Journal of Photochemistry, *24* (1984) 355 - 371

LUMINESCENCE SPECTRA OF HARMINE, HARMALINE, RESERPILINE AND 3-DEHYDRORESERPINES

B. SAVORY and J. H. TURNBULL

Department of Chemistry and Metallurgy, Royal Military College of Science, Shrivenham, Wilts. SN6 8LA (Gt. Britain)

(Received September 13, 1983; in revised form October 10, 1983)

Summary

Fluorescence and phosphorescence spectra of harmine, harmaline and 3-dehydroreserpines were determined in neutral, acidic and basic solution at 298 and 77 K. Harmine and harmaline display normal behaviour. The dehydroreserpines, in contrast, act as pseudobases, undergoing reversible conversion to carbinolamine and keto–indole forms with characteristic spectral changes.

The conversion of reserpines to 3-dehydroreserpines by molecular oxygen in acetic acid media is described. The reaction is catalysed by trifluoroacetic acid and is inhibited by quenchers of singlet oxygen. Reserpiline undergoes similar oxidation under these conditions.

1. Introduction

In a previous paper [1] we discussed the luminescence spectra of reserpine and some related derivatives. We now turn to the Harmala alkaloids harmine (I) and harmaline (II) which are of pharmacological interest as central stimulants, hallucinogens and paralysants of cardiac muscle. (Structures I - VII are shown in Fig. 1.) Structurally these compounds relate to reserpine (IIIa) and to its dehydro derivatives (IVa and Va). We have now determined the fluorescence and phosphorescence spectra of harmine and harmaline in neutral, acidic and alkaline solution, and we have made similar spectral measurements on 3-dehydroreserpines. The spectral changes observed as the pH and temperature are varied illustrate a significant difference between the harmaline and the dehydroreserpine systems. We also describe the oxidation of reserpines by molecular oxygen in acetic acid solution in the presence of proton donors, particularly trifluoroacetic acid. 3-dehydroreserpines are produced, the intense green fluorescence of which has been used for the determination of reserpines in fluids [2, 3]. We have included the stereochemically related Rauwolfia alkaloid reserpiline (VI) in these studies. Reserpiline is easily oxidized to the 3-dehydroreserpilinium

