at the 2- and 4-positions, and two 1H singlets, centered at δ 7.12 and 7.67 were assignable to the proton located at the 5- and 8-positions respectively. These data clearly showed that the glucose in **1** is located at the 6-position, so that tripteroside is norathyriol 6-*O*-β-D-glucoside. The *n*-butanol fraction of the methanolic extract of the fresh herb *G. flavo-maculata* was chromatographed on a polyamide column. Rutin and quercetin, identified by direct comparison (NMR, IR) with authentic samples, were eluted from the column with water and water–methanol (20:1), respectively. The identification of flavonols in this species of *Gentiana* is unusual, since the general flavonoid pattern of the genus is one based on flavones and glycoflavones [5].

EXPERIMENTAL

All mps were uncorr. UV spectra were determined in MeOH and IR spectra in KBr. NMR spectra were measured at 60 MHz with TMS as int. standard using $CDCl_3$ as solvent unless otherwise stated.

Extraction and separation. The fresh herb *T. taiwanense* (3.6 kg), collected at Kuentzuling, Tainan Hsieng, Taiwan, in Aug. 1976, was extracted with hot MeOH. After removal of oleanolic acid, the MeOH extract was evaporated under red. pres. and then treated as described previously [1]. The EtOAc fraction afforded mangiferin and the filtrate was chromatographed on Si gel, eluting with $CHCl_3$, $CHCl_3$–MeOH and MeOH to afford norathyriol in $CHCl_3$–MeOH (6:1) and tripteroside in $CHCl_3$–MeOH (4:1) respectively.

The fresh herb *G. flavo-maculata* (0.68 kg), collected in Aug. 1974, at Mt. Alishan, Chiayi Hsieng, was extracted with hot MeOH and was treated as above. The *n*-BuOH fraction was chromatographed on a polyamide column, eluting with H_2O and H_2O–MeOH (20:1) to afford rutin and quercetin respectively.

Oleanolic acid was identified by IR spectral comparison with an authentic sample. Norathyriol was identified by direct comparison (NMR, IR, UV) with an authentic sample, and by preparation of the tetra-acetate.

Tripteroside, **1**. Pale yellow needles (MeOH), mp 263–265°. red with Mg–HCl, greenish brown with $FeCl_3$; the needles appeared orange under UV light. PC R_f: 0.21 (15% HOAc), 0.35 (30% HOAc). Found: C, 54.03; H, 4.27. $C_{19}H_{18}O_{11}$ requires: C, 54.01; H, 4.30%.

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ROTENOIDS FROM ROOTS OF *MILLETTIA PACHYCARPA*

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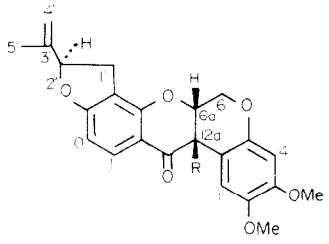
Key Word Index—*Millettia pachycarpa*; Leguminosae; Lototoidae; rotenone; *cis*-12*a*-hydroxyretenone; rot-2′-enonic acid; *cis*-12a-hydroxyrot-2′-enonic acid.

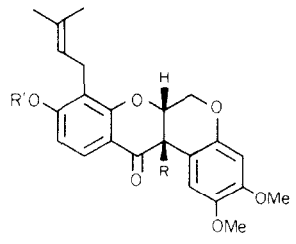
Abstract—Roots of *Millettia pachycarpa* furnished retenone, *cis*-12a-hydroxyrotenone, rot-2′-enonic acid and *cis*-12a-hydroxyrot-2′-enonic acid.

