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LEAF ALKALOIDS OF *RAUWOLFIA VOLKENSII*

BAMIDELE A. AKINLOYE and WILLIAM E. COURT

Postgraduate School of Studies in Pharmacy, University of Bradford, West Yorkshire, BD7 1DP, U.K.

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Key Word Index—*Rauwolfia volkensii*; Apocynaceae; leaf; indole alkaloids.

Abstract—Thirteen alkaloids were isolated and identified from the leaves of *Rauwolfia volkensii*. The alkaloids included E-*seco* heteroyohimbine, heteroyohimbine, sarpagan, dihydroindole, pleiocarpamine, picrinine and akuammicine types together with peraksine.

INTRODUCTION

The East African species *Rauwolfia volkensii* Stapf occurs as a shrub attaining a height of 2 m and is confined to the area around Mount Kilimanjaro and the Pare Mountains [1]. Pichon [2], classifying the *Rauwolfia* species, grouped the African species into 4 sections, Ophioxylanthus, Afrovolfia, Endolobus and Rhopalanthus, but Rao [3] merged the last two groups as the section Endolobus. The two species *R. volkensii* and *R. oreogiton* Markgraf, which comprise the section Ophioxylanthus, are regarded as dubiously distinct by some authorities. In order to discover whether the botanical classification is related to phytochemical variation we have initially investigated the occurrence of alkaloids in *R. volkensii* leaves.

RESULTS

Rvolf 1, tetrahydroalstonine, was identified by comparison with authentic alkaloid and Rvolf 2, geissoschizine, by comparison with published data.

Rvolf 3 demonstrated a normal indole UV spectrum which was unaffected by pH change. The IR spectrum showed carbonyl or conjugated carbomethoxy absorption (1730 cm^{-1}) and absorption at 740 cm^{-1} suggested an *ortho*-disubstituted aromatic ring. The compound could not be acetylated using acetic anhydride and pyridine (absence of free OH or active H) but MS confirmed the presence of COOMe. The MS pattern was not typical of any *Rauwolfia* alkaloid so far encountered and did not resemble yohimbine (absence of prominent $M^+ - 1$ peak) or sarpagan (absence of *m/e* 168 and 169 peaks) structures. The data obtained agreed closely with published data for pleiocarpamine, an alkaloid isolated from *Pleiocarpa mutica* Benth, a related Apocynaceous plant [4].

The compound Rvolf 4 resembled Rvolf 3 but the IR spectrum indicated a trisubstituted *ar*-ring (830 and 790 cm^{-1}). The MS fragmentation pattern resembled that of pleiocarpamine [5] but there was a shift of 30 amu at the higher end of the spectrum. The ^1H NMR signal at δ 3.68 indicated a methoxy substituent and signals at δ 6.6–7.3 confirmed the substitution of the *ar*-ring. NMR data also revealed the presence of COOMe (δ 3.76) and an exocyclic ethylidene sidechain (δ 5.45, *q*, 1H and δ 1.56, *d*, 3H). Accurate mass measurements proved the molecular formula $C_{21}H_{24}N_2O_3$ and confirmed the loss of a COOMe group. As Rvolf 4 could not be acetylated it was identified as 10-methoxypleiocarpamine.

Rvolf 5 exhibited the UV spectrum and chromogenic reactions of a typical dihydroindole chromophore. MS fragmentation resembled that of 2,7-dihydropleiocarpamine [6] but the indole fragments at *m/e* 174, 161 and 160 and IR absorption at 820 cm^{-1} indicated methoxy substitution of the indoline nucleus. The IR peak at 1730 cm^{-1} confirmed the presence of a COOMe group and, by consideration of the preceding compounds, it was concluded that Rvolf 5 was 10-methoxy-2,7-dihydropleiocarpamine.

Compound Rvolf 6 exhibited UV characteristics and chromogenic reactions of a dihydroindole and UV absorption at 305 nm suggested substitution of the *ar*-ring. ^1H NMR signals indicated the presence of two OMe groups (δ 3.72, *s*, 3H; δ 3.6, *s*, 3H), COOMe (δ 3.8, *s*, 3H), N_a – Me (δ 2.88, *s*, 3H) and an exocyclic ethylidene sidechain (δ 5.32, *q*, 1H; δ 1.44, *d*, 3H). MS fragmentation was similar to that of picrinine [7] and suggested 10,11-dimethoxy-N_a-methyl-picrinine as there was a shift of 74 amu (2 OMe + CH_2). The loss of 99 amu ($C_5H_7O_2$) from the parent molecule is probably due to rupture of the C-15, C-20 bond with loss of C-14, C-15, C-16 and the attached COOMe. Data for Rvolf 6 thus resembled published information on quaternine (**7**) isolated from *Alstonia quaternata* Heurck et Muell. Arg. [8] although no shift in 70% $HClO_4$ was observed.

