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LEAF ALKALOIDS OF *RAUWOLFIA OREOGITON*

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Key Word Index—*Rauwolfia oreogiton*; Apocynaceae; leaf alkaloids; E-*seco* heteroyohimbine; heteroyohimbine; akuammiline; picraline; picrinine; pleiocarpamine; akuammicine; dihydroindole; sarpagan.

Abstract—Twenty-one indole alkaloids were isolated from the leaves of *Rauwolfia oreogiton* and identified. The alkaloids comprised E-*seco* heteroyohimbine, heteroyohimbine, akuammiline, akuammicine, pleiocarpamine, picraline, picrinine, dihydroindole and sarpagan types. No chemical differentiation between the leaves of *R. oreogiton* and *R. volkensii* could be established.

INTRODUCTION

The East African species *Rauwolfia oreogiton* Markgraf occurs as a shrub attaining a height of *ca* 2 m. It is indigenous to Tanzania at elevations in excess of 1200 m [1, 2]. Local enquiries in Tanzania indicated that the roots are employed in indigenous medicine in the treatment of gonorrhoea and snakebite and to increase lactation in nursing mothers [2].

As some authorities regard *R. oreogiton* as doubtfully distinct from *R. volkensii* Stapf which also occurs in East Africa and we have already investigated the alkaloids of *R. volkensii* leaves [3], the leaves of *R. oreogiton* have now been examined in order to establish whether there is any phytochemical variation supporting the botanical classification.

RESULTS

Known Apocynaceous alkaloids were identified by physical and spectroscopic analyses and by reference to published data [4] as indicated in Table 1.

For alkaloid OR3 the absence of chromogenic reaction, the UV spectrum and the UV bathochromic shift in concentrated acid medium indicated the presence of an indolenine chromophore. MS revealed β-carboline peaks at *m/e* 182, 168 and 156 and UV, IR and ^{1}H NMR evidence confirmed the absence of substitution on the *ar*-ring. MS peaks at $M^+ - 15$, $M^+ - 32$, $M^+ - 42$, $M^+ - 59$, $M^+ - 73$ and $M^+ - 91$ were consistent with the loss of Me, MeOH, CH_2CO, MeCOO, CH_2OCOMe and MeOH + MeCOO, respectively. ^{1}H NMR signals at δ3.8 (*s*, 3H) and 1.56 (*s*, 3H) confirmed the MeCOO and OCOMe protons, respectively. Evidence of an exocyclic ethylidene side-chain was given by NMR signals at δ 5.52 (*q*, 1H) and 1.64 (*d*, 3H). It was also concluded that the MS peak at *m/e* 279 ($M^+ - 145$) probably represented the loss of a C-16 bridge atom with attached substituents (MeCOO·CH·CH_2·OCOMe). The IR spectrum showed OH absorption (3400 cm^{-1}) and that from an unconjugated ester (1740 cm^{-1}). On acetylation an amorphous monoacetyl derivative (MW 466) was formed.

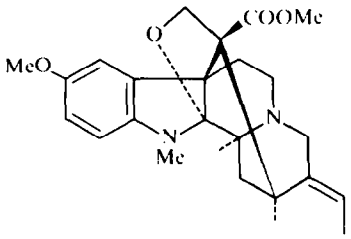
The general MS fragmentation pattern resembled that of akuammiline [5]. The loss of a MeOH and the presence

