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ESTERS OF QUINOLIZIDINE ALKALOIDS FROM THE GENUS *PEARSONIA*

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Key Word Index—*Pearsonia cajanifolia* subsp. *cryptantha*; *P. sessilifolia* subsp. *marginata*; Leguminosae; cajanifoline; cryptanthine; 3β-hydroxylupanine; pearsonine; sessilifoline; chemotaxonomy.

Abstract—Alkaloidal extracts of two species from the genus *Pearsonia* yielded several quinolizidine alkaloids. Amongst these were four new esters of hydroxylated lupanines, cajanifoline (3β-hydroxylupanine-13α-*O*-angelate), sessilifoline (3β-hydroxylupanine-4α-*O*-angelate), pearsonine (3β,8α-dihydroxylupanine-13α-*O*-angelate) and cryptanthine (8α-hydroxylupanine-13α-*O*-angelate). The correct structure for a hydroxylated lupanine (previously believed to be nuttalline), namely 3β-hydroxylupanine, is reported.

INTRODUCTION

In our systematic studies of the tribe Crotalarieae, (Fabaceae, subfamily Papilionoideae) we have found alkaloids to be useful generic characters in determining relationships amongst 14 genera of the tribe [1–6]. Pyrrolizidine alkaloids occur in *Lotononis*, *Buchenroedera* [2, 7] and *Crotalaria* [8], while piperidyl alkaloids were found as major constituents in the alkaloidal extracts of *Dichilus* [5] and as minor constituents in several other genera. Quinolizidine alkaloids occur in practically all genera of the Crotalarieae; esters of quinolizidines were only reported from the genus *Rothia* [9]. We have recently investigated the major alkaloids of the genus *Pearsonia* [10]. Quinolizidine alkaloids such as sparteine, lupanine (**1**), α-isolupanine, nuttalline (**2**) and a piperidyl alkaloid, ammodendrine, were amongst the major components in six species and subspecies of *Pearsonia*. Interestingly, esters of hydroxylated lupanines were also found in significant quantities in all of the specimens investigated. Lupanine-13α-*O*-angelate (**3**), a known ester from *Cadia purpurea* and *Calpurnia aurea* [11] was isolated from *Pearsonia* as well as three new esters of higher oxidized lupanines, cajanifoline (3β-hydroxylupanine-13α-*O*-angelate) (**4**), sessilifoline (3β-hydroxylupanine-4α-*O*-angelate) (**5**) and pearsonine (3β,8α-dihydroxy-lupanine-13α-*O*-angelate) (**6**). Continued investigation of *Pearsonia* revealed yet another unknown ester, namely 8α-hydroxylupanine-13α-*O*-angelate (cryptanthine) (**7**). The structural elucidation of these novel esters is reported in this paper. The identity of a product, previously believed to be nuttalline [10], seemed doubtful in view of the biosynthetic relationship of the hydroxylated lupanines; structural analysis of this compound, using various NMR experiments, showed that the compound was in fact 3β-hydroxylupanine (**8**).

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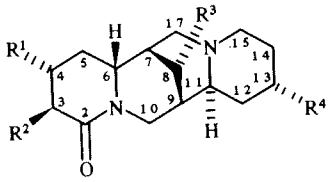
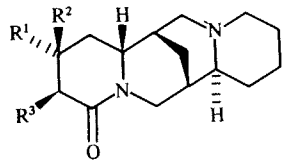
RESULTS AND DISCUSSION

Details on the plant material used as well as procedures for the extraction and isolation of the new esters from the various species of *Pearsonia* have been reported elsewhere [10]. The alkaloids included in this study were isolated from *P. cajanifolia* subsp. *cryptantha* and *P. sessilifolia* subsp. *marginata*. The mass spectrum of the least polar compound (**3**) from *P. cajanifolia* subsp. *cryptantha* showed a weak $[M]^+$ *m/z* 346 and a base peak *m/z* 246. It was evident from the fragmentation pattern that the molecule consisted of a substituted lupanine skeleton and the ^{1}H NMR spectrum showed the presence of an angeloyl moiety. Van Eijk and Radema [11] reported the ^{1}H NMR spectrum of a mixture of the angelic and tiglic acid esters of 13α-hydroxylupanine (**3** and **9**) which were isolated from *Calpurnia aurea* and this spectrum correlated closely with that of the ester isolated from *Pearsonia*. We do, however, differ from the authors in the interpretation of the ^{1}H NMR data. In the spectrum of the ester from *Pearsonia*, the olefinic proton of the angeloyl moiety showed a quartet of quartets at δ6.0 with $J = 7.2$ and 1.4 Hz for the vicinal and allylic couplings, respectively. H-13, centred at δ5.1, showed a narrow quintet with coupling constants in the order of 2.8 hz which is in accordance with a β-orientation for H-13 and dihedral angles of *ca* 60° with all neighbouring protons. The chemical shifts of these two protons were reported incorrectly for the angelate-tiglate esters of 13α-hydroxylupanine [11]. The ^{13}C NMR spectrum (for chemical shifts see Table 1) was virtually identical to that reported by Hussain *et al.* [9] for the same product from species of the genus *Rothia*. Mass spectral data reported for **3** by other workers [12, 13] complemented our assignment of the structure. This compound, on the basis of its mass spectrum and ^{1}H and ^{13}C NMR spectra (Table 1), represents only the *Z*-isomer, lupanine-13α-*O*-angelate (**3**).

