Tetrahedron Vol. 40, No. 13, pp. 2541 to 2545, 1984
Printed in Great Britain.

0040-4020/84 $3.00 + .00

REVISED STRUCTURE AND SYNTHESIS OF PIPEROLEIN ACIDS, GUINEENSINE AND WISANINE FROM *PIPER GUINEENSE*

S. K. OKWUTE*
Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria

and

J. I. OKOGUN and D. A. OKORIE
Department of Chemistry, University of Ibadan, Nigeria

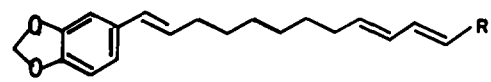
(*Received in the UK 22 October* 1982)

Abstract—The structures of piperolein acids guineensine and wisanine have been confirmed by synthesis. UV irradiation of trans piperolein B acid ester gave the *cis*-isomer reported in the literature as the *trans*-isomer. The *trans*-2, *trans*-4 ethylenic bonds in guineensine and wisanine were introduced by reacting piperolein B aldehyde and 2-methoxy piperonal with the appropriate Wittig or Reformatsky reagent.

Recently we reported[1] the isolation and constitution of guineensine, **1** from the fruits of *Piper guineense*. We required piperolein B acid, **2** as intermediate in our scheme for the synthesis of guineensine. Piperolein B acid had earlier been synthesised[2] using a Wittig reaction. Having in mind the reported[3,4] condition of the Wittig reaction, viz the use of reactive ylides, polar solvents with special reference to DMF and the presence of nucleophiles such as halide ions, which favour the formation of the *cis*-olefin bond over the *trans*-, we expected the reported[2] piperolein B acid should be the *cis*-isomer rather than the *trans*-isomer as assumed in that synthesis. In the synthesis of piperolein B acid to confirm the constitution of the non-crystalline amide, piperolein B, **3** isolated from the fruits of *Piper nigrum* ethyl suberate hemialdehyde was reacted with piperonyl-triphenylphosphonium bromide using sodium ethoxide as base in DMF. Synthetic piperolein B acid was reported to have m.p. 50–52° but no melting point was reported for the acid derived from the natural product.

It was decided to use an alternative route for the synthesis of the intermediate piperolein B acid required for that of guineensine. Part of this paper reports on the structure of piperolein B acid and that of guineensine.

Also recently reported was the isolation and structure of wisanine, **4** from the stem[5] and root[6] of *Piper guineense*. The synthesis of wisanine has been reported[7,8] by two, independent groups. We have however observed that the two groups recorded different physical data for the intermediate ester, **5**. To obtain **5** Crombie *et al.*[7] reacted 2-methoxy piperonal with 3-ethoxy carbonyl-but-2-enyltriphenylphosphorane and reported m.p. 64–66°. On the other hand Vig *et al.*[8] reacted the same aldehyde with the modified Wittig reagent, ethyl-γ-diethyl-phosphonocrotonate, and recorded the ester **5** as a viscous oil boiling at 155–156°/4–5 mm Hg. In view of the above conflicting results we also wish to record our work on the synthesis of wisanine.



