SPECTRAL PROPERTIES OF RING-C-OXYGENATED 4-AZAFLUORENES AND 4-AZAFLUORENONES. THE STRUCTURES OF NATURAL ONYCHINE DERIVATIVES

Dragana Tadić, Bruce K. Cassels, and André Cavé
Laboratoire de Pharmacognosie, UA 496 CNRS, Faculté de Pharmacie, 92296 Châtenay-Malabry, France

Abstract — 4-Azafluorenes bearing a methoxy group at C-5, -6, -7 or -8 and a methyl at C-1 or -3 were synthesized by thermolysis of *O*-crotyloximes of appropriately substituted indan-1-ones. The corresponding azafluorenones were prepared, and the methoxy-1-methyl-4-azafluoren-9-one isomers were *O*- demethylated. The proton nmr, uv-visible and mass spectra of these compounds support the structures assigned to the more complex azafluorenone alkaloids kinabaline, daricnine and macondine, and provide additional guidelines for the structure elucidation of other natural products belonging to this class.

Recent work in our laboratory has led to the isolation and structure elucidation of four phenolic azafluorenone alkaloids from the Malaysian *Meiogyne virgata*[1] and from an *Oxandra* species from the Darien region of Colombia originally recognized as close to *O. major*[2] and reclassified more recently as *O. xylopioides* (Annonaceae). The spectroscopic studies carried out on these compounds leave no doubt that they are derivatives of onychine (1-methyl-4-azafluoren-9-one or 4-methyl-5*H*-indeno[1,2-*b*] pyridine-5-one),[3,4] but although the positions of the hydroxy and methoxy groups on the benzene ring could be deduced from the nmr spectra of these substances, the lack of literature precedent in this series begs for some synthetic support for their structures We therefore decided to prepare the four benzene ring monomethoxylated onychine analogues and the corresponding phenols so that more complete nmr analyses could be carried out and for comparison of their electronic spectra with those of the substances from *Meiogyne* and *Oxandra*

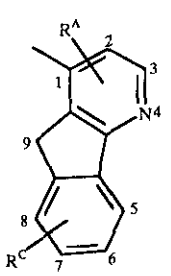
Of the previously described onychine syntheses, the classically designed scheme of Bowden et al.[5] could be expected to give mixtures of isomers differing in the position of the benzene ring substituent, an undesirable situation in the present context. The Prostakov synthesis[6] suffers from the same drawback, compounded with very rigorous reaction conditions which might make the isolation of methoxylated derivatives impossible. On the other hand, the route described by Koyama et al.,[4] which involves the thermolysis of oxime *O*-allyl ethers as the key step,[7,8] could be hoped to afford the eight methoxy-1-(and 3-)methyl-4-azafluorenes in moderate yield starting from the easily accessible methoxyindan-1-ones. No ambiguity exists regarding the substitution of the benzene ring in the products of this reaction, and we anticipated that the oxidation of the azafluorenes to azafluoren-9-ones would pose no problem.

5-Methoxyindan-1-one was available commercially. We obtained its 4- and 6-methoxy isomers by classical methods.[9,10] It should be stated here that a more recent, poorly described and roundabout route to 4-methoxy indan-1-one[11] offers no advantages. The 7-methoxy compound was obtained by a method adapted from the literature;[12,13] we

have included the procedure in the experimental section as the details have not been published previously. *O*-Crotylhydroxylamine was obtained as described.[8]

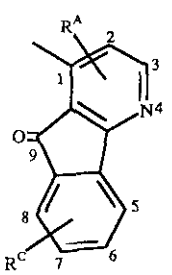
The first step in our synthetic program was the preparation of the *O*-crotyloximes of the four indanones. 7-Methoxyindan-1-one gave a single oxime, presumably the (*E*) isomer, which could be explained by the steric repulsion between the methoxyl group and the bulky substituent on the nascent oxime function. In the cases of the 4-, 5- and 6-methoxylated substances a mixture of geometric isomers was formed, resolved chromatographically and the products characterised. It should be pointed out that the pairs of stereoisomers differ markedly in the chemical shifts of the benzene ring protons at C-7. Although no direct proof is available at this time, it seems reasonable to assume that the H-7 resonance undergoes a large downfield shift due to the (*E*) oxime function, while in the case of the (*Z*) isomers the deshielding attributable to the magnetic anisotropy of the oxime group is counterbalanced by diamagnetic shielding due to the butenyl substituent. Experiments in which the *E* and *Z* isomers of the *O*-crotyloxime of 5-methoxyindan-1-one were thermolysed separately showed by TLC that the oximes are interconverted at the temperature required for ring closure and that therefore the same products are obtained in practically identical yields regardless of the stereochemistry of the starting material. Consequently, the unresolved mixtures of stereoisomers were used in later work.

We carried out the thermolyses under air at 170-180°C as described for onychine and its isomers.[4] The pyridine ring was not formed at lower temperatures, and at 200°C the reaction mixture became an intractable tar, so we retained the original conditions throughout. It should be noted that the oximes are appreciably volatile under these conditions, and that the tubes in which the thermolyses are carried out must either be sealed as in the literature references[4,7] or, more simply, be covered with a well-fitting funnel to ensure adequate reflux. In each case, the expected mixture of 1- and 3-methyl-4-azafluorenes bearing a methoxyl group at the appropriate position of the benzene ring was obtained, but these substances were accompanied by the respective azafluoren-9-ones, obviously formed by air oxidation of the initial products. In those cases in which larger amounts of the ketones were required, these were prepared by oxidation of the azafluorenes with $KMnO_4$ in acetone at room temperature.



1-8

	R^A	R^C	
1	1-CH_3	5-OCH_3	**9**
2	1-CH_3	6-OCH_3	**10**
3	1-CH_3	7-OCH_3	**11**
4	1-CH_3	8-OCH_3	**12**
5	3-CH_3	5-OCH_3	**13**
6	3-CH_3	6-OCH_3	**14**
7	3-CH_3	7-OCH_3	**15**
8	3-CH_3	8-OCH_3	**16**



9-16

O-Demethylation of methoxy-1-methyl-4-azafluoren-9-ones **9-12** with 48% HBr afforded the corresponding phenols.[14]

SPECTRAL PROPERTIES OF BENZENE RING-METHOXYLATED 4-AZAFLUORENES.

