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SHORT COMMUNICATION

TRITERPENOID SAPONINS FROM *PHYTOLACCA DODECANDRA*

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Abstract—Two aglycones from the saponins of the molluscicidal fruit of *Phytolacca dodecandra* have been identified as oleanolic acid and bayogenin.

THE FRUITS of *Phytolacca dodecandra* (Phytolaccaceae) (known in Ethiopia as "Endod") have been extensively used as a poison in Africa[1,2] and are currently receiving considerable attention as a potential molluscicide for the control of bilharzia.[1,2] It has been suggested[1] that the toxic principle which is present in various parts of the plant is a steroidal saponin. Through the courtesy of Dr. B. A. Hems of Glaxo Research Ltd., we have been able to examine a quantity of the fruits and have carried out a preliminary investigation of the saponins.

The dried, crushed fruits were defatted with petroleum ether and then extracted with methanol to furnish a water-soluble gum having the general properties of a saponin. This extract was tested against young adult snails of a Puerto Rican strain of *Australerbis glabratus* with the following reproducible results: (*a*) 1:7500 parts in water, all snails killed in 4 days; (*b*) 1:3250 parts in water, all snails killed after 48 hr.

Hydrolysis of the crude saponin gave a high melting product which was devoid of ester groups but which contained hydroxyl and carboxyl groups (i.r. spectrum) and which was acetylated and then methylated. Separation of the mixed product by chromatography furnished methyl *O*-acetyl oleanolate (I) and methyl tri-*O*-acetylbayogenin[3] (II), thereby indicating the presence of the oleanolic acid and bayogenin moieties as aglycones in the original saponins. The mass spectrum of (II) showed a base peak at *m*/*e* 203 (accurate mass measurement) corresponding to the ion (IV) produced by way of the retro-Diels-Alder product (III). The NMR spectrum of methyl tri-*O*-acetylbayogenin showed, *inter alia*, signals at τ 4·6 (multiplet, 2 protons, H-3 and H-12), 5·05 (doublet, $J=4$ c/s, 1 proton, H-3), 6·2 (close AB system, 2 protons, —CH_2OCOCH_3), 6·35 (singlet, 3 protons, —COOCH_3), 7·9 (singlet, 6 protons, 2 × —OCOCH_2), 8·0 (singlet, 3 protons, —OCOCH_3), 8·8, 8·9, 8·95, 9·2 (singlets, 3 protons each, $\rightarrow$C.CH_3) and 9·1 (singlet, 6 protons, 2 × C.CH_3). The coupling constant between H-2 and H-3 of 4 c/s is in agreement with the assigned stereochemistry of the acetoxyl groups as 2β, 3β. The chemical shift of the close-coupled AB system attributed

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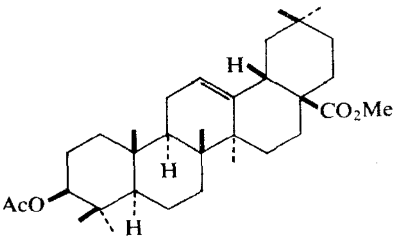
[1] J. M. WATT and M. BREYER, *Medicinal and Poisonous Plants of Southern and Eastern Africa*, Brandwijk (1962).

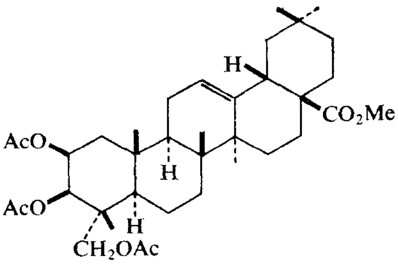
[2] C. WEISS, JR., *Scient. Res.* 64–74 (1967).

[3] R. A. EADE, J. J. H. SIMES and B. STEVENSON, *J. Australian Chem.* 900 (1963).

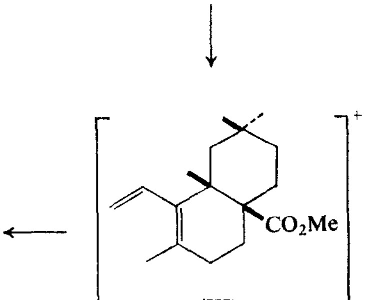
to the protons on C-23 is within the range given by Gaudemer *et al.*[4] for an equatorial —CH_2OCOCH_3 attached to C-4. Thus the NMR and mass spectral data are fully in accord with the structure and stereochemistry previously assigned[3] to bayogenin.



(I)

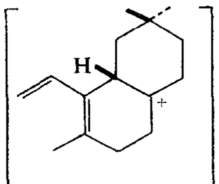


(II)



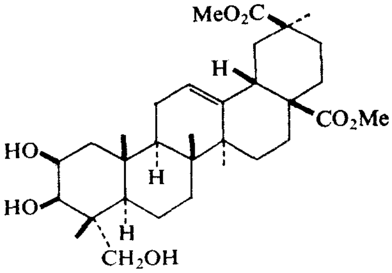
(III)

$C_{17}H_{26}O_2 = 262$ (71 %)



(IV)

$C_{15}H_{23} = 203$ (100%)



(V)

The close structural relationship between bayogenin and phytolaccagenin[5] (V) from *P. americana* L. ("pokeroot") is in accord with the close botanical relationship between the two plant species.

At this stage of our work we had become aware of the more extensive investigation upon this project being carried out by the Tropical Products Institute, who have also reported the isolation of oleanolic acid.[6] We have thus discontinued this investigation.

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[4] A. Gaudemer, J. Polonsky and E. Wenkert, *Bull. Soc. Chim. Fr.* 407 (1964).

[5] G. H. Stout, B. M. Malofsky and V. F. Stout, *J. Am. Chem. Soc.* **86**, 957 (1964).

[6] T. A. King, K. Jewers, H. Richardson and C. P. Falshaw, Abstracts of 5th International Symposium on the Chemistry of Natural Products, F43, London (1968).

EXPERIMENTAL

The NMR spectra were determined in deuterio-chloroform solution on a Varian A 60-A spectrometer.

Extraction of Dried Fruit from Phytolacca dodecandra

The dried fruit (610 g) was coarsely crushed and defatted (Soxhlet) with petroleum ether (b.p. 60–80°) during 8 hr. Subsequent extraction with methanol during 24 hr yielded crude saponin as a brown gum (310 g). Hydrolysis of this saponin (72 g) in boiling methanol (600 ml) containing conc. HCl (150 ml) occurred during 90 min, with the separation of a semi-crystalline product (11·6 g), m.p. 345–350°. After collection of the product, further heating of the filtrate under reflux (2 hr) furnished an additional quantity (2 g) of a similar material.

Separation of the Mixed Aglycones

Crude aglycone (2·7 g) dissolved in pyridine (20 ml) and Ac_2O (50 ml) was kept at 20° during 48 hr. On isolation the mixture of crude acetates, dissolved in methanol (50 ml), was treated with ethereal CH_2N_2 [from nitrosomethylurea (15 g)], during 18 hr at 0°. A solution of the product in benzene (10 ml) was chromatographed on silica gel. Elution with ethyl acetate/benzene (4%) gave methyl *O*-acetyloleanolate (0·6 g) which formed prisms, m.p. 216–222°, from alcohol: further elution with ethyl acetate/benzene (10–20 per cent) yielded methyl tri-*O*-acetylbayogenin in prisms (0·5 g), m.p. 195–203°, from methanol. Both specimens were identical (m.p., mixed m.p., i.r., NMR and mass-spectra) with authentic specimens.

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