THE SAPONIN OF *DORYANTHES PALMERI* W. HILL*

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Doryanthes palmeri W. Hill is a member of a small, exclusively Australian, genus belonging to the family Amaryllidaceae, subfamily Agavoideae (Rendle 1930). The members of this genus are commonly known as " spear " or " giant lilies " and during a survey of the Australian flora for the presence of saponins several were found to give strongly positive results (Dunstan and Simes 1950). Marker *et al.* (1943) have isolated steroidal saponins from a number of American Agavoideae.

The saponin from the roots and crowns of *D. palmeri* was isolated by alcoholic extraction, hydrolysed to the sapogenin, and purified by chromatography on a column of alumina. One major and two minor fractions were obtained.

The major fraction was identified from physical properties and derivatives as the steroidal sapogenin sarsasapogenin, previously obtained from the saponins of other plants including *Smilax* spp. and *Yucca elata* (Engelm.) (van der Haar 1929 ; Marker *et al.* 1943 ; Shabica 1943).

The infra-red spectrum of the acetate is consistent with this conclusion and shows absorption bands in accord with those stated by Wall *et al.* (1952*a*) to be characteristic for steroidal sapogenins. The molar absorptivity indicates that it has a " normal " configuration as the 918 cm^{-1} band is stronger than the 892 cm^{-1} band ; sarsasapogenin is the only common " normal " sapogenin (Wall *et al.* 1952*a*, 1952*b*).

The small amounts of genins obtained from the minor fractions have not yet been fully investigated.

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Experimental

(*a*) *Isolation of Saponin.*—Dried milled roots and crowns of *D. palmeri* (7 kg) collected at Mt. Mistake were extracted eight times with boiling ethanol (22 l.), the combined extracts evaporated to small bulk (2·5 l.), poured into ether (10 l.), and stirred, when the crude saponin separated as a thick syrup. The supernatant ether was decanted and the crude saponin stirred with dry ether (2 l.) until it solidified. The crude saponin (425 g after drying *in vacuo*) was dissolved in water (3 l.) and the solution filtered under pressure. Concentrated hydrochloric acid (350 ml) was added to the filtrate, the mixture refluxed for 3 hr, the crude black amorphous sapogenin filtered off, washed well with water, and dried *in vacuo* at 100 °C.

The crude dry sapogenin (62·4 g) was Soxhlet extracted with ether and the solvent evaporated giving a brownish solid. Recrystallization from methanol (charcoal) formed white crystals (3·8 g), which were dissolved in chloroform-light petroleum (1 : 3 ; 500 ml), and the solution adsorbed on a column of activated alumina (35 × 2·5 cm). Elution with chloroform-light petroleum (1 : 3 ; 900 ml) gave colourless plates (I) (3·3 g). Elution with chloroform (150 ml) gave colourless needles (0·2 g) which after recrystallization from methanol had m.p. 286–290 °C (II).

The column was finally eluted with chloroform-methanol (6 : 1 ; 100 ml) colourless crystals (0·3 g) being obtained which after recrystallization from methanol had m.p. 278–281 °C (III).

I was redissolved in chloroform-light petroleum (1 : 3 ; 375 ml) and rechromatographed on a column of activated alumina (35 × 2·5 cm). Elution with chloroform-light petroleum (1 : 3 ; 300 ml) gave colourless plates (3·0 g) which after recrystallization from methanol had m.p. 199·5 °C (IV), and gave a bluish Liebermann-Burchard test suggesting a steroidal compound, $[\alpha]_D^{24}$ —75·1° (*c*, 4·23 in chloroform) (Found : C, 77·75 ; H, 11·0%. M, 400 ; cryoscopic in camphor. Calc. for $C_{27}H_{44}O_3$: C, 77·8 ; H, 10·7%. M, 416). Sarsasapogenin, $C_{27}H_{44}O_3$ (Simpson and Jacobs 1935 ; Askew, Farmer, and Kon 1936), has m.p. 199–200 °C, $[\alpha]_D^{25}$ —75° (*c*, 0·498 in chloroform). Elution of the column with chloroform (100 ml) gave colourless needles (0·1 g), which on recrystallization from methanol had m.p. 286 °C (V), and with chloroform-methanol (6 : 1 ; 100 ml) gave colourless crystals (0·1 g), m.p. 290 °C (VI). Compounds II, III, and VI appear to be identical substances in differing states of purity.

(*b*) *Preparation of Acetate.*—The acetyl derivative of IV, prepared by refluxing with acetic anhydride and fused sodium acetate, crystallized from methanol as colourless needles, m.p. 146 °C. The infra-red absorption spectrum (*c*, 10·0 g/l in carbon disulphide) showed bands at 852, 892, 918, and 984 cm^{-1}. The molar absorptivity at the 892 band was 82 l. mol^{-1} cm^{-1} and at the 918 band was 236 l. mol^{-1} cm^{-1} (Found : C, 75·8 ; H, 9·9%. Calc. for $C_{29}H_{46}O_4$: C, 75·9 ; H, 10·1%).

Sarsasapogenin acetate, $C_{29}H_{46}O_4$, has m.p. 145 °C (Askew, Farmer, and Kon 1936). Infra-red absorption spectrum (*c*, 10·0 g/l in carbon disulphide) shows bands at 852, 897, 922, and 987 cm^{-1}. The molar absorptivity at the 897 band is 69·9 l. mol^{-1} cm^{-1} and at the 922 band is 239 l. mol^{-1} cm^{-1} (Wall *et al.* 1952*a*).

(*c*) *Oxidation.*—IV (0·3 g) was dissolved in glacial acetic acid (10 ml) and chromic oxide (0·1 g) in glacial acetic acid (30 ml) added. After heating 30 min on the steam-bath the mixture was poured into water and extracted with ether. The extract was washed with sodium bicarbonate solution then water and evaporated. The residue after recrystallization from acetone formed white plates, m.p. 221–223 °C (Found : C, 78·0 ; H, 10·2%. Calc. for $C_{27}H_{42}O_3$: C, 78·2 ; H, 10·2%). The semicarbazone melted at 182 °C (decomp.) after crystallization from aqueous ethanol (Found : N, 9·15%. Calc. for $C_{28}H_{45}O_3N_3$: N, 8·9%). The oxime separated from acetone as colourless plates, m.p. 127 °C. Sarsasapogenone melts at 223–224 °C, its oxime at 127 °C (Jacobs and Fleck 1930) and the semicarbazone at 180 °C (decomp.) (Marker and Rohrmann 1939).

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