Tetrahedron Vol. 23, pp 3521 to 3532. Pergamon Press Ltd 1967. Printed in Great Britain

THE ALKALOIDS OF *ANISOTES SESSILIFLORUS* C.B.Cl. (ACANTHACEAE)—FIVE NEW 4-QUINAZOLONE ALKALOIDS

R. R. ARNDT, S. H. EGGERS and A. JORDAAN
National Chemical Research Laboratory, C.S.I.R., Pretoria, S. Africa

(*Received* 9 *December* 1966; *accepted for publication* 17 *December* 1966)

Abstract—The structures of five new 4-quinazolone alkaloids II–VI have been elucidated by the extensive use of spectrographic techniques and a few selected chemical reactions.

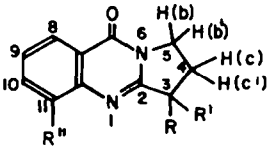
THE alkaloid mixture extracted from *Anisotes sessiliflorus* C.B.Cl. with ethanol, consisted of one major and five minor, optically inactive alkaloids. The mixture was separated by liquid–liquid distribution, and chromatography.

The major alkaloid, m.p. 211–212°, λ_{max}^{EtOH} 226, 303 mμ (ε 12,500 and 9000, respectively) analysed for the empirical formula $C_{11}H_{12}N_2O$, in agreement with the mass spectrum obtained, M^+ 188. This alkaloid was identical with dl-vasicine (peganine)[1] I (m.p., mixed m.p. chromatographic behaviour, UV and IR spectra). The nuclear magnetic resonance (NMR) spectrum in $CDCl_3$ showed four aromatic protons at τ 2·7–3·2, a one-proton triplet (a) at τ 5·20 (J = 7 c/s), two multiplets each representing two protons, centred at τ 6·5 and τ 7·2 which were assigned to the b,b′ and c,c′-protons, respectively. The two-proton singlet at τ 5·38 was assigned to the d,d′-protons.

The five minor alkaloids *anisotine* II, *anisessine* III, *aniflorine* IV, *deoxyaniflorine* V and *sessiflorine* VI are closely related and the structures II–VI were assigned on the evidence described below.

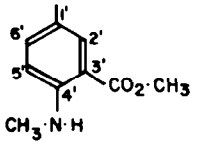
Anisotine II, m.p. 189–190° from acetone-hexane analysed for $C_{20}H_{19}N_3O_3$. The UV spectrum was very similar to that of 4-quinazolone[2] and remained practically unaltered in acid or alkaline solution. The IR spectrum indicated the presence of an >NH (2·99 μ), and two carbonyl functions, assigned to an amide (6·09 μ) and an aromatic carbomethoxy (5·95 μ). The amine present consisted of the grouping —NH · Me, detected in the NMR spectrum as a doublet at τ 7·1 (J = 5 c/s), which collapsed to a singlet on equilibration with deuterium oxide. The unresolved amino-proton signal in the region τ 2·1–2·8 disappeared simultaneously. The —OMe signal appeared at τ 6·20. The NMR spectrum, when compared with the spectra of desoxyvasicinone VII, 3-, and 2-benzyl-4-quinazolone[3,4] VIII and IX, respectively, was exceedingly informative (see Table 1). The total of seven aromatic protons indicated the presence of the second aromatic ring. The doublet at lowest field τ 1·73 (J = 9 c/s) was characteristic for the C-8 proton[5] situated *peri* to the amide carbonyl

[1] E. Späth and E. Nikawitz, *Ber Dtsch. Chem. bis.* **67**, 45 (1934).
[2] J. M. Hearn, R. A. Morton and J. C. E. Simpson, *J. Chem. Soc.* 3318 (1951).
[3] M. J. Bogert and G. A. Geiger, *J. Am. Chem. Soc.* **34**, 524 (1912).
[4] S. C. Pakrashi, J. Bhattacharyya, L. F. Johnson and H. Budzikiewicz, *Tetrahedron* **19**, 1011 (1963).
[5] S. Goodwin, J. N. Shoolery and L. F. Johnson, *J. Am. Chem. Soc.* **81**, 3065 (1959).



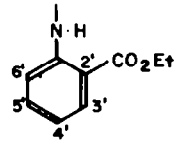
II ANISOTINE

R' = R'' = H



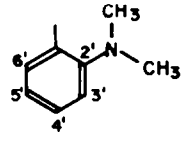
III ANISESSINE

R' = R'' = H



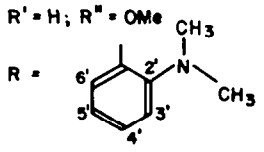
IV ANIFLORINE

R' = OH; R'' = OMe



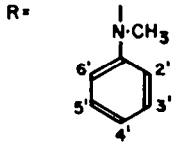
V DEOXYANIFLORINE

R' = H; R'' = OMe



VI SESSIFLORINE

R' = H; R'' = OMe



VII DESOXYVASICINONE

R = R' = R'' = H

in a 4-quinazolone moiety. The substitution pattern of the extra phenyl group was deduced from the presence of a one-proton doublet at an exceptionally high field position, τ 3·36 (J = 9 c/s). This was ascribed to the shielding effect of an ortho amino group.[6] The proton was coupled to an ortho proton, with no meta coupling observed. Further, the proton found as a doublet at τ 2·17 (J = 3 c/s) must be situated next to the deshielding carbomethoxy group,[7] coupled to a meta proton—a situation met in structure II. That this phenyl group was attached to the vasicinone moiety on C-3 was concluded from the analysis of the chemical shift values for the methylene protons in comparison with the values for the corresponding protons in compounds VII, VIII, and IX (see Table 1). The τ-values for protons b,b' and c,c' in II and VII were of the same order, whereas the signal ascribed to the a-proton (R') in II had shifted downfield into the τ 5·4–6·1 region. This was in agreement with the value found for the a,a'-protons in IX, but not with the much lower value for the b,b'-protons in VIII. The mass spectrum (Fig. 1) of anisotine II was simple, but nevertheless diagnostic.

