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AZAFLUORENONES FROM *OXANDRA* cf. *MAJOR* AND BIOGENETIC CONSIDERATIONS*

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Key Word Index—*Oxandra* cf. *major*; Annonaceae; alkaloids; azafluorenones; darienine; macondine; ursuline; biogenesis.

Abstract—The stem bark of *Oxandra* cf. *major*, which contains large amounts of 7,7′-bisdehydroaporphine alkaloids, has also yielded three commonplace steroids, reticuline, four known aporphinoids and the new azafluorenones darienine, macondine and ursuline. Three biogenetic hypotheses are discussed in the light of the structures of the azafluorenones found to date in the Annonaceae.

INTRODUCTION

The genus *Oxandra* (Annonaceae) consists of about 25 species of trees and shrubs, native to tropical America and the West Indies [1–3]. Fries [1] and Hutchinson [2] place it in the primitive, pantropical tribe Uvarieae, although they differ as to some of its relationships to other genera, while Walker [3] includes it in his almost exclusively New World *Malmea* tribe, largely on the basis of its primitive pollen morphology. The chemistry of this genus is almost unknown. An earlier analysis of Colombian material classified provisionally as *O.* cf. *major* Fries led to the isolation of three new 7,7′-bisaporphines [4], and the only other study of which we are aware is a very recent description of three new azafluorenones from the stem bark and twigs of *O. xylopioides* [5]. This paper deals with the isolation and structure elucidation of the alkaloids of *O.* cf. *major* stem bark, especially of the three azafluorenones found in this material, and discusses alternative biogenetic schemes attempting to explain the origin of the latter type of compound.

RESULTS

The petrol extract of the stem bark of *O.* cf. *major*, in addition to rather large amounts of the new 7,7′-bisaporphines urabaine and its *N*-methyl and *N,N′*-dimethyl derivatives [4], provided the probably ubiquitous sitosterol, sitostenone and stigmast-4-en-3-one. The basic fraction (0.1%) of the methylene chloride extract of the dry plant material, made alkaline with ammonia, afforded reticuline, the noraporphines nornuciferine (the monomeric unit of urabaine) and anonaine, the corresponding oxoaporphines lysicamine and liriodenine, additional small quantities of the bisaporphines isolated from the petrol extract, and three minor alkaloids named darienine (**1**), macondine (**2**) and ursuline. These results are summarized in Table 1.

The molecular formula of darienine (**1**), deduced from the HREIMS of its *O*-acetyl derivative, is $C_{15}H_{13}NO_4$. The presence of a carbonyl group in the darienine molecule was indicated by an IR band at 1708 cm^{-1}. Its UV spectrum exhibited several absorption maxima in the same regions as onychine (1-methyl-4-azafluoren-9-one, **3**) [6, 7]; these underwent bathochromic shifts on adding base and also, to a much lesser extent, upon acidification, raising the possibility that darienine might be a phenolic derivative of onychine. The ^1H NMR spectrum of darienine (Table 2) indicated the presence of a methyl group bonded to an aromatic ring, two methoxyl groups, an AB pair of hydrogen atoms assignable to the α- and β-positions of a pyridine ring and a third, uncoupled

Table 1. Alkaloids isolated from the trunk bark of *Oxandra* cf. *major*

Type	Name	% Yield*
Benzylisoquinoline	reticuline	1
Noraporphine	nornuciferine	0.5
	anonaine	0.5
7,7′-*bis*-Dehydroaporphine	urabaine [4]	31†
	N-methylurabaine [4]	30†
	N,N′-dimethylurabaine [4]	27†
Oxoaporphine	lysicamine	5
	liriodenine	2.5
Azafluorenone	darienine (**1**)	1.2
	macondine (**2**)	0.8
	ursuline	0.1

*As percentage of total alkaloids.
†Alkaloids isolated from the petrol and CH_2Cl_2 extracts.

*Part 80 in the series 'Alcaloïdes des Annonacées'. For part 79, see [16].