The UV spectrum of Rvolf 7 indicated a dihydroindole chromophore with *ar*-ring substitution and was unaffected by pH change. ^1H NMR signals corresponded to COOMe (δ 3.78, *s*, 3H), OMe (δ 3.74, *s*,

3H), OMe (δ 3.64, *s*, 3H) and =CH-Me (δ 5.36, *q*, 1H and δ 1.48, *d*, 3H). The MS resembled the *nor*-base corresponding to Rvolf 6, the M^+ being 14 amu less. MS–DIS* indicated that only one TMSi group was taken up, suggesting N_a-H. The M^+-18 peak is prominent in the MS of picrinine and picralstonine [7], compounds also possessing N_a-H. Such data indicated that Rvolf 7 was 10,11-dimethoxypicrinine. As this is a new alkaloid and the major alkaloid of *R. volkensii* leaves, the trivial name volkensine is proposed.

For Rvolf 8, the UV spectrum indicated a phenolic-2-methyleneindoline chromophore with a bathochromic shift of up to 10 nm in 0.1 N NaOH. The MS resembled that of akuammicine except for 16 amu at the upper end of the spectrum (prominent fragments at *m/e* 121, 107 and 92 at the lower end and at *m/e* 338, 279 and 232 at the upper end corresponding to *m/e* 322, 263 and 216 in akuammicine). On acetylation only one acetyl group was found and was attached to the indole moiety (*m/e* 232 peak appeared at *m/e* 274). The position of the phenolic OH group was deduced by comparing the magnitude of the UV bathochromic shift with those of *p*-hydroxyaniline and *m*-hydroxyaniline as recommended by Ahmad *et al.* [9]. Rvolf 8 was thus identified as 10-hydroxyakuammicine, also known as sewarine, and occurring in the related Apocynaceous species *Rhazya stricta* Decaisne [9].

UV, IR and MS of Rvolf 9 resembled those of methoxypleiocarpamine (Rvolf 4) but the MS also revealed a 16 amu increase in the M^+. Rvolf 9 chromatographed near the baseline in most neutral solvent systems employed. This suggested pleiocarpamine-*N*-oxide, which was prepared from pleiocarpamine using *m*-chloroperbenzoic acid in chloroform at room temperature as described by Craig and Purushothaman [10] and found to be identical by co-TLC.

Although UV and IR of Rvolf 10 were typically heteroyohimbinoid, it remained at the baseline in most basic and neutral TLC systems. MS suggested that Rvolf 10 was a quaternary base as it decomposed readily on electron impact and the spectrum resembled malonin-A (N_b-methyl-tetrahydroalstonine) [11]. Rvolf 10 was subsequently found to be identical with synthetic N_b-methyltetrahydroalstonine (UV, IR, MS, co-TLC). The compounds Rvolf 11–13 were identified as nortetraphyllicine, peraksine and normacusine B, respectively ($[\alpha]_D^{20}$, UV, IR, MS, co-TLC, fluorogenic and chromogenic reactions).

DISCUSSION

Studies of the occurrence of alkaloids in the roots of various *Rauwolfia* species [12–14] have agreed with the currently accepted theory that E-*seco* indole alkaloids yield by C-16–C-5 linkage the sarpagan compounds which, in turn by C-17–C-7 linkage, produce dihydroindoles, the latter group occurring in wide variety and large amount [12, 14]. The E-*seco* alkaloids are apparently also precursors of the yohimbine and heteroyohimbine alkaloids although the mechanisms involved are not fully understood. The alkaloids found in *R. volkensii* leaves included the E-*seco* compound geissoschizine (**1**), which is regarded as one of the first alkaloids formed in the biogenetic scheme after the nitrogenous glycosides [15], although the latter have yet to be isolated from *Rauwolfia* species.

The occurrence of the sarpagan normacusine B (**2**) and the dihydroindole nortetraphyllicine (**3**) is in agreement with earlier work on the leaves of *R. mombasiana* Stapf [16] and *R. cumminsii* Stapf [17] and can be related to the presence of geissoschizine. The alkaloid peraksine (= vomifoline) (**4**) occurred in low yield and is formed from a sarpagan intermediate by C-20–C-16 ring closure. Peraksine would appear to be a minor alternative to dihydroindole formation and was similarly found in the leaves of *R. caffra* Sond. [18], *R. mombasiana* [16] and *R. vomitoria* Afz. [19].