[6] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.* 35, 731 (1961).

[7] P. Diehl, *Helv. Chim. Acta* 44, 829 (1961).

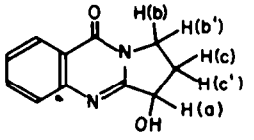
TABLE 1. CHEMICAL SHIFT VALUES (τ, ppm) OF PROTONS IN COMPOUNDS II–IX

	Compound	VII	II	III	IV	V	VI	VIII	IX
Methyl protons	OCH_3	—	s 6·20	—	s 6·12	s 6·15	s 6·06	—	—
	NCH_3	—	s 7·12	—	s 7·20	s 7·41	s 7·05	—	—
Aromatic protons	C_8	df 1·80 J 8 c/s	df 1·73 J 9 c/s	df 1·73 J 4 c/s	dd 2·05 J 8,1 c/s	dd 2·12 J 8,1 c/s	dd 2·11 J 8,1 c/s	df 1·75 J 8 c/s	df 1·74 J 8 c/s
	$C_{2'}$	—	d 2·17 J 3 c/s	—	—		df 3·21 J 6 c/s	—	—
	$C_{3'}$	—	—	dd 2·00 J4,1c/s	2·70–2·95	2·70–3·10	m 2·40–2·80	—	—
	$C_{4'}$	—	—	t 3·27 J 4 c/s			m 2·90–3·00	—	—
	$C_{5'}$	—	d 3·36 J 9 c/s				m 2·40–2·80	—	—
	$C_{6'}$	—		d 3·10 J 4 c/s			df 3·21 J 6 c/s	—	—
Methylene protons	a	t 6·85 J 8 c/s	5·40–6·10 (3H)	m 4·97 (1H)	—	dd 5·05 J 10,6 c/s (1H)	m 5·20–5·85 (3H)	—	s 5·92
	a'				—			—	
	b	t 5·82 J 7 c/s		m 5·30–6·20	m 5·40–5·90	m 5·60–5·95		s 4·86	
	b'								
	c	m 6·65–7·00	m 7·20–8·00	dm 7·10–7·84	m 7·00–7·50	m 7·10–8·15	m 7·10–7·60	—	—

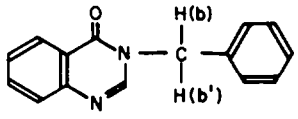
d = doublet
df = doublet with fine splitting
dd = double doublet
dm = double multiplet
m = multiplet
t = triplet
s = singlet

The fact that the ester group was situated ortho with respect to the amino substituent on the aromatic ring, was evident from the loss of methanol (*m/e* 317, M-32) fragment *z* (scheme A) or *m/e* 316 (M-1-32) fragment *y*, explained by the "ortho effect".[8] This interpretation was supported by the loss of methanol-d (M-33) to give fragment *z* from the N-d-methyl compound obtained by treatment with deuterium oxide, and also by the loss of water in the mass spectrum of the acid formed by hydrolysis of II.

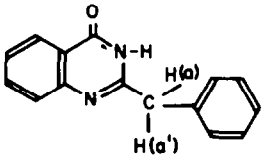
[8] K. Biemann, *Angew. Chem.* 74, 102 (1962).



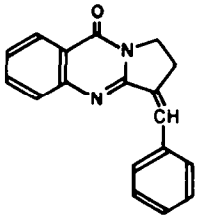
VIII



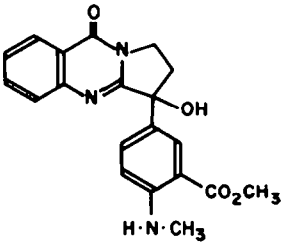
IX



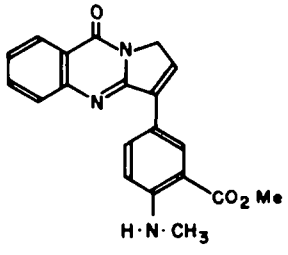
X



XI



XII



The mode of attachment of the aromatic substituent on the desoxyvasicinone moiety on C-3 received further support from the appearance of the peak at *m/e* 185. (Found: 185·0714, calc. for $C_{11}H_9N_2O$ 185·0715), represented by fragment *x*. The peak at *m/e* 290 was ascribed to fragment *w*, formed by the loss of the carbomethoxy group.

Chemical evidence for the position of attachment was obtained from the failure of formation of the benzal derivative of II, a derivative which readily formed in the case of desoxyvasicinone,[9] to yield X. Potassium permanganate oxidation of II in acetone (24°) afforded a product XI, m.p. 185–187°, $C_{20}H_{19}N_3O_4$, M^+ 365. The NMR spectrum of this compound was nearly identical with that of II, the only difference being the absence of the signal for the C-3 proton in the τ 5·4–6·1 region. The UV spectrum of this oxidation product was also very similar to that of II. In acid medium no immediate change was observed. However, after standing for 10 hr at room temperature (24°), a considerable hyperchromic shift of all the bands except the 212 and 222 mμ absorption bands was observed. This UV spectrum was very similar to that obtained for the benzal derivative X. Therefore, the oxidation product must be the 3-hydroxyanisotine XI and the dehydration product obtained in acid solution can be represented

[9] R. C. Morris, W. E. Hanford and Roger Adams, *J. Am. Chem. Soc.* **57**, 951 (1935).

