPONINS AND SAPOGENINS*

## XXVII.† ON THE UNIDENTIFIED ACID AND NEUTRAL SAPOGENINS FROM THE SEEDS OF LUFFA AEGYPTICA MILL (BLACK VARIETY)

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The seeds of *Luffa aegyptica* Mill, locally known as "ghia torai" (family Cucurbitaceae), have earlier been studied for the saponin and sapogenin contents and found to contain a mixture of colourless saponins which on hydrolysis yields two acid and a neutral sapogenin. The acetates of the two acid genins melted at 266–268° and 176–181° while the neutral genin acetate melted at 262–264°.[1] The acid genin acetate, m.p. 266–268°, has earlier been identified as oleanolic acid acetate.[1] The presence of only oleanolic acid has been reported in other species[2,3] while *Luffa operculata*[4] from South America has been reported to contain gypsogenin and an unidentified neutral genin for which no physical constants are found in the literature.

It has been found that the second acid genin acetate, m.p. 176–181°, in the process of recrystallization from methanol slowly and successively transforms into a product, m.p. 262–264°, identical with the neutral genin acetate. The acid genin acetate and the neutral genin acetate have ultimately been identified as acetyl gypsogenin and acetyl gypsogenin lactone by transformation of both of these into oleanolic acid and hederagenin through Wolff–Kishner and sodium borohydride reduction respectively. Finally, direct comparison of the acid genin acetate was made with a sample of gypsogenin acetate kindly provided by Dr. K. Schaffner. Ruzicka and Giacomello[5] have reported the transformation of gypsogenin into its lactone.

### *Experimental*

All melting points were measured on a Kofler hot-stage microscope and are corrected.

#### *Extraction of Saponin*

The well-defatted dry seed powder (800 g) on exhaustive extraction with ethanol gave a brown syrup. This was processed in the usual manner for saponin, which after precipitation a number of times in ether/acetone was a colourless powder which gave all the tests for saponins.

#### *Hydrolysis of the Saponin*

The saponin (4·0 g) in water (1 l.) was hydrolysed with sulphuric acid (10%). The genin obtained was filtered and washed free of acid.

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*Separation of the Acid and the Neutral Genins*

The genin (3 g) was transformed into a potassium salt and the resulting mixture was extracted with ether. The residue obtained from the ethereal extracts on crystallization with methanol gave a colourless neutral genin (800 mg), m.p. 286–288°. Acetylation with pyridine and acetic anhydride on the water-bath yielded an acetate, m.p. 262–264°, which gave no colour with tetranitromethane. The alkaline solution left after the ether extraction, on acidification with hydrochloric acid, gave a colourless precipitate of the acid genin. Acid genin (200 mg) was acetylated with pyridine and acetic anhydride on the water-bath and was separated by crystallization from methanol into two products, m.p. 266–268° and m.p. 176–181°. The product, m.p. 266–268°, was identified earlier as oleanolic acid.[1] Further recrystallizations of the acetate, m.p. 176–181°, gave two products, m.p. 176–181° and m.p. 262–264°. The product, 262–264°, was found to be identical (mixed m.p.) with the neutral genin acetate, m.p. 262–264°. Repeated crystallizations of the product, m.p. 176–181°, gave more of the product, m.p. 262–264°. The acid genin acetate 176–181° gave a positive test with tetranitromethane while the neutral genin acetate gave a negative test.

*Transformation of Acid Genin Acetate and Neutral Genin Acetate into Oleanolic Acid*

Acid genin acetate, m.p. 176–181° (50 mg) and neutral genin acetate, were separately reduced with hydrazine hydrate (4 ml) in diethylene glycol (20 ml) and sodium (0·6 g). The same product was obtained from both of these as colourless needles, m.p. 292–294°. Mixed melting point with an authentic sample of oleanolic acid showed no depression. This product on acetylation with pyridine and acetic anhydride gave the same acetate in both cases, m.p. 260–263°. Mixed m.p. with authentic sample of oleanolic acid acetate, 264–265°.

*Transformation of Neutral Genin Acetate and Acid Genin Acetate into Hederagenin*

Neutral genin acetate and acid genin acetate, m.p. 176–181° (30 mg), were separately reduced by refluxing for 10 hr with sodium borohydride (90 mg) in methanol (5 ml). Both the products obtained on crystallization after the usual treatment gave the same product, m.p. 170–172°. Mixed m.p. with an authentic sample of hederagenin acetate showed no depression.

*Deacetylation of Reduction Products*

The above products on deacetylation with methanolic potassium hydroxide (5%) gave the same product in both cases, m.p. 323–326° (mixed m.p. with authentic hederagenin, 327–329°).

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