The alkaloid pleiocarpamine (**5**) has not previously been isolated from any *Rauwolfia* species although it was discovered in the Apocynaceous species *Pleiocarpa mutica* [4]. The pleiocarpamine skeleton is probably derived from an E-*seco* compound by direct attachment of C-16 to the indolic nitrogen. The pleiocarpamine group of compounds may act as a reservoir of potential E-*seco* compounds for further biosynthesis.

The picrinine bases volkensine (**6**) and quaternine (**7**) occurred in significantly high yield. Although picrinine and desacetyl-desformoakuammiline were obtained from *R. vomitoria* leaves [19] and picrinine and deacetylpicraline from *R. cumminsii* leaves [17], the occurrence of typical *Picralina* alkaloids in *Rauwolfia* species is uncommon. Such compounds have been regarded as byproducts of biosynthesis but their occurrence in large quantities suggests a greater significance and can be tentatively related to the presence of reserpiline in the roots. The heteroyohimbine reserpiline was not found in the leaves but the *allo* (C-3–Hα, C-20–Hα) configuration compound tetrahydroalstonine (**8**) and its N_b-methyl relative (**9**) were isolated.

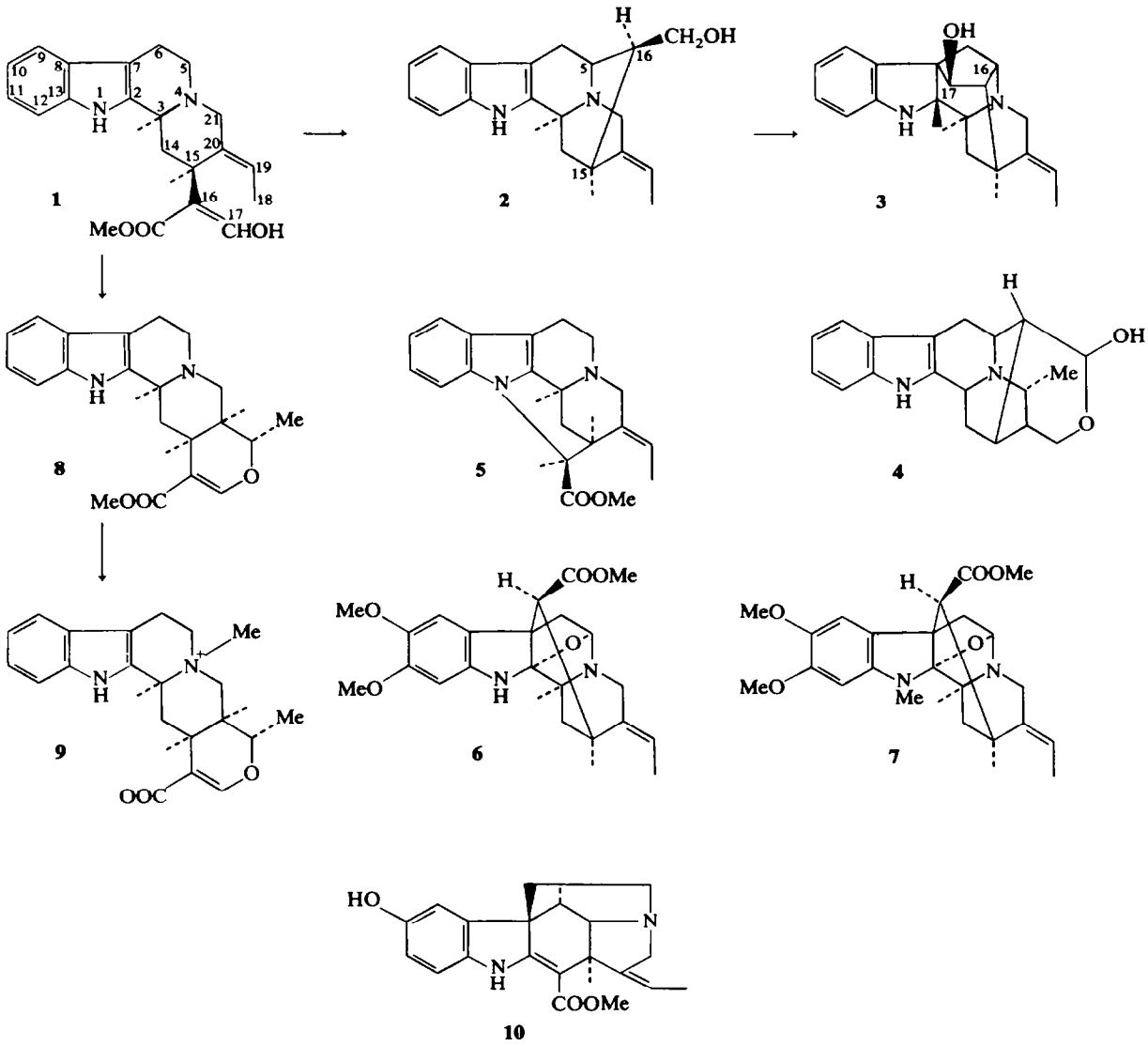
The detection of sewarine (10-hydroxyakuammicine) (**10**) has not previously been reported in *Rauwolfia* species. Sewarine was isolated from *Rhazya stricta* [9] and Scott [20] and Battersby and Hall [2] employing labelling experiments demonstrated that geissoschizine can be a precursor of akuammicine in *Vinca* species.