The proton chemical shifts of the azafluorenes **1-8** are summarized in Table **1**. It can be seen that the pyridine ring AB system ($J_{2,3}$ = 5.1, $J_{1,2}$ = 7.6 Hz) allows the 1- and 3-methyl isomers to be differentiated quite easily, as an α proton (H-3) resonates 0.7-0.9 ppm further downfield than a γ proton (H-1). The *C*-methyl group, similarly, resonates at lower fields when it is located at C-3, although the difference is only about 0.25 ppm. The methylene protons (H-9) appear as a singlet which is at somewhat lower fields in the isomers bearing the alkyl ether function at C-5. It is noteworthy that the methoxyl at C-5 is the most deshielded of all due to the proximity of the pyridine ring, while the C-7 methoxyl group appears somewhat further upfield than the others. The benzene ring proton resonances are almost unaffected by the position of the *C*-methyl, but the signals of the protons on the pyridine ring seem to shift slightly depending on the position of the methoxyl group.

Table **1**. ^{1}H Nmr chemical shifts (δ, ppm from TMS) of methoxy-substituted 4-azafluorenes **1-8** (500 MHz, $CDCl_3$).

^{1}H	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
H-1	—	—	—	—	7.67 *d*	7.69 *d*	7.62 *d*	7.76 *d*
H-2	7.02 *d*	7.02 *d*	6.95 *d*	7.02 *d*	7.02 *d*	7.06 *d*	6.97 *d*	7.09 *d*
H-3	8.60 *d*	8.45 *d*	8.40 *d*	8.47 *d*	—	—	—	—
H-5	—	7.64 *d*	8.03 *d*	7.72*d*	—	7.69 *d*	8.03 *d*	7.82 *d*
H-6	6.96 *d*	—	7.01 *dd*	7.44 *dd*	6.93 *d*	—	6.99 *dd*	7.44 *dd*
H-7	7.40 *dd*	6.99*dd*	—	6.93 *d*	7.35 *dd*	6.98 *dd*	—	6.94 *d*
H-8	7.20 *d*	7.45 *d*	7.09 *d*	—	7.16 *dd*	7.44 *d*	7.08 *d*	—
H-9	3.81 *s*	3.71 *s*	3.73 *s*	3.72 *s*	3.82 *bs*	3.75 *s*	3.76 *s*	3.77 *s*
C-CH_3	2.45 *s*	2.43 *s*	2.40 *s*	2.44 *s*	2.71 *s*	2.68 *s*	2.64 *s*	2.70 *s*
O-CH_3	4.10 *s*	3.91 *s*	3.88 *s*	3.96 *s*	4.07 *s*	3.93 *s*	3.87 *s*	3.95 *s*

The uv spectra of the azafluorenes **1-8** (Tables **2-3**) are characterised by strong absorption near 210 and 300-310 nm, with several intervening maxima or shoulders which are almost always less intense. It is probably significant that the long-wavelength absorption bands of the isomers methylated at C-3 occur several nm closer to the visible region of the spectrum. Upon adding acid, the intermediate portions of the spectra are flattened by a series of batho- and hypochromic effects, while the long-wavelength maxima are shifted towards the visible region by about 30 nm with slight intensity changes of either sign.

The general appearance of the electron impact-induced mass spectra (EIMS) of these compounds is independent of the position of the methyl group on the pyridine ring. Two extreme situations may be distinguished, however, depending

Table 2. Uv -visible spectral data of 1-methyl-4-azafluorenes **1-4** (in EtOH), λ_{max} in nm, log ε in parentheses.

1	1[a]	2	2[a]	3	3[a]	4	4[a]
				206 (4.26)	206 (4.22)		208 (4.29)
212 (4 21)	211 (4 10)	213 (4.35)				212 (4.42)	
218sh (4 15)			218 (4.35)		220sh (4.01)		216 (4.30)
228sh (3 91)	224sh (4 05)	226sh (4.19)					222sh (4.26)
						243 (4.08)	
250 (3.94)	250 (3 68)	256 (3.85)			250 (3.74)	250sh (4.07)	254sh (3.82)
262sh (3.82)				264 (3.97)		260sh (3.94)	262 (3.84)
	270 (3 62)	278sh (3.79)			268 (3.70)		
				285 (4.03)			
292sh (3 9)		290 (3.90)	290sh (3.82)			290 (4.20)	
					295 (3 70)	296 (4 21)	
300 (3 92)							
312 (3.89)	308 (3 90)	316 (3.96)	306 (3.99)				
				314 (4.19)			314 (4.29)
	337 (3.86)		344 (3.87)		344 (4.28)		

[a] HCl added.

Table 3. Uv -visible spectral data of 3-methyl-4-azafluorenes **5-8** (in EtOH), λ_{max} in nm, log ε in parentheses.

5	5[a]	6	6[a]	7	7[a]	8	8[a]
208 (4.28)	206 (4.13)	208 (4.21)		208 (4.26)	206 (4.16)	210sh (4.22)	210 (4.13)
			214 (4.39)		216sh (4 02)	214 (4.23)	
	224 sh (4 00)	220 (4.20)	228sh (4.39)				225sh (4.10)
244 (3 93)							
251 (3 93)	248 (3 66)	258 (3.70)	252 (3.59)		256 (3.79)	250 (3.96)	
261sh (3.85)				260 (3.95)		262sh (3.88)	260 (3.84)
	271 (3.66)			266 (3.97)	272 (3.78)		
				290 (4.02)	286 (3.68)		
		294 (3.91)			298 (3.71)	298 (3.98)	
304 (4 12)						304sh (3.98)	
314sh (4.10)	315 (4.03)	312sh (4.11)	312 (4.19)			308sh (3.91)	
		320 (4 12)		322 (4.23)			325 (4.06)
	348 (4 08)		348 (4.39)		354 (4.33)		

[a] HCl added.

on the location of the methoxyl. When this group is attached to C-6, -7 or -8, the molecular ion gives the base peak of the spectrum (or, in the case of 6-methoxy-1-methyl-4-azafluorene, a signal with an intensity of 90%). The dominant fragmentation process is the loss of a methyl group from the molecular ion, a reaction which seems to be facilitated in the 6- and 8-methoxy compounds. A fragment formed by loss of 29 m.u. from the molecular ion, as seen in the mass-analysed ion kinetic energy (MIKE) spectra, barely exceeds 3% relative abundance. The [M-1] peak appears with intensities between 4 and 21% when the methoxyl is at C-6, -7 or -8. On the other hand, when the methoxyl is at C-5 the molecular ion is less abundant (77%) and the [M-1] ion gives the base peak. Here the loss of a methyl group from the molecular ion is a very minor process (2 to 4% relative abundance), while the loss of 29 m.u. from the molecular ion and also, with a somewhat lower probability, from the [M-1] fragment, occurs rather easily. Doubly charged molecular ions and major fragments are common features in these spectra.