Table 1. Identification of known Apocynaceous alkaloids

Compound	Identity	Formula	Analytical methods
OR 1	geissoschizine	**9**	$[\alpha]_D$, UV, IR, MS, co-TLC
OR 2	aricine	**18**	$[\alpha]_D$, UV, IR, MS, co-TLC
OR 5	akuammiline	**2**	$[\alpha]_D$, UV, IR, MS
OR 7	picrinine	**11**	$[\alpha]_D$, UV, IR, MS, co-TLC
OR 8	quaternine	**13**	$[\alpha]_D$, UV, IR, MS, co-TLC
OR 10	10-methoxyakuammine	**1**	mp, $[\alpha]_D$, UV, IR, MS
OR 11	picraline	**10**	mp, $[\alpha]_D$, UV, IR, MS
OR 13	pleiocarpamine	**7**	$[\alpha]_D$, UV, IR, MS, co-TLC
OR 14	volkensine	**12**	mp, $[\alpha]_D$, UV, IR, MS, co-TLC
OR 16	akuammicine	**16**	$[\alpha]_D$, UV, IR, MS, co-TLC
OR 17	sewerine	**17**	$[\alpha]_D$, UV, IR, MS, co-TLC
OR 18	10-methoxypleiocarpamine	**8**	$[\alpha]_D$, UV, IR, MS, NMR, co-TLC
OR 19	nortetraphyllicine	**19**	$[\alpha]_D$, UV, IR, MS, NMR, co-TLC
OR 20	peraksine	**14**	$[\alpha]_D$, UV, IR, MS, co-TLC
OR 21	normacusine B	**15**	$[\alpha]_D$, UV, IR, MS, co-TLC

of β-carboline peaks at *m/e* 182, 168 and 156 are characteristic of tetrahydro-β-carboline compounds with substituents at the C-5 position [6,7]. $M^+ - 32$ must therefore be CH_2OH + H, the loss of the substituent at C-5 being usually accompanied by expulsion of a hydrogen ion [8]. This is probably due to the N_b-nitrogen atom having the ability to stabilize positive charges and, on electron impact, substituents at adjacent positions are released with an accompanying hydrogen atom and an iminium ion is formed [9]. The ^1H NMR signal at δ 3.2 (s, 2 H) confirmed the CH_2OH substituent at C-5 and it was therefore concluded that OR 3 was 5-hydroxymethyl-akuammiline (**4**).

The UV spectrum and chromogenic reactions of OR4 indicated a dihydroindole chromophore. Strong IR carbonyl absorption at 1740 cm^{-1} was observed but no OH absorption was found. Attempted methylation and acetylation proved unsuccessful. The NMR spectrum



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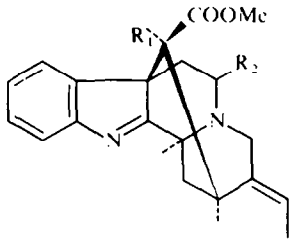
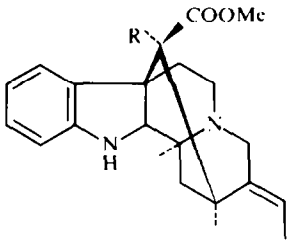
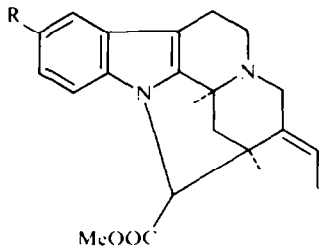


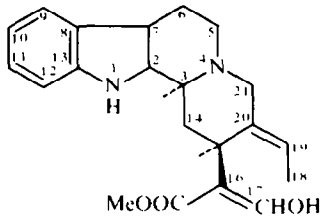
2 R_1 = $AcOCH_2$; R_2 = H
3 R_1 = $HOCH_2$; R_2 = H
4 R_1 = $AcOCH_2$, R_2 = CH_2OH



5 R = $AcOCH_2$
6 R = $HOCH_2$



7 R = H
8 R = MeO



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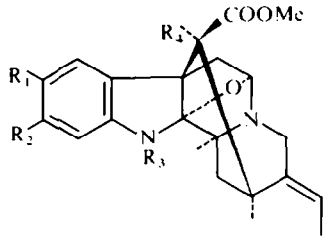
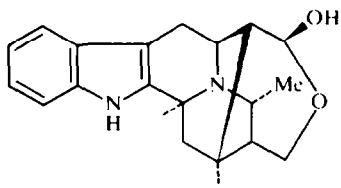


10 R_1 = R_2 = R_3 = H; R_4 = $AcOCH_2$
11 R_1 = R_2 = R_3 = R_4 = H
12 R_1 = R_2 = MeO, R_3 = R_4 = H
13 R_1 = R_2 = MeO, R_3 = Me; R_4 = H



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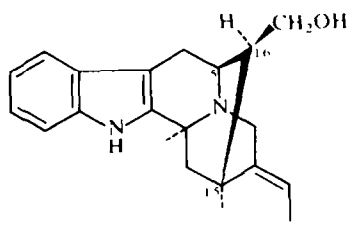

