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SHORT REPORTS

ACACIPETALIN IN *ACACIA CONSTRICTA* FROM NORTH AMERICA

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Key Word Index—*Acacia constricta*; Leguminosae; cyanogenic glycoside; acacipetalin.

Abstract—Acacipetalin, previously known only from the African legumes *Acacia sieberiana* var. *woodii* and *Acacia hebeclada*, has been isolated from an American species of the genus, *Acacia constricta*.

DISCUSSION AND RESULTS

We wish to report the presence of the cyanogenic glucoside, acacipetalin, in an American legume, *Acacia constricta*. This compound has previously been found in certain African species of the genus, but is unknown from other plant groups.

Bentham recognized 6 series within the genus *Acacia*. Of these, 3 are principally Australian and 2 others are widely distributed in Asia, Africa and the Americas [1]. In a recent revision of the genus, Vassal combined the 3 Australian series into one subgenus but otherwise accepted Bentham's basic groups. He did, however, reorganize taxa within the proposed subgenera [2], which are more or less equivalent to Bentham's series. He further divided his proposed subgenus *Acacia*, section *Acacia* into 2 subsections: the *Uniseriae* and the *Pluriseriae*.

Two African members of the subsection *Uniseriae*, namely *Acacia sieberiana* var. *woodii* (≡ *A. stolonifera*) and *Acacia hebeclada* (≡ *A. lasiopetala*), have been shown to contain acacipetalin [3]. A revised structure for this compound has recently been proposed [4], and the presence of a closely related compound, dihydroacacipetalin, has also been reported [5]. Other members of the subsection *Uniseriae* are known to be cyanogenic (*A. chiapensis* [6], *A. tortilis* [7,8] and *A. robusta* [7]) but the structures of the cyanogenic compounds from these have not been elucidated. One species of the subsection *Pluriseriae*, *Acacia giraffae* has also been shown to contain acacipetalin*. Other members of this subsection (*A. farnesiana* [8] and *A. cochliacantha* X *hindsii* [6] are known to possess cyanogenic abilities but again the compounds responsible have not been examined.

Our discovery of acacipetalin in an American species of the subsection *Uniseriae* suggests that a chemical survey for cyanogenic glycosides in the genus might provide some insight into the relationship between African and American acacias.

EXPERIMENTAL

Young leaves and shoots (68 g) collected from a single specimen of *Acacia constricta* (Acc. No. 61.6764, Desert Botanical Garden, Phoenix, Arizona, voucher 9807 deposited in herbarium (DES) of the Garden) were ground in a Waring Blender with 200 ml hot 80% aq EtOH, filtered and the residue washed once with additional aq EtOH. The filtrate was taken to dryness at RT, dissolved in 17 ml 60% aq EtOH and chromatographed on Whatman 3MM sheets in 2-butanone–Me_2CO–H_2O (15:5:3). The cyanogenic material on the chromatogram was located as previously described (4) and then eluted with 80% aq EtOH, taken to dryness at RT, and dissolved in a minimum of H_2O. Preliminary tests on this material disclosed the cyanogenic material to be hydrolyzable with β-glucosidase preparations from either almonds or flax-seedlings but not by alkali. The amount of HCN-producing material corresponded at this stage to 7 μmol/g (fr. wt) of the original plant material. Qualitative tests of the enzymic hydrolysate disclosed that glucose was the sugar released on hydrolysis. The major amount of the glycoside was then chromatographed a second time on Whatman 3MM sheets in the above solvent, eluted with aq EtOH, evaporated and redissolved to yield a further purified sample. Aliquots in duplicate were taken for quantitative analysis for the HCN [9] and glucose released [10], the latter assayed using the Glucostat reagent. The amounts of HCN (1·85 and 1·79 μmol) corresponded to the glucose present (1·82 and 1·81 μmol); thus the unknown is a monoglucoside.

A field desorption mass spectrum [11] of the glucoside had an M + 1 peak at *m/e* 260 (acacipetalin MW = 259) and a peak at *m/e* 283 corresponding to an $(M + 1 + Na)^+$ ion. The trimethylsilyl (TMS) ether of the glycoside was prepared in the manner previously described [12] and its NMR spectrum determined (100 MHz). The spectrum obtained was identical in all respects (chemical shifts, coupling constants and integral values of the aglycone peaks) with that of the TMS ether of authentic acacipetalin [4].

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A NEW NATURALLY OCCURRING 1,2-DITHIOLANE FROM *BRUGUIERA CYLINDRICA*

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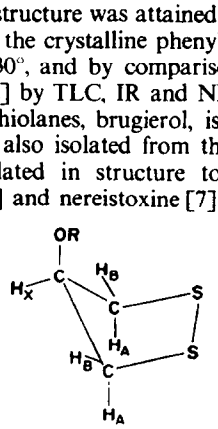
Key Word Index—*Bruguiera cylindrica*; Rhizophoraceae; 4-hydroxy-1,2-dithiolane; phenylaminocarbonyl ester.