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Table 2. ^{1}H NMR chemical shifts of azafluorenones from *Oxandra* cf. *major* ($CDCl_3$)*

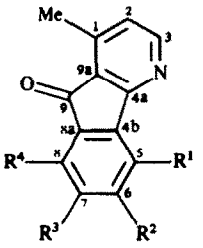
H	1†	1a‡	1b†	2†	2a†	2b†
2	6.85 *d* (5.4)	6.93 *d* (6.0)	6.85 *d* (6.0)	6.89 *d* (5.3)	6.96 *d* (5.3)	6.90 *d* (6.0)
3	8.40 *d*	8.47 *d*	8.42 *d*	8.35 *d*	8.44 *d*	8.36 *d*
5	—	—	—	7.47 *d* (7.9)	7.58 *d* (7.9)	7.53 *d* (7.5)
6	—	—	—	7.08 *d*	7.25 *d*	7.04 *d*
8	7.11 *s*	7.20 *s*	7.10 *s*	—	—	—
1-CMe	2.59 *s*	2.60 *s*	2.60 *s*	2.60 *s*	2.64 *s*	2.64 *s*
5-OMe	4.07 *s*	4.07 *s*	4.08 *s*	—	—	—
6-OMe	4.07 *s*	3.99 *s*	3.95 *s*§	—	—	—
7-OMe	—	—	3.98 *s*§	—	—	3.95 *s*
8-OMe	—	—	—	4.22 *s*	4.14 *s*	4.12 *s*
7-OAc	—	2.35 *s*	—	—	2.36 *s*	—

*J (Hz) in parentheses.
†250 MHz.
‡90 MHz.
§Assignments may be interchanged.

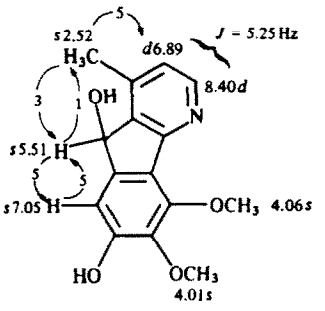
aromatic ring hydrogen. Proof of the phenolic character of darienine was obtained by preparation of the *O*-acetyl (**1a**) and *O*-methyl (**1b**) derivatives.

Comparison of the ^{1}H NMR spectra of darienine (**1**) and its *O*-acetyl derivative (**1a**) indicated a downfield acetylation shift of the lone aromatic ring proton resonance, while one of the methoxyl groups appeared to be shielded by the ester function, strongly suggesting that the phenol group is located between the lone hydrogen atom and a methoxyl [8]. Borohydride reduction of darienine afforded a dihydro derivative (**1c**). NOEDS of this compound (Fig. 1) showed reciprocal positive NOE's between the proton geminal to the alcoholic hydroxyl group (H-9) on the one hand and the *C*-methyl and the isolated aromatic ring protons on the other. The NOE's between H-9 and the *C*-methyl protons can be taken as a demonstration that darienine possesses the heterocyclic skeleton of onychine proved by synthesis (3) [7], and not the 4-methyl-1-aza-fluoren-9-one ring system proposed originally [6]. Irradiation at the resonance frequency of the *C*-methyl group also led to an enhancement of the pyridine β-proton signal, while the methoxyl groups exhibited no NOE's at all. We therefore propose the structure of 5,6-dimethoxy-7-hydroxy-1-methyl-4-aza-fluoren-9-one (8,9-dimethoxy-7-hydroxy-4-methyl-5*H*-indeno[1,2-*b*]pyridine-5-one, **1**) for darienine. A simpler, semisystematic name is 5,6-dimethoxy-7-hydroxyonychine.

The EIMS of macondine indicated the molecular formula $C_{14}H_{11}NO_3$. Its IR spectrum presented an intense absorption at 1706 cm^{-1}, and its UV spectra in neutral, acid and basic solution were almost identical to those of darienine. Its ^{1}H NMR spectrum (Table 2) exhibited the same 4-methyl-2,3-disubstituted pyridine pattern as darienine, a single methoxyl resonance at the unusually large chemical shift of 4.22 ppm, and two *ortho*-coupled benzene ring proton doublets. It thus seemed that macondine must be a close analogue of darienine, but with one methoxyl group instead of two. Acetylation afforded an *O*-acetyl derivative (**2a**) in which both benzene ring protons were deshielded to different degrees and the methoxyl group was shielded [8], showing that a phenol function lies between the methoxyl and one of the



1 $R^1 = R^2 = OMe$, $R^3 = OH$, $R^4 = H$
1a $R^1 = R^2 = OMe$, $R^3 = OAc$, $R^4 = H$
1b $R^1 = R^2 = R^3 = OMe$, $R^4 = H$
2 $R^1 = R^2 = H$, $R^3 = OH$, $R^4 = OMe$
2a $R^1 = R^2 = H$, $R^3 = OAc$, $R^4 = OMe$
2b $R^1 = R^2 = H$, $R^3 = R^4 = OMe$
3 $R^1 = R^2 = R^3 = R^4 = H$