INTRODUCTION

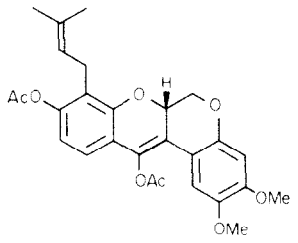
In earlier articles [1, 2] we described the isolation of several new prenylated isoflavonoids and one new prenylated dihydroflavonol from the aerial parts of *Millettia pachycarpa*. The roots of this species are occasionally used as a fish poison and are reputed to be insecticidal; the presence of rotenone has been reported although no details were given[3]. We now report the isolation from the roots of rotenone (**1a**), *cis*-12a-hydroxyrotenone (**1b**), rot-2′-enonic acid (**2a**)



1a R = H
1b R = OH
1c R = OAc



2a R = H, R' = H
2b R = OH, R' = H
2c R = OH, R' = Me



3

and *cis*-12a-hydroxyrot-2-enonic acid (**2b**). Recently **2a** has been shown to be an intermediate on the biosynthetic pathway to other rotenoids in *Amorpha fruticosa* [4] and **2b** is new.

RESULTS AND DISCUSSION

Rotenone (**1a**), the main and least polar constituent of the roots was identified by comparison with an authentic sample. A second slightly more polar compound had an NMR spectrum which agreed with that reported for **1b** [5]; direct comparison established identity. The structure was further confirmed by reduction (Zn–$AcOH$–$ZnCl_2$ [6]) to **1a**.

A third constituent appeared to be rot-2'-enonic acid (**2a**) as indicated by the m.p. [7, 8] and NMR spectrum [8]. According to Crombie and co-workers [8], **2a** on treatment with Ac_2O–$NaOH$ gives the expected monoacetate, but Ac_2O–pyridine affords an enol diacetate **3**, m.p. 132–133° which was obviously identical with a diacetate, m.p. 131°, prepared by this method from our material. Unfortunately, the British workers did not describe the NMR spectrum of **3** except for the statement that it exhibited "the absence of shielding effects of C=O"; this was certainly true of the NMR spectrum of our diacetate (see Experimental).

The most polar constituent of the roots was a non-crystalline substance **2b**, $C_{22}H_{24}O_7$, whose NMR spectrum and that of its monomethyl ether **2c** indicated that it was related to **2a**, as **1b** is to **1a**. Ring E was opened as in rot-2'-enonic acid; that it was a *cis*-12a-hydroxy derivative of **2a** was evident because of the absence of the H-12a signal and the downfield shift of H-1 [5, 9].

EXPERIMENTAL

Ground roots, wt *ca* 2 kg, of *M. pachycarpa* Benth, collected in the Mealong Forest, Sibsagar District, Assam, on 26 March 1980 were extracted with $CHCl_3$ in a Soxhlet apparatus for 12 hr. Evaporation of solvent at reduced pressure gave 5 g of residue which was dissolved in 500 ml of MeOH containing 50 ml H_2O. Insoluble material was rejected. The soln was washed with petrol and the washings again rejected. Most of the MeOH was removed at reduced pressure. The residue was extracted with $CHCl_3$ (7 × 200 ml). The washed and dried extracts were evaporated at reduced pressure and the residue (2–5 g) was chromatographed over 300 g of Si gel. 200 ml fractions were collected as follows: 1–5 (C_6H_6), 6–10 (C_6H_6–EtOAc, 9:1), 11–20 (C_6H_6–EtOAc, 4:1), 21–30 (C_6H_6–EtOAc, 2:1), 31–35 (C_6H_6–EtOAc, 1:1), 36–40 (C_6H_6–EtOAc, 1:2), 41–50 (EtOAc), 51–52 (EtOAc–MeOH, 19:1).

Fractions 4–14 which showed a single spot on TLC (C_6H_6–EtOAc, 9:1) were combined to give 0.8 g of rotenone, m.p. 162°, lit. m.p. 163° [10], identical (m.p., mmp) with an authentic sample, IR bands 1675, 1600, 1510, 1350, 1300, 1090, 1000, 900 cm^{-1}; NMR (270 MHz, $CDCl_3$) 7.88*d* and 6.52*d* (9, H-11 and H-10), 6.78 (H-1), 6.45 (H-4), 5.24*tbr* (8, H-2'), 5.08*br* (H-4'a), 4.94*br* (H-4'b superimposed on H-6a), 4.62*dd* (12,3) and 4.19*dbr* (12, H-6eq and H-6ax), 3.84*m* (15,9, H-1'a,b) and 1.79*br* (H-5'); MS (*m/z*) 394 (M^+), 379, 346, 208, 193, 192 (base peak), 191 and 177.