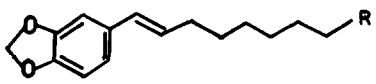
1 R = −CONHBu^i

12 R = −CO_2CH_3

13 R = −CO_2H

RESULTS AND DISCUSSION

Guineensine. Acylation of methylene-1, 2-dioxybenzene[9,10] with azelayl chloride monomethyl ester in symmetrical tetrachloroethane gave methyl ω-piperonyloctanoate, **6**, m.p. 52–53°. Sodium borohydride reduction of **6** gave the alcohol, **7** which was dehydrated to yield the ester **8**. The ester was over 95% pure on GLC. The spectral properties of the ester confirmed the *trans* configuration of the ethylenic bond as established for natural piperolein B[2], pipataline[11] and guineensine.[1] The high trans stereospecificity of the dehydration step is easily explained on the basis of the accepted carbonium ion intermediate[12] in such reactions even though it was possible for any *cis*-isomer resulting from the reaction to be isomerised by toluene-p-sulphonic acid to the *trans*-isomer. On hydrolysis with methanolic KOH, the ester, **8** gave the corresponding acid **2** m.p. 80–81° (lit[2] for piperolein B acid 50–52°) showing that the sample of **2** was different stereochemically from the literature sample. To obtain the *cis*-isomer of the ester **8**, the ester in benzene was UV irradiated. The photolysis product was shown by GLC to be over 95% homogeneous as one substance but its retention time was lower that that of the ester **8**. The photoproduct had a very weak IR absorption at 960 cm^{-1}.



2 R = $-CO_2H$

3 R = $-CON$⟨⟩

8 R = $-CO_2Me$

10 R = $-CH_2OH$

11 R = $-CHO$

Hydrolysis of the photo-product by methanolic KOH gave crystals, m.p. 49–52° (cyclohexane) in good agreement with the data previously published[2] for piperolein B acid which further supported the *cis* ethylenic bond stereochemistry of the acid **9**. There are hyperchromic and bathochromic shifts in λ_{max} on going from the spectrum of **9** to that of **2** and its ester.[13] Lithium aluminium hydride reduction of piperolein B acid ester **8** gave the primary alcohol, **10** m.p. 53–54°. Modified Collins oxidation[14] of **10** gave piperolein B aldehyde, **11** as a highly dense colourless oil. Introduction of the *trans*-2, *trans*-4 ethylenic bonds into the trienoate, **12**, was achieved by condensing **11** with 3-carbomethoxy-propen-2-ylidene-1-triphenylphosphorane in CH_2Cl_2 (16%). Hydrolysis of **12** with methanolic KOH gave the trienoic acid **13** which was converted to the amide **1** by treatment with $SOCl_2$ in the cold followed by excess isobutylamine in dry C6H6. Pure **1**, m.p. 117–119° (lit[1] 115°) was obtained by preparative TLC over Silica/gel. Mixed m.p. (116–118°) with an authentic sample showed no depression and co-TLC gave a single spot. Also all spectra agreed with those reported for the natural amide except the molar extinction coefficients.

Thus the earlier reported[2] piperolein B acid should be the *cis* (Z) and not the *trans* (E) isomer as assumed in that report. The present results also provided further support for the conclusions[3,4] that in the Wittig reaction, the use of reactive ylides, polar solvents (particularly DMF) and the presence of nucleophiles (for example halide ions) enhance the formation of the *cis* (Z-) isomer over the *trans*-

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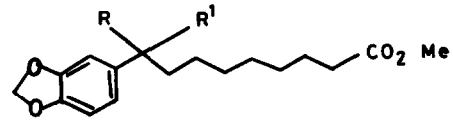
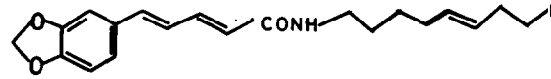
isomer. Also by this synthesis the proposed structure for guineensine, **1** has been confirmed. Recently an amide was isolated from the fruits of *Piper guineense* by Dwuma Badu *et al.*[16] and was assigned structure **14**. Mixed m.p. and co-TLC with an authentic sample from the group as well as direct comparison of the spectra confirmed that they isolated guineensine, **1** and not sylvatine,[17] **14**. Furthermore, from the fact that tetrahydropiperic acid was the product of acid hydrolysis of hexahydrosylvatine, and since the IR spectrum and MS of **14** lacked the 960 cm^{-1} (styryl) band and *m/e* 161 ion, respectively, it is obvious that **14** as reported[17] does not contain the system **2** in it structure.[1,2] However, the position of the isolate ethylenic bond appears biogenetically unusual and i is probably the first of its kind ever reported.