1c

Fig. 1. ^{1}H NMR (500 MHz, $CDCl_3$) data for dihydrodarienine (**1c**) → NOE.

hydrogen atoms bonded to the benzene ring as is the case with darienine. The *O*-methyl derivative (**2b**) was also prepared. It has recently been shown [9] that the UV–Vis spectrum of synthetic 6-hydroxy-1-methyl-4-azafluoren-9-one, recorded in the presence of base, exhibits a clear absorption maximum near 450 nm, associated with the conjugation of the phenolate function with the *para*-situated carbonyl group, while the corresponding spectrum of 7-hydroxy-1-methyl-4-azafluoren-9-one shows no maximum beyond 400 nm. In this respect, the UV–Vis spectra of darienine (**1**) and macondine (**2**), recorded in basic solution, support the assignment of the hydroxyl group to C-7. Therefore, macondine should be 7-hydroxy-8-methoxy-1-methyl-4-aza-fluoren-9-one (7-hydroxy-6-methoxy-5*H*-indeno[1,2-*b*]pyridine-5-one, **2**). The large deshielding of the methoxyl protons can now be explained by the proximity of the *O*-methyl group to the carbonyl function, forced into this position by the combination of its tendency to lie in the plane of the benzene ring [10, 11] and the repulsion of the C-7 hydroxyl group. In spite of the shielding effects of the acetyl and methyl groups on the neighbouring oxygen atom, the downfield methoxyl group protons of *O*-acetyl (**2a**) and *O*-methylmacondine (**2b**) still resonate at δ4.14 and 4.12, respectively.

Ursuline could only be separated from macondine as its *O*-acetyl derivative, of which 1 mg was obtained. Its mass spectrum showed it to be isomeric with *O*-acetylmacondine (**2a**). Its ^{1}H NMR spectrum (Table 2) differs from that of *O*-acetylmacondine in that the methoxyl group resonates somewhat further upfield, and both benzene ring protons, constituting an *ortho*-coupled AB system, also appear to be significantly more shielded. *O*-Acetylursuline was subjected to deacylative methylation with diazomethane [12, 13] and the reaction product was found to be different from *O*-methylmacondine (**2b**), ruling out the possibility that ursuline is oxygenated at C-7 and C-8. Two other oxygenation patterns are compatible with the *ortho*-coupling of the benzene ring protons; namely C-5/C-6 and C-5/C-8, but the data available at this time do not permit a more precise structure assignment.

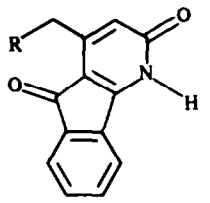
DISCUSSION

With our present knowledge of the structures of at least 10 natural azafluorenone derivatives [5–7, 14–16] we have a much broader base on which to construct biogenetic hypotheses. We may therefore hope that our speculations will stand up better to the test of future biosynthetic work. The first azafluorenone alkaloid, onychine (**3**), was formulated originally as 4-methyl-1-azafluoren-9-one instead of the 1-methyl-4-aza isomer, and it was suggested that it might be derived biogenetically from phenylalanine and mevalonate [6]. This view is clearly untenable if the correct structure is considered. We have pointed out [15] that derivatives of 1-methyl-4-azafluoren-9-one could arise by a regiospecific decarbonylation of 1-methyl-4-azaanthraquinone analogues which have been found together with them in several instances [14, 15, 17]. The azaanthraquinones, in turn, may be regarded as remnants of extensively oxidised aporphinoids [15], an enticing idea considering the abundance of oxoaporphines in many members of the family Annonaceae [18] and most significantly in most of the plants which have yielded azaanthraquinones and/or azafluorenones to date [5, 14, 15, 17, 19], which includes *Annona cherimolia* [Cortes, D. and Ríos, J. L., unpublished results]. Onychine would thus be derived from the abundant, widespread liriodenine, lysicamine or some other 1,2-dioxygenated oxoaporphine, via the azaanthraquinone cleistopholine [15]. Dielsine (**4**) and dielsinol (**4a**), from *Guatteria dielsiana* [14, 16], must

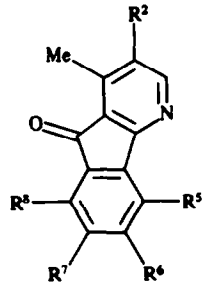
Table 3. ^{13}C NMR chemical shifts of darienine (**1**) and macondine (**2**)*

C	1	2
1	151.8	151.6
2	124.3	125.0
3	152.7	152.7
4a	164.9	164.8
4b	125.9†	125.6‡
5	148.6	120.2
6	145.4	116.8
7	146.8	145.5
8	107.2	147.4
8a	127.3†	124.1‡
9	192.1	190.8
9a	131.6	135.6
1-Me	17.2	17.2
5-OMe	61.8	—
6-OMe	61.5	—
8-OMe	—	62.8

*$CDCl_3$, 125.7 MHz.
†,‡Assignments may be interchanged.