The mass spectrum of the second compound isolated from *P. cajanifolia* subsp. *cryptantha* (**4**) had a base peak

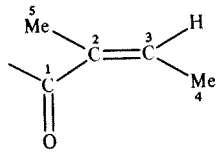


	R^1	R^2	R^3	R^4
1	H	H	H	H
3	H	H	H	OAng
4	H	OH	H	OAng
6	H	OH	OH	OAng
7	H	H	OH	OAng
8	H	OH	H	H
9	H	H	H	OTig
10	H	H	H	OH
11	H	OH	H	OH
12	OH	OH	H	H



	R^1	R^2	R^3
2	H	OH	H
5	OAng	H	OH

Ang =



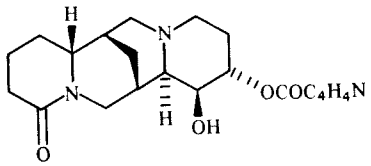


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Table 1. Comparison of ^{13}C chemical shifts of alkaloids isolated from *Pearsonia* with other hydroxylated lupanines

C	3	4	5	6	7	8	10*	11*	12†
2	170.9 *s*	173.8 *s*	171.5 *s*	173.7 *s*	171.0 *s*	173.6 *s*	170.9 *s*	173.8 *s*	171.5 *s*
3	32.9 *t*	67.7 *d*	70.9 *d*	67.9 *d*	32.7 *t*	67.9 *d*	32.9 *t*	68.2 *d*	73.8 *d*
4	19.6 *t*	24.3 *t*	70.3 *t*	24.6 *t*	19.7 *t*	24.4 *t*	19.6 *t*	26.3 *t*	68.4 *d*
5	26.5 *t*	26.1 *t*	26.3 *t*	27.5 *t*	27.6 *t*	26.2 *t*	26.6 *t*	24.5 *t*	26.6 *t*
6	60.6 *d*	61.2 *d*	57.8 *d*	60.4 *d*	59.3 *d*	61.5 *d*	60.8 *d*	61.6 *d*	58.2 *d*
7	34.0 *d*	33.5 *d*	34.0 *d*	40.9 *d*	41.0 *d*	34.4 *d*	34.2 *d*	33.9 *d*	34.3 *d*
8	27.4 *t*	27.2 *t*	32.5 *t*	72.7 *d*	72.9 *d*	27.1 *t*	27.3 *t*	27.4 *t*	33.0 *t*
9	32.2 *d*	32.2 *d*	31.7 *d*	39.2 *t*	39.2 *d*	32.1 *d*	31.6 *d*	39.2 *d*	32.0 *d*
10	46.6 *t*	49.7 *t*	48.3 *t*	45.1 *t*	45.1 *t*	47.7 *t*	46.8 *t*	47.8 *t*	48.3 *t*
11	57.9 *d*	57.8 *d*	64.1 *d*	58.1 *d*	57.6 *d*	64.0 *d*	57.0 *d*	57.3 *d*	64.0 *d*
12	36.4 *t*	35.8 *t*	30.2 *t*	38.9 *t*	38.9 *t*	33.2 *t*	39.9 *t*	39.6 *t*	31.7 *t*
13	67.7 *d*	67.9 *d*	24.4 *t*	66.6 *d*	66.5 *d*	24.2 *t*	64.0 *d*	64.3 *d*	24.8 *t*
14	28.8 *t*	28.3 *t*	24.3 *t*	29.7 *t*	29.6 *t*	25.0 *t*	32.4 *t*	31.5 *t*	24.5 *t*
15	49.8 *t*	47.8 *t*	55.4 *t*	49.6 *t*	49.3 *t*	55.3 *t*	49.2 *t*	49.3 *t*	55.3 *t*
17	52.0 *t*	51.7 *t*	52.1 *t*	52.4 *t*	52.1 *t*	52.7 *t*	52.4 *t*	52.3 *t*	52.6 *t*
1′	167.4 *s*	167.3 *s*	167.8 *s*	167.2 *s*	167.1 *s*	—	—	—	—
2′	128.2 *s*	128.1 *s*	127.8 *s*	128.0 *s*	127.9 *s*	—	—	—	—
3′	137.6 *d*	137.5 *d*	139.2 *d*	137.7 *d*	137.7 *d*	—	—	—	—
4′	16.0 *q*	15.9 *q*	15.5 *q*	16.0 *q*	15.8 *q*	—	—	—	—
5′	20.8 *q*	20.7 *q*	20.1 *q*	20.8 *q*	20.6 *q*	—	—	—	—

*Data from ref. [16].
†Data from ref. [6].

with *m/z* 262 as the first significant fragmentation from the $[M]^+$ (*m/z* 362). A molecular mass 16 mass units higher than that of lupanine-13α-*O*-angelate (**3**) and a similar fragmentation pattern, indicated the presence of a free hydroxyl group in a tetracyclic lupanine skeleton closely related to **3**. It was essential to establish the nature and position of the ester moiety as well as the position of the hydroxyl group in the molecule. Standard ^1H and