6 R, R^1 = =O

7 R, R^1 = $-H, -OH$

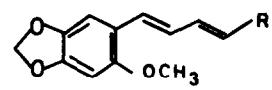
Wisanine. To obtain wisanine, **4** the intermediat dienoate, **5** was prepared via two alternate pathway: 2-Methoxy-piperonal was first subjected to Re formatsky reaction with ethyl-γ-bromocrotonate i THF to give **5** (60%) as bright yellow needles, m.p



14

88–90°. Considering the much lower m.p. recorde for **5** by previous workers (lit[7] m.p. 64–66°) w decided to prepare **5** in accordance with literatu procedure. Consequently, 2′-methoxypiperonal wa condensed with 3-ethoxycarbonylbut-2-enyltr phenylphosphorane in benzene. This gave **5** in much lower yield (40%), m.p. 88–90°. Mixed m.p with the product of Reformatsky reaction showed n depression and co-TLC gave a single spot. Also a spectra for the two samples were identical in a respects. To obtain **4** the ester, **5** was hydrolysed t the acid **15** with methanolic KOH, m.p. 218–220 Treatment of **15** with oxalylchloride followed b piperidine in dry benzene gave **4** as pale yello prisms, m.p. 178–180° (lit[5] 176–178°); m.m.p 178–180°.

In their report Vig *et al.*[8] quoted the weak I absorption band at 3050 cm^{-1} to support the pre ence of a diene system in **5**. We consider the ver strong absorptions at 1700 and 1010 cm^{-1} mor



4 R = $-CON$⟨⟩

5 R = $-CO_2C_2H_5$

15 R = $-CO_2H$

characteristic of a conjugated *trans, trans*,-diene ca bonyl system. It is therefore apparent that previo workers failed to obtain an isomerically pure samp of the dienoate, **5** arising from the difficulty preparing either 2-methoxypiperonal or the yli which is known to contain at least 25% *cis* (Z)-isom in $CDCl_3$ solution at room temperature.[19] Thus tl very high yield of over 75% recorded for **5** by son workers[8] is rather unexpected.

Table 1. M.ps of *trans*-2,4-pentadienoates

Pentadienoates	Melting points Methyl	Ethyl
5-Phenyl-2,4-pentadienoate	—	39–40°[19]
5-(3:4-Methylenedioxyphenyl)-2,4-pentadienoate	146°[20]	
	145–146°[21]	78°[20]
5-(2-Methoxy-3:4-methylene disxyphenyl)-2,4-pentadienoate	150–2°[21]	88–90°[22]
		64–66°[7]
		oil[8]

EXPERIMENTAL

M.ps were determined on a Kofler hot-stage apparatus and were uncorrected. IR and UV spectra were taken with Perkin–Elmer 137 instruments. ^{1}H NMR spectra ($CDCl_3$ + TMS solns) were taken with Varian T60A instrument. Mass spectra except where otherwise stated were obtained with a Perkin–Elmer Hitachi RMU 6E spectrometer. Gas chromatograms were obtained using a Packard Becker 417 instrument with stationary phase 3% SP 2100, N_2 as carrier gas, isothermal column temperature of 230° and flame ionisation detector. Silica gel refers to the appropriate Merck Silica gel for column or thin layer chromatography. The irradiation during photolysis was carried out using a 125W GEC, MBW/U mercury arc lamp. Methylene-1,2-dioxybenzene was obtained using the procedure of Shorygin *et al.*[9] γ-Bromocrotonates were prepared according to ref. 23. 3-Methoxy-, and 3-ethoxy carbonylbut-2-enyltriphenylphosphoranes were prepared according to ref 24, m.ps 160–165° and 157–160°, respectively. 3,4-Methylenedioxyanisole was obtained by methylation of sesamol (from Aldrich Chemical Co. Ltd.,).

Azelayl chloride monomethyl ester. Azelaic acid monomethyl ester was treated in the usual manner at room temperature over-night with thionyl chloride to give the required chloride (85% yield, b.p. 121–122°, 1 mm).