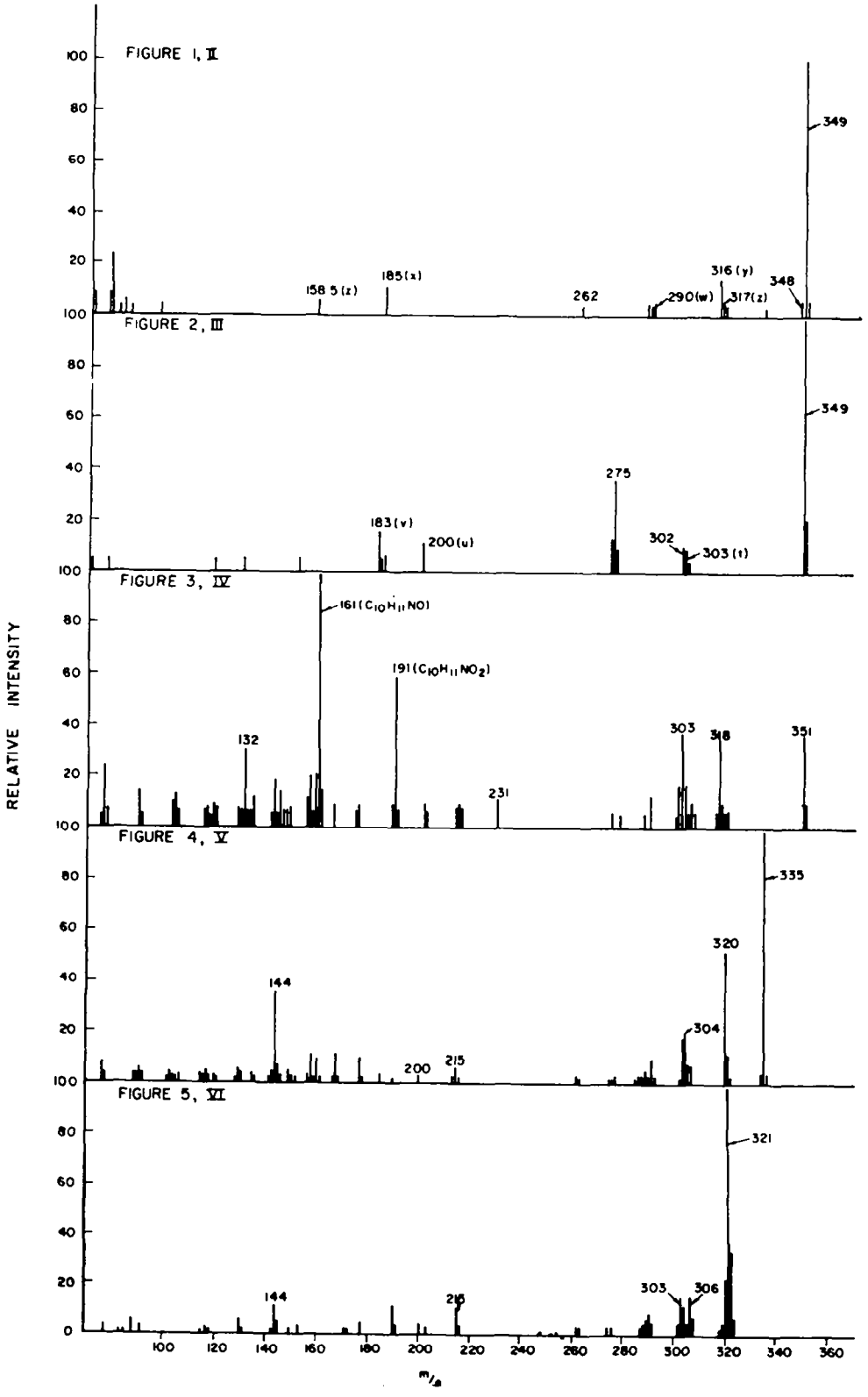
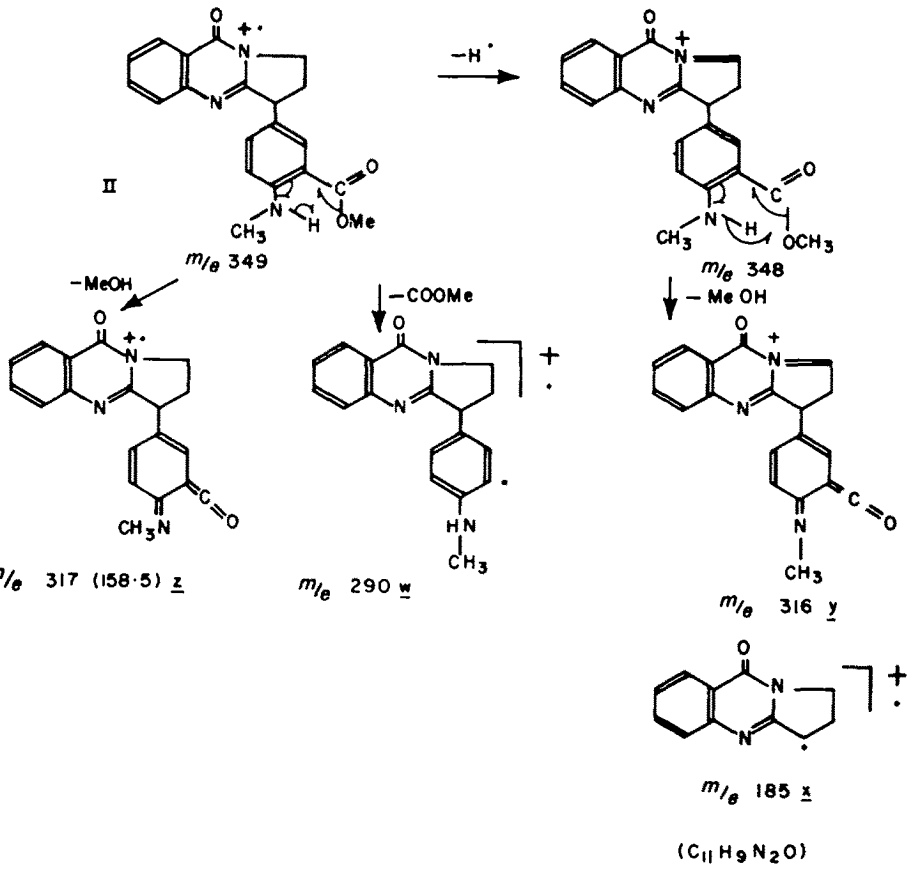