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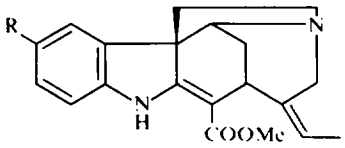
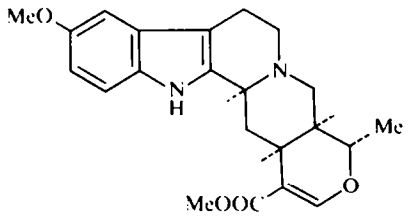


16 R = H
17 R = MeO



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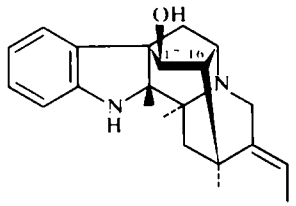

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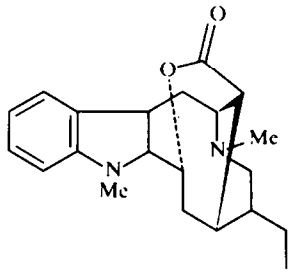

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revealed an ethyl side-chain (δ 1.28, *d*, 2H, C-19; δ 1.0, *t*, 3H, C-18), two aliphatic N-Me groups (δ 2.76, *s*, 3H; δ 2.72, *s*, 3H) and non-substitution of the *ar*-ring (δ 7.4-6.72, *m*, 4H). The MS fragmentation pattern resembled that of acyl indole alkaloids, indole peaks at *m/e* 158 and 144 confirming N_a-Me substitution. Peaks at *m/e* 182, 168, 138 and 122 corresponded in intensity to peaks at *m/e* 196, 182, 152 and 122 in tabernaemontanine [10]. The prominent $M^+ - 28$ peak is characteristic of a ketone group expelled from a ring system [11]. As OR 4 is not a quaternary base, the C-3–N_b bond must be absent and the C-16 COOH group is probably bonded to C-3. Therefore, the formula **20** is proposed for OR 4.

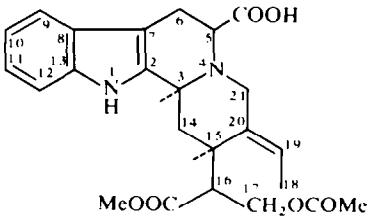
The UV spectrum of OR 6 indicated an indolenine chromophore and the IR spectrum revealed a broad OH band at 3350 cm^{-1}. In general the IR, MS and ^{1}H NMR spectra resembled those of akuammiline. The MS, however, showed a M^+ 42 amu less than that of akuammiline and the NMR spectrum lacked the Me proton signal corresponding to the acetate group. A signal (δ 2.96, *d*, 2H) suggesting a CH_2OH substituent was observed. Therefore, it was concluded that OR 6 was deacetylakuammiline (**3**) [12]. The acetyl derivative was prepared and found to be identical with akuammiline (mp, mmp, UV, IR, MS, ^{1}H NMR).

The UV spectrum and chromogenic reactions of OR 9 indicated a dihydroindole chromophore and the MS fragmentation pattern resembled that of akuammiline although the M^+ was 2 amu greater. The ^{1}H NMR spectrum showed an NH proton signal at δ 7.88 and MS revealed distinct indole peaks at *m/e* 144 and 130, the relative intensities of which suggested a C-2-Hβ dihydroindole [11]. OR 9 was identified as 2β-dihydroakuammiline (**5**). Catalytic hydrogenation of akuammiline (10% Pd on alumina, pH 10, 12 hr) yielded an identical compound (UV, IR, MS, co-TLC).

Spectral data for OR 12 closely resembled that of deacetylakuammiline (OR 6). MS, however, showed a M^+ at *m/e* 354, 2 amu greater than that for deacetylakuammiline. UV and chromogenic data indicated the presence of a dihydroindole chromophore and MS showed distinct indole peaks at *m/e* 144, 143 and 130. Catalytic hydrogenation of deacetylakuammiline (10% Pd on alumina, pH 10, 12 hr) yielded an identical compound (mmp, UV, IR, MS, ^{1}H NMR). Therefore, OR 12 was identified as deacetyl-1,2β-dihydroakuammiline (**6**).