The occurrence of alkaloids in the leaves of *R. volkensii* (section Ophioxylanthus) differs from reported accounts of the alkaloids occurring in the leaves of *R. cumminsii* [17], *R. mombasiana* [16] and *R. vomitoria* [19] (section Endolobus) and *R. caffra* [18] and *R. obscura* K. Schum. [22] (section Afrovolfia). The presence of typical *Picralina*, *Pleiocarpa* and *Rhazya* alkaloids in *R. volkensii* suggests that further work may enable the differentiation of this section Ophioxylanthus chemically as well as morphologically.

EXPERIMENTAL

Leaves of *Rauwolfia volkensii* Stapf were collected in the Kindoroko Forest Reserve, Same District, Kilimanjaro Region, Tanzania in January 1974 by the Silviculture Research Section, Ministry of Natural Resources and Tourism, Tanzania. Voucher specimen RAU 111-743 was deposited with

* Mass spectroscopy with direct inlet silylation.



the Collection of Materia Medica and Herbaria, University of Bradford. *Analytical methods* used for TLC, UV, IR, ^{1}H NMR, MS and fluorescence and chromogenic tests have been described previously [23, 24].

Extraction. Finely powdered leaves (3 kg) were defatted by overnight maceration using 10 l. petrol (bp 40–60°). The petrol was separated by filtration and the marc dried at room temp. before being successively re-extracted for 24 hr with 10 l. MeOH and twice with 10 l. MeOH + 2% NH_3. The resultant extracts were bulked and reduced to dryness under red. pres. The resultant dried extract was dissolved in 200 ml HCl and the insoluble resinous matter removed by filtration. Filtrate was extracted with $CHCl_3$ (6 × 100 ml) to yield, on bulking and evaporation to dryness, the weak base fraction (10.5 g). Residual aq. phase was rendered alkaline (pH 8). Extraction with $CHCl_3$ (6 × 100 ml) as before yielded the intermediate base fraction (800 mg). The aq. phase was again rendered alkaline (pH 12) and extracted with $CHCl_3$ as before to yield the strong base fraction (200 mg).

Separation. The total weak base fraction (10.5 g) was separated by column chromatography using a 50 × 3.5 cm glass column packed with Al_2O_3 (activated neutral Brockmann grade I). The column was eluted with 500 ml volumes of the solvents hexane, hexane–EtOAc (4:1, 2:1, 1:1), EtOAc, EtOAc–MeOH (6:1, 4:1, 2:1, 1:1) and MeOH. 100 ml fractions were collected and monitored by TLC using Si gel layers, solvent systems $CHCl_3$–MeOH (9:1) and EtOAc–*iso*PrOH–NH_3 (17:3:1), and $FeCl_3$–$HClO_4$ and $Ce(SO_4)_2$ spray reagents. Fractions yielding spots of identical R_f values and colour reactions were bulked to yield alkaloid fractions, A, B and C. Fraction A separated by PLC (solvent Me_2CO–$CHCl_3$ (4:5)) gave alkaloids Rvolf 1 (8 mg), Rvolf 2 (10 mg), Rvolf 3 (8 mg), Rvolf 4 (60 mg) and Rvolf 5 (5 mg), in order of decreasing R_f values. Fraction B similarly separated (solvent $CHCl_3$–MeOH (9:1)) yielded compounds Rvolf 6 (60 mg), Rvolf 7 (600 mg) and Rvolf 8 (15 mg). Fraction C separated using solvent system $CHCl_3$–MeOH (3:1) gave alkaloids Rvolf 9 (10 mg) and Rvolf 10 (15 mg). Intermediate and strong base fractions were separated by PLC (solvent system, $CHCl_3$–Me_2CO–petrol (9:7:4) in an atmosphere of NH_3) to yield Rvolf 11 (8 mg), Rvolf 12 (8 mg) and Rvolf 13 (5 mg).