^{13}C NMR spectra were recorded for the compound and DEPT, COSY and HETCOR experiments were commissioned and used in the determination of the structure of the molecule. In the ^{1}H NMR spectrum of the compound, a broad singlet (δ4.65), exchangeable with D_2O, confirmed the presence of a free hydroxyl group in the molecule. Of special interest was the quartet of quartets centred at δ6.04. This signal, together with a three-proton quintet at δ1.86 and a three-proton doublet of quartets at δ1.95, indicated a 2-methyl-(*Z*)-but-2-enoyl (angeloyl) moiety as the ester functionality in the molecule. No trace of the *E*-isomer (tigloyl) was found in the proton spectrum. The position of the ester group was disclosed by the presence of a narrow quintet at δ5.13, very similar in nature to the H-13 signal of **3**. In the COSY spectrum, this proton showed spin interaction with protons in the crowded upfield region (δ1.61–1.86) where the methylene proton resonances occurred. In the HETCOR spectrum of the compound, this low field proton signal showed spin–spin interaction with a carbon resonance at δ67.9. The chemical shift of this carbon resonance (a doublet in the DEPT spectrum) is quite similar to the chemical shift of the C-13 signal of **3** and is *ca* 1 ppm downfield from the corresponding carbon signal in the ^{13}C NMR spectrum of 13α-hydroxylupanine (**10**) [14]. The position of the ester moiety is therefore at C-13, identical to the ester position of **3**.

The presence of another doublet in the ^{13}C NMR region of **4**, where carbon atoms which are directly substituted with oxygen show resonance, indicated the carbinol carbon atom. In the HETCOR spectrum, this carbon resonance (δ67.7) showed coupling with a proton signal at δ3.96. The position of the hydroxyl group could be deduced from the coupling constants of this doublet of doublets. The stronger coupling constant represented a vicinal *trans* diaxial relationship with a neighbouring proton whereas the medium strength coupling constant ($J = 5.58$ Hz) may result from spin interaction with a *vicinal* equatorial proton of a neighbouring methylene group. The absence of any other coupling suggested that the carbinol moiety lay between a methylene group and a quarternary carbon atom. The only possible position of such nature in the tetracyclic skeleton is C-3 which is adjacent to the carbonyl group of the lactam ring. It was also possible to deduce the relative stereochemistry of C-3 from the coupling constants. For a β-orientated hydroxyl group, the α-orientated proton is *trans* diaxially and *cis* axial–equatorially orientated with respect to H-4β and H-4α, respectively. Inspection of a Dreiding model of the proposed structure showed that this orientation is possible even for the half-chair conformation of the lactam ring which is evident from X-ray structural analysis of lupanine derivatives [15]. The inverted stereochemistry, that is an α-orientation for H-3, would result in the H-3/H-4α and H-3/H-4β dihedral angles being nearly equal and therefore equivalent values for the two coupling constants of H-3. A similar molecule, 3β,13α-dihydroxylupanine (**11**) [16], showed the same multiplicity and coupling constants for the proton signal of the C-3 carbinol group. Removal of the ester moiety of **4** with aqueous sodium hydroxide in methanol gave the diol (**11**). The ^{13}C NMR spectrum of this product was identical to that reported for 3β,13α-dihydroxylupanine (**11**) (Table 1) from *Cytisus scoparius* [16] and confirmed the proposed regio- and stereochemistry for the carbinol moiety. The spectral evidence indicated that cajanifoline (**4**) has the structure of 3β-hydroxylupanine-13α-*O*-angelate {(*Z*)-2-methyl-2-butenoic acid [2*S*-(2α,7β,7aβ,10β,14β,14aα)]dodecahydro-10-hydroxy-11-oxo-7,14-methano-2H,6H-dipyrido[1,2-*a*:1′,2′-*e*][1,5]diazocin-2-yl-ester}.

The ^{1}H NMR spectrum of compound (**6**) from the alkaloidal extract with the lowest mobility on TLC was strikingly similar to that of cajanifoline (**4**). A new signal in the medium field region (δ3.61) suggested further substitution of the molecule. This concept was confirmed by the mass spectrum which showed a $[M]^+$ *m/z* 378, 16 mass units higher than that of **4**. These data indicated the presence of a second free hydroxyl group in the molecule in addition to the 3β-hydroxy group evident from the doublet of doublets at δ4.0 (as in the spectrum of **4**). Irradiation of the triplet at δ3.61 resulted in coagulation of a multiplet at δ2.27 and one in the crowded upfield region (δ1.6–1.9) of the spectrum. The lack of any decay in the other carbinol proton signal at δ4.0 upon the decoupling of the signal at δ3.61, eliminated the possibility of a vicinal dihydroxylated lupanine as it is found in some other polyhydroxylated lupanines [17, 18]. From the decoupling experiments it was not possible to deduce the position of the second hydroxyl group unambiguously. The multiplicity of H-10eq, however, gave an undisputable indication of the position of the second hydroxyl group as well as the relative stereochemistry at the carbinol carbon atom.