The UV spectrum of OR 15 was typically indolic with a well-defined minimum at 252 nm. The chromogenic reaction and MS pattern suggested an E-*seco* indole structure. MS peaks at $M^+ - 31$, $M^+ - 46$, $M^+ - 59$ and $M^+ - 73$ probably represented the loss of MeO, COOH + H, COOMe and CH_2OCOMe fragments, respectively. As β-carboline peaks occurred at *m/e* 182, 168 and 156 instead of *m/e* 184, 170 and 156 as in the common E-*seco* indoles, C-5 substitution was probable. That a COOH group was attached at C-5 is evident from the loss on electron impact of 46 amu from the M^+. This is attributable to the loss of COOH + H [7], analogous peaks being observed in the MS of adirubine and 5-carboxytetrahydroalstonine [7, 8]. The IR spectrum revealed OH (3400 cm^{-1}), NH (2950 cm^{-1}) and carbonyl ester (1740 cm^{-1}) groups. Bohlmann IR bands occurred at 2800 and 2760 cm^{-1} indicating a *cis* relationship between H-3 and H-15 and confirming the C-15 H α orientation. As geissoschizine, aricine and akuammiline co-occur with OR 15, it is probable that C-3 H is also α-oriented.

The MS peak at *m/e* 250 probably represents the M^+ less the substituents at C-5 (COOH) and C-16 ($MeCOO{\cdot}CH{\cdot}CH_2{\cdot}OCOMe$). Thus OR 15 closely resembles adirubine acetate [7] but the M^+ is 2 amu less. The iminium ion of adirubine acetate (*m/e* 396) can be represented by *m/e* 394 in OR 15, the ethyl substituent being replaced by an ethylidene side-chain at C-20. ^{1}H NMR examination was unsatisfactory but trace alkaloid OR 15 has been provisionally identified as 19,20-dehydroadirubine acetate (**21**).



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DISCUSSION

Thirteen indole alkaloids were obtained from a 3 kg sample of *R. volkensii* leaves [3] and 21 indole alkaloids have now been isolated from 6 kg *R. oreogiton* leaves. The general distribution of the alkaloids is similar for both species, the akuammiline (**2–6**) and picraline (**10–13**) bases predominating.

Although the main groups of alkaloids detected in *Rauwolfia* roots conform to the biosynthetic progression from E-*seco* indole (e.g. geissoschizine, **9**) to sarpagan (e.g. normacusine B, **15**) and dihydroindole (e.g. nortetraphyllicine, **19**) with accompanying heteroyohimbine (e.g. tetrahydroalstonine, aricine **18**) and yohimbine (e.g. α-yohimbine), such compounds occur in small quantities only in the leaves.

The function of the picraline bases is not understood but it is plausible that pleiocarpamine (**7–8**), akuammiline (**2–6**) and picraline (**10–13**) bases are a reserve of compounds readily reverting to E-*seco* indole bases for further synthesis via the sarpagan route. This suggestion could account for large amounts of volkensine (10,11-dimethoxypicrinine, **12**) in the leaves only and large amounts of reserpiline (10,11-dimethoxytetrahydroalstonine) in the stems and roots [13, 14]. We were unable, however, to detect any dimethoxyakuammilines or dimethoxygeissoschizine but it is probable that such compounds would be rapidly removed from the biosynthetic pool. Peraksine (**14**) and the akuammicine bases (**16, 17**), occurring in small quantities only, may be by-products of the biosynthetic cycle although 10-methoxyakuammine (**1**) and OR 4 (**20**), also occurring in small amounts, are less likely to be end-products.

Although the total alkaloidal yield of *R. oreogiton* leaves (0.015%) was lower than for *R. volkensii* leaves (0.027%) [3] and the volkensine yield was markedly lower (0.0017% as opposed to 0.02%), no variation in the alkaloid pattern could be found which would enable differentiation of the two species. Further work is proceeding in order to establish whether other *Rauwolfia* species yield akuammiline and picraline type bases in their aerial parts.