FIGURE I, II
349
316 (y)
348
158 5 (z)
185 (x)
262
290 (w)
317 (z)
FIGURE 2, III
349
275
183 (v)
200 (u)
302
303 (t)
FIGURE 3, IV
161 ($C_{10}H_{11}NO$)
191 ($C_{10}H_{11}NO_2$)
132
303
318
351
231
FIGURE 4, V
335
320
144
304
200
215
FIGURE 5, VI
321
144
215
303
306
RELATIVE INTENSITY
m/e

SCHEME A



by XII (M^+ 347). Compound XII, also obtained on refluxing XI in acetic acid with *p*-toluene-sulphonic acid for 30 min, was found to be extremely unstable, rapidly going over into a dark blue polymer.

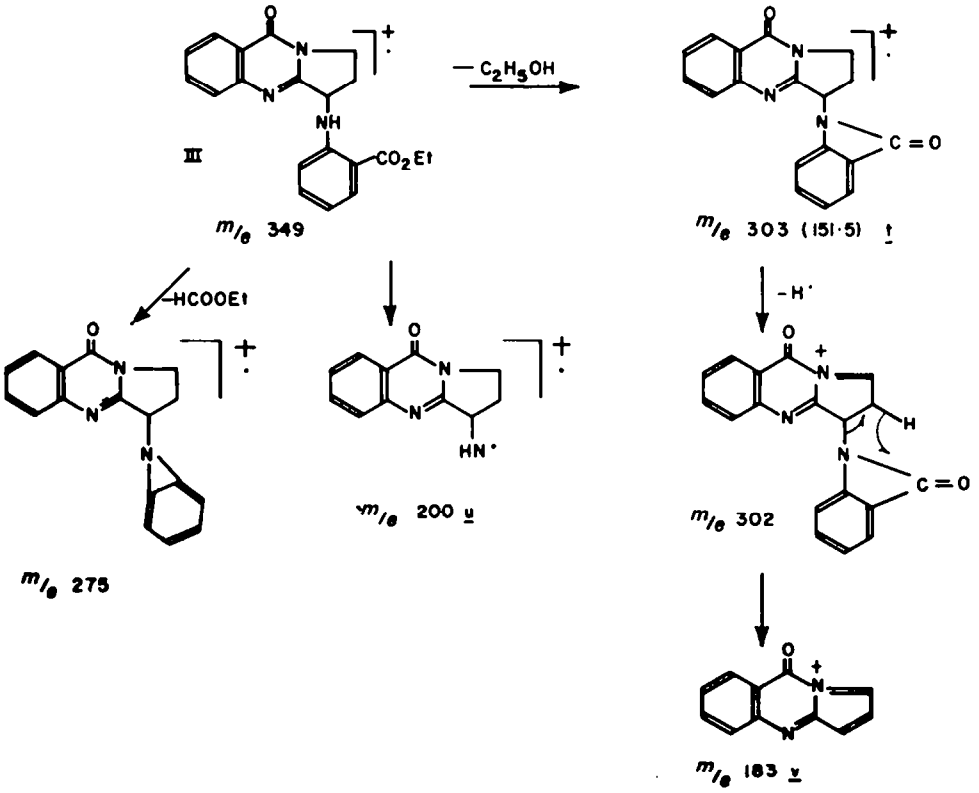
Anisessine III m.p. 170° from acetone/hexane, analysed for $C_{20}H_{19}N_3O_3$. The UV spectra of II and III were essentially superimposable. The IR spectrum indicated the presence of an NH-group (2·95 μ), amide and aromatic ester carbonyls (6·05 and 5·95 μ, respectively). The NMR and mass spectra showed marked differences when compared with the spectra obtained for II. The presence of an ethyl ester was evident from the characteristic A_2X_3 ethyl pattern, a triplet centred at τ 8·63 (J = 7 c/s), and a quartet centred at τ 5·62 (J = 7 c/s). No N-CH_3 signal was present, but that a secondary amine did occur was indicated by the disappearance on equilibration with deuterium oxide of a one-proton doublet at τ 1·52 (J = 3 c/s) and the collapse of a multiplet centred at τ 4·97 (C-3 proton), to a triplet representing the four lines of the X-proton of an ABX system where $J_{AX} = J_{BX}$ = 4 c/s. A total of eight aromatic protons suggested that the phenyl substituent on the desoxyvasicinone skeleton was disub-

stituted. The analysis of the aromatic proton signals (Table 1) showed the C-8 low-field proton signal at τ 1·73 (J = 4 c/s). Another proton appeared at low field τ 2·00 as a double doublet (J = 4 and 1 c/s), typical of an aromatic proton next to an ester grouping, coupled to ortho and meta protons. Two aromatic proton signals at higher field τ 3·1 (doublet, J = 4 c/s) and τ 3·27 (triplet, J = 4 c/s) indicated the presence of protons ortho and para to the amino group, the spin–spin coupling pattern being in accordance with the substitution pattern shown in III. In a decoupling experiment performed on a Varian HA-100, the proton signal at τ 4·97 was irradiated with a frequency of 2985 c/s. This caused marked simplification of the multiplets at τ 7·1 and 7·84, and no change in the multiplet at τ 5·3–6·2, supporting the assignments made to these various protons as given in Table 1.