0047-2670/84/$3.00

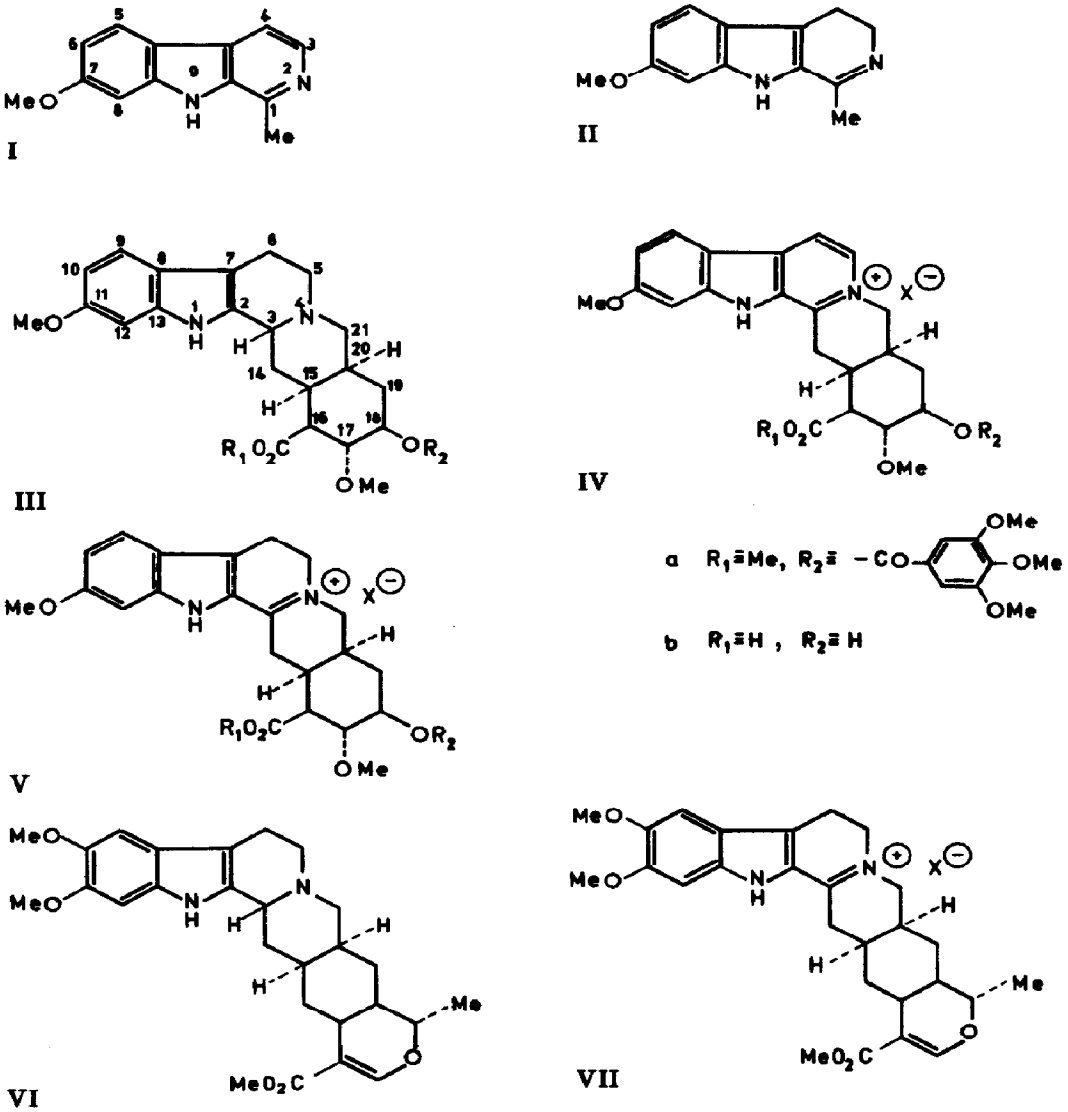


Fig. 1. Chemical structures of harmine (I), harmaline (II), reserpine (IIIa), 3,4,5,6-dehydroreserpine (IVa), 3,4-dehydroreserpine (Va), 3,4-dehydroreserpic acid (Vb), reserpiline (VI) and 3,4-dehydroreserpiline (VII).

cation (VII) in trifluoroacetic acid solution. The cation possesses a distinctive yellow fluorescence.

2. Experimental details and materials

The spectroscopic techniques and corrections were as described in earlier papers [4].

Harmine, harmaline and harmaline hydrochloride were purum grades supplied by Fluka AG. 3-dehydro derivatives of reserpine and reserpiline

were prepared from the parent alkaloids by oxidation in trifluoroacetic acid solution and isolated as their respective trifluoroacetate and perchlorate salts.

3. Results and discussion

Spectral measurements were made in ethanolic solutions of harmine, harmaline and 3-dehydro derivatives of reserpine, reserpic acid and reserpiline.

3.1. Absorption spectra (cf. ref. 5)

The absorption spectrum of harmine (I) in neutral ethanol (Fig. 2 and Table 1) shows well-defined peaks at λ_{max} = 241 nm and λ_{max} = 301 nm with smaller peaks at λ_{max} = 325 nm and λ_{max} = 338 nm. This spectrum is unchanged in aqueous alkaline (NaOH) ethanol. In aqueous acidic (HCl) ethanol, however, the spectrum is significantly modified (Fig. 2 and Table 1), showing λ_{max} = 250 nm and λ_{max} = 326 nm with the emergence of a distinct shoulder at 360 nm and a very weak absorption at 410 nm ($\epsilon \approx 500$ $dm^3\ mol^{-1}\ cm^{-1}$). These changes reflect protonation of the base to give the cationic species VIII (Fig. 3). Acidic solutions are faintly yellow owing to the weak band at 410 nm.

The absorption spectrum of harmaline (II) in neutral ethanol (Fig. 4 and Table 1) (λ_{max} = 261 nm and λ_{max} = 337 nm) is also modified in an acidic medium (λ_{max} = 259 nm and λ_{max} = 383 nm) (Fig. 4 and Table 1). The acidic solution of harmaline, corresponding to a solution of crystalline

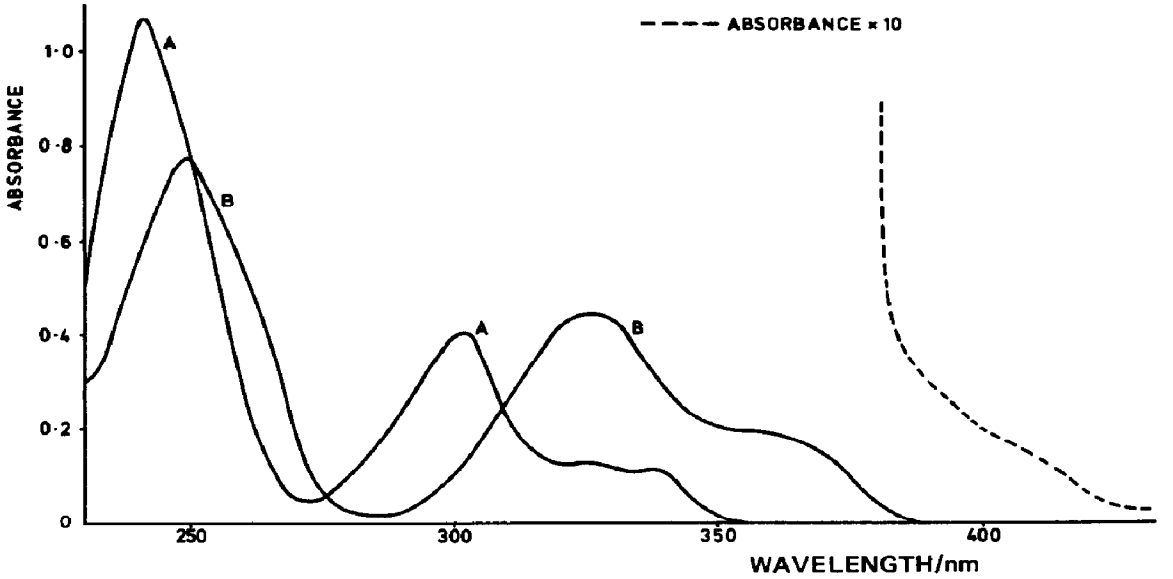
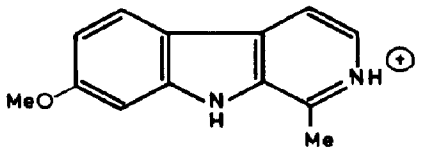


