H. curvistigma F. Maekawa (0·38%); *H. hexaloba var. perfecta* F. Maekawa (0·30%).

Group B: *Asarum caulenscens* Maxim**†; *Asarum hirsutisepalum* Hatsushima**; *A. yakusimense* Masam**; *Asiasarum heterotropides var. seoulense* F. Maekawa; *A. sieboldii* F. Maekawa; *Heterotropa albivenium* F. Maekawa; *H. asaroides* Morr. et Decne; *H. crassa* F. Maekawa; *H. kiusiana* F. Maekawa; *H. megacalyx* F. Maekawa; *H. muramatsui* F. Maekawa; *H. nipponica* F. Maekawa; *H. savatieri* F. Maekawa; *H. tamaensis* F. Maekawa.

Acknowledgements—The authors wish to thank Prof. Y. Saiki for providing us with the air-dried materials tested in our experiments.

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** Collected in Yakushima in middle of November.

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TRITERPENES FROM LATEX OF *EUPHORBIA BALSAMIFERA*

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(*Received* 12 *August* 1975)

Key Word Index—*Euphorbia balsamifera*; Euphorbiaceae; tabaiba dulce; germanicol; germanicone; lupeol; lupenone; β-amyrin; cycloartenol; dihydroagnosterol; cycloartanone.

Plant. Euphorbia balsamifera Ait. Source: Collected on the coast of Guia de Isora, Tenerife, Canary Isles. *Previous work*: germanicol, cycloartenol and lanosterol [1–3].

Present work. The unsaponifiable of the latex (1l.) was chromatographed on silica gel, yielding the following compounds which were characterized by their physical and spectroscopic data: *germanicol* (3·1 g), *germanicone* (89 mg), *lupeol* (4·5 g), *lupenone* (38 mg), *β-amyrin* (140 mg) and *cycloartenol* (300 mg) which were identified by comparison with authentic samples; *dihydroagnosterol* (80 mg), obtained as alcohol, was characterized as the acetate, mp 165–171° (MeOH), $[\alpha]_D$ +62 ($CHCl_3$; *c* 0·76); its UV spectrum [λ_{max}(EtOH) nm (log ε): 236 (3·89), 243 (3·95), 253 (3·79)] was in agreement with an homoannular dienic system which was corroborated by the NMR ($CDCl_3$) signal at δ 5·74 (2H, *m*, $W_{1/2}$ 15 Hz); *cycloartanone* (50 mg), isolated for the first time in nature, mp 95–99° (MeOH), IR ν_{max}($CHCl_3$) cm^{-1}: 3020, 1695; MS (probe) 70 eV *m/e* (rel. int.): 426 M^+, 411 ($M^+ - 15$; 100), 355, 342, 313, 288, 257, 245, 231, 175, 163, 161, 159, displaying characteristic fragments of tetracyclic triterpenes with a cyclopropane ring between C-9 and C-10 [4,5]; NMR (60 MHz, $CDCl_3$): δ 0·60 (2H, *dd*); its IR and NMR spectra were superimposable with those of a synthetic sample.

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Phytochemistry, 1976, Vol 15, pp 427–429. Pergamon Press. Printed in England.

TRITERPENOIDS OF THE STEMS OF SIX *CASTANOPSIS* SPECIES OF HONG KONG

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(*Received* 8 *July* 1975)

Key Word Index—*Castanopsis concinna, C. cuspidata, C. eyrei, C. fabri, C. fissa* and *C. hickelii*; Fagaceae; triterpenoids; rearranged oleananes, lupanes, hopanes and ursanes; steroids.

Plants. Castanopsis concinna A. DC., *C. cuspidata* (Thunb.) Schky., *C. eyrei* (Champ.) Tutch., *C. fabri* Hance, *C. fissa* Rehd. and Wils., and *C. hickelii* A. Camus.

Previous work. From the leaves, 5 friedelane derivatives including canophyllol (28-hydroxyfriedelan-3-one), glutinol, 22-hydroxyhopan-3-one, 3β,22-dihydroxyhopane, lupeol and taraxasterol, sitosterol, ellagic acid and digallic acid [1,2].

Present work. Light petrol extracts of the stems of the 6 species were examined for triterpenoids and steroids by chromatography on alumina. Fifteen different triterpenoids, 7 belonging to the D:A-friedooleanane, 3 to the hopane, 2 to the lupane, and 1 to each of the ursane, D:B-friedooleanane and D-friedooleanane group have been isolated. Friedelan-3β-yl-acetate, friedelan-2,3-dione, hop-17(21)-en-3β-yl acetate, hop-17(21)-en-3α-ol (**1**), betulin and taraxerol, obtained in this study, have not been found in the leaves [2]. Of the steroids, stigmast-4-en-3-on-6β-ol was obtained from 2 while sitosterol was found in all species. Each of the plant materials, after extraction with petrol, was further extracted with 95% EtOH and tested for acidic triterpenoids. Negative result was obtained in every case.