In practically all the quinolizidine alkaloids the H-10eq (H-10α) signal occurs in the medium field region (*ca* δ4.30) and shows strong geminal coupling ($J = 13.6$ Hz) with H-10ax and weak coupling with H-9 ($J = 1.95$ Hz). In addition to these spin–spin interactions, H-10eq shows a weak coupling ($J = 1.95$ Hz) with H-8eq in the spectra of similar molecules such as **1**, **8** and **3**. This coupling arises from long range spin interaction due to the *W*-conformation [19] for the H-8eq/C-8/C-9/C-10/H-10eq fragment of the molecule. This spin correlation is also clearly evident in the COSY spectrum of **4**. However, in the case of this molecule, H-10eq is only a doublet of doublets and lacks one of the fine couplings. Furthermore, the signal for H-8ax (present in the spectrum of **4** at δ1.27), is absent in the spectrum of this molecule. C-7 and C-9 in the ^{13}C NMR spectrum are both shifted downfield by *ca* 6 ppm compared to the chemical shifts of the corresponding carbon atoms in related structures (see Table 1). The position of the free hydroxyl group is therefore believed to be equatorial (or α) on C-8 as indicated by the above-mentioned NMR data. The structure assigned to this compound, pearsonine (**6**), is 3β,8α-dihydroxylupanine-13α-*O*-angelate {(*Z*)-2-methyl-2-butenoic acid [2*S*-(2α,7β,7aβ,10β,14β,14aα)]-dodecahydro-10-hydroxy-11-oxo-7,14-α-hydroxymethano-2H,6H-dipyrido[1,2-*a*:1′,2′-*e*] [1,5]diazocin-2-yl-ester}.

A compound of special interest was the third ester isolated from *P. cajanifolia* subsp. *cryptantha*. This alkaloid (**5**), which was first isolated from *P. sessilifolia* subsp. *marginata*, occurs only in trace amounts in *P. cajanifolia* subsp. *cryptantha*. Material could be isolated in ample quantities from *P. sessilifolia* subsp. *marginata* for the recording of spectroscopic data. The mass spectrum of this compound had a $[M]^+$ *m/z* 362 which showed that it is an isomer of **4**. Unlike **4** and **6** which have base peaks of *m/z* 262, this molecule has a base peak *m/z* 263. This difference in the fragmentation pattern suggested that the molecule may contain an α-hydroxy ester moiety. The

loss of a fragment of *m/z* 100, as in the case of **4** and **6**, can be explained in terms of a single hydrogen transfer during a McLafferty rearrangement [20] to liberate an angelic acid fragment from the $[M]^+$. The loss of a fragment of *m/z* 99 (angeloyloxy moiety) in this compound pointed to a different mechanism of fragmentation, probably the formation of a radical cation stabilized by the presence of an adjacent hydroxyl group to form a protonated oxirane radical ion. A similar fragmentation pattern was reported for 13-(2′-pyrrolylcarboxyl)calpurmenine (**13**) [21], a quinolizidine alkaloid from *Calpurnia aurea* subsp. *sylvatica*, which has an α-hydroxy ester substitution in the D-ring. Despite the mass spectral data, it was essential to use NMR spectrocopy to establish the exact position of the two functional groups in the compound. We have recently isolated lebeckianine (3β,4α-dihydroxylupanine) (**12**) from the genus *Lebeckia* [6]. The ^{1}H NMR spectrum of the new ester was somewhat reminiscent of the structure of lebeckianine. Surprisingly, compound **5** also proved to be an angelate ester. Chemical shifts for protons of the ester moiety are virtually identical to the corresponding values for **3**, **4** and **6** and no trace of the *E*-isomer was found in the ^{1}H NMR spectrum. In comparing the ^{1}H NMR spectra of this product and **12**, the following similarities were used to determine the structure of the molecule. The H-4 multiplet centred at δ3.69 in the proton spectrum of **12** was shifted to δ5.0 in the spectrum of the new compound. Irradiation of this multiplet resulted in the doublet at δ4.14 to coagulate to a singlet. This doublet at δ3.83 represents H-3 in the spectrum of **12**. The mutual coupling of these two protons, together with the significant downfield shift of the eight line multiplet and the slight deshielding experienced by H-3 proved that C-4 is esterified. Other protons in the medium field regions of the two molecules compared favourably as did the ^{13}C NMR spectra of the two compounds (Table 1). The structure of this ester, sessilifoline (**5**), was therefore assigned as 3β-hydroxylupanine-4α-*O*-angelate {(*Z*)-2-methyl-2-butenoic acid [2*R*-(2α,3β,7β,7aα,14β,14aβ)]-dodecahydro-3-hydroxy-4-oxo-7,14-methano-4H,6H-dipyrido[1,2-*a*:1′,2′-*e*] [1,5]diazocin-2-yl-ester}.

The final ester (**7**) isolated from *P. cajanifolia* subsp. *cryptantha*, was detected in the crude alkaloidal extract by eluting the TLC with 10% MeOH in EtOAc. This product has the same R_f value as sessilifoline in our standard eluent ($CHCl_3$–C_6H_{12}–$HNEt_2$ 4:5:1) but was slightly more mobile in the above-mentioned eluent. Mass spectral analysis of the compound showed that it is a structural isomer of **4** and **5**. Comparison of the ^{1}H NMR spectrum of the novel compound and those of the other esters was indicative of the structure of the compound. The only difference between the spectra of this compound and **6** is the absence of the H-3 in the medium field region and slight differences in the crowded upfield region. The free hydroxyl group is on the 8α-position as indicated by the narrow triplet at δ3.55 and the absence of the *W*-conformation coupling ($J_{8eq,10eq}$) in the H-10eq doublet centred at δ4.45. An α-orientation for H-13 was evident from the narrow quintet at δ5.04. The chemical shifts of the carbon atoms in the ^{13}C NMR spectrum were virtually identical to those of **6** except for C-3 which was strongly shifted to the aliphatic region (see Table 1). All the spectroscopic data support the 8α-hydroxylupanine-13α-*O*-angelate structure as that of cryptanthine (**7**) {(*Z*)-2-methyl-2-butenoic acid [2*S*-(2α,7β,7aβ,14β,14aα)]-dodecahydro-11-oxo-7,14-α-hydroxymethano-2H,6H-dipyrido[1,2-*a*: 1′,2′-*e*] [1,5]diazocin-2-yl-ester}.