Taxonomic note

The African species of the section *Ophioxylanthus* (*R. oreogiton* and *R. volkensii*) are differentiated from other African *Rauwolfia* species by the presence of short, thick stamen filaments [15]. Confusion regarding the identities of *R. volkensii* and *R. oreogiton* resulted in the assumption by silviculturists that the species were synonymous or dubiously distinct (R. L. Willan, private communication). Subsequently it was shown that typically *R. volkensii* possessed corollas 24–30 mm long with stamens somewhat below the middle of the corolla tube, whilst *R. oreogiton* revealed corollas 16–23 mm long and stamens somewhat above the middle of the corolla tube [16]. *R. volkensii* is confined to the region around Mount Kilimanjaro and the Pare Mountains of Tanzania and material from East and West Usambaras is considered to be *R. oreogiton* [7].

EXPERIMENTAL

Leaves of *R. oreogiton* were collected in April 1970 in the Mkussu Forest Reserve, West Usambaras, Tanzania. Voucher specimens reference number RAU 106-701 are lodged with the Pharmaceutical Society of Great Britain Collection of Materia Medica and Herbaria, University of Bradford, U.K.

Analytical methods used for TLC, UV, IR, ^{1}H NMR, MS and fluorescence and chromogenic tests have been described earlier [17–19].

Extraction. Powdered leaves (6 kg) were extracted by the method described earlier for *R. volkensii* leaves [3] yielding 15 g crude weak base fraction, 8.5 g crude intermediate base fraction and 5.2 g crude strong base fraction.

Separation. The weak base fraction fractionated by column chromatography as described earlier [3] yielded fractions 1–6. Fraction 1 yielded 3 alkaloids, OR 1 (4 mg), OR 2 (8 mg) and OR 3 (10 mg), when separated on Si gel layers using Me_2CO–petrol–CCl_4–*iso*-octane (7:6:4:3) solvent system. OR 4 (50 mg) crystallized from a MeOH soln of fraction 2 and separation of the supernatant soln using the system Et_2O–MeOH (9:1) yielded OR 5 (100 mg) and OR 6 (50 mg). OR 10 (100 mg) crystallized from a MeOH soln of fraction 3 and separation of the supernatant soln by TLC using the system EtOAc–*iso*-PrOH–NH_3 (16:3:1) provided OR 7 (5 mg), OR 8 (15 mg) and OR 9 (100 mg). Fraction 4, similarly treated, yielded OR 11 (150 mg), OR 12 (120 mg), OR 13 (5 mg) and OR 14 (100 mg). Fraction 5 produced OR 15 (5 mg), OR 16 (10 mg) and OR 17 (10 mg) on separation using the system Et_2O–MeOH (1:1). Fraction 6 yielded OR 18 (30 mg) when separated in the system $CHCl_3$–MeOH–petrol (8:1:1). The intermediate and strong base fractions were combined and on separation by TLC on Si gel using the system EtOAc–*iso*-PrOH–NH_3 (17:3:1) gave OR 19 (10 mg), OR 20 (10 mg) and OR 21 (20 mg).

Identification of alkaloids. Known *Rauwolfia* alkaloids were identified as indicated in Table 1. *OR* 3, *5-hydroxymethylakuammiline*, off-white amorphous powder; $[\alpha]_D^{21} - 141°$ (MeOH); UV λ_{max}^{MeOH} nm (log ε): 223 (4.20), 265 (3.73); λ_{min}^{MeOH} nm: 248 (3.72); $\lambda_{max}^{MeOH+HCl}$ nm: 229, 283; $\lambda_{max}^{MeOH-HCl}$ nm: 225; IR ν_{max}^{KBr} cm^{-1}: 3400 *m*, 2925 *m*, 1740 *s*, 1620 *w*, 1600 *w*, 1440 *m*, 1360 *w*, 1240 *s*, 1120 *m*, 1080 *m*, 750 *m*; MS *m/e* (rel. int. %): 424 (80), 409 (50), 392 (20), 382 (20), 367 (25), 365 (30), 351 (100), 333(60), 292 (20), 279 (20), 260 (20), 247 (35), 232 (25), 218 (20), 206 (20), 194 (25), 182 (30), 168 (30), 156 (25); ^{1}H NMR ($CDCl_3$): δ 7.80–7.12 (*m*, 4 H), 5.52 (*q*, 1 H), 4.48 (*s*, 1 H), 4.08 (*s*, 1 H), 3.80 (*s*, 3 H), 3.48 (*s*, 2 H), 3.20 (*s*, 2 H), 3.00 (*s*, 1 H), 2.36 (*s*, 1 H), 2.16 (*s*, 1 H), 1.96 (*d*, 1 H), 1.64 (*d*, 3 H), 1.56 (*s*, 3 H), 1.24 (*s*, 1 H); no reaction with $FeCl_3$–$HClO_4$ or $Ce(SO_4)_2$ reagents.

