collections were identical with respect to the flavonoid constituents. The apparent lack of variation of flavonoids as characters in *Leptarrhena* is in accord with the invariant flavonoid profiles seen in several other taxa studied in this series [12]. The major polyphenol in all populations of *Leptarrhena* studied is (+)-dihydromyricetin; this is its first reported occurrence in the Saxifragaceae.

EXPERIMENTAL

Plant material was obtained from the following: Canada: Mt. Baldy, B.C. (BAB-1273); Goldie Lake, Mt. Seymour Prov. Park, B.C. (BAB-1274); Strachan Meadow, Cypress Bowl Prov. Park, B.C., two specimens (BAB-1232 and BAB-1233); Yew Lake, Cypress Bowl Prov. Park (BAB-1159); Mt. Becher, Courtenay, Vancouver Island, B.C. (BAB-1153); and United States: Washington: Chelan Co., summit, North Cascades Highway (BAB-1103). Vouchers are deposited in UBC.

Isolation procedures and chromatographic procedures were described by Wilkins and Bohm [8]. NMR spectra were determined in Me_2CO-d_6 with TMS as internal standard. Optical rotation was measured in Me_2CO. Acetylation was carried out with Ac_2O/Py and the product recrystallized from MeOH.

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NEW PYRROLIZIDINE ALKALOIDS FROM *CROTALARIA CANDICANS**

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(*Revised received* 22 *January* 1979)

Key Word Index—*Crotalaria candicans*; Leguminosae; pyrrolizidine; crocandine; isocrocandine; turneforcidine; 3-hydroxy-2,3,4-trimethylglutaric acid.

Abstract—Crocandine and isocrocandine, isolated from the seeds of *C. candicans*, have been shown by spectroscopy and chemical evidence to be macrocyclic diesters of turneforcidine and 3-hydroxy-2,3,4-trimethylglutaric acids.

INTRODUCTION

Crotalaria candicans W. & A. 184 [1], which grows wild in Western ghats in the Nilgiris (India) at *ca* 2000 m, is characterized by broadly cordate, acute, persistent, shining viscous and black (when dry) bracts and bracteoles, considered to be synonymous with *C. madurensis* Wight in Wall and has been investigated for alkaloids. Isolated constituents have been characterized as two new macrocyclic diesters, named here as crocandine (CC-I) and isocrocandine (CC-II), which are different from the ones reported from *C. madurensis* [2–6]. These chemotaxonomical data are further justification for considering *C. candicans* a different species as proposed by W. & A. A survey of literature [7] shows that only two esters of turneforcidine, viz. turneforcine and retusine, have been described hitherto.

RESULTS AND DISCUSSION

Structure of crocandine (1)

The ^1H NMR spectrum ($CDCl_3$) of the alkaloid exhibits signals at δ 1.15 (*d*, J = 7 Hz, $C\underline{H}_3$—CH—COO), 1.23 (*d*, J = 7 Hz, $C\underline{H}_3$—CH—COO), 1.28 (*s*, $C\underline{H}_3$—C—OH), 3.2 (OH), 3.78 and 4.73 (H-9) and 5.05 (*m*, H-7). The unusual width of the H-7 multiplet, 24.0 cps, is characteristic of esters of hastanecine and turneforcidine

* Part 37 in the series "*Genus* Crotalaria". For Part 36 see Siddiqi, M. A., Suri, K. A., Suri, O. P. and Atal, C. K., Indian Pharmaceutical Congress (held at Calcutta, 26–28 December, 1978).

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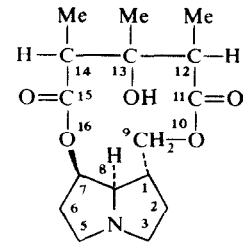

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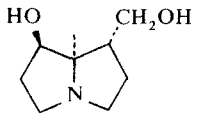

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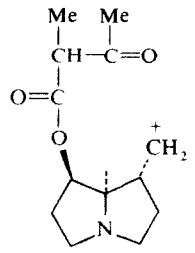

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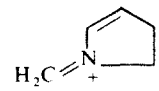
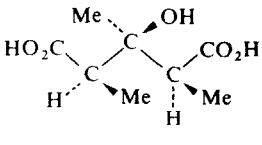
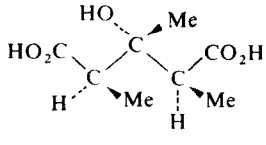
3



m/e 82 (100%)
4



5a



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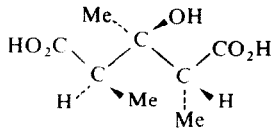
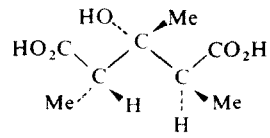


5c



5d

[8]. The positions of the H-9 and H-7 signals indicate that the alkaloid has a structure similar to that of retusine [9], another ester of turneforcidine. The position of the OH at δ 3.2 was ascertained by D_2O exchange.