Fractions 18–20 which gave a single spot on TLC were combined. The oily material was identical on TLC with an authentic sample of **1b** [5]; in an earlier reference it was reported as a solid, m.p. 88° [11]. It had IR bands at 1725, 1670, 1610, 1325, 1290, 1105, 1085, 950; NMR (60 MHz, $CDCl_3$) 7.80 (8, H-11), 6.65 (H-1), 6.54 (H-4), 6.50*d* (8, H-10), 5.30*m* (H-2'), 5.02*m* (2*p*, H-4'), 4.90*t* (3.5, H-6a), 4.60*m* (H-6), 3.83, 3.73 (2 × OMe), 3.0*m* (2*p*, H-1'), 1.80 (3*p*, H-5'); MS (*m/z*) 410 (M^+), 392, 279, 377, 363, 349, 321, 284, 208 (base peak), 142. Acetylation of 25 mg of **1b** (Ac_2O–pyridine 24 hr) followed by usual work up gave 25 mg of crystalline **1c**, m.p. 151°, previously [5] reported as an oil, NMR (60 MHz, $CDCl_3$) 7.90*d* (8, H-11), 6.90 (H-1), 6.50*d* (8, H-10), 6.50 (H-4), 5.40*m* (H-2'), 5.05*m* (2*p*, H-4'), 4.45*t* (3.5, H-6a), 4.45*m* (H-6), 3.85, 3.80 (OMe), 2.15 (Ac), 1.80 (Me), MS (*m/z*) 452 (M^+), 392, 377, 363, 349, 345, 312, 279, 270, 250 (base peak), 208, 182, 105. Reduction of 25 mg of **1b** in 3 ml of HOAc and 1.5 ml of H_2O with 0.2 g Zn dust and 50 mg of $ZnCl_2$ (no reduction took place when $ZnCl_2$ was omitted) [6] at 100° for 2.5 hr, dilution with H_2O, extraction with $CHCl_3$ and evaporation of the washed and dried extract gave 20 mg of crystalline rotenone, m.p. 162°.

Fractions 24–28 were combined to give 200 mg of crystalline **2a**, m.p. 203°, lit. m.p. 206–208° [7], 206–207° [8], UV λ_{max} 292 nm; IR bands at 1670, 1600, 1500, 1440, 1345, 1145, 1100, 1080 and 1025 cm^{-1}; NMR (270 MHz, $CDCl_3$) 7.72*d* and 6.50*d* (8, H-10 and H-11), 6.79 (H-1), 6.45 (H-4), 5.25*tbr* (7, H-2'), 4.90*t* (3.5, H-6a), 4.62*dd* (12,3) and 4.12*dbr* (12, H-6eq and H-6ax), 3.85*m* (H-12a) partly under 3.97, 3.81 (OMe), 3.37*m* (2*p*, H-1'), 1.81*br* and 1.72*br* (3*p* each, H-4' and H-5'); MS (*m/z*) 396 (M^+), 379, 363, 349, 284, 208, 192 (base peak), 177, 149, 121. Acetylation of 25 mg of **2a** (Ac_2O–pyridine, 24 hr) followed by usual work up gave 20 mg of crystalline **3**, m.p. 131°, lit. m.p. 132–133° [8], IR bands at 1755, 1615, 1510, 1450, 1365, 1085, 1040, 925; NMR (270 MHz, $CDCl_3$) 7.39 (H-1), 6.89*d* and 6.68*d* (8, H-10 and H-11), 6.45 (H-4), 5.54*dd* (10,5, H-6a), 5.11*tbr* (7, H-2'), 4.50*dd* (10,5) and 4.28*t* (10, H-6ax and H-6eq), 3.88 (2 OMe), 3.23 (2*p*, H-1'), 2.43, 2.31 (Ac), 176*br* and 1.70*br* (3*p* each, H-4' and H-5'); MS (*m/z*) 480 (M^+), 438, 396, 380, 367, 365, 349, 340, 325, 311, 297, 295, 284, 208, 205, 194, 192, 191.