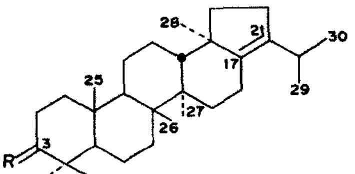
The distribution of compounds isolated in this study together with similar compounds from the leaves of the same species [2] is listed in Table 1.

Hop-17(21)-en-3α-ol (**1**) has never been isolated as a natural product, though it has been prepared from hop-17(21)-en-3-one (**2**) by reduction with sodium in n-pentanol, and its corresponding 3β-ol (**3**) and 3β-yl acetate have been isolated once from *Quercus championi* [3]. In this study, (**1**), $C_{30}H_{50}O$ (M^+, *m/e* 426) had mp 189–191°, $[\alpha]_D + 37{\cdot}2°$ (lit. [3], mp 187–190°, $[\alpha]_D + 34{\cdot}6°$), ν_{max} 3460 (OH), 1650 (>C=C<). Its NMR spectrum showed a one proton signal for the equatorial C-3 methine hydrogen at δ 3·40 (approx. *t*, $W_{1/2}$ 7 Hz) (cf. 3-*epi*moretenol (**4**) [4]). The chemical shifts of 5 of the 8 Me protons also agreed well with those reported for (**4**) [4] (Table 2). These can be assigned to the Me groups at C-23 to C-27.

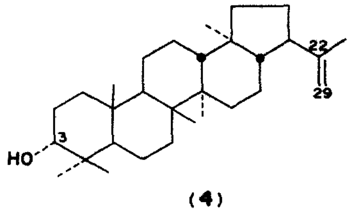
Oxidation of (**1**) with Jones' reagent gave (**2**), and (**1**) was finally confirmed to be hop-17(21)-en-3α-ol by repeating the reduction of (**2**), which resulted in the formation of 2 alcohols, separable by preparative TLC. The major (80%) and less polar epimer was found to be identical with (**1**).

Table 1. Triterpenoids and sterols from six *Castanopsis* species

Class	Compounds isolated	Species	
		Stems	Leaves
D:A Friedo-oleanane	Friedelan-3β-yl acetate	*C. cuspidata*	
	Friedelan-3α-yl acetate	*C. cuspitada*	*C. cuspidata*
	Friedelin	All species	All species
	Friedelan-3β-ol	All species	All species
	Friedelan-3α-ol	*C. cuspidata*	*C. cuspidata*
	Friedelan-3-on-28-ol (Canophyllol)	*C. concinna*	*C. concinna*
	Friedelan-2,3-dione	*C. fabri*	
D:B-Friedo-oleanane	Glutinol	*C. hickelii*	*C. fabri*
D-Friedo-oleanane	Taraxerol	*C. fissa*, *C. hickelii*	
Ursane	Taraxasterol	*C. concinna*, *C. cuspidata* *C. eyrei*,	*C. fabri* *C. hickelii*
Lupane	Lupeol	*C. cuspidata*,	*C. cuspidata*, *C. fissa*
	Betulin	*C. concinna*, *C. eyrei*	
Hopane	Hop-17(21)-en-3β-yl acetate	*C. hickelii*	
	Hop-17(21)-en-3α-ol	*C. fissa*	
	Hopan-3-on-22-ol (Hydroxyhopanone)	*C. eyrei*	*C. eyrei* *C. hickelii*
	Hopan-3β.22-diol		*C. eyrei*
Stigma-stane	Sitosterol	All species	All species
	Stigmast-4-en-3-on-6β-ol	*C. cuspidata*, *C. hickelii*	



(**1**) R = α-OH, β-H
(**2**) R = O
(**3**) R = α-H, β-OH



(**4**)

EXPERIMENTAL

IR spectra were recorded for KBr discs, NMR spectra in $CDCl_3$, UV spectra in 95% EtOH 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.

Extraction. For each of the 6 species, air-dried stems were milled, then extracted with light petrol 2× for 7 days at room temp. Combined extracts were evaporated to a small vol. and chromatographed on alumina.