Identification of alkaloids. Rvolf 1, *tetrahydroalstonine.* Off-white amorphous powder; $[\alpha]_D^{20}$, UV, IR, MS, chromogenic and fluorogenic colours, co-TLC (6 systems). Rvolf 2, *geissoschizine.* White amorphous powder; $[\alpha]_D^{20}$, UV, IR, MS,

and chromogenic reactions agreed with published data [25]; acetyl derivative also agreed (UV, IR, MS). Rvolf 3, *pleiocarpamine*. White crystals; mp 158–160°; $[\alpha]_D^{20}+135°$ (MeOH, *c* 0.1); UV λ_{max}^{MeOH} nm: 227 (log ε 4.4), 285 (3.9); λ_{min}^{MeOH} nm: 265; IR ν_{max}^{KBr} cm^{-1}: 3450 *s*, 2950 *s*, 1730 *m*, 1670 *m*, 1580 *s*, 1500 *w*, 1460 *m*, 1420 *s*, 1260 *w*, 1200 *w*, 1120 *s*, 1040 *w*, 840 *w*, 740 *w*; MS *m/e* (rel. int.): 322 (M^+, 100), 321 (15), 307 (11), 291 (71), 263 (95), 249 (7), 246 (11), 234 (33), 232 (22), 223 (30), 218 (15), 205 (26), 194 (22), 182 (22), 181 (26), 180 (82), 167 (33), 155 (27), 140 (56), 131 (34), 125 (55), 121 (41), 108 (56); ^1H NMR ($CDCl_3$): δ 7.76–7.04 (*m*, 4H), 5.48 (*q*, 1H), 4.72 (*bd*, 1H), 4.16 (*s*, 1H), 3.88 (*s*, 1H), 3.68 (*s*, 3H), 2.52 (*s*, 2H), 1.56 (*d*, 3H), 1.28 (*s*, 1H); grey colour with $FeCl_3$–$HClO_4$ reagent, pale pink with $Ce(SO_4)_2$ reagent. Rvolf 4, *10-methoxy-pleiocarpamine*. Pale yellow amorphous powder; $[\alpha]_D^{20}-75.3°$ ($CHCl_3$, *c* 0.1); UV λ_{max}^{MeOH} nm (log ε): 230 (4.4), 283 (3.8); λ_{min}^{MeOH} nm: 263 (3.6); IR ν_{max}^{KBr} cm^{-1}: 3450 *m*, 2950 *s*, 1730 *s*, 1650 *w*, 1600 *s*, 1485 *s*, 1440 *s*, 1360 *m*, 1330 *w*, 1305 *w*, 1200 *m*, 1170 *w*, 1120 *m*, 1100 *m*, 1060 *m*, 1040 *s*, 1000 *w*, 990 *w*, 960 *w*, 940 *m*, 910 *w*, 880 *w*, 850 *m*, 830 *m*, 790 *m*, 780 *m*, 760 *w*, 740 *w*; MS *m/e* (rel. int.): 352.17735 (M^+, 100: $C_{21}H_{24}N_2O_3$ calc. as 352.178682, error 0.00133), 351 (66), 321 (11), 307 (8), 293.16494 (47: $C_{19}H_{21}N_2O$ calc. as 293.16537, error 0.00043), 271 (11), 264 (14), 262 (12), 253 (5), 244 (8), 238 (6), 212 (10), 210 (15), 198 (8), 197 (8), 186 (18), 168 (8), 167 (8), 154 (8), 146 (13), 121 (18); ^1H NMR ($CDCl_3$) δ: 7.36–6.6 (*m*, 3H), 5.45 (*q*, 1H), 4.64 (*d*, 1H), 4.12 (*s*, 1H), 3.92 (*s*, 1H), 3.8 (*s*, 3H), 3.68 (*s*, 3H), 3.48 (*bd*, 1H), 3.16 (*s*, 1H), 3.0 (*s*, 1H), 2.68 (*m*, 3H), 2.16 (*s*, 1H), 2.08 (*d*, 1H), 1.56 (*d*, 3H), 1.26 (*s*, 1H); grey colour with $FeCl_3$–$HClO_4$ reagent, yellow with $Ce(SO_4)_2$ reagent. Rvolf 5, *10-methoxy-2,7-dihydro-pleiocarpamine*. Off-white amorphous powder: UV λ_{max}^{MeOH} nm (log ε): 210 (4.47), 249 (4.06), 297 (3.48); λ_{min}^{MeOH} nm: 265; IR ν_{max}^{KBr} cm^{-1}: 3400 *s*, 2910 *s*, 2850 *w*, 1730 *s*, 1660 *m*, 1610 *s*, 1500 *w*, 1460 *s*, 1400 *w*, 1340 *w*, 1260 *w*, 1200 *m*, 1160 *s*, 1130 *m*, 1030 *s*, 820 *m*, MS *m/e* (rel. int.): 354 (M^+, 100), 339 (31), 323 (13), 295 (22), 281 (13), 263 (13), 232 (13), 224 (13), 200 (14), 180 (13), 174 (13), 173 (13), 161 (19), 160 (13); red-brown colour with $FeCl_3$–$HClO_4$ reagent; red colour with $Ce(SO_4)_2$ reagent.