SPECTRAL PROPERTIES OF BENZENE RING-METHOXYLATED 4-AZAFLUOREN-9-ONES

The ^{1}H nmr chemical shifts and multiplicities of the methoxy azafluorenones **9-16** are shown in Table **4.** The pyridine ring proton resonances again make the 1- and 3-methylated isomers readily recognizable, although in these substances H-1 is slightly deshielded by the carbonyl group, and H-2 and -3 tend to resonate at higher fields. The C-1 methyl resonance is displaced to such an extent that it becomes indistinguishable from its counterpart at C-3. As with the azafluorenes, the benzene ring proton chemical shifts are practically unaffected by the position of the *C*-methyl group On the other hand, the introduction of the ketone function causes predictable displacements of these resonances: H-6 and -8 are deshielded by up to 0.2 ppm in comparison to their counterparts in the azafluorene series; H-5 is unexpectedly shielded by as much as 0.3 ppm in all these substances, and a smaller effect is noticeable on H-7 when C-6 bears a

Table 4. ^{1}H Nmr chemical shifts (δ, ppm from TMS) of benzene ring-methoxylated 4-azafluoren-9-ones **9-16** (500 MHz, $CDCl_3$).

^{1}H	9	10	11	12	13	14	15	16
H-1	—	—	—	—	7.75 *d*	7.75 *d*	7.71 *d*	7.77 *d*
H-2	6.91 *d*	6.96 *d*	6.88 *d*	7.05	7.00 *d*	7.05 *d*	6.96 *d*	7.06 *d*
H-3	8.49 *d*	8.39 *d*	8.34 *d*	8.41 *d*	—	—	—	—
H-5	—	7.35 *d*	7.73 *d*	7.59 *d*	—	7.37 *d*	7.74 *d*	7.48 *d*
H-6	7.15 *bd*	—	7.07 *dd*	7.58 *dd*	7.14 *dd*	—	7.05 *dd*	7.54 *dd*
H-7	7.40 *dd*	6.87 *dd*	—	7.00 *dd*	7.38 *dd*	6.86 *dd*	—	6.96 *d*
H-8	7.34 *dd*	7.64 *d*	7.21 *d*	—	7.34 *dd*	7.64 *d*	7.23 *d*	—
C-CH_3	2.62 *s*	2.63 *s*	2.60 *s*	2.67 *s*	2.67 *s*	2.64 *s*	2.61 *s*	2.65 *s*
O-CH_3	4.07 *s*	3.94 *s*	3.88 *s*	4.01 *s*	4.04 *s*	3.94 *s*	3.88 *s*	4.01 *s*

methoxyl group. The deshielding of the C-5 methoxyl by the neighbouring aromatic heterocycle, which is also clearly observed in the azafluorenone series, is somewhat larger than the comparable effect of the carbonyl group on the C-8 methoxyl. The C-7 methoxyl group resonates upfield from all the others, as in the case of the corresponding azafluorenes. The position of the methoxyl group affects the pyridine ring proton resonances to a small extent, as noted for the azafluorenes.

In the uv spectra of the azafluorenones (Tables **5-6**), the dominant peak occurs between 242 and 248 nm with the exception of the 7-methoxy compounds, where it appears near 260 nm. A doublet in the vicinity of 290 nm is relatively weak in the 5-, 7-, and 8-methoxylated isomers, while in the 6-methoxy compounds its intensity approaches that of the major peak. The near-visible absorptions of the 3-methyl isomers appear at slightly longer wavelengths, as for the azafluorenes. Acid-induced bathochromic shifts of the long-wavelength maxima of about 25 nm, with little change in the generally low extinction coefficient, are clearly visible only in the spectra of the 5- and 7-methoxy isomers, where the substituent is *ortho* or *para* with respect to the 2-pyridyl moiety.

The cims of these substances fall into the same two major groups as those of the azafluorenes. Here again, the [M-1] ion gives the base peak when the methoxyl group is located at C-5, but is much less prominent in all other situations. The loss of a methyl group from the molecular ion is only favored when the methoxyl group is located at C-7, in which case neither the molecular ion nor the [M-1] fragment lose a presumed COH fragment easily. This moiety leaves the molecular ion and the [M-1] fragment of the other isomers rather readily, and in the case of the 8-methoxy compounds accounts for the base peak at *m/z* 196. It must be remembered that the mikes of the molecular ions and the M-1 fragments of the 5-methoxy-4-azafluorenes explain the intense peaks at *m/z* 182 and 181 as resulting from the loss of a 29 m.u. neutral fragment which cannot involve a carbonyl group. The extrusion of CO from the azafluorenones does not appear to be an important primary process, judging from the mikes. As with the azafluorenes, doubly charged major ions are usually detected.

SPECTRAL PROPERTIES OF HYDROXYLATED 1-METHYL-4-AZAFLUOREN-9-ONES

With the exception of the intramolecularly hydrogen-bonded 8-hydroxy isomer, these compounds were rather insoluble in $CDCl_3$. We therefore recorded their ^1H nmr spectra in CD_3OD, and for this reason the chemical shifts are not strictly comparable to those tabulated for the methyl ethers. Nevertheless these results, summarised in Table **7**, show the same general trends.

The uv-vis spectra of the benzene ring-hydroxylated 1-methyl-4-azafluoren-9-ones, recorded in neutral or acid solution, showed similar features to those of the corresponding methoxy compounds. Upon adding base, however, all isomers exhibited very large bathochromic shifts of the longest wavelength absorption band which extended well into the visible region. This effect could be observed with the naked eye, as the practically colorless solutions in the spectrometer cells became distinctly colored when NaOH was added. The spectra of the alkaline solutions of the compounds bearing a phenol function at C-6 or -8 showed a fairly intense absorption band near 450 nm. When the hydroxyl group was located at C-5 or -7, this band was considerably weaker, but shifted to about 500 nm. These results are summarised in Tables **8** and **9**. A further diagnostic criterion for the presence of a hydroxyl group at C-8 is the $AlCl_3$-induced,

Table 5. Uv-visible spectral data of 1-methyl-4-azafluoren-9-ones 9-12 (in EtOH), λ_{max} in nm, log ε in parentheses.

9	9[a]	10	10[a]	11	11[a]	12	12[a]
207 (4.16)	212 (4.19)	214 (4.09)	216 (4.05)	207 (3.97)	206 (3 97)	208 (4.17)	208 (4.22)
					218 (3.94)		
228 (4 15)	230 (4.06)	225sh (4.36)	230sh (4.09)		223 (3.94)	227 (4.24)	227 (4.24)
		235sh (4 36)	240sh (4.21)				
248 (4.33)	248 (4.08)	245 (4.36)	248 (4.26)			248 (4.34)	247 (4 23)
				265 (4.51)	264 (4.37)		
		276sh (4.36)	276sh (4.09)			278sh (3 81)	
		280 (4.21)	283 (4.11)	283sh (3 84)			
	290sh (3.76)	292 (4.36)	294 (4.09)	294 (3.84)	295 (3.85)	290 (3.91)	290sh (3.94)
298 (3.85)					300(3.85)	301 (3.94)	302 (3.98)
310 (3 85)			308sh (3.74)	314 (3.67)			
	322 (3.89)	326 (3.44)	328 (3.36)	327 (3.51)	329 (3.65)		
344 sh (3.35)		340 (3.44)	343 (3.36)		348 (3.7)	340 (3.45)	
	384 (3.35)						374sh (3.48)

[a] HCl added.