4 R = H
4a R = OH

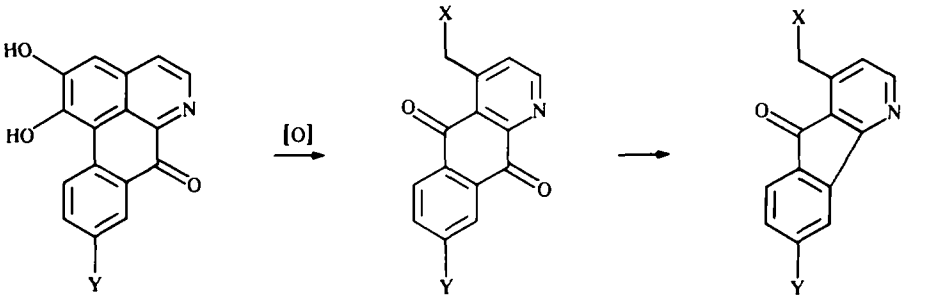


	R²	R⁵	R⁶	R⁷	R⁸
5	H	H	OMe	H	H
5a	H	H	OH	H	H
6	H	OH	OMe	H	H
7	OMe	H	OMe	OH	H
8	H	OMe	OH	H	OMe

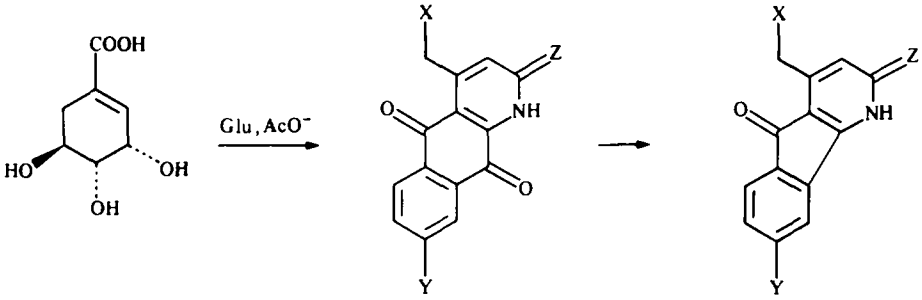
almost certainly be derived from onychine or cleistopholine by oxidation of C-3 and of the *C*-methyl group, although the hydroxymethyl group of dielsinol could also be regarded as a biogenetic remnant resulting from the degradation of the hypothetical oxoaporphine precursor [15].

By now, azafluorenones have been described with oxygen substituents on all four available positions of the benzene ring. Two derivatives of onychine bearing a single oxygen atom on the benzene ring have been described as natural products: 6-methoxyonychine (**5**), from *G. dielsiana*, the structure of which has recently been revised and confirmed by synthesis [14, 16], is congruent with the oxoaporphine lanuginosine, which occurs in several Annonaceae [18]; its relationship to 6-hydroxyonychine (**5a**), from *O. xylopioides* [5], is trivial. The onychine derivatives with two oxygen substituents on the benzene ring appear to be four: the *O.* cf. *major* metabolite macondine (**2**) exhibits an oxygenation pattern which may be derived formally from that of glaunine; 5-hydroxy-6-methoxyonychine (**6**) and 2,6-dimethoxy-7-hydroxyonychine (**7**), from *O. xylopioides* [5], have been assigned structures which may similarly be related to oxocrebanine and oxoglaucine, respectively. Neither glaunine nor oxocrebanine, nor other oxoaporphines with the same oxygenation patterns, are known as constituents of this family [18]. Ursuline may also be related to oxocrebanine, unless its substitution pattern should correspond to some hitherto unknown 8,11-oxygenated oxoaporphine. Two azafluorenone alkaloids with three oxygen atoms on the benzene ring are now known: darienine (**1**) and kinabaline (**8**), from *O.* cf. *major* and *Meiogyne virgata* [15], respectively, and neither of them corresponds in its substitution to any known oxoaporphine. Within the context of the aporphinoid biogenesis of these compounds (Scheme 1), we prefer to postulate that one, two or even three oxygen atoms may be introduced at different positions of the benzene ring either at the azaanthraquinone stage or once the azafluorenone skeleton has been formed, rather than assume that all these patterns arise independently.