In the MS, the presence of characteristic ions at *m/e* 82, 95, 96, 108, 121, 122, 138, 154 suggests it to be an ester of a saturated pyrrolizidine-1,9-diol. The presence of the base peak at *m/e* 82 (**4**) is characteristic of esters of platynecine and its diastereoisomers [8]. The appearance of a significant ion at *m/e* 238 (35%) fixes the position of the OH group in the acid part [10].

On acid hydrolysis the alkaloid afforded a necine HCl, mp 115°, and an acid, mp 111–112°. ^{1}H NMR ($CDCl_3$) of the acid shows signals at δ 1.32 (*d*, J = 7.2 Hz, 2 × $C\underline{H}_3$—CH), 1.41 (*s*, $C\underline{H}_3$—C—OH) and 2.95 (*q*, J = 7.2 Hz, 2 × —C$\underline{H}$—CH_3). The MS of the acid corresponds to the fragmentation pattern of 3-hydroxy-2,3,4-trimethylglutaric acid which exists in 4 isomeric forms, viz. crispatic acid, mp 133–134°; fulvinic acid, mp 113–114°; cromaduric acid, mp 138–139° and isocromaduric acid, mp 129–130°. The mp of the necic acid obtained by hydrolysis of crocandine corresponded to fulvinic acid with which it gave superimposable IR and undepressed mmp. Necine HCl was converted into the free base by elution through a column of ion exchange resin A-540 (OH form). The eluates, on concentration *in vacuo* and crystallization (Me_2CO) afforded colourless crystals, mp 118°, $[\alpha]_D$ −16° (*c* 0.5%, MeOH) (lit. turneforcidine, mp 118.5–120°, $[\alpha]_D$ −18° in MeOH and −3.5° in EtOH [8]; mp 118.5–120°, $[\alpha]_D$ −10.5° in MeOH [11]). Thus crocandine was established to be a macrocyclic diester of turneforcidine with fulvinic acid and could be structurally represented as 1β-H-13-hydroxy-12,13,14-trimethyl crotalanine.

Structure of isocrocandine

^{1}H NMR and MS of isocrocandine and crocandine were similar. However, non-superimposable IR, TLC pattern and mp led us to consider it an alkaloid different but isomeric with crocandine.

Acid hydrolysis of isocrocandine yielded turneforcidine HCl and a necic acid, mp 136–137°; mmp with cromaduric acid, 138–139°, [5] was undepressed. Out of 4 isomeric 3-hydroxy-2,3,4-trimethylglutaric acids, two are optically inactive *meso* forms (**5a** and **5b**) and two are optically active (**5c** and **5d**).

Edwards [12] synthesized the 4 isomeric acids and assigned *S-meso* and *R-meso* configurations to crispatic and fulvinic acids, respectively. However, another group of workers [13] synthesized the acids through another route and reversed the assigned configurations on the basis of Cram's asymmetric induction rule and other chemical relations.

EXPERIMENTAL

Mps are uncorr. ^{1}H NMR were recorded at 60 MHz using TMS as internal reference in $CDCl_3$. R_f values are recorded on Si gel G plates. The seed source was identified by scientists of the Herbarium Section of R. R. L., Jammu Tawi, India and a specimen has been preserved in the section against No. RRL 14836.

Extraction and separation of alkaloids from the seeds of C. candicans. Powdered seeds (2 kg), 3.5% tertiary base and 0.1% of *N*-oxides were defatted with *n*-hexane and the marc extracted with 95% EtOH in a Soxhlet. The EtOH extract was concd under red. pres. and the residue processed for the extraction of alkaloids [14]. The $CHCl_3$ soln, on concn, separated an amorphous substance which was found to be impure on TLC. The basic substance was loaded onto a column of neutral Al_2O_3, when elution with $CHCl_3$–MeOH (99:1) gave pure alkaloid. R_f 0.54 ($CHCl_3$–MeOH–NH_4OH, 85:14:1), which on further crystallization from MeOH gave colourless needles (CC-1), mp 244–246°, $[\alpha]_D$ +130° (*c* 1%, MeOH). (Found: C, 61.36; H, 7.91; N, 4.56. $C_{16}H_{25}NO_5$ (M^+, 311) requires: C, 61.73; H, 8.03; N, 4.50%). ν_{max}^{Film} cm^{-1}: 1735 (ester CO) 3550 (OH). The mother liquor left behind after the separation of CC-I was evapd to dryness and crystallized from EtOAc to afford colourless crystals, mp 172–174° (CC-II); R_f 0.56; $[\alpha]_D$ +36° (*c* 1%, MeOH). (Found: C, 61.95; H, 7.85; N, 4.43. $C_{16}H_{25}NO_5$ (M^+, 311) requires: C, 61.73; H, 8.03; N, 4.50%). ν_{max}^{Film} cm^{-1}: 1735 (ester CO), 3550 (OH).