The presence of esters of higher oxidized lupanines in *Pearsonia* is of special taxonomic significance. The only other genus in the tribe Crotalarieae known to produce esters of lupanine is *Rothia* [9]. Not only does this indicate a close taxonomic relationship between *Pearsonia* and *Rothia*, but it also serves to support the concept of *Pearsonia* as a unique genus for two reasons. The esters that were found are all angelates; no traces of tiglic acid esters were detected in any of the species included in this study. Secondly, the four new esters isolated from *Pearsonia* are all of higher oxidized lupanines; such compounds have previously only been reported from the genus *Calpurnia* [17, 21].

The similarity in the position of hydroxyl groups in **4**–**6** suggests a biosynthetic relationship between these compounds. These three new esters all have hydroxyl groups on the 3β-position. Should the alkaloids from this genus be biosynthetically related, it posed the question whether the hydroxylupanine, previously identified as nuttalline (**2**) on the basis of its mass spectrum and ^{13}C NMR spectrum [10], was in fact 3β-hydroxylupanine. It was decided to reinvestigate this alkaloid to either confirm its structure as that of **2** or to show that it may be biosynthetically related to the other quinolizidine alkaloids present in the genus. The alkaloid was isolated from *P. sessilifolia* in a small quantity. In order to obtain more material for structural elucidation purposes, an extract was made of *Lebeckia melilotoides* (for voucher specimen see ref. [6]) which provided ample quantities of alkaloid. Comparison of the hydroxylupanines isolated from the two different plant species showed that they were in all respects (physical and spectroscopical) identical. Analysis of the ^{1}H, ^{13}C NMR, COSY, DEPT, HETCOR and COLOC spectra of the compound indeed showed that it was not 4β-hydroxylupanine (nuttalline) (**2**) but 3β-hydroxylupanine (**8**) {[3*S*-(3β,7β,7aα,14β,14aβ)]-dodecahydro-3-hydroxy-7,14-methano-4H,6H-dipyrido-[1,2-*a*:1′,2′-*e*] [1, 5]diazocin-4-one}. The carbinol proton, with a chemical shift of δ3.91, showed two couplings, $J = 11.45$ and 5.62 Hz. As in the case of **4** and **6**, these data support a 3β-position for the free hydroxyl group. In the COSY spectrum, this proton signal shows correlation with only two other signals, both in the upfield region (*ca* δ1.60). The ^{13}C NMR spectra of **4**–**6**, **8** and **11** [16] were compared and the resonances of the carbon atoms of the hydroxylated lactam ring were quite similar for the different compounds. The spectroscopical evidence showed that the position of the hydroxyl group is 3β and not 4α. Gerrans and Nattrass [22] earlier reported the isolation of **2** from *Lebeckia plukenetiana*. These authors verified the structure of the compound by direct comparison of the mass spectrum and IR spectrum with those of an authentic sample of nuttalline from *Lupinus nuttallii* [23]. In spite of the absolute identical spectra of the two products, the melting points were significantly different (108–109° for **2** from *Lupinus nuttallii* [23] and 64–65° for **2** from *Lebeckia plukenetiana* [22]), whereas the melting point of **8** is 94–94.5°. We have earlier investigated the major alkaloids of the genus *Lebeckia* [6] and the product now correctly identified as 3β-hydroxylupanine was a major component in the alkaloidal content of all species investigated. Interestingly, the IR spectrum of **8** is significantly similar to the IR data reported for **2** from *L. nuttallii* [23]. Our results render the findings concerning the

alkaloid from *Lebeckia plukenetiana* doubtful; in addition it leaves the true structure of nuttalline open for speculation. We could not find any direct evidence in the form of ^{1}H and ^{13}C NMR data for nuttalline in the literature for comparison with our own data even though **2** was recently reported from other species of *Lupinus* [24, 25].

The position of the hydroxyl group in **8** is an indication of the probable biosynthetic relationship between 3β-hydroxylupanine and the esters **3**–**5**. Interestingly, four of the esters from *Pearsonia* have the ester moiety attached to the C-13 position. This position seems to be the favoured position for esterification among derivatives of lupanine as is also the case in other quinolizidine alkaloid ester derivatives [9, 11, 15, 17, 26]. In the case of *Pearsonia*, further hydroxylation of the skeleton occurs preferentially at C-3, followed by hydroxylation at C-8. One of the esters, namely sessilifoline (**5**), has the ester moiety at quite an unexpected position; the position of the free hydroxyl group does, however, appeal to a biogenetic relationship with the other esters. The fact that *Pearsonia* specializes in the production of only angelate esters, together with the higher oxidation of the lupanine derivatives, suggests an evolutionary advanced status for this genus.

