cone, m.p. 192°, from acetone identified as 3,7,3′,4′-tetramethyl ether of quercetin by m.p. (lit. 192–194°) and spectral properties.[21,22] (Found C, 63·55; H, 5·2. Calc. for $C_{19}H_{18}O_7$: C, 63·68; H, 5·02%.)

2,3,4-tri-*O*-methyl-L-rhamnose was obtained as the sugar. On warming the solution with a mixture of aniline and aniline hydrochloride in methanol, a product was obtained which crystallized from light petroleum as colourless needles, m.p. 123° confirming the identity of the sugar (lit., m.p. 124–125°).[30]

Aglycone. The coloured aglycone gave characteristic colour reactions of 5-hydroxy flavonols with three methoxyl groups. (Found: C, 62·95; H, 4·5; OCH_3, 26·2. Calc. for $C_{18}H_{16}O_7$: C, 62·8, H, 4·65; OCH_3, 27·03%.) Acetylation with Ac_2O and pyridine gave a diacetate, m.p. 180°. (Found: $COCH_3$, 20·8. Calc. for $C_{18}H_{14}O_7$ $(COCH_3)_2$: $COCH_3$, 20·96%), and $KMnO_4$ gave veratric acid.

Ether extract (*quercetin*). The residue obtained from above was extracted with Et_2O yielding quercetin, m.p. 316°. (Found: C, 59·60; H, 3·31. Calc. for $C_{15}H_{10}O_7$: C, 59·46; H, 3·21%.) It formed a penta acetate, m.p. 195°. (Found: $COCH_3$, 39·88. Calc. for $C_{15}H_5O_7$ $(COCH_3)_5$: $COCH_3$, 41·21%.)

Acknowledgement—We are thankful to the Council of Scientific and Industrial Research (India) for the award of a research fellowship to one of us (O.P.Y.)

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Phytochemistry, 1971, Vol. 10, pp. 2263 to 2265. Pergamon Press. Printed in England.

SWARTZIAGENIN: A MIXTURE OF OLEANOLIC AND *O*-ACETYLOLEANOLIC ACIDS

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INTRODUCTION

THE SEED pods of the tree *Swartzia madagascariensis* Desv. have been reported to have been used effectively in controlling the populations of bilharzia-transmitting snails in African ponds.[1] Chemical studies by one of us have shown that the pods contain two acidic saponins, swartziasaponins A and B, which afford swartziagenin, a triterpene dicarboxylic acid of unknown constitution, on hydrolysis with Kiliani's reagent.[2,3] As part of a continuing study of saponins derived from tropical plants as potential molluscicides,[4] we have re-examined swartziagenin and have found it to be a mixture of oleanolic (Ia) and *O*-acetyloleanolic (Ib) acids.

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[1] A. MOZELEY, *Molluscicides*, Lewis, London, p. 22 (1952).

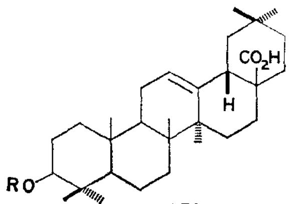
[2] F. SANDBERG, B. AHLENIUS and R. THORSEN, *Svensk. Farm. Tidskr.* **62**, 541 (1958).

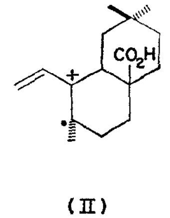
[3] F. SANDBERG, *Pakistan J. Sci. Indust. Res.* **4**, 258 (1961).

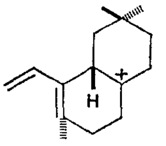
[4] *Report of the Tropical Products Institute* H.M.S.O., London, p. 13 (1967).

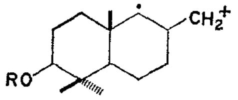
RESULTS AND DISCUSSION

Acid hydrolysis of a mixture of glycosides from *Swartzia madagascariensis* seed pods furnished the aglycones, which were separated by chromatography into a triterpene carboxylic acid and a flavone. The triterpene acid, $C_{30}H_{48}O_3$, m.p. 300–304°, ($M^+ = 456$), showed in its IR spectrum strong absorption at 3440, 1690 and 1030 cm^{-1} indicating the presence of hydroxyl and carboxyl groups. The base peak of the mass spectrum of this compound was observed at $m/e = 248$, and this ion (II) fragmented with the loss of a formyl group to give the ion (III) $m/e = 203$. The presence of these ions in the spectrum suggested that the acid was either an ursa-12-en or oleana-12-en-28-carboxylic acid, and the ion (IV) observed at $m/e = 207$ indicated that the hydroxyl group was probably located at C_3. Methylation of the acid afforded a monomethyl ester, $C_{31}H_{50}O_3$, m.p. 190°, ($M^+ = 470$), ν_{max} 3300 and 1720 cm^{-1}, which was found to be identical with an authentic sample of methyl oleanolate.