The mass spectrum (Fig. 2) of anisessine showed the loss of ethanol m/e 3·3 (M-46), fragment t, while water was lost in the case of the free acid obtained on hydrolysis of III, through the "ortho effect" (scheme B). The different mode of attachment of the phenyl substituent was apparent from peaks at m/e 200 and m/e 183, fragments u and v. The possible routes for the formation of the other prominent peaks in the spectrum at m/e 302 and m/e 275 are given in scheme B.

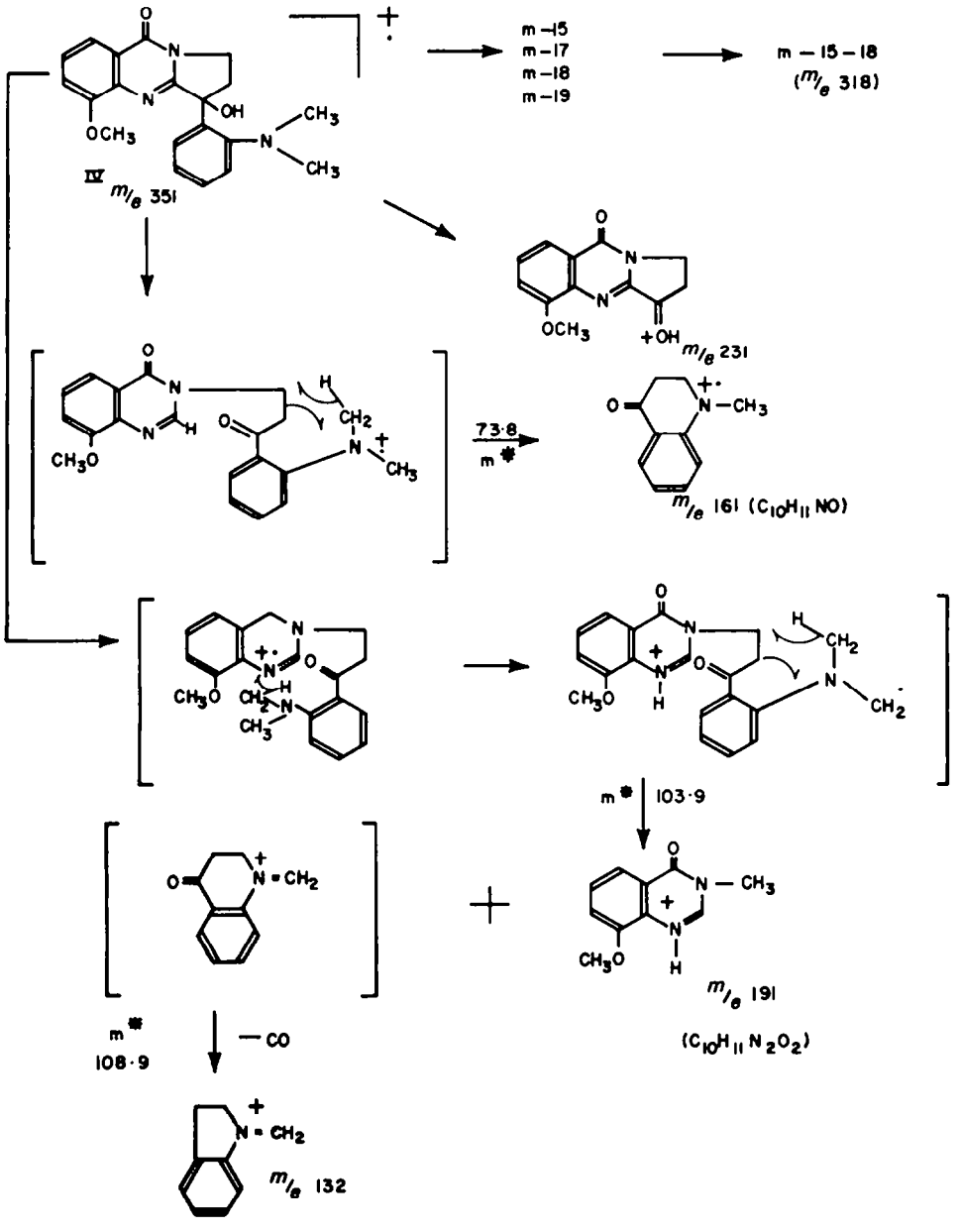
From the oxidation of III with potassium permanganate in acetone (24°), ethyl anthranilate was isolated.