Table 6. Uv-visible spectral data of 3-methyl-4-azafluoren-9-ones 13-16 (in EtOH), λ_{max} in nm, log ε in parentheses.

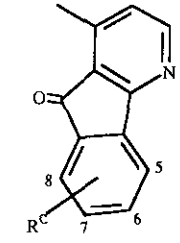
13	13[a]	14	14[a]	15	15[a]	16	16[a]
208 (4.01)	207 (4.22)	206 (4.08)	206sh (4.08)	210 (4.00)	205 (3.96)	208sh (3.81)	
229 (4 22)		220sh (4.13)		226 (3.99)	221 (3.96)	228 (3.96)	228 (3.82)
		234sh (4.16)	234sh (4.16)				
241sh (4.33)	243 (4.22)	242 (4.20)	242 (4.18)			244 (4.01)	244 (3.89)
247 (4.40)							
				260 (4.37)	257 (4.25)		
		286sh (4.42)	286sh (4.04)				
302 (4 00)	300sh (3.88)	298 (4.06)	298 (4.06)	295 (4.04)	295 (3.95)	293 (3.71)	293sh (3.67)
308sh (3.99)						304 (3.73)	305 (3.73)
	313 (4.35)		314sh (3.76)	317 (3 75)			320sh (3.53)
	332 (3.39)	326 (3.67)		331sh (3 67)	330 (3.67)		
340sh (3.39)		345 (3.56)	342 (3.59)				
				362sh (3.05)	355 (3.72)	360 (3.11)	
					401 (3.14)		375 (3.11)

[a] HCl added.

acid-reversible bathochromic shift of the long-wavelength band to 450 nm.

Table 7. ^{1}H Nmr chemical shifts (δ, ppm from TMS) of benzene ring-hydroxylated 1-methyl-4-azafluoren-9-ones (**17**, **19**, **20**, 500 MHz, **18**, 200 MHz, CD_3OD).

^{1}H	**17**	**18**	**19**	**20**
H-2	7.02 *d*	7.13 *d*	7.00 *d*	7.13 *d*
H-3	8.30 *d*	8.35 *d*	8.25 *d*	8.36 *d*
H-5	—	7.24 *d*	7.63 *d*	7.30 *d*
H-6	7.03 *d*	—	6.98 *dd*	7.46 *dd*
H-7	7.30 *t*	6.82 *t*	—	6.87 *d*
H-8	7.15 *d*	7.56 *d*	7.04 *d*	—
CH_3	2.57 *s*	2.62 *s*	2.57 *s*	2.62 *s*



	R^C
17	5-OH
18	6-OH
19	7-OH
20	8-OH

The eims of the phenols are characterised by stable molecular ions which give the base peak in every case. The fragment peaks are all quite weak with the exception of those due to the [M-CO] ion, documented by mikes, in the 5-, 6-, and 8-hydroxy isomers (19-36%). 7-Hydroxy-1-methyl-4-azafluoren-9-one, on the contrary, does not give an appreciable [M-CO] fragment, and the initial loss of COH is preferred, followed by decarbonylation. The COH group is lost from the [M-CO] ions in all the other cases, followed by the extrusion of HCN. Considering the ratio of the intensities of the peaks at *m/z* 183 and 154, the [M-CO] ion seems to be much less stable in the cases of the 6- and especially the 7-hydroxy isomers.

NATURAL ONYCHINE DERIVATIVES

Our spectroscopic data for the simple benzene ring-methoxylated and hydroxylated 1-methyl-4-azafluoren-9-ones should be helpful in the structure elucidation and the interpretation of the spectra of new alkaloids belonging to this class. The more subtle effects of polysubstitution on the ^{1}H nmr and mass spectra may not be easily predictable, but the uv-vis spectra of onychine derivatives can be considered as a very useful indication of the positions of hydroxyl groups. The appearance in the spectrum, after adding NaOH, of an absorption band about 450 nm with a log ε in the 3.4-3.6 range points to the presence of a phenol function at C-6 or C-8; these two possibilities may be distinguished by the $AlCl_3$-induced shift in the spectrum of 8-hydroxylated azafluoren-9-ones. If the base-shifted spectrum instead shows a much weaker maximum near 500 nm, with a log ε of about 2.6, it may be concluded that the hydroxyl group is situated

Table 8. Uv-vis data of 1-methyl-4-azafluoren-9-ones **17** and **19**, bearing a phenol function *meta* with regard to the carbonyl group (in EtOH), λ_{max} in nm, log ε in parentheses.

17	17[a]	17[b]	19	19[a]	19[b]
206 (3 85)	206 (3.85)	208 (3.77)	205 (3.97)	205 (3.94)	
	214sh (3.83)				214 (3.93)
				221sh (3 89)	222sh (3.89)
230 (3.80)		235sh (3.85)	231sh (3.77)	232sh (3.83)	238 (3.79)
249 (4.00)	248 (3.73)	244 (3.88)			
		255sh (3.81)		256sh (4.18)	
			265 (4.30)	264 (4.23)	
			284 (3.77)		281 (4 16)
298 (3 48)	294 (3 48)		295 (3 80)	296 (3.78)	
310 (3.48)	324 (3.50)		316 (3.62)	302sh (3.77)	310 (3.94)
340sh (2 98)	335sh (3.39)	335sh (3.39)	330sh (3.53)	354 (3.60)	358 (3.83)
400sh (2.60)	400sh (2.91)				
		490 (2.61)			510 (2 62)

[a] HCl added; [b] NaOH added

Table 9. Uv-vis data of 1-methyl-4-azafluoren-9-ones **18** and **20**, bearing a phenol function *para* or *ortho* with regard to the carbonyl group (in EtOH), λ_{max} in nm, log ε in parentheses.

