Chemical Investigation of Indian Soapnut, *Sapindus laurifolius* Vahl.

Plants belonging to the genus *Sapindus* (Fam. Sapindaceae) are very good sources of saponins. A survey[1-4] of the literature shows that no triterpene except hederagenin[2] has so far been reported from any of the species of *Sapindus*.

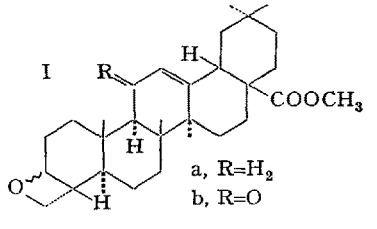
Sapindus laurifolius Vahl. is cultivated throughout Northwest India, West Bengal and Assam, and is wild on the Himalayas up to 1.2 km. Fruits are commonly used as detergent. They are sometimes used as expectorant, in salivation, chlorosis and epilepsy.

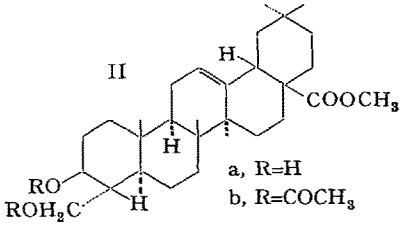
The ethanolic extract of the defatted fleshy pericarp of the nuts of *S. laurifolius* furnished a good amount of saponin which on alcoholic hydrolysis (ethanol–water–conc. HCl = 7:3:2) gave a crude acid sapogenin. The latter, on treatment with diazomethane and subsequent column chromatography on active alumina, gave 3 colorless compounds, A, B and C.

Compound A (Ia) [m.p. 258–260°, $[\alpha]_D$ + 84.78° ($CHCl_3$); ν in cm^{-1} (KBr): 1710 (ester carbonyl), 1360, 1380 (*gem*-dimethyl), 1116 (ether function). Anal. calc. for $C_{31}H_{48}O_3$: C, 79.49; H, 10.25; found: C, 79.27; H, 10.14] responded to the test of a triterpene (Liebermann-Burchard) and gave a pale yellow color with tetranitromethane showing the presence of unsaturation. As indicated in IR-spectrum, this compound contained no hydroxyl group and it failed to give any acetyl derivative on heating with pyridine and acetic anhydride on steam-bath. That the ether function was not present as a methoxyl or ethoxyl group was shown by their absence in Zeisel method of determination. It appeared to be the methyl ester of a new compound, named as 'Sapindic acid'.

Methyl sapindate was recovered unchanged after treatment with osmium tetroxide in dry pyridine for 7 days at room temperature thus indicating the hindered nature of the double bond. Direct proof of the presence of a typical 12:13 double bond of the α- or β-amyrin series was obtained by oxidation of Ia with chromium trioxide-acetic acid on steam-bath to yield the α,β-unsaturated ketone Ib[$C_{31}H_{46}O_4$ m.p. 301–304°, $[\alpha]_D$ + 24.1°, λ_{max}^{MeOH} 246.5 nm[5,6] (log ε 4.25); ν in cm^{-1} (KBr): 1665 (α,β-unsaturated ketone)]. Methyl sapindate consumed 1 mole of perbenzoic acid at a rate typical of the triterpenes of the β-amyrin series, having a double bond at 12:13[7].

The ether linkage in Ia is present within the frame-work of the compound and not as an ether oxygen joining 2 different units. Ia, on refluxing with acetic anhydride and conc. HCl for $1^1/_2$ h furnished methyl diacetyl hederagenate (IIb)[2].





Correlation of methyl sapindate with methyl hederagenate suggests the structure and stereochemistry of sapindic acid as 3ξ.23α-oxido-olean-12-ene-28-oic acid.

In order to prove that sapindic acid is not an artifact of hederagenin[2], the major constituent of acid sapogenin fraction, pure methyl hederagenate was refluxed with ethanolic hydrochloric acid (ethanol–conc. HCl = 5:1) and the reaction product on chromatography over active alumina furnished methyl hederagenate in almost quantitative yield.

Compound B, $C_{31}H_{50}O_3$, m.p. 198–200°, $[\alpha]_D^{36}$ + 74.0° ($CHCl_3$), responded to Liebermann-Burchard test and gave a pale yellow color with tetranitromethane. This methyl ester which formed a monoacetate, $C_{33}H_{52}O_4$, m.p. 219–220°, $[\alpha]_D^{35}$ + 69.5° ($CHCl_3$) and a monoketo compound, $C_{31}H_{48}O_3$, m.p. 185–186°, did not depress the m.p. of an authentic sample of methyl oleanolate[8].

Compound C, $C_{31}H_{50}O_4$, m.p. 238–239°, $[\alpha]_D^{36}$ + 78.3° ($CHCl_3$) gave a diacetate, $C_{35}H_{54}O_6$, m.p. 191–192°, $[\alpha]_D^{36}$ + 76.2° ($CHCl_3$), on heating with pyridine and acetic anhydride on steam-bath. Compound C was proved to be methyl hederagenate (IIa)[2,9].

Zusammenfassung. Aus der Fleischschale der Nüsse von *Sapindus laurifolius* wurden ausser Hederagenin 2 Triterpene isoliert. Das eine wurde als Oleanolsäure identifiziert, und das andere (Sapindic-Säure) erwies sich als Δ^{12} 3ξ,23α-oxido-oleanen-28-säure.

P. C. Maiti[10], S. Roy and A. Roy

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[10] Central Forensic Science Laboratory, Calcutta-14.