SCHEME B



Aniflorine IV, m.p. 197° from methanol, analysed for $C_{20}H_{21}N_3O_3$. The similarity of the UV spectrum with those of alkaloids II and III indicated a close relationship with these alkaloids. The IR spectrum indicated the presence of a hydroxyl group (2·90 μ), an amide group (6·02 μ) and the absence of an ester carbonyl. In the NMR spectrum, the presence of a dimethylamino group was evident from the six-proton

SCHEME C



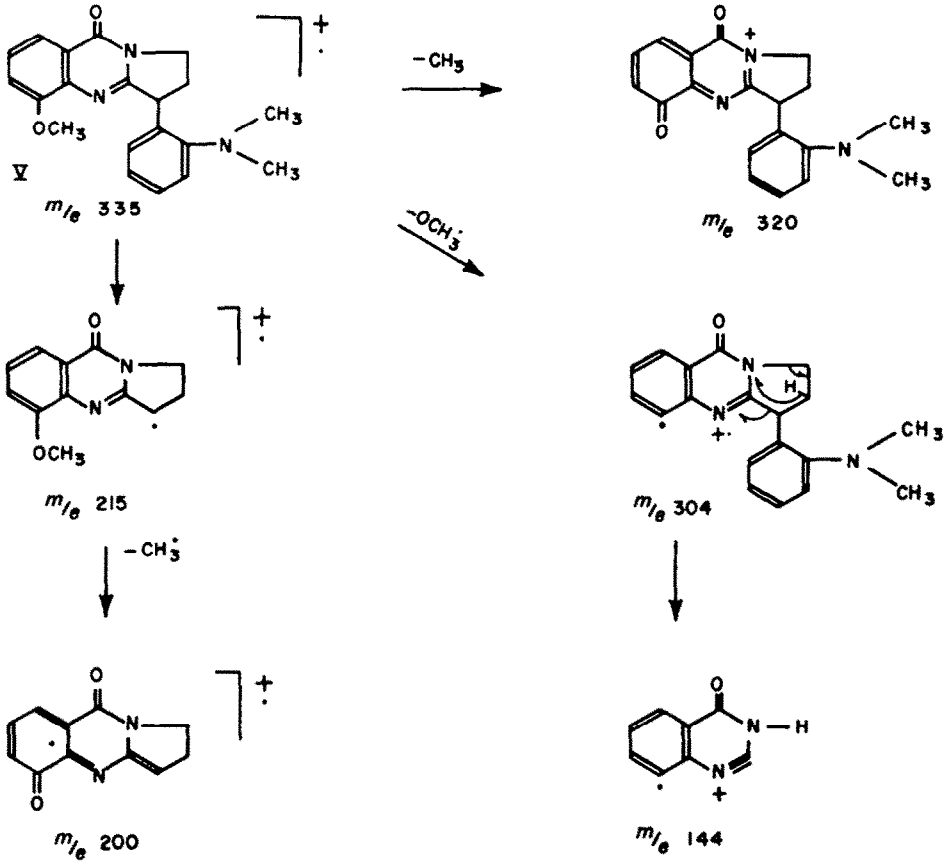
singlet at τ 7·20, while an aromatic methoxyl gave rise to a singlet at τ 6·12. That this methoxyl group was attached to the quinazolone aromatic ring was concluded from the mass spectrum discussed below, whereas its position on this ring became evident from the C-8 proton spin–spin coupling pattern. This showed ortho and meta coupling (J = 8 and 1 c/s), which is only possible with the methoxyl in the 11-position. The other six aromatic protons gave rise to signals in the rather narrow region of τ 2·70–2·95. The absence of any aromatic proton signal at higher field, as anticipated for protons ortho and para with respect to the amino group, needs an explanation. The position of the hydroxyl became evident from the absence of the C-3 proton signal. The tertiary nature of this alcohol was in accordance with the failure of acetylation under non-forcing conditions (Ac_2O/pyridine), and resistance to chromic oxide oxidation. If the $-N \cdot (Me)_2$ substituent is placed ortho to the carbon attached to the five-membered ring as in IV, the crowded situation would prevent the methyl groups from becoming co-planar with the aromatic nucleus and thus prevent the donation of electrons from the amino group and therefore its shielding effect. Attempts to dehydrate aniflorine under conditions found to be effective in the case of compound XI were unsuccessful. It is suggested that this was due to the close proximity of the two functional groups, of which the amino group would be preferentially protonated, thus preventing protonation of the hydroxyl group. The para position (C-4′) for the dimethylamino group is ruled out by the absence of a symmetrical A_2B_2 pattern in the NMR spectrum. It would also be difficult to explain the absence of shielding effects of the 3′-, 5′-protons. The latter argument also holds for substitution in the meta positions (C-3′ or C-5′).

The mass spectrum of IV (Fig. 3) was completely compatible with the structure suggested. Scheme C shows possible routes for the formation of the most prominent peaks. The ions *m/e* 191 (60%) and *m/e* 161 (100%) are considered to result from the transfer of two hydrogens from the N-dimethyl- and one from the hydroxyl group. The latter assumption was proved to be correct by the spectrum obtained after deuterium exchange of the hydroxyl proton, in which peaks appeared at *m/e* 192 and *m/e* 161. Such hydrogen transfer would only appear possible provided the dimethylamino group is situated ortho to the point of attachment of the phenyl ring. Information with regard to the correctness of this argument will be provided by the synthesis of suitably labelled analogues at present in progress.

Alkaloid IV on treatment with Raney nickel in ethanol under hydrogen, yielded deoxyaniflorine which was found to be identical in all respects with the isolated alkaloid V, m.p. 168–172° from methanol ($C_{20}H_{21}N_3O_2$). The NMR data obtained are given in Table 1. Scheme D shows possible routes for the formation of the more intense peaks in the mass spectrum (Fig. 4) of deoxyaniflorine.