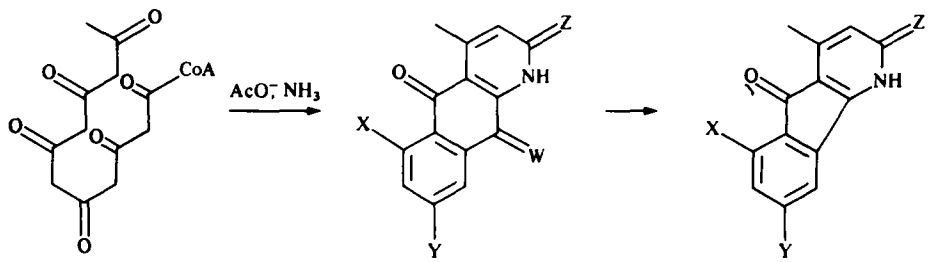
An ingenious proposal to explain the origin of azaanthraquinones, and therefore also of azafluorenones, depicts these alkaloids as shikimate derivatives formed by way of 2-aminonaphthoquinones (Scheme 2) [14]. Although the details of such a pathway have not been



Scheme 1



Scheme 2



Scheme 3

worked out, it is well worth noting that the three oxygen atoms of darienine (**1**) are located precisely at the positions (C-5, C-6 and C-7) which would have borne the hydroxyl groups of shikimic acid, while 6-methoxy- (**5**), 6-hydroxy- (**5a**), 5-hydroxy-6-methoxy- (**6**), 2,6-dimethoxy-7-hydroxyonychine (**7**) and possibly ursuline could be envisioned as partially deoxygenated derivatives. Macondine (**2**) and kinabaline (**8**), however, require the introduction of a non-shikimate oxygen atom at C-8 of the azafluorenone skeleton.

By analogy with the biosynthesis of a number of anthraquinones [19], the azaanthraquinones could also be derived from an appropriately folded polyketide (Scheme 3). If this were the case, one could expect to find oxygen atoms at C-6 and/or C-8 of the resulting azafluorenones, which is true for all the benzene ring oxygenated alkaloids of this type, although additional oxidation at C-5 or C-7 would be required in every instance except for 6-methoxy- (**5**) and 6-hydroxyonychine (**5a**).

In conclusion, none of these postulated routes provides a wholly satisfactory explanation of the distribution of oxygen substituents in the natural azafluorenones. If it is admitted as likely that azaanthraquinones are intermediates in their biosynthesis, it may be of some significance that the only known compounds of this latter type lack oxygen atoms in their benzene ring. Unless this merely reflects our present ignorance, it would seem to support the idea that biosynthetically late oxygenations are the key to the already wide variety of patterns found in the azafluorenone alkaloids.

EXPERIMENTAL

Plant material. Stem bark of *Oxandra* cf. *major* was collected near the gulf of Urabá in the Darien region of Colombia in August, 1984, and classified provisionally by Dr P. J. M. Maas. Voucher specimens have been deposited in the herbaria of the Joaquín Antonio Uribe Botanical Garden, Medellín, Colombia, under reference J.B. 1240, and of the Institute of Systematic Botany of the Rijksuniversiteit, Utrecht.

Extraction and separation. The dried, powdered trunk bark was defatted with petrol. The air-dried marc was made alkaline with aq. NH_3 and extracted with CH_2Cl_2. The conc solution was extracted with HCl and the aq. layer was made alkaline and re-extracted with CH_2Cl_2, which was removed *in vacuo* to afford 0.1% (dry wt basis) of crude alkaloids. These were separated by flash chromatography [20] on silica gel eluting with CH_2Cl_2–Me_2CO (98:2), followed by prep. TLC on silica gel with CH_2Cl_2–Me_2CO–MeOH (10:0.3:0.3) and crystallization when possible. The yields of individual alkaloids are summarized in Table 1. ^{1}H NMR 90, 250 and 500 MHz in $CDCl_3$; ^{13}C NMR 125.7 MHz in $CDCl_3$; IR: film; EIMS: 70 eV.

