(15 mg), 224–226°, $C_{32}H_{52}O_2$ ($M^+$ at *m/e* 468). [α], UV, IR, NMR, mmp co-TLC which, on hydrolysis afforded α-amyrin mp, mmp co-TLC, [α] IR.

The last crystalline compound was isoursenol acetate, (126 mg) mp 214–216°. $C_{32}H_{52}O_2$; $[\alpha]^{24}_{589}$ +34·8; $[\alpha]_{578}$ +35·0; $[\alpha]_{546}$ +40·1 $[\alpha]_{436}$ +68·8°, $[\alpha]_{365}$ +115·2°; $[\alpha]_{316}$ +187·2°; ($CHCl_3$). UV, NMR, IR. (M ± at *m/e* 468, base peak at *m/e* 203); hydrolysis gave isoursenol, mp [α] IR. NMR.

The ethanolic residue (80 g) was shaken with $CHCl_3$ (600 ml) and filtered. A solid was obtained which on crystallization ($H_2O$–EtOH) afforded needles of (+)-pinitol (3·0 g) mp 187–189° $[\alpha]^{24}_{589}$ +51·1° ($CHCl_3$) IR, NMR, co-TLC mmp with an authentic specimen; pentacetate, mp, mmp and co-TLC. The $CHCl_3$ soluble material was percolated on a Si gel column but no pure compounds were isolated.

This is only the second time that isoursenol (found earlier in *Olearia paniculata*, Compositae [4]) has been isolated from plant sources, and its presence in other members of the caryophyllaceae needs to be looked for.

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# TERPENOIDS AND STEROIDS FROM *MACARANGA TANARIUS**

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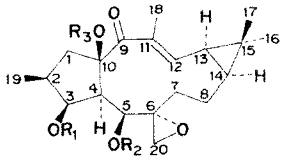
**Key Word Index**—*Macaranga tanarius*; Euphorbiaceae; diterpenoids: 6:20-epoxylathyrol-5,10-diacetate-3-phenylacetate and macarangonol; triterpenoids: β-amyrenone, β-amyrin, friedel-3-ene, friedelin, friedelan-3β-ol; steroids: sitosterol, 5α-stigmastan-3,6-dione, 6β-hydroxystigmast-4-en-3-one; ellagic acid.

*Plant. Macaranga tanarius* Muell.-Arg. (Hong Kong Herbarium voucher Specimen No. 23238). *Previous work.* Diterpene ketol, macarangonol from stems.* Hardwoods for pulp and paper making [1]. On sister species: *M. triloba* (preliminary chemical and pharmacological screening) [2]. *M. denticulata* (taraxerone, 3-*epi*taraxerol and sitosterol [3]).

*Present work.* The light petrol extract of the stems of *M. tanarius* has been found to contain diterpenoids: besides macarangonol*, 6:20-epoxylathyrol-5,10-diacetate-3-phenylacetate (**1**) [4], which has previously been isolated only from *Euphorbia lathyris* (Euphorbiaceae), and triterpenoids: friedel-3-ene, friedelin, friedelan-3β-ol, β-amyrenone and β-amyrin. Friedel-3-ene was first prepared in the pure state by Brownlie *et al.* [5] by dehydration of friedelan-3β-ol, and its natural occurrence has been reported only from *Vaccinium*



( **1** ) $R_1$ = PhAc, $R_2$=$R_3$=Ac

( **2** ) $R_1$ = $R_2$= $R_3$= H

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* Part X in the series "An Examination of the Euphorbiaceae of Hong Kong". For Part IX, see Hui W. H., Ng K. K., Fukamiya N., Koreeda M. and Nakanishi K. (1971) *Phytochemistry*, **10**, 1617.

*membranaceum* (Ericaceae) [6]. The steroids, sitosterol, 5α-stigmastan-3,6-dione and 6β-hydroxystigmast-4-en-3-one have also been found in the same extract. The former was first reported from *Metasequoia glyptostroboides* [7] in 1969, though its synthesis from sitosterol [8] had been achieved in 1942. This is its second natural occurrence. 6-β-Hydroxystigmast-4-en-3-one has been isolated twice from plants as inseparable mixtures: one with 6β-hydroxycampest-4-en-3-one from *Melia azedarach* [9], and the other with 6β-hydroxystigmasta-4,22-dien-3-one from *Phaseolus vulgaris* [10]. We reported here its first isolation in the pure state as indicated by both its IR and MS being completely identical with those of authentic samples prepared from sitosterol [11]. The EtOH extract of the stems (after extraction with light petroleum) yielded ellagic acid, and the light petroleum extract of the leaves gave friedelin, friedelan-3β-ol, β-amyrin and sitosterol.