The last member of the group of alkaloids isolated, VI sessiflorine m.p. 195–197° from methanol, had molecular formula $C_{19}H_{19}N_3O_2$. (Found: M^+ 321·148 $C_{19}H_{19}N_3O_2$ requires 321·147.) Sessiflorine rapidly decolorized potassium permanganate in acetone as might be expected of an N-substituted aniline. No identifiable products were isolated. The IR spectrum showed an amide carbonyl (6·05 μ). The NMR spectrum showed an aromatic OMe at τ 6·06, and a tertiary methylamino group at τ 7·05. The double doublet for the C-8 proton at τ 2·11 (J = 8 and 1 c/s) together with the mass spectral data (scheme E) placed the methoxyl at C-11. Three aromatic protons (two ortho on C-2′ and C-6′ and one para on C-4′) appear at

SCHEME D

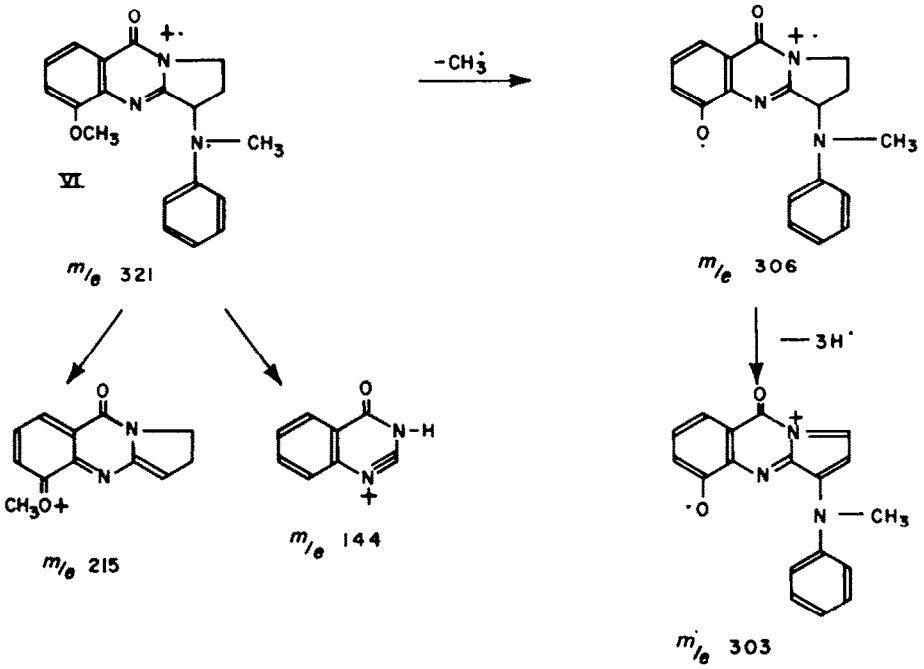


higher field due to the shielding effect of the amino group. The mass spectrum (Fig. 5) was consistent with the proposed structure VI. An accurate mass determination of the peak at *m/e* 303 (303·103 ≡ $C_{18}H_{13}N_3O_2$) showed that this fragment was not due to the loss of water from the molecular ion ($C_{19}H_{17}N_3O$ requires 303·137), but due to loss of a methyl group and three additional hydrogens (scheme E). The absence of a hydroxyl was also proved by failure of deuterium exchange and the absence of IR absorption in the 2·8–2·9 μ region.

The UV spectrum of VI in ethanol was similar to those of alkaloids IV and V. However, in acid solution electron transfer from the exocylic nitrogen to the aromatic ring was eliminated with a corresponding decrease in the intensity of the spectrum, as in the case of N-dimethylaniline. In the spectra of IV and V only a very slight change in intensity of the absorption band at 235 mμ was observed.

It may therefore be concluded that in alkaloids IV and V, electron transfer from the exocyclic nitrogen was inhibited due to steric effects. This may be regarded as final evidence for placing the N-dimethyl substituent on the carbon ortho to the point of linkage in alkaloids aniflorine and deoxyaniflorine.

SCHEME E



EXPERIMENTAL

UV absorption spectra refer to ethanol, and IR absorption spectra refer to chloroform solutions. The latter were recorded on a Perkin–Elmer Infracord 237 spectrometer. Nuclear magnetic resonance spectra were determined with a Varian A-60 instrument, with T.M.S. as internal standard (τ 10·00) unless otherwise stated. Mass spectra were determined with an A.E.I., MS-9 spectrometer, using the direct insertion technique. Melting points were determined on a Kofler block.

Extraction and isolation of alkaloids. Ground, air-dried branches and leaves (22 kg) of *Anisotes sessiliflorus* were exhaustively extracted with ethanol, the extract concentrated, and shaken with 2% aqueous tartaric acid. The acid solution was made alkaline, and the crude alkaloids (11·8 g) isolated with chloroform. The crude alkaloid mixture was subjected to a 10-tube Craig counter-current distribution between chloroform and aqueous buffer solution (citric acid-phosphate; pH 7·4, 100 ml of each phase per tube). Tube 10 yielded alkaloid I (7·4 g) m.p. 211–212° (methanol–benzene). (Found: C, 69·9; H, 6·5; N, 14·6; O, 8·8; Calc. for $C_{11}H_{12}N_2O$: C, 70·2; H, 6·4; N, 14·9; O, 8·5%.) This alkaloid (I) was found to be identical in all respects with d,l vasicine, kindly supplied by Dr. K. Schreiber (Inst. für Kulturpflanzenforschung Gatersleben der Deutschen Akademie der Wissenschaften zu Berlin). Tubes 1 and 2 yielded a mixture of the minor alkaloids (3·5 g), contaminated with some vasicine which was removed by chromatographing the mixture through formamide-impregnated cellulose powder. Elution with benzene afforded the mixture of minor alkaloids (3·0 g), and vasicine (400 mg) was eluted with 9:1 benzene–methylene chloride. Finally, the minor alkaloids were separated into five alkaloids II, III, V, VI, and IV in decreasing order of their R_f values, by preparative thin-layer chromatography on silica gel.