OR 4, white crystals; mp 180–181°; UV λ_{max}^{MeOH} nm (log ε): 214 (4.23), 249 (4.00), 284 (3.67); λ_{min}^{MeOH} nm (log ε): 234 (3.91), 273 (3.54); IR ν_{max}^{KBr} cm^{-1}: 3400 *w*, 3150 *w*, 2950 *s*, 2850 *s*, 1740 *s*, 1610 *m*, 1480 *s*, 1450 *s*, 1420 *w*, 1390 *w*, 1380 *m*, 1360 *m*, 1330 *w*, 1120 *m*, 1070 *m*, 1020 *w*, 940 *m*, 790 *w*, 740 *s*; MS *m/e* (rel. int., %): 340 (10), 312 (16), 295 (1), 282 (3), 267 (7), 255 (22), 239 (9), 224 (40), 210 (4), 199 (16), 196 (18), 182 (21), 168 (100), 158 (54), 144 (78), 138 (57), 131 (13), 122 (13), 108 (15), 96 (33), 94 (89); ^{1}H NMR ($CDCl_3$): δ 7.4–6.72 (*m*, 4 H), 3.92 (*s*, 1 H), 3.72 (*br. d*, 3 H), 3.44 (*s*, 1 H), 3.36 (*s*, 1 H), 2.76 (*s*, 3 H), 2.72 (*s*, 3 H), 2.64 (*s*, 1 H), 2.52 (*s*, 1 H), 1.84 (*s*, 1 H), 1.72 (*s*, 1 H), 1.56 (*dd*, 3 H), 1.28 (*d*, 2 H), 1.0 (*t*, 3 H);

chromogenic reactions, instant red colour with $FeCl_3$ $HClO_4$ and $Ce(SO_4)_2$ reagents.

OR 6, *deacetylakuammiline*, pale yellow amorphous powder; $[\alpha]_D^{21}$ + 19.7° (MeOH); UV λ_{max}^{MeOH} nm (log ε): 222 (4.25), 267 (3.76); λ_{min}^{MeOH} nm (log ε): 247 (3.70); IR ν_{max}^{KBr} cm^{-1}: 3350 *s*, 2950 *s*, 1730 *s*, 1660 *m*, 1620 *w*, 1600 *m*, 1440 *s*, 1230 *s*, 1100 *m*, 1070 *m*, 960 *w*, 920 *w*, 840 *m*, 780 *m*, 750 *s*; MS *m/e* (rel. int., %): 352 (100), 335 (11), 321 (95), 307 (5), 293 (23), 261 (14), 249 (18), 232 (18), 206 (14), 194 (14), 180 (23), 170 (18), 168 (23), 156 (16); ^1H NMR ($CDCl_3$): δ 7.84–7.24 (*m*, 4 H), 5.56 (*q*, 1 H), 4.24 (*s*, 1 H), 4.12 (*s*, 1 H), 3.9 (*s*, 3 H), 3.76 (*dd*, 1 H), 3.28 (*s*, 1 H), 3.08 (*s*, 1 H), 2.96 (*d*, 2 H), 2.68 (*s*, 1 H), 2.56 (*s*, 1 H), 2.36 (*m*, 1 H), 2.0 (*s*, 1 H), 1.64 (*d*, 3 H), 1.28 (*s*, 1 H); no colour reaction with $FeCl_3$–$HClO_4$ or $Ce(SO_4)_2$ reagents.