Rvolf 6, *10,11-dimethoxy-N_a-methyl-picrinine* (*quaternine*). Off-white crystals; mp 153°; $[\alpha]_D^{20}-27°$ ($CHCl_3$, *c* 0.4); UV λ_{max}^{MeOH} nm: 210 (log ε 4.70), 243 (4.10), 305 (3.90); λ_{min}^{MeOH} nm: 232 (3.90); 272 (3.30); IR ν_{max}^{KBr} cm^{-1}: 3450 *m*, 2950 *s*, 1730 *s*, 1610 *m*, 1500 *s*, 1460 *m*, 1410 *w*, 1390 *w*, 1360 *w*, 1320 *w*, 1270 *w*, 1240 *m*, 1200 *m*, 1160 *m*, 1070 *s*, 1020 *s*, 990 *m*, 820 *s*, 750 *m*; MS *m/e* (rel. int.): 412.19681 (M^+, 100: $C_{23}H_{28}N_2O_5$ calc. as 412.199809, error 0.00299), 397 (20), 383 (9), 381 (5), 353 (24), 325 (8), 313.15591 (77: $C_{18}H_{21}N_2O_3$ calc. as 313.155208, error 0.00007), 276.12285 (38: $C_{15}H_{18}NO_4$ calc. as 276.123574, error 0.00072), 268 (6), 254 (6), 231 (16), 218 (7), 204 (9), 169 (9), 136 (14), 135 (12); ^1H NMR ($CDCl_3$): δ 7.24 (*s*, 1H), 7.2 (*s*, 1H), 5.32 (*q*, 1H), 4.72 (*d*, 1H), 3.8 (*s*, 3H), 3.72 (*s*, 3H), 3.6 (*s*, 3H), 2.88 (*s*, 3H), 1.44 (*d*, 3H); red-brown colour with $FeCl_3$–$HClO_4$ reagent, bright yellow colour with $Ce(SO_4)_2$ reagent.

Rvolf 7, *10,11-dimethoxy-picrinine* (*volkensine*). White needles; mp 280°; $[\alpha]_D^{20}-63.4°$ ($CHCl_3$, *c* 0.1); UV λ_{max}^{MeOH} nm (log ε): 213 (4.3), 244 (4.0), 303 (3.9); λ_{min}^{MeOH} nm: 231 (4.0), 267 (3.2); IR ν_{max}^{KBr} cm^{-1}: 3400 *m*, 2900 *s*, 1730 *s*, 1610 *m*, 1500 *s*, 1460 *s*, 1380 *w*, 1330 *m*, 1250 *w*, 1230 *w*, 1195 *m*, 1160 *s*, 1120 *s*, 1070 *m*, 1030 *m*, 1020 *m*, 1000 *m*, 870 *m*, 820 *m*; MS *m/e* (rel. int.): 398.19063 (M^+, 100: $C_{22}H_{26}N_2O_5$ calc. as 398.184159, error 0.00648), 383 (13), 381 (25), 380 (79), 365 (29), 339 (25), 321 (13), 307 (8), 299.14391 (50): $C_{17}H_{19}N_2O_3$ calc. as 299.139558, error 0.00435), 292 (13), 269 (13), 262.10674 (28: $C_{14}H_{16}NO_4$ calc. as 262.107925, error 0.00118), 254 (10), 232 (13), 217 (13), 213 (13), 204 (10), 190 (17), 136 (25), 108 (21); ^1H NMR ($CDCl_3$): δ 7.24 (*s*, 1H), 6.36 (*s*, 1H), 5.36 (*q*, 1H), 4.8 (*s*, 1H), 3.78 (*s*, 3H), 3.74 (*s*, 3H), 3.64 (*s*, 3H), 3.26 (*s*, 1H), 1.48 (*d*, 3H); MS-DIS *m/e* (rel. int.): 470 (M^+, 25) 455 (10), 398 (100), 383 (13), 380 (79), 365 (29), 339 (25), 321 (13), 307 (8), 299 (50), 292 (13), 269 (13), 262 (28), 254 (10), 232 (13), 217 (13), 213 (13), 204 (10), 190 (17); orange–yellow colour with $Ce(SO_4)_2$ reagent, red-brown with $FeCl_3$–$HClO_4$ reagent.