18	18[a]	18[b]	20	20[a]	20[b]
204 (3.96)	204 (3.97)	209 (3.98)	206 (4.07)	206 (4.07)	
			228 (4.04)	228 (4.00)	218 (3.93)
240sh (4.08)	240sh (4.05)				242 (4.24)
246 (4 13)	246 (4 10)	248 (4.10)	248 (4.30)	249 (4.11)	249 (4.23)
		260sh (3.96)			
272sh (3 93)	272sh (3 87)		278sh (3.60)		
284 (4.01)	284 (3.95)	282 (3.53)			
295 (3.96)	295 (3.95)	295sh (3.67)	290 (3.76)	290sh (3.82)	294 (3.86)
	308sh (3.53)		302 (3.79)	301 (3.89)	305 (3.85)
332 (3 23)		320 (3.87)			
343 (3.19)	346 (3.23)				
		360sh (3.35)	366 (3.30)		
		372 (3.30)		378 (3.24)	
390sh (2.93)					
		453 (3.38)			450 (3.60)

[a] HCl added; [b] NaOH added.

at C-5 or -7. It must be kept in mind, however, that stronger absorption at this wavelength (log ε approximately 3.8) may indicate the presence of a 4-azafluoren-3-ol-9-one chromophore, as in dielsine.[16]

6-Methoxyonychine (**10**) (6-methoxy-1-methyl-4-azafluoren-9-one) has been isolated from the Amazonian tree *Guatteria dielsiana*,[16] and the revised structure of this natural product was confirmed by the synthesis described above.[15] Onychine and several of its natural phenolic derivatives have been isolated in our laboratory, and the structures of kinabaline (5,8-dimethoxy-6-hydroxyonychine) from *Meiogyne virgata*,[1] darienine (5,6-dimethoxy-7-hydroxyonychine) and macondine (7-hydroxy-8-methoxyonychine) from *Oxandra xylopioides*[2] are sufficiently well established. The general features of the ^{1}H nmr spectra of these alkaloids agree well with those described in this paper. The uv-vis spectra recorded after adding NaOH are especially valuable, as they clearly support the proposed positions of the phenol functions. Thus, a basified solution of kinabaline shows a fairly strong absorption maximum at 450 nm, in accord with the placement of its hydroxyl group at C-6. Similar behavior could not be observed in the corresponding spectra of darienine and macondine, as is reasonable considering the low intensity of the long-wave absorption band associated with a phenoxy group at C-7. After adding base, the uv-vis spectrum of ursuline (6-hydroxy-5-methoxyonychine), found initially in *O. xylopioides* [2] and characterized more completely as a constituent of *Unonopsis spectabilis*,[17] exhibits a diagnostically useful absorption peak at 460 nm. Isoursuline (5-hydroxy-6-methoxyonychine), also isolated from *U. spectabilis*,[17] shows a weaker maximum at 484 nm in accordance with the presence of the phenol function at C-5. In conclusion, once a substituted azafluorenone structure is suspected for a natural product, its uv-vis spectra are of crucial importance for a rapid assignment of the position of any hydroxyl group which may be present.

EXPERIMENTAL

Phenyl 3-Chloropropanoate A suspension of phenol (5.0 g) and recently distilled 3-chloropropanoyl chloride (10 ml) in water (50 ml) containing methyl red as indicator was treated dropwise with 5M NaOH, with good stirring, until the yellow color persisted. The reaction mixture was extracted with Et_2O, the extract dried and the solvent removed under reduced pressure to give 7.68g of the ester (78%). 60 MHz ^{1}H nmr (DMSO-d_6) δ 3.08 (2H, *t*, *J* = 5.4 Hz, $ClCH_2$), 3.90 (2H, *t*, *J* = 5.4 Hz, $COCH_2$), 6.96-7.57 (5H, *m*, ArH).

7-Hydroxyindan-1-one. Phenyl 3-chloropropanoate (7.0 g) and $AlCl_3$ (21 g) were mixed at room temperature, and heated in an oil bath, keeping at 90-100°C for 1 h and then at 180°C for 2 h. The mixture was taken up with 1M HCl and CH_2Cl_2, and the organic layer was washed with water, dried and concentrated to give 1.5 g of the title compound (26%), which was pure enough for use in the next step. Reddish needles from MeOH, mp 104-106°C. 60 MHz ^{1}H nmr ($CDCl_3$ with drops of C_5D_5N) δ 2.55 (2H, *t*, *J* = 6 Hz, H-3), 3.1 (2H, *br t*, *J* = 6 Hz, H-2), 7.0 (2H, *m*, H-4 and -6), 7.58 (1H, *t*, *J* = 4.5 Hz, H-5), 9.93 (1H, *br s*, OH).

7-Methoxyindan-1-one 7-Hydroxyindan-1-one (1.30 g) was dissolved in DMF (2 ml) containing powdered, dry K_2CO_3 (2.47 g), Me_2SO_4 (2 ml) was added, and the mixture was stirred overnight at 60°C. After pouring into water, extracting with CH_2Cl_2, drying and removing the solvent, the product was purified by column chromatography on silica gel,

eluting with CH_2Cl_2-hexane (3:1), and crystallised in MeOH to give 0.56 g (40%) colorless prisms, mp 86-87°C from CH_2Cl_2. 60 MHz ^{1}H nmr ($CDCl_3$) δ 2.70 (2H, *t*, *J* = 6 Hz, H-3), 3.10 (2H, *t*, *J* = 6 Hz, H-2), 3.90 (3H, *s*, OMe), 6.73 (1H, *br d*, J_o = 8 Hz, H-6), 6.98 (1H, *br d*, J_o = 8 Hz, H-4), 7.48 (1H, *t*, J_o = 8 Hz, H-5).

Preparation of Monomethoxyindan-1-one *O*-Crotyloximes A mixture of monomethoxyindan-1-one (1.8 g, 11 mmol), *O*-crotylhydroxylamine-HCl (1.6 g, 13 mmol), NaOAc (0.60 g, 7.3 mmol) and Na_2CO_3 (1.0 g, 9.4 mmol) in EtOH (15 ml) was refluxed for 2 h. After removing the EtOH under reduced pressure, the residue was extracted with CH_2Cl_2, and the extract dried and concentrated to give the corresponding crude oxime. In those cases in which mixtures of stereoisomers were obtained, these were separated by flash chromatography on silica gel, eluting with CH_2Cl_2.

Thermolysis of Monomethoxyindan-1-one *O*-Crotyloximes The oxime, in a thick-walled test-tube with a well-fitting funnel for reflux, was heated in an oil bath at 170-180°C for 20-24 h. The reaction mixture was taken up with CH_2Cl_2, the basic constituents extracted with 1.2 M HCl, the acid solution made alkaline with conc. aq. NH_3 and extracted with CH_2Cl_2, and the organic phase dried and concentrated to give a mixture of monomethoxylated 1- and 3-methyl-4-azafluorenes and -fluoren-9-ones. These were separated by flash chromatography and PTLC on silica gel, eluting with CH_2Cl_2-MeOH (99:1)

Hydrolysis of Monomethoxy-1-Methyl-4-azafluoren-9-ones. The monomethoxy-1-methyl-4-azafluoren-9-one, dissolved in 48% HBr, was refluxed for 24 to 48 h. After removing excess reagent under reduced pressure, the product was purified by PTLC on silica gel, eluting with CH_2Cl_2-MeOH (98:2).