C. concinna. Stems (15 kg) and alumina (2 kg) were used. Elution with petrol gave friedelin (5·0 g), mp 262–264°, $[\alpha]_D - 28{\cdot}3°$, IR ν_{max}: 1715 cm^{-1}; with petrol–C_6H_6 (1:1), first friedelan-3β-ol (1·05 g), mp 281–284°, $[\alpha]_D + 23{\cdot}9°$, IR ν_{max}: 3630 cm^{-1}, then taraxasterol (1·5 g), mp 222–224°, $[\alpha]_D + 106{\cdot}7°$, IR ν_{max}: 3600, 3050, 1650, 880 cm^{-1} and finally sitosterol (0·30 g), mp 138–140°, $[\alpha]_D - 35{\cdot}8°$; with C_6H_6, canophyllol (0·01 g), mp 279–280° (from C_6H_6), $[\alpha]_D - 9{\cdot}0°$, IR ν_{max}: 3550, 1720 cm^{-1}; and finally with C_6H_6–$CHCl_3$ (1:1), betulin (0·10 g), mp 251–253°, $[\alpha]_D + 18{\cdot}0°$, IR ν_{max}: 3400, 3050, 1650, 880 cm^{-1}, (diacetate, mp 222–223°, $[\alpha]_D + 23{\cdot}0°$, IR ν_{max}: 1750, 1745, 1245, [2 × OAc], 3080, 1640, 890, cm^{-1} [>C=CH_2]).

C. cuspidata. Stems (1·4 kg) and alumina (250 g) were used. Elution with petrol yielded firstly friedelan-3β-yl acetate (10 mg), mp 293–294°, $[\alpha]_D + 43{\cdot}0°$, IR ν_{max}: 1745, 1247 cm^{-1}; secondly friedelan-3α-yl acetate (20 mg), mp 315–317°, $[\alpha]_D - 15{\cdot}0°$, IR ν_{max}: 1745, 1250 cm^{-1}; thirdly friedelin (0·10 g), mp 261–263°, and finally friedelan-3β-ol (0·20 g), mp 288–289°. Elution with petrol–C_6H_6 (1:1) gave lupeol (0·31 g), mp 210–211°, $[\alpha]_D + 28{\cdot}1°$, IR ν_{max}: 3380, 3080, 1645, 882 cm^{-1}, friedelan-3α-ol (0·02 g) mp 301–303° (from $CHCl_3$), $[\alpha]_D + 14{\cdot}0°$, IR ν_{max}: 3600 cm^{-1}(OH), then taraxasterol (0·10 g), mp 220–221° and finally sitosterol (0·50 g). Elution with C_6H_6–$CHCl_3$ (1:1) afforded stigmas-4-en-3-on-6β-ol (15 mg), mp 213–215°, MS: *m/e* 428 (M^+) $C_{29}H_{48}O_2$, IR ν_{max}: 3510

Table 2. Chemical shifts of compounds **1** & **4**

Compound	C-23	C-24	C-25	C-26	C-27	C-28	C-29	C-30
(1)	0·94	0·84	0·84	0·94	0·94	0·81	1·01*	1·01*
(4)	0·95 –0·98	0·83	0·83	0·95 –0·98	0·93 –0·98	0·68	—†	1·68†

* Pr^i *J*, 6 Hz. † CMe = CH_2.

(OH), 1695, 1620 cm^{-1} ($>C{=}\overset{|}{C}{-}\overset{|}{C}{=}O$), UV λ_{max}: 246 nm (ϵ 12,900).

C. eyrei. Stems (11 kg) and alumina (2·2 kg) were used. Elution with petrol gave friedelin (5·0 g) friedelan-3β-ol (1·5 g) and taraxasterol (0·01 g); with C_6H_6, sitosterol (1·3 g), then 22-hydroxyhopan-3-one (0·20 g), mp 250–252°, $[\alpha]_D$ + 67·0°, IR ν_{max}: 3480 (OH), 1720 cm^{-1} ($>C{=}O$), and with C_6H_6–$CHCl_3$ (1:1), betulin (0·10 g), mp 250–252°.

C. fabri. Stems (6 kg) and alumina (3 kg) were used. Elution with petrol yielded friedelin (4·0 g), and friedelan-3β-ol (0·01 g); with petrol–C_6H_6 (1:1), sitosterol (0·10 g), and with $CHCl_3$, friedelan-2,3-dione (3-hydroxyfriedel-3-en-2-one) (5 mg) mp 273–274° [from $(Me)_2CO$–$CHCl_3$], $[\alpha]_D$ + 23·7°, MS: *m/e* 440 (M^+) $C_{30}H_{48}O_2$, IR ν_{max}: 3390 (OH), 1670, 1640 cm^{-1}, ($>C{=}\overset{|}{C}{-}\overset{|}{C}{=}O$) UV λ_{max}: 276 nm (ϵ 9,700).