OR 9,1,2β-*dihydro-akuammiline*, off-white amorphous powder; $[\alpha]_D^{21}$ − 9.4° (MeOH); UV λ_{max}^{MeOH} nm (log ε): 213 (4.19), 244 (3.89), 303 (3.52); λ_{min}^{MeOH} nm (log ε), 227 (3.68), 268 (3.00); IR ν_{max}^{KBr} 3400 *m*, 2950 *s*, 1740 *s*, 1600 *m*, 1580 *m*, 1470 *m*, 1380 *m*, 1200 *m*, 1120 *m*, 1040 *m*, 990 *m*, 920 *w*, 890 *w*, 800 *w*, 780 *m*, 740 *s*; MS *m/e* (rel. int., %): 396 (100), 381 (35), 369 (4), 354 (4), 337 (35), 323 (4), 321 (4), 277 (4), 263 (4), 251 (4), 235 (4), 221 (4), 194 (4), 182 (9), 168 (17), 156 (13), 144 (13), 130 (13); ^1H NMR ($CDCl_3$): δ 7.88 (*d*, 1 H), 7.24–6.52 (*m*, 4 H), 5.58 (*q*, 1 H), 4.92 (*d*, 1 H), 4.12 (*s*, 1H), 4.0 (*s*, 1 H), 3.84 (*s*, 3 H), 3.8 (*s*, 1 H), 3.58 (*s*, 1 H), 3.36 (*s*, 1 H), 3.12 (*s*, 1 H), 2.96 (*s*, 1 H), 2.08 (*s*, 3 H), 1.8 (*d*, 3 H), 1.28 (*s*, 1 H); a red colour was obtained with $FeCl_3$–$HClO_4$ and $Ce(SO_4)_2$ reagents.

OR 12,*deacetyl*-1,2β-*dihydro-akuammiline*, white crystals: mp 228–230°; $[\alpha]_D^{21}$ +99° (MeOH); UV λ_{max}^{MeOH} nm (log ε): 210 (4.04), 244 (3.58), 302 (3.23); λ_{min}^{MeOH} nm (log ε): 227 (3.56), 267 (2.90); IR ν_{max}^{KBr} cm^{-1}: 3450 *s*, 2950 *s*, 2850 *w*, 1720 *s*, 1600 *m*, 1460 *s*, 1440 *s*, 1210 *s*, 1110 *m*, 1040 *m*, 920 *w*, 800 *w*, 740 *s*; MS *m/e* (rel. int., %): 354 (100), 339 (34), 323 (8), 295 (9), 277 (3), 263 (6), 251 (9), 235 (8), 221 (5), 206 (5), 194 (5), 182 (5), 168 (13), 167 (9), 156 (9), 144 (6), 143 (6), 130 (9); ^1H NMR ($CDCl_3$): δ 7.6–6.6 (*m*, 4 H), 5.56 (*q*, 1 H), 4.25 (*s*, 1 H), 4.12 (*s*, 1 H), 3.8 (*s*, 3 H), 3.76 (*dd*, 1 H), 3.28 (*s*, 1 H), 3.08 (*s*, 1 H), 2.96 (*d*, 2 H), 2.68 (*s*, 1 H), 2.56 (*s*, 1 H), 2.36 (*m*, 1 H), 2.0 (*s*, 1 H), 1.64 (*d*, 3 H), 1.28 (*s*, 1 H); red colour with $FeCl_3$–$HClO_4$ and $Ce(SO_4)_2$ reagents.

OR 15, off-white amorphous powder: UV λ_{max}^{MeOH} nm (log ε): 227 (4.40), 285 (3.80), 291 (3.82); λ_{min}^{MeOH} nm (log ε): 252 (3.00); IR ν_{max}^{KBr} cm^{-1}: 3400 *s*, 2950 *m*, 2800 *w*, 2760 *w*, 1740 *s*, 1620 *w*, 1600 *w*, 1440 *m*, 1360 *w*, 1240 *s*, 1120 *m*, 1080 *m*, 740 *s*; MS *m/e* (rel. int., %): 440 (67), 426 (44), 409 (44), 394 (56), 383 (78), 381 (33), 367 (33), 352 (56), 337 (56), 325 (44), 305 (44), 292 (33), 277 (44), 262 (44), 250 (67), 234 (100), 222 (56), 206 (56), 204 (44), 194 (67), 183 (67), 182 (56), 168 (67), 167 (65), 156 (78), 144 (56); grey-brown colour turning green on heating with $FeCl_3$ $HClO_4$ reagent.

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