Darienine (**1**). Amorphous yellow solid. UV λ_{max}^{EtOH} nm (log ε): 206 (4.09), 235 (4.03), 266 (4.33), 292 (4.02), 302 sh (4.00); $\lambda_{max}^{EtOH+NaOH}$ nm (log ε): 218 (4.05), 226 sh (4.04), 285 (4.18), 322 (4.12), 360 (3.78); $\lambda_{max}^{EtOH+HCl}$ nm (log ε): 206 (4.09), 226 (4.03), 265 (4.27), 292 (3.96), 302 sh (3.95). IR ν_{max} cm^{-1} 3350, 2920, 1708, 1600, 1565. MS *m/z* (rel. int.): 271 $[M]^+$ (41), 270 $[M-H]^+$ (21), 256 $[M-CH_3]^+$ (100), 243 $[M-CO]^+$ (3), 242 $[M-H-CO]^+$ (20), 241 (28), 225 (22). ^{1}H NMR, see Table 2. ^{13}C NMR, see Table 3.

O-Acetyldarienine (**1a**). From darienine (**1**) with Ac_2O–pyridine. Mp 143°. IR ν_{max} cm^{-1}: 1765, 1710, 1592, 1560. MS *m/z*: 313.0931 $[M]^+$ (calc. for $C_{17}H_{15}NO_5$: 313.0950) (19); 271.0825 $[M-Ac]^+$ (calc. for $C_{15}H_{13}NO_4$: 271.0844) (26); 256.0591 $[M-Ac-Me]^+$ (calc. for $C_{14}H_{10}NO_4$: 256.0610) (100); 241 $[M-Ac-Me-Me]^+$ (35); 225 $[256-OMe]^+$ (34); 212 (9); 195 (12). ^{1}H NMR, see Table 2.

O-Methyldarienine (**1b**). From darienine (**1**) with CH_2N_2. ^{1}H NMR, see Table 2.

Dihydrodarienine (**1c**). From darienine (**1**) with $NaBH_4$. Mp 85–88°. UV λ_{max}^{EtOH} nm (log ε) 205 (3.94), 230 sh (3.79), 295 (3.66), 308 (3.65); $\lambda_{max}^{EtOH+NaOH}$: 219 (3.86), 242 sh (3.69), 345 (3.75); $\lambda_{max}^{EtOH+HCl}$ 205 (3.90), 242 sh (3.66), 352 (3.75). IR ν_{max} cm^{-1} 3330, 1600, 1565. MS *m/z*: 273 $[M]^+$, 258, 245, 244, 227. ^{1}H NMR, see Fig. 1.

Macondine (**2**). Amorphous. UV λ_{max}^{EtOH} nm (log ε): 208 (3.99), 237 (3.95), 265 (4.11), 294 sh (3.80), 303 (3.87), unchanged on adding HCl; $\lambda_{max}^{EtOH+NaOH}$ nm (log ε): 220 (3.92), 245 (3.90), 283 (3.95), 322 (3.92), 360 sh (3.55). IR ν_{max} cm^{-1}: 3360, 1706, 1600, 1565. MS *m/z*: 241 $[M]^+$, 223, 195, 167. ^{1}H NMR, see Table 2. ^{13}C NMR, see Table 3.

O-Acetylmacondine (**2a**). From macondine (**2**) with Ac_2O–pyridine. Mp173°. UV λ_{max}^{EtOH} nm (log ε): 208 (4.16), 232 sh (4.09), 259 (4.50), 280 sh (4.29); $\lambda_{max}^{EtOH+NaOH}$ nm (log ε): 230 (4.09), 250 sh (4.24), 280 (4.49), 325 (4.13), 360 sh (3.82). IR ν_{max} cm^{-1}: 1758, 1706, 1600, 1565. MS *m/z* (rel. int.): 283 (7) $[M]^+$, 241 (100), 223 (71), 195 (38), 167 (16). ^{1}H NMR, see Table 2.

O-Methylmacondine (**2b**). From macondine (**2**) with CH_2N_2. ^{1}H NMR, see Table 2.

O-Acetylursuline. From the mixture of macondine (**2**) and ursuline with Ac_2O–pyridine. UV λ_{max}^{EtOH} nm (log ε): 208 (3.98), 225 sh (3.92), 250 (4.04), 288 (3.47). IR ν_{max} cm^{-1} 1735, 1708. MS, *m/z*: 283 $[M]^+$, 241, 223. ^{1}H NMR (250 MHz): δ2.36 (3H, *s*, OAc), 2.64 (3H, *s*, C-Me), 4.09 (3H, *s*, OMe), 6.96 and 8.52 (2H, 2*d*, *J* = 5.5 Hz), 7.10 and 7.50 (2H, 2*d*, *J* = 8.0 Hz).

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