Hydrolysis of crocandine. The alkaloid (0.2 g) was treated with HCl (18%, 5 ml) and heated at 100°. The hydrolysis was completed after heating for 35 hr as confirmed by TLC. The hydrolysed mixture was extracted with Et_2O to give a necic acid, R_f 0.5 (C_6H_6–MeOH–HOAc, 20:4:3) which on crystallization from dry C_6H_6 afforded colourless crystals, mp 111–112°,

mmp with authentic fulvinic acid undepressed. The acidic aq. layer was evapd to dryness in a vacuum desiccator, the residue extracted with EtOH and crystallized from EtOH and Et_2O to give colourless crystals, mp 115°.

Hydrolysis of isocrocandine. The alkaloid (0.15 g) was dissolved in 18% HCl (5 ml) and hydrolysed by heating at 100° for 30 hr. Processing of the hydrolysis mixture, using the methods described for crocandine, afforded a necic acid, mp 136–137° and necine HCl, mp 115°, mmp with necine HCl obtained from crocandine undepressed.

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GEIBALANSINE ET *O*-ACÉTYLGEIBALANSINE, NOUVEAUX ALCALOÏDES ISOLÉS DE *GEIJERA BALANSAE**†

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(*Reçu le* 20 *novembre* 1978)

Key Word Index—*Geijera balansae*; Rutaceae; skimmianine; geibalansine; *O*-acetylgeibalansine; hordenine; 3-methoxy-4-hydroxy-*N*,*N*-dimethyl phenylethylamine.

Des sept espèces connues de *Geijera*, originaires de Nouvelle-Guinée, Australie orientale, Nouvelle-Calédonie ou îles Loyauté, deux seulement ont fait, à ce jour, l'objet d'une étude chimique; de ces deux espèces ont été isolés des coumarines, des terpénoïdes et cinq alcaloïdes quinoléiques, déjà trouvés dans d'autres Rutaceae [1] (platydesmine et son acétate, γ-fagarine, skimmianine, flindersine). L'espèce que nous avons étudiée, *Geijera balansae* Schintz. et Guill.‖, a été récoltée á Port-Boisé, dans le Sud de la Nouvelle-Calédonie. Des feuilles, cinq alcaloïdes ont été isolés: la skimmianine, présente dans de nombreuses Rutaceae [2] et quatre composés séparés pour la première fois d'une plante de cette famille: l'hordénine, la methoxy-3 hydroxy-4 *NN* diméthylphényléthylamine, la geibalansine **1** et son dérivé *O*-acétylé **2**.

Les dérivés de la phényléthylamine ont été assez rarement trouvés chez les Rutaceae [3, 4] et si l'hordénine a été isolée à plusieurs reprises de Leguminosae et de Cactaceae, la méthoxy-3 hydroxy-4 *NN* diméthylphényléthylamine ne l'a été que de deux espèces mexicaines de 'peyotl' [5, 6]. Les dérivés pyranoquinoléiques sont, par contre, plus couramment rencontrés chez les Rutaceae. La geibalansine **1** et son acétate **2**, isolés ici, ont été identifiés par les méthodes spectrales classiques. Traitée par l'iodure de méthyle, la geibalansine **1** a été transformée en ribalinine **3** [7]. L'application de la méthode des largeurs de bande en RMN [8] au signal du proton en 3′ (voir Partie Expérimentale) nouse fair proposer pour la geibalansine une configuration équatoriale de l'OH en 3′. Comme la ribalinine, la geibalansine avait été synthétisée avant d'être connue à l'état naturel [7, 9].

*Cette note est dédiée à la mémoire de Monsieur le Professeur Jean Le Men, décédé le 4 Octobre 1978.

† Partie 54 dans la série "Plantes de Nouvelle-Calédonie". Pour la Partie 53, voir référence [11].

‖ Un échantillon botanique a été déposé au Muséum National d'Histoire Naturelle de Paris sous le No. Sévenet-Pusset 1300.