Methyl-ω-piperonoyl octanoate, **6.** Azelayl chloride monomethyl ester (23g, 0.059 mole) and methylene-1, 2-dioxybenzene (8.0g, 0.66 mole) in 1, 1, 2, 2-tetrachloroethane (30 cm^3) in a 3-necked 250 cm^3 round bottomed flask carrying a reflux condenser and a $CaCl_2$ drying tube was cooled (ice bath) and stirred mechanically. Freshly distilled stannic chloride (17 cm^3) was added in small portions over ½ h. On completion of the addition the ice bath was removed and the stirring was continued for a further 15 h at room temp. The reaction mixture was decomposed with a mixture of ice and HCl (1 : 1) and extracted with ether. The ether extract was washed with saturated $NaHCO_3$ and then H_2O (an emulsion may form). The ether was distilled off and the residue steam-distilled. The non-steam volatile aq residue was extracted with ether. The ether extract was washed with $NaHCO_3$ solution, water and dried with Na_2SO_4. Evaporation of ether gave the crude keto-ester. Column chromatography over silica gel with ether/hexane gave the product (8.5 g, 47%) as colourless crystals (m.p. 52–53°, ether/hexane). ν_{max} (Nujol) 1740 (ester C=O), 1675 (ketone C=O) and 925 cm^{-1} (O—CH_2–O); δ6.85–7.73 (3H, m, aromatic), 6.03 (2H, s, O–CH_2–O), 3.66 (3H, s, –OCH_3), 2.83 (2H, t, J = 6Hz, –CH_2CO–) 2.33 (2H, t, J = 6Hz, –CH_2CO_2R) and 1.53 10H, s, –$(CH_2)_5$–; λ_{max}: (methanol) 210 (ε4,500), 22δ (16,400), 273 (2,100) and 308 nm (3,300); *m/e* 306 (M$^+$) 275, 262, 177, 164 and 149. Found: C, 66.91; H, 7.45; $C_{17}H_{22}O_5$ requires: C, 66.65; H, 7.24%.

Trans-Piperolein B ester, **8** *and acid* **2.** Methyl ω-piperonoyl-octanoate (3.42g) was dissolved in CaH_2-dried methanol (100 cm^3) and $NaBH_4$ (1.1 g partially decomposed sample) was added and stirred magnetically for ¼ h at room temp. The methanolic solution was diluted with water and extracted with ether. The ether extract was washed liberally with water, dried with $MgSO_4$ and ether removed. The yield of methyl 9-hydroxy-9-(3, 4-methylene dioxyphenyl)-nonanoate was quantitative (3.7g). ν_{max} (film), 3600 (OH), 1950 (ester C=O), and 925 cm^{-1} (O–CH_2–O). This ester (3.52 g, 01011M) dissolved in sodium dried benzene (1.25 litres) and toluene-p-sulphonic acid (0.7 g) were heated at reflux for 2 h with the azeotropic removal of water using a Dean and Stark apparatus.

The reaction mixture was allowed to cool, washed with sat $NaHCO_3$ water and dried ($MgSO_4$). Evaporation of benzene under reduced pressure, followed by column chromatography of the crude product over silica gel with 10% ether/hexane gave 2.7 g (82%) of the *trans* ester **8** as a dense oil. The gas chromatogram (3% SP 2100, 5 ft × ¼ in. column, atten × 32, isothermal 230°) exhibited a major peak (95% of volatile products). It had ν_{max} (film): 1745 (ester C=O), 960 (styryl C=C), and 925 cm^{-1} (O–CH_2–O); δ6.90–6.70 (3H, m, aromatic), 6.50–5.90 (2H, m, vinyl protons), 5.90 (2H, s, O–CH_2–O), 3.70 (3H, s, –OCH_3), 2.20 (4H, m, CH_2C=C, CH_2C=O) and 1.50 (8H, s, –$(CH_2)_4$–); λ_{max} (methanol) 214 (ε24,500), 260 (15,100), 267 (14,700) and 304 nm (5,600); *m/e* 290 (M$^+$) 161, 148, 135, 131, 115 and 103; Found: C, 70.03; H, 7.32; $C_{17}H_{22}O_4$ requires: C, 70.32; H, 7.64%.

