## CYCLOARTENYL ACETATE, CYCLOARTENOL AND CYCLO-ARTENONE IN THE BARK OF ARTOCARPUS SPECIES\*

GOWSALA PAVANASASIVAM and M. UVAIS S. SULTANBAWA
Department of Chemistry, University of Sri Lanka, Peradeniya Campus,
Peradeniya, Sri Lanka

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THE LIGHT petrol. (b.p. 60-80°) extract of the bark of the endemic species Artocarpus nobilis Thw. (Sinhala-wal del) when chromatographed on a silica gel column gave 3 triterpenes.† The first of these, obtained as white needles m.p.  $118^{\circ}$ ,  $[a]_{D}^{26} + 55^{\circ}$ , had IR band at 1745 cm<sup>-1</sup> assignable to the > CO group of an ester and its NMR spectrum showed the presence of, (a) an olefinic proton ( $\tau$  5·34), (b) a -CHO- group ( $\tau$  5·4), (c) a -C=O Me group  $(\tau 7.96)$ , (d) two vinyl methyl groups  $(\tau 8.32, 8.4)$ , (e) two one proton multiplets  $(\tau 9.42,$ 9.68) assignable to cyclopropane ring protons, and (f) the usual methylene envelope and signals due to tertiary methyl groups. The above evidence suggested that this compound is cycloartenyl acetate (I). This suggestion was confirmed by the observation that (I) on hydrolysis gave cycloartenol (identified by m, m, p., IR and TLC comparison with an authentic sample) which on acetylation gave back the original compound (I) (m. m.p., IR and TLC comparison). The second and third compounds were identical (m. m.p., IR, TLC) with authentic samples of cycloartenol (II) and cycloartenone (III) respectively. As far as we know, this is the first report of the isolation of the three compounds from the bark of an Artocarpus species. However, the isolation of cycloartenol as its acetate together with cycloartenone from the peduncle of the fruits of Artocarpus heterophyllus Lam<sup>1</sup> has been reported. Cycloartenyl acetate is not very common in plants but has been reported from A. chaplasha<sup>2</sup> and Ficus macrophylla,<sup>3</sup> both of which belong to the family Moraceae.

Chromatographic separation on silica gel of the light petrol. extract of the timber of A. nobilis Thw. gave besides other compounds the same three triterpenes, but in low yields (see Table 1). As an extension of this investigation, the light petrol. extracts of the barks of A. heterophyllus Lam (A. integra Merr) A. altilis (Park) Fosb (A. incisa Lam) and A. lakoocha Roxb<sup>4</sup> were studied. The extracts of the first two species gave, after chromatographic separation on silica gel, all three compounds (I, II and III). However, A. lakoocha Roxb gave cycloartenol (II) and cycloartenone (III) and an acetate which was similar but

<sup>\*</sup> Part VI in the series "Chemical Investigation of Ceylonese Plants".

<sup>†</sup> Work is in progress on the other products from the extract.

<sup>&</sup>lt;sup>1</sup> BARTON, D. H. R. (1951) J. Chem. Soc. 1444

<sup>&</sup>lt;sup>2</sup> CHAKRAVARTI, R. N., MAHATA, S. B. and BANNERJEE, S. K. (1971) Phytochemistry 10, 1351.

<sup>&</sup>lt;sup>3</sup> RITCHIE, E., GALBRAITH, N. M., MILLER, C. J., RAWSON, J. W. L. and TAYLOR, W. C. (1966) Colloq. Int. Center Nat. Rech. Sci. 144, 107.

not identical with cycloartenyl acetate. Structural determination of this compound is in progress. The relative proportions of the three compounds in the different species are given in Table 1. The presence of the three compounds I, II and III in various species may have taxonomic value for this genus.

TABLE 1.	DISTRIBUTION	OF	CYCLOARTENOL	AND	RELATED	COMPOUNDS II	N Artocarpus
			SPEC	IES			

% of triterpene in bark							
Bark from	Cycloartenyl acetate	Cycloartenol	Cycloartenone				
A. nobilis Thw.	1 2	0.24	0.006				
A. altilis (Park) Fosb (A. incisa Lam.) A. heterophyllus Lam	0.68	0 07	0.005				
(A. integra Merr)	0.04	0.06	0.15				
A lakoocha Roxb	_	0.004	0 001				
Timber A nobilis Thw.	0.02	0 01	0.001				

<sup>\*</sup> All compounds were identified by m.m.p. IR and Co-TLC.

$$(I) \quad R = \int_{0}^{0} H$$

$$(II) \quad R = \int_{0}^{0} H$$

$$(III) \quad R = 0$$

## EXPERIMENTAL

All rotations were determined in CHCl<sub>3</sub> and m p s. on a Kofler hot Stage. Light petrol. refers to the fraction b.p. 60-80°.

Isolation of cycloartenyl acetate, cycloartenol and cycloartenone. (a) from A. nobilis Thw. Dried powdered bark (5·5 kg) of A. nobilis Thw. (from Peradeniya) was exhaustively extracted with light petrol. Concentration of the extract deposited a yellow solid (15 g) which was filtered off. The filtrate on removal of the solvent yielded a gum (200 g). This gum (15 g) was subjected to column chromatography over silica gel (200 g, Merk 30–70 mesh) and light petrol.— $C_6H_6$  (1:1) fraction gave a yellow sticky liquid (two spots). It was boiled with MeOH and cooled. A yellow liquid settled at the bottom and was separated. The methanolic solution on cooling furnished cycloartenyl acetate as white needles (5 g) m.p. 118°,  $[a]_D^{26} + 55^\circ$  (lit. 122·5–123·5°,  $[a]_D + 58^\circ$ ).  $\nu_{max}^{Nujol}$  1745, 1650, 1250, 1100, 1045, 1030, 1000, 980, 925, 890 and 730 cm<sup>-1</sup>. NMR data in CDCl<sub>3</sub> (100 MHz) are given in the text above.

On hydrolysis, it gave cycloartenol which was shown to be identical with an authentic sample (m m p., IR and Co-TLC). This cycloartenol on acetylation gave back the original compound and it was shown to be identical with it by m m p, IR and Co-TLC

Elution of the column with light petrol.– $C_6H_6$  (1:1) gave a gum which on crystallization from MeOH furnished white scales of cycloartenone (25 mg) m p. 108°,  $[\alpha]_D^{26} + 23^\circ$  (Lit., 109°,  $[\alpha]_D + 24^\circ$ )

Further elution with  $C_6H_6$  gave a gum which on crystallization from MeOH gave cycloartenol (100 mg) m.p. 112°,  $[a]_D^{26} + 55^\circ$  (lit., <sup>1,5</sup> 114°,  $[a]_D + 54^\circ$ ).

(b) from A. altilis Park Fosb, A. heterophyllus Lam and A. lakoocha Roxb the compounds (I-III) were isolated as above and characterised by m.m.p., IR and Co-TLC

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<sup>4</sup> Mahata, S. B., Bannerjee, S. K. and Chakravarti, R. N. (1966) Bull. Calcutta Sch. Trop. Med. 14, 16. <sup>5</sup> Bentley, H. R., Henry, J. A., Irvine, D. S. and Spring, F. S. (1953) J. Chem. Soc. 3673.