

(OH), 1695, 1620 cm^{-1} ($>\text{C}=\text{C}=\text{O}$), 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-3 β -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°, $[\alpha]_{\text{D}} + 67.0^\circ$, IR ν_{max} : 3480 (OH), 1720 cm^{-1} ($>\text{C}=\text{O}$), and with $\text{C}_6\text{H}_6\text{-CHCl}_3$ (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-3 β -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 $(\text{Me})_2\text{CO-CHCl}_3$], $[\alpha]_{\text{D}} + 23.7^\circ$, MS: m/e 440 (M^+) $\text{C}_{30}\text{H}_{48}\text{O}_2$, IR ν_{max} : 3390 (OH), 1670, 1640 cm^{-1} , ($>\text{C}=\text{C}=\text{O}$) 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-3 β -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} ($>\text{C}=\text{CH}-$), hop-17(21)-en-3 α -ol (1) (0.025 g) mp 189–191° $[\alpha]_{\text{D}} + 37.2^\circ$. (Found: M^+ 426. Calc. for $\text{C}_{30}\text{H}_{50}\text{O}$: M^+ 426), IR ν_{max} : 3460 (OH), 1650 cm^{-1} ($>\text{C}=\text{C}-$), 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°, $[\alpha]_{\text{D}} + 43.0^\circ$, 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-3 β -yl acetate (20 mg),

mp 259–261° (from petrol), $[\alpha]_{\text{D}} + 56.7^\circ$, IR ν_{max} : 1740, 1255 (OAc), 1670 cm^{-1} ($>\text{C}=\text{C}-$), friedelin (0.80 g) and friedelan-3 β -ol (0.40 g). Elution with petrol- C_6H_6 (1:1) yielded glutinol (20 mg), mp 210–212°, $[\alpha]_{\text{D}} + 67.0^\circ$ IR ν_{max} : 3500 (OH), 1650, 830 cm^{-1} ($>\text{C}=\text{CH}-$), taraxerol (0.90 g) and sitosterol (0.50 g), and with $\text{C}_6\text{H}_6\text{-CHCl}_3$ (1:1), stigmast-4-en-3-on-6 β -ol (10 mg), mp 213–214°.

Test for acidic triterpenoids. Stems from each plant, after extraction with petrol, were further extracted 2 \times 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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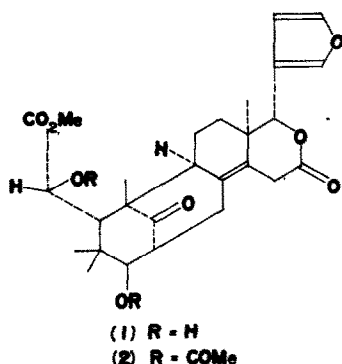
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Key Word Index—*Swietenia macrophylla*; meliaceae; tetranortriterpenoids; swietenine; swietenolide; swietenolide diacetate.

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.

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 $\text{C}_{31}\text{H}_{38}\text{O}_{10}$, mp 227–230°C, $[\alpha]_{\text{D}} = -131^\circ$. 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.



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

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QUERETAROIC (30) CAFFEATE AND OTHER CONSTITUENTS OF *MELIANTHUS MAJOR**

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(Revised received 22 September 1975)

Key Word Index—*Melanthus major*; Sapindaceae; queretaroic (30) caffeate; cyclolaudenol; sitosterol- β -D-glucoside; oleanolic acid; ursolic acid.

Melanthus is a South African plant and one of the species, *M. comosus*, used by natives for medicinal purposes [1] contains four toxic bufadienolides and hellebrigenin-3-acetate [2–5]. Recently the alcoholic extract of the Indian species, *M. major* L. was reported to show a transient hypotensive activity [6] at a dose of 1 mg/kg (20 mm Hg, 5 min) and hypertensive activity at 2.5–10 mg/kg (20–30 mm. Hg, 5–15 min) when administered intravenously to anaesthetized cats.

The hexane, ethylacetate and butanol fractions of the alcoholic extract were separately subjected to repeated chromatography over alumina and silica gel to obtain substances A, B, C, D, E and F. While the hexane fraction was biologically inactive, the ethyl acetate fraction showed mild hypotension at 2.5 mg/kg (60 mm Hg, 45 min) and the butanol fraction caused transient hypertension at 1 mg/kg (24 mm Hg, 4 min) and hypotension at 2.5 mg/kg (36 mm Hg, 35 min). Both the fractions caused death at 5 mg/kg. No pure product could be isolated from the butanol-soluble fraction.

Substance E, mp 230–2°, $C_{39}H_{54}O_7$ was soluble in alkali and gave a green colour with ferric chloride which indicated its phenolic nature whereas positive Liebermann–Burchard and Noller's reactions showed it to be an unsaturated triterpenoid. The IR spectrum exhibited the presence of a hydroxyl group (3380), a carboxyl group (1710) and a trisubstituted double bond (840 cm^{-1}).

It formed a triacetate, mp 225–8°, $C_{45}H_{60}O_{10}$, whose IR and NMR spectra showed that one of the acetoxy groups was secondary aliphatic and the other two were phenolic in nature. The triacetate gave a methyl ester, mp 212–7°. However, the methylation of substance E,

under similar conditions, led to the formation of a mixture of a monomethoxy methyl ester, mp 114–18° and a dimethoxy methyl ester, mp 107–10°.

Substance E on alkaline hydrolysis yielded two products E-A1 and E-A2. The former product (E-A1), mp 318–20°, $C_{30}H_{46}O_4$, (M^+ at m/e 472) formed a diacetate, mp 295–9°. The acetate gave a methyl ester, mp 210° and product E-A1 was characterised (IR, mmp) as queretaroic acid [7].

The second component E-A2, mp 209°, $C_9H_8O_4$, (M^+ at m/e 180) yielded a dimethyl ether, mp 179° and a diacetate, mp 198° and was confirmed as caffeic acid.

Thus, substance E was established as the caffeic acid ester of queretaroic acid whose primary hydroxyl group was involved in the esterification and, therefore, must be queretaroic (30) caffeate [3β -hydroxy-30(3',4'-dihydroxy cinnamoyl)oxy-olean-28-oic acid]. It caused a fall in blood pressure in cat at 1 mg/kg (40 mm. Hg, 15 min) and death at 5 mg/kg.

EXPERIMENTAL

Mp's are uncorrected. R_f values pertain to TLC on Kiesel gel G and IR spectra were recorded in KBr. The alcoholic extract of the plant (aerial parts, 4.5 kg) was successively macerated with hexane and EtOAc. The hexane fraction (68.0 g) was chromatographed on neutral alumina (activity 2.5). Elution with hexane- C_6H_6 (1:1) gave Substance A crystallised from MeOH (1.24 g). The residue (18.90 g) from the C_6H_6 -MeOH (98:2) eluate was crystallised from EtOH to give substance B (10.2 g). The C_6H_6 -MeOH (95:5) eluate (4.60 g) afforded substance C crystallised from EtOH (3.56 g). EtOAc residue (36.0 g) was chromatographed over Si gel, the C_6H_6 -EtOAc (3:1) fraction, on crystallisation from EtOH, gave substance D (3.02 g). The residue from the C_6H_6 -EtOAc (1:1) fraction was rechromatographed and the $CHCl_3$ -MeOH (96:4) eluate

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