Hydrolysis of piperlein B methyl ester with 5% methanolic KOH gave 51% yield of *trans* piperolein B acid **2** recrystallised from cyclohexane m.p. 80–81°. ν_{max} (Nujol), 1695 cm^{-1} (carboxylic C=O); λ_{max} (methanol) 222 (ε20,700), 262 (18,200) and 308nm (8,500); *m/e* 276 (M$^+$), 161, 148, 135, 131, 115 and 103; Found: C, 69.58; H, 7.44; C, 69.56; H, 7.25%.

Cis-piperolein B acid **9.** A solution of piperolein B methyl ester (340 mg) in dry benzene (150 cm^3, 0.23%) was irradiated for 3 h in a 250 cm^3 pyrex glass flask. The solvent was removed under reduced pressure to give an oil which was purified by filtration of its petroleum ether solution through a short silica gel column. GLC (3% SP 2100, 5 ft × ¼ in. column, Atten × 60, 230° isothermal) gave a major peak (96% of volatile materials). Co-injection with the starting olefin-ester gave two major peaks, the photolysis product having a lower retention time. ν_{max} (film) 1750 (ester C=O), 930 cm^{-1} (O–CH_2–O), σ6.40–5.30 (2H, m, vinyl protons), 6.0 (2H, s, O–CH_2–O), 3.60 (3H, s, –OCH_3), 2.20 (4H, m, CH_2 C=C, CH_2 C=O) and 1.50 (8H, s, –$(CH_2)_4$–).

Hydrolysis with methanolic KOH, gave the corresponding acid **9** (m.p. 49–52°). λ_{max} (methanol), 219 (ε15,000), 262 (15,000), 268 (7,300), 302nm (1,800); Found: C, 69.16; H, 7.66; $C_{16}H_{20}O_4$ requires; C, 69.56; H, 7.25%.

Piperolein B alcohol **10** *and aldehyde* **11.** Piperolein B acid ester **8** (3,40 g) was subjected to $LiAlH_4$ reduction in ether (20 cm^3) at 0°. The mixture was decomposed with water and extracted with ether to give 3.0g (94%) of **10** recrystallisable from petroleum ether as colourless flakes, m.p. 53–54°. It analysed for $C_{16}H_{22}O_3$; C, 73.28; H, 8.39%: Calc.; C, 73.28: H, 8.39% ν_{max} (CM^{-1}) 3500 (OH), 960 (Styryl C=C) and 925 (O–CH_2–O). δ($CDCl_3$); 6.50–5.90 (2H, m, vinyl) 1.43 (1H, s, OH, disappeared with D_2O). *M/e* 262 (M$^+$), 161, 148, 135, 103.

1.50 g of **10** in CH_2Cl_2 was oxidised to the corresponding aldehyde **11** using modified Collins procedure.[14] The organic soln of the aldehyde was passed rapidly through a short column of silica gel, dried ($MgSO_4$), and solvent removed under reduced pressure to give a viscous oil (1.04g, 72%). λ_{max} (film cm^{-1} 1740 (aldehyde C=O), 960 (styryl C=C); δ ($CDCl_3$) 9.8 (1H, t_1, J 2H_Z; formyl group).