Fractions 31–33 were combined to give 50 mg of **2b** as a

gum, UV λ_{max} 290 nm; NMR (60 MHz, $CDCl_3$) 7.72*d* and 6.50*d* (8, H-10 and H-11), 6.65 (H-1), 6.55 (H-4), 5.20*tbr* (7, H-2'), 4.90*t* (3.5, H-6a), 4.50*m* (2*p*, H-6), 3.81, 3.77 (OMe), 3.35*m* (2*p*, H-1'), 1.80 and 1.70 (3*p* each, H-4' and H-5'); MS (*m/z*) 412 (M^+), 394, 379, 338, 323, 300, 295, 265, 253, 225, 208 (base peak) 192, 179, 165, 149 (Calculated for $C_{23}H_{24}O_7$: MW 412.1520. Found: MW (MS) 412.1512). Methylation of 25 mg of **2b** with excess CH_2N_2 gave the monomethyl ether as a gum (25 mg); NMR (270 MHz, $CDCl_3$), 7.81*d* and 6.61*d* (8, H-11 and H-10), 6.53 and 6.48 (H-1 and H-4), 5.10*tbr* (6.5, H-2'), 4.59*m* (3*p*-deceptively simple looking ABC system of H-6a, H-6ax and H-6eq), 4.50*br* (-OH), 3.87, 3.81, 3.71 (OMe), 3.28*m* (2*p*, H-1'), 1.77 and 1.65 (3*p* each, vinyl Me): MS (*m/z*) 426 (M^+), 408, 379, 365, 341, 328, 314, 292, 290, 279, 256, 236, 219, 208 (base peak), 192.

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FLAVONOL AND DIHYDROFLAVONOL GLYCOSIDES OF *ECHINOCEREUS TRIGLOCHIDIATUS* VAR. *GURNEYI**

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Key Word Index—*Echinocereus triglochidiatus* var. *gurneyi*; Cactaceae; floral flavonoids; dihydroflavonols; flavonols; chemotaxonomy.

Abstract—Perianth parts, in particular, tepals of *Echinocereus triglochidiatus* var. *gurneyi* yielded a complex mixture of dihydroflavonols and dihydroflavonol 7-*O*-glucosides. Dihydroquercetin and its 7-*O*-glucoside were the predominant compounds while dihydrokaempferol and dihydromyricetin and their 7-*O*-glycosides were present in lesser amounts. Quercetin 7-*O*-glucoside was the principal flavonol glycoside: others present were quercetin and kaempferol 3-*O*-glucosides and 3-*O*-rhamnosylglucosides. The epidermis and spines yielded only traces of presumed flavonols as determined by two-dimensional TLC. No flavonoids were detected in the cortex tissue. This is the first report of dihydroflavonol derivatives from the Cactaceae and constitutes the first record of flavonoids from *Echinocereus*.

INTRODUCTION

Echinocereus triglochidiatus Engelmann is a morphologically variable cactus species that occurs over a wide range in south-western North America and parts of Mexico [1]. Several varieties have been described [1,2]. Populations referable to the variety in question here, *E. triglochidiatus* var. *gurneyi* Benson, occur on mountainsides and outwash plains in the northern Chihuahuan Desert and adjacent regions of New Mexico and Trans-Pecos Texas [1]. This is one of the more variable of the claret-cup cacti in terms of stem and flower size.

The distribution of flavonoids among species of Cactaceae is known only cursorily [3,4] although common flavonols; kaempferol, quercetin, and isorhamnetin, have been reported [5–9]. Here we report

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