EXPERIMENTAL

Mps: uncorr. IR spectra were recorded for thin films of $CHCl_3$ solns. Optical rotations were measured for a pathlength of 1 cm in the solvents stated for each sample. ^{1}H and ^{13}C NMR spectra were recorded at 200 or 500 MHz and 50 or 125 MHz, respectively, in $CDCl_3$ using the $CHCl_3$ signal (δ7.24) as ref. TLC was performed on silica gel plates with a 0.25 mm layer thickness using $CHCl_3$–C_6H_{12}–$HNEt_2$ (4:5:1) or 10% MeOH in EtOAc. Chromatograms were visualized by spraying with iodoplatinate solution. CC using Kieselgel 60 as adsorbent was used to purify the different compounds. Further details on extraction and isolation are reported elsewhere [10].

Lupanine-13α-O-angelate (**3**). $[\alpha]_D^{25}$ +32° ($CHCl_3$; *c* 3.2); ^{1}H NMR (200 MHz, $CDCl_3$): δ6.01 (1H, *dd*, $J_{3',4'}$ = 7.35 and $J_{3',5'}$ = 1.44 Hz, H-3′), 5.11 (1H, *quin*, $J_{12,13} = J_{13,14}$ = 2.81 Hz, H-13), 4.30 (1H, *dt*, $J_{8eq,10eq} = J_{9,10eq}$ = 2.20 and $J_{10ax,10eq}$ = 13.32 Hz, H-10eq), 3.26 (1H, *m*, H-6), 2.85 (1H, *dd*, $J_{7,17eq}$ = 10.41 and $J_{17ax,17eq}$ = 12.30 Hz, H-17eq), 2.58 (1H, *ddd*, $J_{14ax,15eq}$ = 2.27, $J_{14eq,15eq}$ = 4.27 and $J_{15ax,15eq}$ = 12.40 Hz, H-15eq), 2.49 (1H, *dd*, $J_{9,10ax}$ = 2.75 and $J_{10ax,10eq}$ = 13.32 Hz, H-10ax), 2.40–2.00 (5H, *m*, H-7, H-8eq, H-11, H-15ax and H-17ax), 1.93 (3H, *dq*, $J_{3',4'}$ = 7.35 and $J_{4',5'}$ = 1.47 Hz, 3 × H-4′), 1.85 (3H, *dq*, $J_{3',5'}$ = 1.44 and $J_{4',5'}$ = 1.47 Hz, 3 × H-5′), 1.80–1.47 (11H, *m*, 2 × H-3, 2 × H-4, 2 × H-5, H-9, 2 × H-12, 2 × H-14), 1.25 (1H, *dt*, $J_{7,8ax} = J_{8ax,9}$ = 2.39 and $J_{8ax,8eq}$ = 12.26 Hz, H-8ax); EIMS (probe) 70 eV *m/z* (rel. int.): 346 $[M]^+$ (10), 246 $[M-C_5H_8O_2]^+$ (100), 148 (17), 134 (35) (for full spectrum see ref. [12] and [13]).

Cajanifoline (**4**). Mp 87–91°; $[\alpha]_D^{22}$ −11° ($CHCl_3$; *c* 1.4); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 *br* (OH), 1705 (ester C=O), 1640 (lactam C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ6.04 (1H, *qq*, $J_{3',4'}$ = 7.22 and $J_{3',5'}$ = 1.43 Hz, H-3′), 5.13 (1H, *quin*, $J_{12,13} = J_{13,14}$ = 2.80 Hz, H-13), 4.65 (1H, *br s*, OH), 4.26 (1H, *dt*, $J_{8eq,10eq} = J_{9,10eq}$ = 2.15 and $J_{10ax,10eq}$ = 13.39 Hz, H-10eq), 3.96 (1H, *dd*, $J_{3,4ax}$ = 11.36 and $J_{3,4eq}$ = 5.58 Hz, H-3), 3.33 (1H, *ddd*, $J_{5ax,6}$ = 10.55, $J_{5eq,6}$ = 5.07 and $J_{6,7}$ = 1.70 Hz, H-6), 2.91 (1H, *dd*, $J_{7,17eq}$ = 9.24 and $J_{17ax,17eq}$ = 11.58 Hz, H-17eq), 2.65 (1H, *dd*, $J_{9,10ax}$ = 2.54 and $J_{10ax,10eq}$ = 13.39 Hz, H-10ax), 2.60 (1H, *ddd*, $J_{14ax,15eq}$ = 1.89, $J_{14eq,15eq}$ = 4.57 and $J_{15ax,15eq}$ = 12.54, H-15eq), 2.35 (1H, *dt*, $J_{14ax,15ax} = J_{15ax,15eq}$ = 12.54 and $J_{14eq,15ax}$ = 2.61 Hz, H-15ax), 2.21 (1H, *m*, H-4eq), 2.12 (2H, *m*, H-8 and H-11), 2.04 (1H, *dd*, $J_{7,17ax}$ = 3.75 and $J_{17ax,17eq}$ = 11.58 Hz, H-17ax), 1.99 (1H, *m*, H-7), 1.95 (3H, *dq*, $J_{3',4'}$ = 7.22 and $J_{4',5'}$ = 1.43 Hz, 3 × H-4′), 1.86 (3H, *quin*, $J_{3',4'} = J_{4',5'}$ = 1.43 Hz, 3 × H-22), 1.86–1.61 (7H, *m*, 2 × H-5, H-4ax, 2 × H-12 and 2 × H-14), 1.59 (1H, *m*, H-9), 1.27 (1H, *dt*, $J_{7,8ax} = J_{8ax,9}$ = 2.29 and $J_{8ax,8eq}$ = 12.52 Hz, H-8ax); EIMS (probe) (70 eV [10] *m/z* (rel. int.): 362 $[M]^+$ (5), 277 (7), 262 $[M-C_5H_8O_2]^+$ (100), 246 (23), 234 (7), 205 (3), 186 (9), 165 (7), 148 (24), 134 (60), 122 (23), 108 (15), 91 (57), 69 (23), 55 (39).