Methyl 13-(3, 4-*methylenedioxyphenyl*)-2, 4, 12-*tridecatrienote* **12.** A solution of 1.60 g (4.4 mole of 3-ethoxycarbonylbut-2-enyltriphenylphosphorance in CH_2Cl_2 (10 cm^3) was treated dropwise under N_2 at room temp (24 h) with a solution of 1.04 g (4.0 moles) of **11** in CH_2Cl_2 (10 cm^3) with magnetic stirring. The solvent was removed on water bath and the residue extracted with petroleum ether. Evaporation of the solvent gave the crude trienoate which on

column chromatography over silica gel with 5% ether–hexane first gave a mixture (0.04 g) lacking the 1000 cm^{-1} band in the IR spectrum, and then 0.22g (16%) all *trans* trienoate, **12**. Recrystallisation from methanol gave needle-like crystals, m.p. 46–48°. It analysed for $C_{21}H_{26}O_4$: Calc. C, 73.68; H, 7.60%. Found: C, 73.48; H. 7.75%. ν_{max} (Nujol) 1700 (α, β; γ, σ, –unsaturated ester), 1000 (*trans* C=C conjugated with C=O), 960 (styryl C=C) and 925 (O–CH_2–O). λ_{max} (methanol), 216 (ϵ32,400); 261 (51,800) and 305, (9,900) nm; δ ($CDCL_3$); 7.1–6.7 (3H, m, aromatic), 6.50–563 (6H, m, vinyl), 5.90 (2H, s, OCH_2–O), 3.70 (3H, s, $-OCH_3$), and 1.50 (8H, m, $(CH_2)_4$–); *m/e* 342 (M^+), 161, 148, 135, 131 and 103.

Guineensine 1. 405mg of **12** was refluxed with 5% methanolic KOH (3 cm^3) under N_2 (2 h). Most of the methenol was distilled off and the residue diluted with water and extracted with ether. The aqueous layer was acidified with cold dilute HCl and extracted with chloroform. Evaporation of the solvent gave guineensic acid **13** (278 mg, 71%).

220 mg of **13** was added to ice-cold $SOCl_2$ (1 cm^3) and left to stand overnight in an ice-bath. Excess $SOCl_2$ was removed by co-distillation with dry benzene. The crude acid chloride was taken up in dry benzene (10 cm^3) and added drop-wise with stirring to a solution of excess isobutylamine (1.0 g) also in dry benzene (10 cm^3) which was cooled in ice. The mixture was stirred at room temp ($\frac{1}{2}$ h) and diluted with benzene (30 cm^3). It was washed successively with dilute HCl, 5% $NaHCO_3$, water and then dried ($MgSO_4$). The solvent was removed under reduced pressure. Preparative TlC on silica gel gave 79 mg (30% based on acid) of amide **1**, m.p. 117–119°, m.m.p. 116–118° (lit[1] 113–115°, petroleum ether–benzene). (Found: C, 75.39; H, 8.65% M, 3.60. Calc for $C_{24}H_{33}NO_3$ requires; C, 75.15 H, 8.65; N, 3.65%.) All spectral analyses agreed with those reported for the natural product except the molar extinction co-efficient: Natural: λ_{max} (ethanol) 214 (34,000), 261 (35,600), 302 (6,500): Synthetic: λ_{max} (methanol) 216 (21,300) 263 (36,900), and 304 (7,000) nm.

2-Methoxypiperonal. A soln of 3:4-methylene dioxyanisole (2.8 g) in DMF (4 cm^3) was cooled in ice bath for 15 min. Phosphorus oxychloride (5 cm^3) was added and the mixture heated under reflux at 100° (2.5 h). The mixture was then poured into ice, and allowed to stand for several hours at room temp. The precipitated 2-methoxypiperonal 2.3 g, (70%) was filtered off at the pump and dried in vacuo over self indicating silica gel. Recrystallisation from ethanol gave needle-like pale brown cryatals, m.p. 110–112° (lit[25] 111.5–112.5°). (Found: C, 60.85% H, 4.6. Calc for $C_9H_8O_4$ requires: C, 60%, H, 4.5%.)