7-Methoxyindan-1-one *O*-Crotyloxime. 86% yield. 60 MHz ^{1}H nmr ($CDCl_3$) δ 1.73 (3H, *d*, *J* = 3 Hz, *C*-CH_3), 2.90 (4H, *s*, CH_2CH_2), 3.83 (3H, *s*, *O*-CH_3), 4.66 (2H, *m*, *O*-CH_2), 5.77 (2H, *m*, CH=CH), 6.66 (1H, *d*, J_o = 8 Hz, H-6), 6.81 (1H, *d*, J_o = 8 Hz, H-4), 7.20 (1H, *t*, *J* = 8 Hz, H-5). Eims *m/z* (%) 231 (16), 177 (11), 160 (100), 146 (11), 145 (21), 131 (23), 130 (19), 103 (13). Found: C, 72.58; H, 7.44; N, 6.13; $C_{14}H_{17}NO_2$ requires C, 72.70; H, 7.40; N, 6.05%.

5-Methoxy-1-methyl-4-azafluorene (1). Pale yellow glassy solid, subliming as needles, mp 130°C, 19% yield. ^{1}H Nmr see Table 1. Uv-vis see Table 2. Eims*m/z* (%) 211.0990 (77, $[M]^+$ $C_{14}H_{13}NO$ calc. 211.0997), 210 (100), 208 (8), 196 (4), 195 (3), 183 (12), 182 (74), 181 (51), 180 (39), 168 (5), 167 (16), 166 (16), 153 (6), 152 (9), 151 (5), 140 (7), 139 (3), 127 (4), 91 (5), 90.5 (14), 90 (14), 89. (9), 89 (5), 77 (12), 76 (4).

5-Methoxy-3-methyl-4-azafluorene (5). Pale yellow glassy solid, subliming as prisms, mp 111°C, 5% yield. ^{1}H Nmr see Table 1. Uv-vis see Table 3. Eims *m/z* (%) 211.1000 (77, $[M]^+$ $C_{14}H_{13}NO$ calc. 211.0997), 210 (100), 209 (3), 208 (6), 183 (12), 182 (85), 181 (59), 180 (34), 178 (5), 168 (5), 167 (15), 166 (17), 153 (9), 152 (16), 151 (4), 140 (9), 139 (12), 127 (7), 126 (4), 105.5 (5), 91.5 (3), 91 (4), 90.5 (20), 90 (15), 89.5 (7), 89 (6), 84 (4), 83.5 (4), 78.5 (3.5), 77 (16), 76 (9), 75 (3), 63 (5), 51 (6), 39 (5).

5-Methoxy-1-methyl-4-azafluoren-9-one (9). Pale yellow solid, subliming as prisms, mp 180°C, 5% yield. ^{1}H Nmr see Table 4. Uv-vis see Table 5. Eims *m/z* (%) 225.0773 (87, $[M]^+$ $C_{14}H_{11}NO_2$ calc. 225.0790), 224 (100), 211 (4), 197

(6), 196 (66), 195 (56), 194 (13), 167 (17), 166 (19), 141 (4), 140 (11), 139 (16), 126 (3), 112.5 (4), 97.5 (6), 86 (18), 84 (30), 83.5 (10), 70.5 (8), 63 (6), 51 (12), 49 (36), 39 (5).

5-Hydroxy-1-methyl-4-azafluoren-9-one (**17**). Pale yellow amorphous solid, subliming as brownish needles, mp 193°C, 39% yield. ^{1}H Nmr see Table **7**. Uv-vis see Table **8**. Eims *m/z* (%) 212 (10), 211.0623 (100, $[M]^+$ $C_{13}H_9NO_2$ calc. 211.0633), 184 (5), 183 (36), 155 (4), 154 (10), 128 (4), 127 (7), 105.5 (2); mikes *m/z* 211 to 183.

5-Methoxy-3-methyl-4-azafluoren-9-one (**13**). Pale yellow solid, 4% yield. ^{1}H Nmr see Table **4**. Uv-vis see Table **6**. Eims *m/z* (%) 225.0784 (88, $[M]^+$ $C_{14}H_{11}NO_2$ calc. 225.0790), 224 (100), 222 (7), 211 (6), 197 (13), 196 (70), 195 (57), 194 (12), 168 (4), 167 (17), 166 (20), 162 (3), 152 (5), 141 (6), 140 (15), 139 (9), 127 (6), 126 (5), 97.5 (4), 88 (3), 86 (11), 84 (17), 83.5 (10), 77 (5), 70.5 (6), 49 (18).

6-Methoxyindan-1-one (presumably *E*) *O*-Crotyloxime. Yellowish oil, 21% yield. 60 MHz ^{1}H nmr ($CDCl_3$) δ 1.75 (3H, *d*, *J* = 3 Hz, *C*-CH_3), 2.93 (4H, *br s*, CH_2CH_2), 3.80 (3H, *s*, *O*-CH_3), 4.63 (2H, *m*, *O*-CH_2), 5.80 (2H, *m*, CH=CH), 6.91 (1H, *dd*, J_o= 9 Hz, J_m = 2 Hz, H-5), 7.20 (1H, *dd*, J_o = 9 Hz, J_m = 2 Hz, H-4), 7.93 (1H, *d*, *J* = 2 Hz, H-7). Eims *m/z* (%) 231 (30, $[M]^+$), 216 (3), 177 (75), 160 (16), 146 (10), 131 (6), 117 (7), 103 (18).

6-Methoxyindan-1-one (presumably *Z*) *O*-Crotyloxime. Colorless needles, 62% yield. 60 MHz ^{1}H nmr ($CDCl_3$) δ 1.78 (3H, *d*, *J* = 3 Hz, *C*-CH_3), 2.91 (4H, *br s*, CH_2CH_2), 3.80 (3H, *s*, *O*-CH_3), 4.66 (2H, *m*, *O*-CH_2), 5.78 (2H, *m*, CH=CH), 6.88 (1H, *dd*, J_o = 8 Hz, J_m = 2 Hz, H-5), 7.16 (1H, *d*, J_o = 8 Hz, H-4), 7.16 (1H, *d*, J_m= 2 Hz, H-7). Eims *m/z* (%) 231 (30, $[M]^+$), 216 (2), 177 (75), 160 (16), 146 (10), 131 (6), 117 (7), 103 (18). Found: C, 72.67; H, 7.31; N, 6.01. $C_{14}H_{17}NO_2$ requires C, 72.70; H,7.40; N, 6.05%.