C. fissa. Stems (7·5 kg) and alumina (1·5 kg) were used. Elution with petrol afforded friedelin (0·11 g) and friedelan-3β-ol (0·30 g); with petrol–C_6H_6 (1:1), taraxerol (0·50 g), mp 283–285° (from C_6H_6), IR ν_{max}: 3500 (OH), 1640, 830 cm^{-1} ($>C{=}CH$–), hop-17(21)-en-3α-ol (**1**) (0·025 g) mp 189–191° $[\alpha]_D$ + 37·2°. (Found: M^+ 426. Calc. for $C_{30}H_{50}O$: M^+ 426), IR ν_{max}: 3460 (OH), 1650 cm^{-1} ($>C{=}C<$), and finally sitosterol (0·50 g). Oxidation of (**1**) (20 mg) with Jones' reagent gave a product which was recrystallized from $CHCl_3$ to give (**2**) (15 mg), mp 195–197°, IR ν_{max}: 1720, 1670 cm^{-1}. Reduction of (**2**) (0·10 g) in *n*-pentanol (30 ml) with Na (0·5 g) under reflux for 24 hr gave a product which was separated by preparative TLC into (**1**) (45 mg) mp 189–190°, and (**3**) (15 mg), mp 228–229°, $[\alpha]_D$ + 43·0°, the former being the faster moving component.

C. hickelii. Stems (1·4 kg) and alumina (250 g) were used. Elution with petrol gave hop-17(21)-en-3β-yl acetate (20 mg), mp 259–261° (from petrol), $[\alpha]_D$ + 56·7°, IR ν_{max}: 1740, 1255 (OAc), ·1670 cm^{-1} ($>C{=}C<$), friedelin (0·80 g) and friedelan-3β-ol (0·40 g). Elution with petrol–C_6H_6 (1:1) yielded glutinol (20 mg), mp 210–212°, $[\alpha]_D$ + 67·0° IR ν_{max}: 3500 (OH), 1650, 830 cm^{-1} ($>C{=}CH$–), taraxerol (0·90 g) and sitosterol (0·50 g), and with C_6H_6–$CHCl_3$ (1:1), stigmast-4-en-3-on-6β-ol (10 mg), mp 213–214°.

Test for acidic triterpenoids. Stems from each plant, after extraction with petrol, were further extracted 2× with 95% EtOH at room temp. for 1 week. The extract was vacuum distilled to give a brown residue which was extracted with Et_2O. The ethereal soln was shaken with 2M NaOH and the alkaline soln was acidified with 1M H_2SO_4. A dark brown gummy ppt. was obtained. No triterpenoids could be isolated in each case.

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ISOLATION OF SWIETENOLIDE DIACETATE FROM *SWIETENIA MACROPHYLLA*

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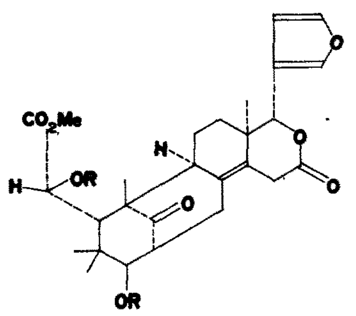
Key Word Index—*Swietenia macrophylla*; meliaceae; tetranortriterpenoids; swietenine; swietenolide; swietenolide diacetate.

The traditional belief and practice (by chewing and then swallowing the seeds of *Swietenia macrophylla*) by the natives and the common folks of Malaysia in providing 'cure' to high blood pressure has prompted us to carry out extraction on the seeds obtained from trees* grown locally for biological testing. Two tetranortriterpenoids, namely swietenine and swietenolide (**1**) (a bitter compound), have been isolated [1,4] from the seeds of *Swietenia macrophylla* and their structures characterized [2–7]. We have now isolated and identified a third compound swietenolide diacetate (**2**) which has not been observed previously in the seeds. Compound **2** was reported to occur in the wood of *Khaya ivorensis* [8] but it was not isolated in pure form for identification.



(**1**) R = H
(**2**) R = COMe

The ground seeds were extracted with *n*-hexane in a Soxhlet. The extract afforded on cooling a yellow powdery solid and after filtering this off, evaporation of the *n*-hexane left behind an oil with the following fatty acid compositions [9–11] determined as their Me esters: palmitic acid (12·9%), stearic acid (12·9%), oleic acid (29·5%), linoleic acid (28·6%), linolenic acid (15·5%), and arachidic acid (0·7%). TLC on silica gel showed that the yellow solid consisted of at least four compounds, two of which corresponded to the previously known terpenoids. Repeated chromatography over a neutral alumina column (10% $CHCl_3$ in benzene) afforded a white crystalline compound analysed to $C_{31}H_{38}O_{10}$, mp 227–230°C, $[\alpha]_D$ = −131°. Its MS showed a molecular ion at *m/e* 570. Its IR, NMR spectra, and R_f value (TLC) were identical to those of authentic **2** prepared by acetylating 1 with Ac_2O–pyridine [7]. No suppression of mixed melting point was observed.

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* Location of trees: Forest Reserve, Forest Research Institute, Kepong, Malaysia (10 miles north-west of Kuala Lumpur).