Hydrolysis. Cajanifoline (**4**) (7 mg) was dissolved in MeOH (1 ml) and stirred for 2 hr at 70° in the presence of 0.2 M NaOH. After evapn of solvent, the residue was dissolved in CH_2Cl_2 and neutralized with HOAc. The crude alkaloid was extracted with CH_2Cl_2 and purified by silica gel CC to afford 4 mg of **11**. The ^{13}C NMR spectrum of this product was identical to the data reported for 3β,13α-dihydroxylupanine (**11**) [16].

Sessilifoline (**5**). $[\alpha]_D^{22}$ −72° ($CHCl_3$; *c* 1.6); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 *br* (OH), 1709 (ester C=O), 1640 (lactam C=O); ^{1}H NMR (200 MHz, $CDCl_3$): δ6.09 (1H, *qq*, $J_{3',4'}$ = 7.24 and $J_{3',5'}$ = 1.41 Hz, H-3′), 5.00 (1H, *ddd*, $J_{3,4}$ = 10.07, $J_{4,5ax}$ = 11.93 and $J_{4,5eq}$ = 4.14 Hz, H-4), 4.24 (1H, *dt*, $J_{8eq,10eq} = J_{9,10eq}$ = 1.95 and $J_{10ax,10eq}$ = 13.43 Hz, H-10eq), 4.14 (1H, *d*, $J_{3,4}$ = 10.07 Hz, H-3), 3.70 (1H, *br s*, OH), 3.44 (1H, *dd*, $J_{5ax,6}$ = 11.72 and $J_{5eq,6}$ = 4.95 Hz, H-6), 2.96 (1H, *dd*, $J_{7,17eq}$ = 10.20 and $J_{17ax,17eq}$ = 11.83 Hz, H-17eq), 2.83 (1H, *m*, H-15eq), 2.71 (1H, *dd*, $J_{9,10ax}$ = 2.24 and $J_{10ax,10eq}$ = 13.43 Hz, H-10ax), 2.36 (1H, *m*, H-8eq), 2.23 (1H, *ddd*, $J_{4,5eq}$ = 4.14, $J_{5ax,5eq}$ = 13.19 and $J_{5eq,6}$ = 4.95 Hz, H-5eq), 2.07 (1H, *m*, H-5ax), 1.99 (3H, *dq*, $J_{3',4'}$ = 7.24 and $J_{4',5'}$ = 1.47 Hz, 3 × H-4′), 1.89 (3H, *dq*, $J_{3',5'}$ = 1.41 and $J_{4',5'}$ = 1.47 Hz, 3 × H-22), 1.75–1.40 (11H, *m*, H-7, H-9, H-11, H-17ax, 2 × H-12, 2 × H-13, 2 × H-14 and H-15ax), 1.38 (1H, *m*, H-8ax); EIMS (probe) 70 eV [10] *m/z* (rel. int.): 362 $[M]^+$ (20), 279 $[M-C_5H_7O]^+$ (4), 263 $[M-C_5H_7O_2]^+$ (100), 245 (60), 233 (3), 221 (2), 205 (3), 191 (1), 177 (3), 163 (6), 148 (27), 136 (54), 122 (8), 110 (17), 98 (31), 84 (23), 67 (11), 55 (43).

Pearsonine (**6**). Mp 93–96°; $[\alpha]_D^{22}$ +7° ($CHCl_3$; *c* 0.6); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 *br* (OH), 1710 (ester C=O), 1640 (lactam C=O); ^{1}H NMR (200 MHz, $CDCl_3$): δ6.06 (1H, *qq*, $J_{3',4'}$ = 7.20 and $J_{3',5'}$ = 1.43 Hz, H-3′), 5.11 (1H, *quin*, $J_{12,13} = J_{13,14}$ = 2.83 Hz, H-13), 4.30 (1H, *dd*, $J_{9,10eq}$ = 2.97 and $J_{10ax,10eq}$ = 13.63 Hz, H-10eq), 4.00 (1H, *dd*, $J_{3,4ax}$ = 11.14 and $J_{3,4eq}$ = 5.28 Hz, H-3), 3.77 (1H, *br s*, OH), 3.61 (1H, *t*, $J_{7,8} = J_{8,9}$ = 2.93 Hz, H-8), 3.32 (1H, *m*, H-6), 2.99 (1H, *dd*, $J_{7,17eq}$ = 10.50 and $J_{17ax,17eq}$ = 11.67 Hz, H-17eq), 2.67 (1H, *ddd*, $J_{14a,15eq}$ = 3.96, $J_{14b,15eq}$ = 2.88 and $J_{15ax,15eq}$ = 11.47 Hz, H-15eq), 2.59 (1H, *dd*, $J_{9,10ax}$ = 2.50 and $J_{10ax,10eq}$ = 13.63 Hz, H-10ax), 2.27 (2H, *m*, H-5eq and H-7), 2.14 (1H, *m*, H-15ax), 2.13 (1H, *dd*, $J_{7,17ax}$ = 2.27 and $J_{17ax,17eq}$ = 11.67 Hz, H-17ax), 1.96 (3H, *dq*, $J_{3',4'}$ = 7.27 and $J_{4',5'}$ = 1.55 Hz, 3 × H-4′), 1.86 (3H, *dq*, $J_{3',5'}$ = 1.43 and $J_{4',5'}$ = 1.55 Hz, 3 × H-22), 1.96–1.59, (8H, *m*, 2 × H-3, 2 × H-4, H-9, H-11, 2 × H-12 and 2 × H-14); EIMS (probe) 70 eV [10] *m/z* (rel. int.): 378 $[M]^+$ (25), 363 $[M-Me]^+$ (9), 298 $[M-C_5H_7O]^+$ (6), 278 $[M-C_5H_8O_2]^+$ (100), 262 (29), 246 (12), 206 (6), 193 (5), 183 (19), 164 (15), 150 (28), 134 (24), 108 (18), 96 (20), 82 (31), 67 (21), 55 (42).