Rvolf 8, *10-hydroxy-akuammicine* (*sewarine*). Off-white amorphous powder; $[\alpha]_D^{20}-720°$ (EtOH, *c*, 0.1); UV λ_{max}^{MeOH} nm: 223, 292, 335; λ_{min}^{MeOH} nm: 262, 302; $\lambda_{max}^{MeOH(alkali)}$ nm: 238, 298, 354; $\lambda_{min}^{MeOH(alkali)}$ nm: 277, 313; IR ν_{max}^{KBr} cm^{-1}: 3450 *s*, 2950 *s*, 1730 *w*, 1660 *m*, 1600 *s*, 1470 *w*, 1440 *m*, 1380 *w*, 1300 *m*, 1260 *m*, 1240 *m*, 1200 *w*, 1150 *w*, 1100 *m*, 1070 *w*, 780 *w*, 750 *w*, 730 *w*; MS *m/e* (rel. int.): 338.16505 (M^+, 64: $C_{20}H_{22}N_2O_3$ calc. as 338.163032, error 0.00202), 324 (9), 322 (9), 309 (9), 307 (9), 295 (9), 279 (19), 268 (9), 265 (9), 263 (9), 250 (9), 232 (17), 222 (9), 212 (9), 199 (9), 196 (9), 182 (14), 180 (9), 172 (18), 170 (18), 169 (12), 121 (100), 107 (55), 92 (55); blue–green colour with $FeCl_3$–$HClO_4$ reagent, steel grey with $Ce(SO_4)_2$ reagent; acetyl derivative; MS *m/e* (rel. int.) 380 (55), 365 (7), 363 (3), 351 (24), 349 (7), 338 (7), 337 (7), 321 (14), 310 (7), 274 (17), 263 (7), 250 (3), 241 (7), 232 (3), 222 (7), 172 (7), 121 (100), 107 (55), 92 (50).

Rvolf 9, *10-methoxy-pleiocarpamine-N_b oxide*. Yellow amorphous powder. UV λ_{max}^{MeOH} nm: 233, 279; λ_{min}^{MeOH} nm: 258; IR ν_{max}^{KBr} cm^{-1}: 3450 *s*, 2950 *m*, 1730 *s*, 1660 *w*, 1600 *s*, 1490 *s*, 1440 *s*, 1360 *w*, 1340 *w*, 1300 *w*, 1280 *s*, 1200 *s*, 1180 *w*, 1160 *w*, 1140 *w*, 1120 *w*, 1100 *w*, 1090 *w*, 1030 *s*, 940 *w*, 930 *w*, 910 *w*, 820 *m*, 780 *w*, 760 *w*; MS *m/e* (rel. int.): 368 (M^+, 71), 352 (100), 351 (82), 337 (11), 321 (11), 310 (12), 293 (39), 291 (21), 277 (9), 271 (9), 263 (18), 250 (22), 224 (14), 210 (18), 198 (12), 197 (12), 186 (21); pale yellow colour with $Ce(SO_4)_2$ reagent, purple colour with $FeCl_3$–$HClO_4$ reagent turning grey on standing for 18 hr.