The chipped stem and bark of *Bruguiera cylindrica* was extracted with $CHCl_3$ and the extract was chromatographed 2× on a Si gel column with i-Pr_2O to yield a yellow oil, which gave a single spot on TLC. Structure **1** was suggested by the IR absorption band at 3320 cm^{-1} due to a hydroxyl group and UV max at 320 nm due to a 1,2-dithiolane ring and by NMR spectrum indicative of a partial structure $-CH_{\mathcal{I}}-CH(OH)-CH_2-$, which showed octet (two double doublets) as AB parts of ABX spectra for two methylenes at 3·06 ppm ($J_{A,X}$ 3·5 Hz) and 3·18 ppm ($J_{B,X}$ 2·2 Hz) with $J_{A,B}$ 11·5 Hz and a multiplet (H_x) for a methine at 4·90 ppm and a broad signal disappearing with D_2O for a hydroxyl centered at 2·41 ppm respectively. On irradiation at the methine proton, the ABX spectra and the doublet collapsed to a pair of AB spectra and singlet respectively thus confirming the arrangement of protons.

Confirmation of structure was attained by combustion and MS analysis of the crystalline phenylaminocarbonyl ester (**2**) mp 129–130°, and by comparison with a synthetic specimen [1,2] by TLC, IR and NMR spectra.

Three known dithiolanes, brugierol, isobrugierol and brugine [3–5] were also isolated from this plant. These compounds are related in structure to α-lipoic acid, asparagusic acid [6] and nereistoxine [7].



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

EXPERIMENTAL

Spectra were obtained at 100 MHz in $CDCl_3$ with TMS internal standard.

Phenylaminocarbonyl ester of **1**. Dry toluene (1 ml) was added to $CHCl_3$ soln of 1 (200 mg) and then the $CHCl_3$ was removed. Phenylisocyanate (280 mg) was added to this toluene soln, which was heated under reflux for 1 hr. The product, ex CCl_4, melted at 129–130°, 250 mg. Anal. Calcd for $C_{10}H_{11}O_2NS_2$: C, 49·79; H, 4·56; O, 13·26; N, 5·81; S, 26·58. Found: C, 50·00; H, 4·27; O, 13·71; N, 5·95; S, 26·07. IR(KBr): 3325 cm^{-1} (=NH), 1700 (–CO–O–). MS: *m/e* 241 (M^+, parent ion), 165 ($M-C_6H_4$), 149 ($M-NHC_6H_5$), 105 ($M-OCONHC_6H_5$), 104 ($M-OCONHC_6H_5$, –H), 77 ($M-OCONHC_6H_5-C_2H_4$), and 41 ($M-OCONHC_6H_5,-S_2$).

Isolation of brugierol (**3**) *and isobrugierol* (**4**). After **1** had been eluted from the Si gel column, elution with $CHCl_3$ gave a mixture of **3** and **4** (200 mg). By using preparative TLC with *n*-hexane–$CHCl_3$ (5:1) as solvent, **3** and **4** were purified. **3**, IR (KBr): 3420 cm^{-1} (–OH), 1035–1065 ($-S_2O$). UV (MeOH)λ_{max}: 252 nm (1,2-dithiolane oxide). NMR: showed signals for 2 sets of ABX spectra. δppm 2·90 (*dd*, 1H), 3·60 (*dd*, 1H), 4·05 (*dd*, 1H), 4·10 (*dd*, 1H) for a pair methylenes, 5·41 (*m*, 1H for methine), 4·40 (*d*, 1H for –OH). **4**, IR (KBr): 3415 cm^{-1} (–OH), 1030–1085 ($-S_2O$). UV (MeOH) λ_{max}: 248 nm (1,2-dithiolane oxide). NMR: ppm 3·45 (*dd*, 1H), 3·54 (*dd*, 1H), 356 (*dd*, 1H), 383 (*dd*, 1H) for a pair methylenes of 2 sets of ABX spectra. 5·43 (m, 1H for methine).

Isolation of brugine (**5**). The chipped stem and bark (24 kg) was extracted with $CHCl_3$ at 50–60°. The extract was concentrated to give dark brown solid, which was chromatographed on Si gel first with $CHCl_3$ and then with MeOH–Me_2CO–C_6H_6 (2:1:1). The second fraction was rechromatographed on Al_2O_3 with $Me_2CO-C_6H_6$ (1:1) to give brugine, (+)-tropine 1,2-dithiolane-3-carboxylate (50 mg). $[\alpha]_D^{25}$ −23 (*c*, 3·5 in $CHCl_3$), IR ($CHCl_3$): 1727 (–CO–O–), UVλ_{max} (EtOH): 278 nm (ε, 360), 324·3 (sh). NMR: ppm 4·93 (*t*, 1H, $-\overset{CH_2}{\underset{CH_2}{}}>CH-O-$), 4·17 (*dd*, 1H, $-\overset{CO}{\underset{S}{}}>C\overset{H}{\underset{CH_2-}{}}$), 3·8–2·5 (*m*, 6H), 2·27 (*s*, 3H, –N–Me), 1·55–2·02 (*m*, 8H). MS: *m/e* 273