Cryptanthine (**7**). Mp 108–110°; $[\alpha]_D^{23}$ +117° ($CHCl_3$; *c* 1.4); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 *br* (OH), 1710 (ester C=O), 1640 (lactam C=O); ^{1}H NMR (200 MHz, $CDCl_3$): δ5.99 (1H, *qq*, $J_{3',4'}$ = 7.22 and $J_{3',5'}$ = 1.42 Hz, H-3′), 5.04 (1H, *quin*, $J_{12,13} = J_{13,14}$ = 2.78 Hz, H-13), 4.45 (1H, *dd*, $J_{9,10eq}$ = 2.96 and $J_{10ax,10eq}$ = 13.82 Hz, H-10eq), 4.0 (1H, *br s*, OH), 3.55 (1H, *t*, $J_{7,8} = J_{8,9}$ = 2.84 Hz, H-8), 3.22 (1H, *ddd*, $J_{5ax,6}$ = 10.53, $J_{5eq,6}$ = 4.47 and $J_{6,7}$ = 1.21 Hz, H-6), 2.81 (1H, *dd*, $J_{7,17eq}$ = 10.56 and $J_{17ax,17eq}$ = 11.42 Hz, H-17eq), 2.59 (1H, *dt*, $J_{14ax,15eq} = J_{14eq,15eq}$ = 3.57 and $J_{15ax,15eq}$ = 11.45 Hz, H-15eq), 2.40 (1H, *dd*, $J_{9,10ax}$ = 2.26 and $J_{10ax,10eq}$ = 13.82 Hz, H-10ax), 2.30–2.05 (4H, *m*, H-7, H-11, H-15ax and H-17ax), 1.90 (3H, *dq*, $J_{3',4'}$ = 7.27 and $J_{4',5'}$

= 1.49 Hz, 3 × H-4'), 1.81 (3H, *dq*, $J_{3',5'}$ = 1.42 and $J_{4',5'}$ = 1.49 Hz, 3 × H-22), 2.0–1.30 (11H, *m*, 2 × H-3, 2 × H-4, 2 × H-5, 2 × H-12, 2 × H-14 and H-9). EIMS (probe) 70 eV *m/z* (rel. int.): 362 $[M]^+$ (10), 282 (4), 262 (100), 247 (9), 235 (9), 223 (4), 205 (4), 194 (2), 182 (3), 164 (13), 150 (31), 147 (27), 134 (15), 123 (12), 112 (37), 108 (19), 98 (22), 96 (18), 82 (22), 67 (14), 55 (76).

3β-Hydroxylupanine (**8**). Mp 94–94.5°; $[\alpha]_D^{20}$ 0° (EtOH; *c* 2.1); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3479 *br*, 2813, 2769, 1633, 1012; ^1H NMR (500 MHz, $CDCl_3$): δ4.19 (1H, *dt*, $J_{8eq,10eq} = J_{9,10eq}$ = 2.33 and $J_{10ax,10eq}$ = 13.26 Hz, H-10eq), 3.91 (1H, *dd*, $J_{3,4ax}$ = 11.45 and $J_{3,4eq}$ = 5.59 Hz, H-3), 3.90 (1H, *br s*, OH), 3.23 (1H, *ddd*, $J_{5ax,6}$ = 10.45, $J_{5eq,6}$ = 5.18 and $J_{6,7}$ = 1.33 Hz, H-6), 2.75 (1H, *dd*, $J_{7,17eq}$ = 10.15 and $J_{17ax,17eq}$ = 11.75 Hz, H-17eq), 2.64 (1H, *m*, H-15eq), 2.53 (1H, *dd*, $J_{9,10ax}$ = 2.75 and $J_{10ax,10eq}$ = 13.26 Hz, H-10ax), 2.13–2.04 (3H, *m*, H-5eq, H-8 and H-9), 1.93 (1H, *m*, H-7), 1.79 (1H, *dd*, $J_{7,17ax}$ = 3.90 and $J_{17ax,17eq}$ = 11.75 Hz, H-17ax), 1.80–1.10 (11H, *m*, 2 × H-4, H-5ax, H-8ax, H-11, 2 × H-12, 2 × H-14 and H-15ax); EIMS (probe) 70 eV *m/z* (rel. int.): 264 $[M^+]$ (97), 247 (38), 235 (14), 218 (7), 206 (5), 191 (8), 179 (10), 165 (15), 150 (61), 136 (100), 134 (61), 122 (30), 110 (33), 98 (53), 84 (43), 69 (27), 55 (41).

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