Rvolf 10, *tetrahydroalstonine-N_b-methyl*. White crystalline powder, mp 260°; $[\alpha]_D^{20}-119\pm2°$ ($.Cl^-$, H_2O, *c* 0.1); UV λ_{max}^{MeOH} nm (log ε): 225 (4.80), 279 (4.00), 290 (3.80); IR ν_{max}^{KBr} cm^{-1} 3450 *s*, 2920 *m*, 1695 *w*, 1610 *s*, 1580 *s*, 1450, *s*, 1410 *s*, 1340 *m*, 1300 *m*, 1280 *w*, 1195 *m*, 1100 *m*, 1050 *m*, 1020 *s*, 940 *m*, 750 *m*; MS *m/e* (rel. int.): 366 (M^+, 30), 365 (18), 352 (100), 351 (75), 337 (14), 329 (9), 321 (14), 307 (9), 293 (11), 279 (11), 265 (11), 249 (9), 239 (11), 225 (14), 223 (11), 209 (18), 198 (29), 184 (57), 183 (23), 156 (75), 144 (14), 130 (11); pale yellow colour with $Ce(SO_4)_2$ reagent, grey colour with $FeCl_3$–$HClO_4$ reagent. Rvolf 11, *nortetraphyllicine*. Off-white crystals; $[\alpha]_D^{20}$, UV, IR, MS, chromogenic reactions, co-TLC (6 systems) agreed with an authentic sample. Rvolf 12, *peraksine* (= *vomifoline*). Off-white amorphous powder; $[\alpha]_D^{20}$, UV, IR, MS, chromogenic reactions, co-TLC (6 systems) agreed with an authentic sample. Rvolf 13, *normacusine B*. Off-white amorphous powder; $[\alpha]_D^{20}$, UV, IR, MS, chromogenic reactions, co-TLC (6 systems) agreed with an authentic sample.

REFERENCES

1. Stapf, O. in Thiselton Dyer, W. T. (1904) *Flora of Tropical Africa* Vol. IV, p. 108. Lovell, Reeve, London.
2. Pichon, M. (1947) *Bull. Soc. Bot. Fr.*, **94**, 31.
3. Rao, A. S. (1956) *Ann. Mo. Bot. Gard.* **43**, 253.

4. Kump, W. G. and Schmid, H. (1961) *Helv. Chim. Acta*, **44**, 1503.
5. Leuzinger, F., Hesse, M. and Schmid, H. (1968) *Helv. Chim. Acta*, **51**, 1641.
6. Hesse, M., Philipsborn, W. V., Schumann, D., Spiteller, G., Spiteller-Friedmann, M., Taylor, W. I., Schmid, H. and Karrer, P. (1964) *Helv. Chim. Acta*, **47**, 878.
7. Rackhimov, D. A. (1969) *Khim. Prir. Soedin.* 521.
8. Mamatas-Kalamaras, S., Sevent, T., Thal, C. and Potier, P. (1975) *Phytochemistry* **14**, 1849.
9. Ahmad, Y., Le Quesne, P. W. and Neuss, N. (1970) *Chem. Commun.* 538.
10. Craig, J. C. and Purushothaman, K. K. (1970) *J. Org. Chem.* **35**, 71.
11. Hesse, M., Vetter, W. and Schmid, H. (1965) *Helv. Chim. Acta*, **48**, 674.
12. Iwu, M. M. and Court W. E. (1977) *Planta Med.* **32**, 88.
13. Timmins, P. and Court, W. E. (1976) *Planta Med.* **29**, 282.
14. Habib, M. S. and Court, W. E. (1974) *Planta Med.* **25**, 261.
15. Cordell, G. A. (1974) *Lloydia*, **37**, 219.
16. Iwu, M. M. and Court, W. E. (1978) *Planta Med.* **33**, 232.
17. Iwu, M. M. and Court, W. E. (1978) *Planta Med.* **33**, 360.
18. Habib, M. S. and Court, W. E. (1974) *Phytochemistry* **13**, 661.
19. Pousset, J.-L. and Poisson, J. (1965) *Ann. Pharm. Fr.* **23**, 733.
20. Scott, A. I. (1970) *Acc. Chem. Res.* **3**, 151.
21. Battersby, A. R. and Hall, E. S. (1969) *Chem. Commun.* 793.
22. Timmins, P. and Court, W. E. (1975) *Planta Med.* **27**, 105.
23. Habib, M. S. and Court, W. E. (1974) *Planta Med.* **25**, 331.
24. Timmins, P. and Court, W. E. (1975) *Planta Med.* **27**, 319,
25. Gabetta, B. and Mustich, G. (1975) *Spectral Data of Indole Alkaloids*. Inverni della Beffa, Milan.