

had identical spectral and electrophoretic properties (λ_{\max} 548 nm; mobility relative to betanin 0.72 at pH 2.4, 0.80 at pH 4.5). Since Oleracin I gave on acid hydrolysis the diastereoisomeric aglycones betanidin and isobetanidin and Oleracin II only isobetanidin, the former is a betanidin and the latter an isobetanidin derivative. Since Oleracin I treated with aq. citric acid [1] gave a mixture of Oleracin I and II, they are clearly diastereoisomers. On alkali treatment, the mixture yielded ferulic acid and two new diastereoisomeric pigments (DO1 and DO2) which were separated by chromatography on polyamide. These pigments had indistinguishable spectral properties (λ_{\max} 537 nm). DO 1 gave on complete acid hydrolysis a mixture of betanidin and isobetanidin and compound DO2 only isobetanidin; thus DO1 is a betanidin and DO2 the corresponding isobetanidin derivative. Controlled acid hydrolysis of DO1 and DO2 mixture with 10% acetic acid (3.5 hr under reflux) gave 2 sugars, identified as glucose and cellobiose by comparison with authentic materials. When a mixture of Oleracin I and II was methylated with CH_2N_2

followed by alkali fusion, 5-hydroxy-6-methoxyindole-2-carboxylic acid was obtained. Thus cellobiose is bound to the hydroxyl group at position 5 and the phenolic hydroxylic group at position 6 is free. Since controlled acid hydrolysis (1 N HCl; 10 min at 80°) of DO1 + DO2 gave in addition to the products of total hydrolysis, small amounts of betanin and isobetanin, the disaccharide-aglycone linkage is β . Thus DO1 is betanidin 5-*O*-cellobioside and DO 2 is isobetanidin 5-*O*-cellobioside.

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TECLEANONE FROM *DIPHASIA KLAINEANA* AND *TECLEA VERDOORNIANA*

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Key Word Index—*Diphasia klaineana*; *Teclea verdoorniana*; Rutaceae; acridone alkaloid; tecleanone; chemotaxonomy.

Plants. *Diphasia klaineana* Pierre-Enti 490A and Enti 490B; *Teclea verdoorniana* Exell et Mendonca-Enti 390 and Enti R 789. Voucher specimens have been deposited at the herbarium of the Royal Botanic Garden, Edinburgh. *Source.* *D. klaineana* from beside the Awutu-Winneue road and *T. verdoorniana* from the Neung Forest Reserve, Tarkwa, Ghana. *Uses.* Both species are used by the indigenous population as a cure for

various ailments [1]. *Previous work.* On the stem and root barks of *D. klaineana* [2] and *T. verdoorniana* [2–3] and on other species of *Teclea* [4–5].

Present work. The isolation of small quantities of an unidentified alkaloid, designated DK/1, from *D. klaineana* (8 mg) and *T. verdoorniana* (5 mg) has been described previously [2]. From a second, larger, collection of *D. klaineana* root bark (Enti 490B, 1 kg) more of this compound

has now been isolated by column chromatography of the CHCl_3 extract over silica gel. Elution of the column with C_6H_6 yielded evoxanthine (875 mg) identified as before [2]. Further elution with CHCl_3 gave the new alkaloid (65 mg) recrystallized from MeOH as yellow needles mp $189-191^\circ$. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ) 230 (4.45), 263 (3.90), 269 (3.91) and 395 (3.88), indicative of an acridone nucleus [6]. IR ν_{max} cm^{-1} (KCl): 3300 (NH), 1640 (CO), 1580, 1525. Accurate mass measurement gave M^+ 301.1316, $\text{C}_{17}\text{H}_{19}\text{NO}_4$ requires 301.1314, with major ions at m/e 270 ($M^+ - \text{MeO}$, 60%), 168 ($\text{C}_9\text{H}_{12}\text{O}_3$, 100%), 133 ($\text{C}_8\text{H}_7\text{NO}$, 30%), 105 ($\text{C}_7\text{H}_7\text{N}$, 60%). This is unlike the fragmentation patterns recorded for acridones by Bowie *et al.* [7] and suggested the compound was a benzophenone with *N*-substitution on one ring (m/e 133 and 105) and *O*-substituents on the other (m/e 168). This was confirmed by an NMR study (60 MHz, CDCl_3): δ 9.10 (1H, *m*, N-H, replaceable on addition of D_2O), 6.50–7.40 (4H, *m*, $4 \times \text{H-Ar}$), 6.20 (2H, *s*, $2 \times \text{H-Ar}$), 3.87 (3H, *s*, OMe), 3.70 (6H, *s*, $2 \times \text{OMe}$), 2.97 (3H, *d*, NH-Me, on addition of D_2O the signal collapsed to a singlet, due to exchange to ND-Me).

Therefore combined MS and NMR data suggested the alkaloid was a benzophenone substituted in one ring with NH-Me and in the other with $3 \times \text{OMe}$. A further study of the aromatic proton signals in the NMR spectrum allowed conclusions to be made regarding the substitution pattern. By analogy with NMR spectra of acridones [8] the two protons at δ 6.20 can be assigned to the *O*-substituted ring and because of their lack of *ortho* coupling and their relatively highfield position they can be neither adjacent to each other nor *ortho* to the carbonyl function of the benzophenone thereby limiting them to the *meta* positions with respect to the latter. The pattern of the remaining aromatic protons is typical of the non-substituted ring of acridones [8] and indicates that the NH-Me group probably occurs in the biogenetically anticipated position *ortho* to the carbonyl bridge.

Very recently an *o*-amino benzophenone alkaloid, tecleanone, has been reported in *Teclea gran-*

difolia Engl. [5]. Comparison of IR, NMR and MS showed close agreement with those obtained in the present work and the co-identity of the alkaloid from *T. verdoorniana* and *D. klaineana* with tecleanone was confirmed by the preparation of the *NN*-dimethyl derivative mp $127-128^\circ$ (lit. [5] 128°).

Biological significance. As pointed out by Casey and Malhotra [5] the isolation of an *o*-amino benzophenone offers strong support to the proposal that acridone alkaloids, found in many rutaceous species [4], are formed via the condensation of anthranilic acid and acetate [9].

The distribution of tecleanone may also have chemotaxonomic value. Its co-occurrence in *T. grandifolia* and *T. verdoorniana* is in support of the contention [1] that these two taxa are conspecific and its presence in *D. klaineana* offers further biochemical evidence that the affinities of that species are with *Teclea* Delile rather than *Oricia* Pierre [2].

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