## EXPERIMENTAL

IR spectra were recorded for KBr discs, NMR spectra in $CDCl_3$, UV spectrum in 95% ethanol and optical rotations in $CHCl_3$ solns. Light petrol had bp 60–80°. Known compounds were identified by TLC, mmp and IR spectral comparisons with authentic samples.

*Stems.* Milled dried stems (61 kg) were extracted twice with light petrol, and the combined extracts were concentrated to give crystals (9·0 g) which were filtered and recrystallized twice from $CHCl_3$ to give friedelan-3β-ol, mp 284–287°. The filtrates were combined, evaporated to dryness and chromatographed on alumina (3 kg) in light petrol soln. Elution with light petrol gave plates of friedel-3-ene (20 mg), mp 258–260° (from light petrol), $[\alpha]_D$ +52·9°, $C_{30}H_{50}$, $M^+$ 410, $\nu_{max}$ 3050, 1670, 832 $cm^{-1}$ ($\gt C{=}CH{-}$), identical with an authentic sample prepared by dehydration of friedelan-3β-ol with $POCl_3$ in pyridine [5], then β-amyrenone (10 mg), mp 179–181°, $[\alpha]_D$ + 104·5°, and friedelin (5·0 g), mp 261–262°, and finally friedelan-3β-ol (2·5 g); light petrol–$C_6H_6$ (1 : 1), β-amyrin (1·2 g), mp 198–200°, $[\alpha]_D$ +85·0°, then sitosterol (3·0 g), mp 139–140°, and finally a semicrystalline solid which on recrystallization from light petrol–$CHCl_3$ yielded needle-shaped crystals (0·2 g), mp 200–202°, $[\alpha]_D$ +12·0°, $C_{29}H_{48}O_2$, $M^+$ 428, $\nu_{max}$ 1710, 1720 ($\gt C{=}O$), identical with a sample of 5α-stigmast-3, 6-dione synthesized from sitosterol by chromium trioxide oxidation followed by zinc dust reduction [8]; benzene, a black gum which after removal of coloured material with acetone, crystallized from light petrol to give colourless needles (20 mg), mp 204–207°, (Found: $M^+$ 552. C, 69·3; H, 7·3. Calc. for $C_{32}H_{40}O_8$: $M^+$ 552. C, 69·5; H, 7·3%.) $\nu_{max}$ 1730, 1260 (RCOO–), 1660, 1620 ($\gt C{=}\overset{|}{C}{-}\overset{|}{C}{=}O$), 1600, 1580, 730, 700 $cm^{-1}$ (mono-substituted $C_6H_6$ ring), δ2·05 (3H,*s*,–OCOMe), 2·15 (3H,*s*,–OCOMe), 7·25 (5H,*s*, –$C_6H_5$), and 3·95 (2H,*s*,–$OCOCH_2Ar$), (identical with an authentic sample of 6 : 20-epoxylathyrol-5,10-diacetate-3-phenylacetate, **1** [4]), hydrolyed by boiling with KOH in MeOH to give 6:20-epoxylathyrol (**2**), mp 205–208°, $C_{20}H_{30}O_5$, $M^+$ 350, $\nu_{max}$ 3520 (OH), 1690, 1640 $cm^{-1}$($\gt C{=}\overset{|}{C}{-}\overset{|}{C}{=}O$). Continued elution with $C_6H_6$ yielded plate-like crystals (20 mg), mp 211–212°, $[\alpha]_D$ +27·5°, (Found: C, 81·1; H, 11·1. Calc. for $C_{29}H_{48}O_2$: C, 81·3; H, 11·3%, MS, $M^+$ 428, (b.p.) (no appreciable peak at *m/e* 426 or 414), $\nu_{max}$ 3510, (OH), 1695, 1620 $cm^{-1}$($\gt C{=}\overset{|}{C}{-}\overset{|}{C}{=}O$), $\lambda_{max}$ 246 nm (ϵ 12900) (Lit. [9] 239, Lit. [10] 238 nm), identical with samples of 6β-hydroxystigmast-4-en-3-one (from Professor Katsui [10] and our own) prepared by oxidation of pure sitosterol with $Na_2Cr_2O_7$ in HOAc [11]; and $C_6H_6$–$CHCl_3$ (1:1) gave macarangonol, $C_{20}H_{30}O_2$ (0·10 g). The stems, after extraction with light petrol, were further extracted twice with EtOH. The combined conc extracts deposited a yellow solid (100 g), mp > 360°, which after several recrystallizations from pyridine, gave needles of ellagic acid, $\nu_{max}$ 3500, 1720, 1600, 1520 $cm^{-1}$ (tetraacetate, mp 310–316°; tetramethyl ether, mp 350°).

*Leaves.* Milled dry leaves (20 kg) were extracted with light petrol, and chromatographed as for the stems. Compounds obtained were friedelin, friedelan-3β–ol, β-amyrin and sitosterol.

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