Ethyl 2-methoxypiperate **5**

(i) Zinc (0.85 g) in THF (2 cm^3) was refluxed with a crystal of iodine for about 10 min. A soln of 2-methoxypiperonal (1.4 g) in THF (6 cm^3) was added followed by a solution of ethyl γ-bromocrotonate (3.85 g) in THF (6 cm^3), and the mixture refluxed with magnetic stirring. After the reaction had subsided another portion of bromoester (3.85 g) in THF (6 cm^3) was added and stirring continued under reflux for 2 h. The mixture was decomposed with dil. H_2SO_4 and extracted with ether (3 × 50 cm^3). The ether extract was washed to neutral and evaporated. Dehydration of the intermediate alcohol was completed by refluxing in benzene (150 cm^3) with toluene-p-sulphonic acid using the Dean–Stark apparatus for 2 h. Column chromatography of the crude product on Solica gel gave pure *trans, trans*-diene ester **5** (1.2 g, 60%), recrystallisable from benzene as yellow needles m.p. 88–90°. λ_{max} (MeOH); 225 (ϵ 6,300), 250 (9,400) 300 (8,200) and 366 (16,800) nm: γ_{max} (KBr); 1700, 1610 and 1010 cm^{-1}; δ ($CDCl_3$): 7.4–5.8 (6H, aromatic and vinyl protons), 5.9 (3H, S, O–CH_2–O), 4.3 (2H, q, J 7H_z, $-OCH_2CH_3$), 3.9 (3H, S, $-OCH_3$) and 1.3 (3H, t, J6H_2)–OCH_2CH_3). (Found: C, 65.20%: H, 5.81. Calc for $C_{15}H_{16}O_5C$, 65.22%, H, 5.80%.)

(ii) To a solution of 3-ethoxycarbonylbut-2-eny triphenyl-phosphorane (0.8 g) in dry benzene (20 cm^3) solution of 2-methoxy piperonal (0.3 g) in dry benzer (20 cm^3) was added under N_2 and the mixture heated und reflux for 24 h. Evaporation of the solvent under reduce pressure followed by column chromatography gave tl dienoate **5** (0.162, 40%) as yellow needles, m.p. 88–9((benzene). Co–TLC with product from (i) gave a single spc M.m.p. showed no depression, and all spectra were supe imposable.

Wisanine, 4. Ethyl 2-methoxypiperate **5** (0.7 g) was heate under reflux with 2N methanolic KOH (5 cm^3) for 3 h. Mo of the methanol was then evaporated and the residue dilute with water (10 cm^3) and extracted with ether (2 × 20 cm Acidification of the aqueous layer gave 2-methoxypiper acid **5** (0.280 g, 44%) as yellow crystals, m.p. 218–220° (li 221–224°; EtOAc).

To a soln of the acid (270 mg) in 5 cm^3 dry C_6H_6 1 cm^3 oxalyl chloride was added and the mixture heated at 8 under reflux for 2 h. The solvent was evaporated und reduced pressure and 1 cm^3 of piperidine in 5 cm^3 C_6 added and stirred at room temp overnight. The C_6H_6 so was washed with dil HCl, then water and dried ov anhydrous Na_2SO_4. Column chromatography over neutr alumina gave the piperidide (130 mg, 49%) as pale yello prisms, m.p. 178–180° m.p.p. 178–180° (lit[5] 176–178 EtOAc). Requires: C, 68.57, H, 6.67, N, 4.44%; Found: (68.56; H, 6.73; N, 4.35%. ν_{max} (KBr) 1640, 1610, 1600, 102 and 1010 cm^{-1} δ ($CDCl_3$) 6–7 (6H, m) 5.9 (2H, S), 3.9 (3I S), 3.6 (4H) and 1.5 (6H).

Acknowledgements—We thank Professor Paul L. Schiff, J University of Pittsburgh, School of Pharmacy, Departme Pharmacology, 512, Salt Hall, for sending a sample natural guineensine and its spectra. We also wish to expre our gratitude to Scandinavian Microanalytical Laborat ries, Herlev, Denmark for the elemental analysis of Wi anine, and the University of Ibadan, Ibadan, Nigeria, for postgraduate Scholarship to S. K. O.

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