Anisotine (II), crystallized from acetone–hexane, had m.p. 189–190°, λ_{max} 212, 226, 259, 301, 312, and 356 mμ (ε 37,700, 54,100; 14,800; 4900; 4500, and 5400, respectively.) (Found: C, 68·7; H, 5·7; N, 12·0. $C_{20}H_{19}N_3O_3$ requires C, 68·4; H, 6·0; N, 12·0%.) M^+ 349.

Anisessine (III), when crystallized from methanol, had m.p. 170–171°, λ_{max} 207, 225, 253, 300, 311, and 340 mμ (ε 36,600; 54,100; 14,700; 4900; 4200, and 6300, respectively) (Found: C, 68·6; H, 5·7; N, 12·2. $C_{20}H_{19}N_3O_3$ requires C, 68·4; H, 6·0; N, 12·0%.) M^+ 349.

Aniflorine (IV), crystallized from methanol, had m.p. 195–197°, λ_{max} 207, 235, 286, 312, and 324 mμ (ε 31,300; 19,900; 7000; 6600 and 5800, respectively.) $\lambda_{max}^{EtOH-HCl}$ 207, 236, 291, 312, and 324 mμ (ε 30,500; 16,100; 6200; 7700, and 7500, respectively.) (Found: C, 68·5; H, 6·3; N, 11·6. $C_{20}H_{21}N_3O_3$ requires C, 68·4; H, 6·0; N, 12·0%.) M^+ 351.

Deoxyaniflorine (V), crystallized from methanol, had m.p. 168–172°, λ_{max} 211, 232, 285, 315, and 330 mμ (ε 33,000; 23,100; 8600; 6900, and 5800, respectively.) $\lambda_{max}^{EtOH-HCl}$ 211, 237, 285, 315, and 320 mμ (ε 33,000; 20,300; 7700; 6900, and 5700, respectively.) (Found: M^+ 335·160; $C_{20}H_{20}N_3O_2$ requires 335·163.)

Sessiflorine (VI), crystallized from methanol, had m.p. 195–197°, λ_{max} 212, 239, 286, 315, and 327 mμ (ε 34,700; 30,300; 9200; 8800, and 6600, respectively). $\lambda_{max}^{EtOH-HCl}$ 212, 239, 286, 315 and 327 mμ (ε 30,100; 19,400; 7000; 6900, and 5900, respectively). (Found M^+ 321·148; $C_{19}H_{19}N_3O_2$ requires 321·147.)

Benzaldesoxyvasicinone (X). Desoxyvasicinone (10 mg) was heated at 145° in the presence of a few drops of freshly distilled benzaldehyde for 45 min. After cooling, the reaction mixture was extracted with methylene chloride, and this solution extracted with dilute sulphuric acid (3N). The acid solution was made alkaline with sodium carbonate and extracted with methylene chloride. Yield 5·0 mg m.p. 135° from hexane, λ_{max} 207, 223, 279, 292, 304, 317, and 332 mμ (ε 35,000; 32,900; 13,600; 11,800; 12,700; 13,200, and 11,000, respectively). (Found M^+ 274·106; $C_{18}H_{14}N_2O$ requires 274·111.)

Oxidation of anisotine (II) *to 3-hydroxyanisotine* (*XI*). To a solution of anisotine (43 mg) in acetone (5 ml) freshly distilled from potassium permanganate, was added solid potassium permanganate (34 mg). Excess of oxidizing agent was destroyed after 12 hr at 24°, the solids removed by filtration and the solution evaporated *in vacuo*. Only one product was formed according to t.l.c. A small amount of starting material was removed by preparative t.l.c. on silica gel (96:4 methylene chloride-methanol). Crystallization from methanol gave crystals m.p. 185–187°, λ_{max} 212, 225, 262, 303, 315, and 354 mμ (ε 31,500; 51,000; 14,100; 7500; 7300, and 5100, respectively.) $\lambda_{max}^{EtOH-HCl}$ after standing for 12 hr 210, 225, 275, 287, 302, 317, 332, and 354 mμ (ε 31,400; 51,200; 17,500; 16,500; 17,500; 16,500; 12,900, and 5800, respectively) M^+ 365.

Oxidation of anisessine (III). Solid potassium permanganate (20 mg) was added to a solution of anisessine (7 mg) in acetone (2 ml) distilled from potassium permanganate. After standing for 30 min at 24°, excess of oxidising agent was destroyed, the solvent evaporated, the residue taken up in methylene chloride and filtered. A fast-moving component on t.l.c. (2 mg) (silica gel, methylene chloride) was recovered and identified as ethyl anthranilate. (Gas chromatography, mass spectroscopy and t.l.c.).

Hydrogenolysis of aniflorine (IV) *to deoxyaniflorine* (V). Aniflorine (2 mg) in ethanol (2 ml) was shaken with hydrogen in the presence of Raney nickel (100 mg) for 4 days. The product consisted of two major components separated by preparative t.l.c. (silica gel, 98:2 methylene chloride-methanol). One of these components was identified as starting material and the second as deoxyaniflorine (chromatographic behaviour and mass spectroscopy).

Acknowledgement—This work was supported by Messrs. Smith, Kline and French, Philadelphia, U.S.A.