6-Methoxy-1-methyl-4-azafluorene (**2**). Colorless amorphous solid, 4% yield. ^{1}H Nmr see Table **1**. Uv-vis see Table **2**. Eims *m/z* (%) 212 (16, $[M+1]^+$), 211.0990 (90, $[M]^+$ $C_{14}H_{13}NO$ calc. 211.0997), 210 (12), 197 (14), 196 (100), 195 (4), 181 (6), 180 (9), 168 (20), 167 (20), 166 (8), 153 (6), 140 (5), 139 (5), 105.5 (6).

6-Methoxy-3-methyl-4-azafluorene (**6**). Colorless amorphous solid, 4% yield. ^{1}H Nmr see Table **1**. Uv-vis see Table **3**. Eims *m/z* (%) 212 (11, $[M+1]^+$), 211.0990 (100, $[M]^+$ $C_{14}H_{13}NO$ calc. 211.0997), 210 (9), 197 (8), 196 (67), 180 (9), 168 (14), 167 (10), 166 (4), 153 (3), 140 (3), 139 (3), 105.5 (3).

6-Methoxy-1-methyl-4-azafluoren-9-one (**10**). Pale yellow amorphous solid, 1.6% yield. ^{1}H Nmr see Table **4**. Uv-vis see Table **5**. Ir (film) ν_{max} (cm^{-1}) 1700, 1610, 1570, 1470, 1355. Eims *m/z* (%) 226 (15), 225.0795 (100, $[M]^+$ $C_{14}H_{11}NO_2$ calc. 225.0790), 224 (11), 211 (4), 210 (10), 196 (11), 195 (14), 182 (8), 167 (6), 166 (4), 154 (8), 140 (3), 139 (3), 128 (4), 127 (9), 126 (4), 112.5 (2), 86 (12), 84 (22), 77 (3), 75 (3), 51 (9), 49 (33).

6-Hydroxy-1-methyl-4-azafluoren-9-one (**18**). Pale yellow amorphous solid, subliming as needles, mp 312°C, 62% yield. ^{1}H Nmr see Table **7**. Uv-vis see Table **9**. Eims *m/z* (%) 212 (16), 211.0634 (100, $[M]^+$ $C_{13}H_9NO_2$ calc. 211.0633), 210 (4), 183 (19), 182 (5), 155 (7), 154 (12), 128 (5), 127 (6), 126 (4), 105.5 (8), 82 (9), 64 (23); mikes *m/z* 211 to 183.

6-Methoxy-3-methyl-4-azafluoren-9-one (**14**). Pale yellow amorphous solid, 1.4% yield. ^{1}H Nmr see Table **4**. Uv-vis see Table **6**. Ir (film) ν_{max} (cm^{-1}) 2900, 1700, 1605, 1575. Eims *m/z* (%) 225.0773 (100, $[M]^+$ $C_{14}H_{11}NO_2$ calc.

225.0790), 226 (5), 224 (21), 210 (8), 197 (4), 196 (12), 195 (29), 182 (15), 173 (4), 168 (2), 167 (11), 166 (5), 154 (10), 149 (5), 144 (3), 140 (6), 139 (5), 127 (18), 126 (5), 112.((3).

5-Methoxyindan-1-one (presumably *E*) *O*-Crotyloxime. Yellowish oil, 20% yield. 60 MHz ^{1}H nmr ($CDCl_3$) δ 1.71 (3H, *d*, *J* = 4 Hz, *C*-CH_3), 2.93 (4H, *m*, CH_2CH_2), 3.80 (3H, *s*, *O*-CH_3), 4.57 (2H, *m*, *O*-CH_2), 5.73 (2H, *m*, CH=CH), 6.76 (2H, *m*, H-4 and -6), 8.21 (1H, *d*, *J* = 9 Hz, H-7). Eims *m/z* (%) 231 (30, $[M]^+$), 216 (6), 177 (100), 160 (39), 146 (52), 131 (29), 117 (10), 103 (41), 77 (17).

5-Methoxyindan-1-one (presumably Z) *O*-Crotyloxime. Colorless needles, 71% yield. 60 MHz ^{1}H nmr ($CDCl_3$) δ 1.75 (3H, *d*, *J* = 4 Hz, *C*-CH_3), 2.96 (4H, *s*, CH_2CH_2), 3.83 (3H, *s*, *O*-CH_3), 4.60 (2H, *m*, *O*-CH_2), 5.80 (2H, *m*, CH=CH), 6.80 (2H, *m*, H-4 and -6), 7.62 (1H, *d*, *J* = 9 Hz, H-7). Eims*m/z* (%) 231 (30, $[M]^+$), 216 (4), 177 (100), 160 (20), 146 (43), 131 (14), 117 (6), 103 (22), 77 (9). Found: C, 72.81; H, 7.33; N, 6.01; $C_{13}H_{17}NO_2$ requires C, 72.70; H, 7.40; N, 6.05%.

7-Methoxy-1-methyl-4-azafluorene (**3**). Pale yellow needles from CH_2Cl_2, sublimed, mp 112°C, 3.3% yield. ^{1}H Nmr see Table 1. Uv-vis see Table 2. Ir (film) ν_{max} (cm^{-1}) 2900, 1600, 1375, 1240. Eims*m/z* (%) 212 (13), 211.1010 (100, $[M]^+$ $C_{14}H_{13}NO$ calc. 211.0997), 210 (5), 197 (6), 196 (33), 180 (3), 169 (4), 168 (28), 167 (17), 166 (4), 153 (4), 139 (3), 105.5 (3).

7-Methoxy-3-methyl-4-azafluorene (**7**). Colorless amorphous solid, sublimes as microneedles, mp 180°C, 14% yield. ^{1}H Nmr see Table 1. Uv-vis see Table 3. Ir (film) ν_{max} (cm^{-1}) 2900, 1580, 1400, 1240. Eims *m/z* (%) 212 (12), 211.0990 (100, $[M]^+$ $C_{14}H_{13}NO$ calc. 211.0997), 210 (4), 197 (5), 196 (42), 169 (3), 168 (26), 167 (10), 140 (3), 127 (4), 105.5 (5).

7-Methoxy-1-methyl-4-azafluoren-9-one (**11**). Pale yellow amorphous solid, sublimes as needles, mp 179°C, 1.9% yield. ^{1}H Nmr see Table 4. Uv-vis see Table 5. Ir (film) ν_{max} (cm^{-1}) 1705, 1590, 1555, 1290. Eims *m/z* (%) 226 (18), 225.0795 (100, $[M]^+$ $C_{14}H_{11}NO_2$ calc. 225.0790), 210 (47), 183 (3), 182 (27), 154 (20), 153 (5), 128 (3), 127 (11), 126 (5), 112.5 (3), 101 (4).