(I)
(a) R = H
(b) R = CH$_3$CO


(II)


(III)


(IV)
(a) R = H
(b) R = CH$_3$CO

As the fresh sample of seed pods had afforded as its major triterpene sapogenin a monocarboxylic acid, oleanolic acid (Ia), and not swartziagenin, we decided to examine the homogeneity of swartziagenin. Comparison of the two compounds by TLC showed that swartziagenin was a mixture comprised of oleanolic acid and a small quantity of a less polar compound. Separation of the mixture by preparative TLC furnished oleanolic acid and a small quantity of the minor component, $C_{32}H_{50}O_4$, m.p. 265–268°, ($M^+ = 498$). The IR spectrum of the latter compound showed strong absorption at 1730, 1680 and 1255 cm^{-1}, indicating the presence of acetoxy and carboxyl groups. Strong ions were observed in its mass spectrum at $m/e = 438$, 423, 249, 248 (base peak) and 203, which could be formulated as $M^+ - CH_3CO_2H$, $M^+ - CH_3CO_2H - CH_3$ and (IVb; II; III) respectively. Consideration of the spectroscopic data, together with the fact that oleanolic acid was present in swartziagenin made us conclude that the minor component was probably *O*-acetyloleanolic acid (Ib), and this was confirmed by comparison with an authentic specimen prepared from oleanolic acid. We cannot rule out the possibility that *O*-acetyloleanolic acid is an artefact produced during hydrolysis of swartziasaponins with Kiliani's reagent and work is in progress to settle this point.

The flavone, $C_{15}H_{10}O_6$, m.p. 276–279° ($M^+ = 286$), ν_{max} 3330, 3100, 1650 and 1605, had strong ions at $m/e = 258$, 152 and 134 in its mass spectrum, which were formed by elision of carbon monoxide and retro-Diels-Alder fragmentation of the molecular ion. The spectroscopic data and the m.p. suggested that the compound was kaempferol, and this was confirmed by preparation of the tetramethyl ether and the tetra-acetate whose physical constants and spectroscopic data were in agreement with recorded values.

EXPERIMENTAL

Isolation of oleanolic acid and kaempferol from seed pods. Ground seed pods of *Swartzia madagascariensis* (940 g) were exhaustively extracted with ether, acetone, and methanol. Evaporation of the extracts gave 13, 53 and 315 g of solid respectively. Hydrolysis of a portion of the methanol extract (87 g) in aqueous ethanol (47%; 1 l.) with 10 N HCl (250 ml), afforded a mixture of aglycones which were chromatographed on kieselgel. Elution with petrol–ether (2:3) gave oleanic acid, $C_{30}H_{48}O_3$, (1·7 g; m.p., IR, MS, TLC; methyl ester, $C_{31}H_{50}O_3$, m.p., IR, MS, TLC), and ether furnished kaempferol, $C_{15}H_{10}O_6$ (1·6 g; m.p., IR, MS; trimethyl ether, m.p., IR, MS, NMR; tetraacetate, m.p., IR, MS).

Separation of swartziagenin by PLC. Swartziagenin (334 mg) was chromatographed on 3 × 20 × 40 cm plates coated with 0·75 mm layers of kieselgel using $CHCl_3$–MeOH (9:1) as eluant. Extraction of the band R_f *ca.* 0·75 with $CHCl_3$ gave oleanolic acid (232 mg; m.p., IR, MS, TLC), and the band R_f *ca.* 0·95 with $CHCl_3$ afforded *O*-acetyloleanolic acid, $C_{32}H_{50}O_4$ (60 mg; IR, MS, TLC).

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ROSACEAE

ANTHOCYANINS IN PETALS OF *CHAENOMELES SPECIOSA*

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Abstract—*Chaenomeles speciosa* petals are pigmented with previously unrecorded diglycosides of pelargonidin and cyanidin containing glucose and galactose, together with cyanidin 3-galactoside and 3-glucoside, pelargonidin 3-galactoside and traces of pelargonidin 3-glucoside.

INTRODUCTION

ALTHOUGH anthocyanins of the Rosaceae have been identified,[1] those of the genus *Chaenomeles* (sub-family Pomoideae) have been studied only once, by Hayashi,[2] who found that petals of *Chaenomeles lagenaria* (= *Chaenomeles speciosa*) contained a cyanidin 3-diglucoside.

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[1] J. B. HARBORNE, *Comparative Biochemistry of the Flavonoids*, pp. 130, 154, 236, Academic Press, London (1967).

[2] K. HAYASHI, *Acta Phytochim.* **14**, 47 (1944).