

NEW AMIDES FROM THE EXTRACTS OF *PIPER GUINEENSE*

JOSEPH I. OKOGUN*, B. LUCAS SONDENGAM† and SAMUEL F. KIMBU†

*Department of Chemistry, University of Ibadan, Ibadan, Nigeria;

†Department of Chemistry, University of Cameroon, B.P. 812, Yaounde, Cameroon

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Among compounds previously isolated from the fruit of *Piper guineense* are piperine and related amides, lignans, guineensine and its lower homologue [1-3]. We have recently indicated [3] that the components of the fruits of *P. guineense* vary with plant location. We have now examined the extracts of the fruits stems and roots of *P. guineense* collected near Buea in Cameroon and isolated two new amides. The ground dried plant material was extracted overnight with hexane. The crude extract from the fruits (1 kg) was chromatographed on neutral alumina (Brockmann). Hexane eluted a fraction (10 g) which crystallized from C₆H₆-hexane (1:1) and could be recrystallized from Et₂O. It had mp 99° and analysed for C₁₈H₂₃NO₄; MS, *m/e* 317 (M⁺), 165, 135, 84 and 77; IR (KBr), CM⁻¹ 1625 (C=O), 1600 (aromatic ring), 990 (trans-CH=CH-), 920 (-CHO₂O-), UV (MeOH), 217 (ε 16200), 235 (12700) and 302 nm (5800); NMR, δ, 7.1-6.1 (2H, *m*, vinyl H), 6.5 (1H, *s*, aromatic H), 6.7 (1H, *s*, aromatic H), 5.9 (2H, *s*, -OCH₂O-), 3.8 (3H, *s*, OMe), 3.5 (4H, *bs*, piperidine α-H), 2.8-2.1 (4H, *m*, -CH₂CH₂-), 1.6 (6H, piperidine β-H and γ-H). These results compared well with observations for piperine and its derivatives [3, 4] (see below) and are in agreement with the structure (1a), 4,5-dihydro-2'-methoxy piperine.

The stem (500 g) yielded a hexane extract which was chromatographed on neutral alumina (Brockmann) and yielded crystals (250 g) on elution with hexane. The crystals had mp 176-178° (C₆H₆-hexane). It analysed for C₁₈H₂₁NO₄; MS, *m/e* 315 (M⁺), 285, 284, 232, 231,

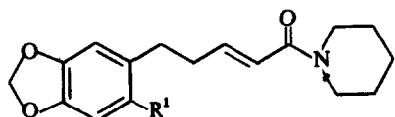
204, 202, 201, 183, 182, 165, 145, 115, 102 and 84; IR (KBr) 3050, 3010, 1620sh (unsaturation), 1630 (C=O), 1590 (aromatic ring), 995 (trans-CH=CH-), 920 cm⁻¹ (-OCH₂O-); UV 220 (ε 6900), 230sh (5600), 251 (6000), 258 (5900), 301 (9500), 308 (9400), 372 nm (13500); NMR δ 7.4-6.2 (4H, *m*, vinyl H), 6.9 (1H, *s*, aromatic H), 6.5 (1H, *s*, aromatic H), 5.9 (2H, *s*, -OCH₂O-), 3.8 (3H, *s*, OMe), 3.6 (4H, *bs*, piperidine -H), 1.6 (6H, *bs*, piperidine β- and γ-H). Comparison of these spectroscopic data with those of piperine and its derivatives [2, 3] led to the structure (2) 2'-methoxy-piperine.

The roots (500 g) yielded a hexane extract which was chromatographed on neutral alumina (Brockmann). Elution with hexane gave on crystallization from C₆H₆ hexane 4,5 dihydro-piperine (1b) mp 74° (lit. [4] mp 78°). Its IR, UV, NMR and MS were in agreement with published data.

Though these results confirm that there is variation in fruit contents with plant location, other results, which have demonstrated the presence of 2'-methoxypiperine in Nigerian [5] and Ghanain [6] varieties, indicate that the variation may be quantitative rather than qualitative, i.e. the relative proportion of the various components vary. Hitherto all the piperine amides isolated from *P. guineense* possess substituted benzene rings similar to the benzene rings of the lignans (for example sesamine) which cooccur with the amides. The present isolation of piperine amides with a tetrasubstituted benzene ring from *P. guineense* complements the earlier isolation [2] of aschatin, a lignan with a tetrasubstituted benzene ring from the same source.

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1a R¹ = OMe1b R¹ = H