7-Hydroxy-1-methyl-4-azafluoren-9-one (**19**). Pale yellow amorphous solid, sublimes as needles, mp above 340°C, 57% yield. ^{1}H Nmr see Table 7. Uv-vis see Table 8. Eims *m/z* (%) 212 (16), 211.0644 (100, $[M]^+$ $C_{13}H_9NO_2$ calc. 211.0633), 210 (3), 183 (3), 182 (7), 156 (1), 155 (4), 154 (12), 128 (2), 127 (6), 126 (1), 105 (3).

7-Methoxy-3-methyl-4-azafluoren-9-one (**15**). Pale yellow amorphous solid, sublimes as needles, mp 195°C, 2.4% yield. ^{1}H Nmr see Table 4. Uv-vis see Table 6. Ir (film) ν_{max} (cm^{-1}) 1705, 1590, 1560, 1400, 1280, 1240. Eims m/z (%) 226 (17), 225.0773 (100, $[M]^+$ $C_{14}H_{11}NO_2$ calc. 225.0790), 210 (54), 182 (17), 154 (15), 153 (4), 127 (9), 126 (4), 112.5 (4).

4-Methoxyindan-1-one (presumably *E*) *O*-Crotyloxime. Colorless needles, 18% yield. 60 MHz ^{1}H nmr δ ($CDCl_3$) 1.72 (3H, *d*, *J* = 4 Hz, *C*-CH_3), 2.88 (4H, *br s*, CH_2CH_2), 3.82 (3H, *s*, *O*-CH_3), 4.60 (2H, *m*, *O*-CH_2), 5.80 (2H, *m*, CH=CH), 6.85 (1H, *d*, *J* = 8 Hz, H-5), 7.25 (1H, *t*, *J* = 8 Hz, H-6), 7.93 (1H, *d*, *J* = 8 Hz, H-7). Eims *m/z* (%) 231

(35, $[M]^+$), 216 (6), 177 (70), 160 (16), 146 (6), 131 (7), 117 (3), 103 (15), 55 (100).

4-Methoxyindan-1-one (presumably *Z*) *O*-Crotyloxime. Light yellow oil, 60% yield. 60 MHz ^{1}H nmr δ ($CDCl_3$) 1.75 (3H, *d*, J = 4 Hz, *C*-CH_3), 2.85 (4H, *br s*, CH_2CH_2), 3.78 (3H, *s*, *O*-CH_3), 4.60 (2H, *m*, *O*-CH_2), 5.78 (2H, *m*, CH=CH), 6.76 (1H, *dd*, J_o = 7 Hz, J_m = 2 Hz, H-5), 7.23 (2H, *m*, H-6 and -7). EIMS *m/z* (%) 231 (34, $[M]^+$), 216 (5), 177 (53), 160 (14), 146 (7), 131 (5), 117 (3), 103 (13), 55 (100).

8-Methoxy-1-methyl-4-azafluorene (**4**). Colorless needles from CH_2Cl_2, sublimed, mp 151°C, 4.3% yield. ^{1}H Nmr see Table 1. Uv-vis see Table 2. Eims *m/z* (%) 212 (14), 211 0990 (100, $[M]^+$ $C_{14}H_{13}NO$ calc. 211.0997), 210 (17), 197 (9), 196 (66), 182 (3), 181 (9), 180 (14), 168 (20), 167 (13), 166 (9), 152 (3), 139 (4), 115 (3), 105.5 (4), 90.5 (7); mikes *m/z* 211 to 196 + 182.

8-Methoxy-3-methyl-4-azafluorene (**8**). Colorless needles from CH_2Cl_2, mp 120-121°C, 2.7% yield. ^{1}H Nmr see Table 1. Uv-vis see Table 3. Eims *m/z* (%) 212 (14), 211.0990 (100, $[M]^+$ $C_{14}H_{13}NO$ calc. 211.0997), 210 (21), 197 (10), 196 (87), 182 (3), 181 (9), 180 (20), 178 (4), 177 (5), 168 (21), 167 (12), 166 (12), 153 (3), 152 (4), 140 (4), 139 (4), 105.5 (2), 90.5 (7); mikes *m/z* 211 to 196 +182, and 196 to 181 + 168.

8-Methoxy-1-methyl-4-azafluoren-9-one (**12**). Pale yellow amorphous solid, sublimes as needles, mp 193°C, 2% yield. ^{1}H Nmr see Table 4. Uv-vis see Table 5. Eims *m/z* (%) 225.0773 (96, $[M]^+$ $C_{14}H_{11}NO_2$ calc 225.0790), 224 (9), 207 (10), 198 (3), 197 (16), 196 (100), 195 (19), 194 (6), 182 (6), 179 (6), 178 (5), 169 (12), 168 (13), 167 (20), 166 (20), 154 (5), 153 (5), 152 (5), 141 (4), 140 (10), 139 (12), 128 (4), 127 (10), 113 (4), 112.5 (4); mikes *m/z* 225 to 207 + 197 + 196.

8-Hydroxy-1-methyl-4-azafluoren-9-one (**20**). Pale yellow microcrystals, sublimes as prisms, mp 196°C, 44% yield. ^{1}H Nmr see Table 7. Uv-vis see Table 9; $\lambda_{max}^{EtOH+AlCl_3}$ (log ε) 206 (4.07), 230sh (3.97), 252 (4.21), 290 (3.72), 300 (3.72), 311 (3.50), 450 (3.42). Eims *m/z* (%) 212 (10), 211.0623 (100, $[M]^+$ $C_{13}H_9NO_2$ calc. 211.0633), 183 (21), 182 (3), 165 (3), 164 (3), 155 (2), 154 (6), 127 (7), 112 (5); mikes *m/z* 211 to 193 + 183 and 183 to 155.

8-Methoxy-3-methyl-4-azafluoren-9-one (**16**). Pale yellow amorphous solid, sublimes as needles, mp 201°C, 65% yield by permanganate oxidation of **8**. ^{1}H Nmr see Table 4. Uv-vis see Table 6. Eims *m/z* (%) 226 (15), 225.0795 (99, $[M]^+$ $C_{14}H_{11}NO_2$ calc. 225.0790), 224 (33), 197 (22), 196 (100), 195 (40), 194 (8), 182 (9), 180 (3), 179 (11), 169 (26), 168 (21), 167 (12), 166 (21), 153 (12), 140 (14), 139 (12), 127 (10), 126 (11), 112.5 (3); mikes *m/z* 225 to 207 + 197 + 196.

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