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$\Delta^{\alpha\beta}$-DIHYDROPIPERLONGUMININE, A NEW AMIDE FROM *PIPER GUINEENSE**

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Key Word Index—*Piper guineense*; Piperaceae; amide; $\Delta^{\alpha\beta}$-dihydropiperlonguminine.

Plant. Piper guineense Schum. and Thonn. (Piperaceae), also known as West African Black Pepper or Ashanti Pepper, is a woody climber of the forests of Ghana and other parts of West Africa [1]. The plants were collected and identified by Mr. K. Obeng-Darko of the Faculty of Agriculture, and, voucher specimens are on deposit at the Faculty of Pharmacy, University of Science and Technology, Kumasi, Ghana. *Uses.* Condiment and medicinal in the treatment of coughs, intestinal disease, bronchitis, venereal desease, colds, rheumatism and insect infestation [1].

Previous work. On the crude fiber content [2], the lignans yangambin [3,4] and dihydrocubebin [5] and a series of unsaturated aliphatic amides [6].

Plant part examined. Dried fruits were extracted by maceration with Me_2CO. The combined Me_2CO extracts were concentrated to an oily residue which was partitioned between Et_2O and H_2O. Chromatography of the Et_2O soluble compounds over silicic acid in petrol–$CHCl_3$ mixtures afforded a complex mixture of constituents [7]. Repeated rechromatography of various fractions afforded $\Delta^{\alpha\beta}$-dihydropiperlonguminine as white crystals, mp 90–94°C, whose IR and UV spectra were indicative of an α,β-unsaturated secondary amide containing an aromatic function [8,9]. The NMR spectrum was very similar to that of piperlonguminine [6] and further indicated the trans orientation of the two olefinic protons adjacent to the amide carbonyl [δ 5·82 (1H, *d*, J 16 Hz) and 6·87 (1H, *d*, J 16 Hz)]. The mass spectrum showed M^+ at *m/e* 275, two mass units higher than piperlonguminine (M^+ *m/e* 273) [6]. Catalytic reduction of the unsaturated amide over Pd–C gave tetrahydropiperlonguminine, identical (UV, IR, NMR, MS mp, mmp) with the product of the reduction of piperlonguminine (prepared from piperic acid chloride and isobutylamine) in the same manner. Finally, treatment of the dihydropiperlonguminine with OsO_4 followed by KIO_4 [11,12] afforded 3-(3,4-methylenedioxyphenyl)-1-propanal (prepared by synthesis from 3,4-methylenedioxycinnamic acid) as the major product, confirming the α,β-orientation of the double bond of the natural amide. To our knowledge, this is the first reported occurrence of $\Delta^{\alpha\beta}$-dihydropiperlonguminine in nature, although both $\Delta^{\alpha\beta}$ and $\Delta^{\beta\gamma}$-dihydropiperlonguminine have been synthesized previously [13].

Biological significance. Medical [1].

EXPERIMENTAL

Extraction. The dried fruits (500 g) were extracted by maceration with Me_2CO (3 × 3 l.) and the combined extracts concentrated to an oily residue (17·94 g) which was partitioned between Et_2O (0·5 l.) and H_2O (2 × 0·5 l.). Chromatography of the Et_2O soluble compounds (16·83 g) over silicic acid (500 g) in petrol–$CHCl_3$ (3:7) and then petrol–$CHCl_3$ (1:3) afforded fractions containing numerous compounds. Rechromatography of various fractions in the same manner afforded $\Delta^{\alpha\beta}$-dihydropiperlonguminine (75 mg) as white crystals, mp 90–94 [illegible] nm (log ϵ): 208 (4·20), 212 (*sh*) (4·15), 240 (*sh*) (3·81), 290 (3·58) and 339 (3·44); ν_{max}^{KBr} cm^{-1}: 3390, 1667, 1620, 1548, 1503, 1490, 1445, 1250, 1188, 1100, 1035, 925, 857 and 810; NMR (60 MHz, $CDCl_3$): δ 0·90 (6H, *d*, *J* 6 Hz), 1·25–1·58 (3H, *m*), 2·52 (2H, *t*, *J* 7 Hz), 3·10 (2H, *t*, *J* 7 Hz), 5·82 (1H, *d*, *J* 16 Hz), 5·92 (2H, *s*), 6·68 (2H, *s*), 6·82 (1H, *s*) and 6·87 (1H, *d*, *J* 16 Hz); MS (probe) 70 eV *m/e* (rel. int.): 275 M^+ (16%) for $C_{16}H_{21}NO_3$, 203 (3), 175 (3), 135 (100), 105 (2), 77 (4) and 57 (1).

Tetrahydropiperlonguminine. $\Delta^{\alpha\beta}$-dihydropiperlonguminine in MeOH was reduced in the presence of 5% Pd–C (5 mg) for 4 h to afford tetrahydropiperlonguminine, colorless needles from petrol–C_6H_6, mp 45–47°; λ_{max}^{MeOH} nm (log ϵ) 210 (3·77), 237 (*sh*) (3·51) and 290 (3·48); ν_{max}^{KBr} cm^{-1}: 3330, 2940, 1640, 1550, 1490, 1468, 1445, 1245, 1190, 1160, 1100, 1037, 920, 860 and 805; NMR (60 MHz, $CDCl_3$): δ 0·87 (6H, *d*, *J* 6 Hz), 1·59–2·48 (9H, *m*), 2·99 (2H, *t*, *J* 7 Hz), 5·85 (2H, *s*) and 6·60 (3H, *s*); MS (probe) 70 eV (rel. int.): M^+ *m/e* 277 (76%) for $C_{16}H_{23}NO_3$, 262 (3), 234 (5), 205 (28), 204 (54), 177 (8), 163 (3), 149 (5), 148 (52), 142 (17), 135 (100), 128 (20), 115 (70), 114 (9), 105 (8), 100 (9), 77 (27), 72 (22), 60 (40), 57 (7), and 43 (9). The product was identical to authentic tetrahydropiperlonguminine (prepared by the condensation of piperic acid chloride and isobutylamine followed by catalytic hydrogenation with 5% Pd–C) by direct comparison (UV, IR, NMR, MS, mp, mmp).

3-(3,4-*methylenedioxyphenyl*)-1-*propanal.* Oxidation of $\Delta^{\alpha\beta}$-dihydropiperlonguminine in dioxane–H_2O (3:1) with OsO_4 for 5 min followed by treatment with excess KIO_4 (added batchwise) over a period of 20 min and stirring for 1 hr gave an Et_2O soluble oil which after chromatography over silicic acid and elution with C_6H_6 afforded 3-(3,4-methylenedioxyphenyl)-1-propanal (a pale yellow oil, identical UV, IR, NMR, MS) with a sample prepared by synthesis from 3,4-methylenedioxycinnamic acid).

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5-HYDROXY-L-TRYPTOPHAN; TAXONOMIC CHARACTER AND CHEMICAL DEFENCE IN *GRIFFONIA*

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Key Word Index—*Griffonia* (*Bandeiraea*); 5-hydroxy-L-tryptophan.

The seeds of *Griffonia* (*Bandeiraea*) *simplicifolia* (Val ex DC.), a West African legume used in native medicine [1], have been reported [2, 3] to contain high concentrations of 5-hydroxy-L-tryptophan (5-HTP). It has been argued that the accumulation of this amino acid like the accumulation of 3,4-dihydroxy-L-phenylalanine (L-DOPA) in seeds of *Mucuna* species may protect the seeds from insect predation [4], and both the ground seed of *G. simplicifolia* and 5-hydroxy-L-tryptophan itself have proved to be extremely toxic to the larvae of *Prodenia eridania* (the southern army worm) [5] and the larvae of *Callosobruchus maculatus* (the southern cow pea weevil) [6].

In studying the distribution of L-DOPA in *Mucuna* it was possible to obtain seeds of six different species of the genus and show that all of these (but none from other genera examined) accumulated the amino acid at uniformly high levels (6–9% dry wt.) [4]. This finding supported the view that the role of L-DOPA in *Mucuna* seeds is a protective one. No such comparison was possible with *Griffonia* however as only one species of the four described in this small genus was available at the time of the original work and no other 5-HTP accumulating species were found in related genera.

We now report that a few seeds of *G. physocarpa* Baill. (*Bandeiraea tenuiflora* Benth.) from Gabon and of *G. speciosa* (Welw. ex Benth.) Taub. collected in Zaire in 1958 and preserved at the Royal Botanic Gardens, Kew, have been made available to us. The seeds of both these species also contain high concentrations of 5-HTP. On analysis (colorimetrically [7] and by amino acid analyser), 20 individual seeds of *G. simplicifolia* collected in Nigeria gave a mean value of 14.0% ± 0.24 of 5-HTP (calculated on dry seed weight). This uniformly high value is consistent with the view that 5-HTP has a protective role in the seed.

In analysing seeds representing over 250 other genera of the Leguminosae we have failed to find any other species that accumulates 5-HTP, and it is clear that the accumulation of 5-HTP is restricted to a very small number of plant species and may in all probability be a unique biochemical characteristic of this one tropical genus.

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