Fig. 2. Absorption spectra of harmine in neutral (curve A) and acidic (curve B) ethanol.

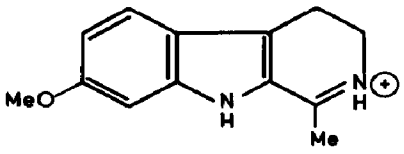
TABLE 1

Compound	*Absorption*			*Fluorescence (298 K)*	*Fluorescence (77 K)*	*Phosphorescence (77 K)*	
	λ_{max} (nm)	ϵ (dm^3 mol^{-1} cm^{-1})	λ_{ex} (nm)	λ_{max}[a] (nm)	λ_{max}[a] (nm)	λ_{max}[a] (nm)	τ_p (s)
Harmine	241	27776					
	301	10795	301	355, 365	346, **361**, 377	409, 419, 434	2.7
	325	3546					
	338	3158					
Harmine + acid	250	20114					
	326	11908	301	412	385, 400	461	3.7
	360	5126					
Harmine + alkali	241	26948					
	301	12866	301	356, **366**	345, **362**	407, 420, **435**	2.7
	325	7844					
	337	7248					
Harmaline	261	14209	261	367, 477	346, 362, **429**, 442	410, 418, **434**	3.4
	337	22131	337	367, 476	361, **427**, 441	411, 419, 433	2.8
	365	5075					
Harmaline + acid	259	11926	261	475	**429**, 446	460	4.4
	383	28644	337	476	**428**, 445	461	3.7
Harmaline + alkali	261	23908	261	366	349, **367**, 380	409, 422, **433**	
	337	28926	337	368	367, 383	410, 421, **435**	2.8
Harmaline hydrochloride	255	6911	255	(351, 365) 476	346, 363, 427, 445	433	
	380	14292	380	476	375, 428, 445		

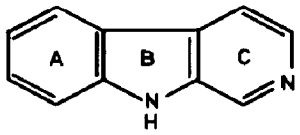
[a] Values in bold type denote the wavelength of the peak with greatest intensity.



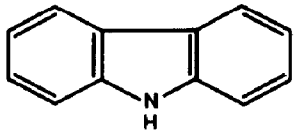
VIII



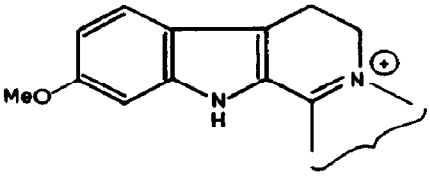
IX



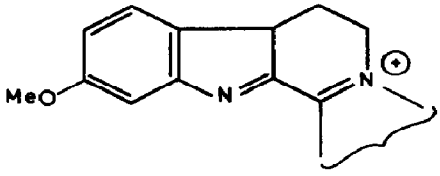
X



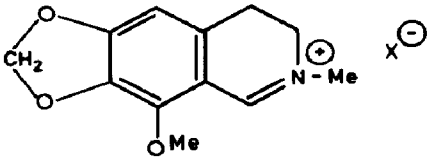
XI



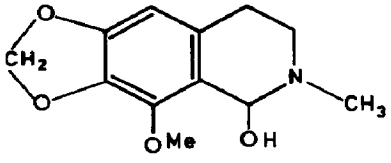
XII



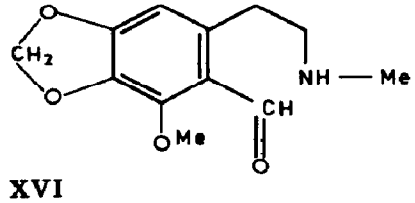
XIII



XIV



XV



XVI

Fig. 3. Chemical structures of protonated harmine (VIII), protonated harmaline (IX), β-carboline (X), carbazole (XI), indole immonium cation (XII), isoindole immonium cation (XIII), cotarnine cationic form (XIV), cotarnine carbinolamine (XV) and cotarnine amino aldehyde form (XVI).

harmaline hydrochloride, is distinctly yellow in colour owing to the strong absorption in the blue region at λ_{max} = 380 nm, arising from the cationic chromophore IX (Fig. 3).

3.2. Emission spectra

Emission spectral data for harmine and harmaline are given in Table 1. The fluorescence of harmine at 298 K (Fig. 5) is characteristic of the β-carboline nucleus (Fig. 3, X). The singlet emission (in neutral ethanol)

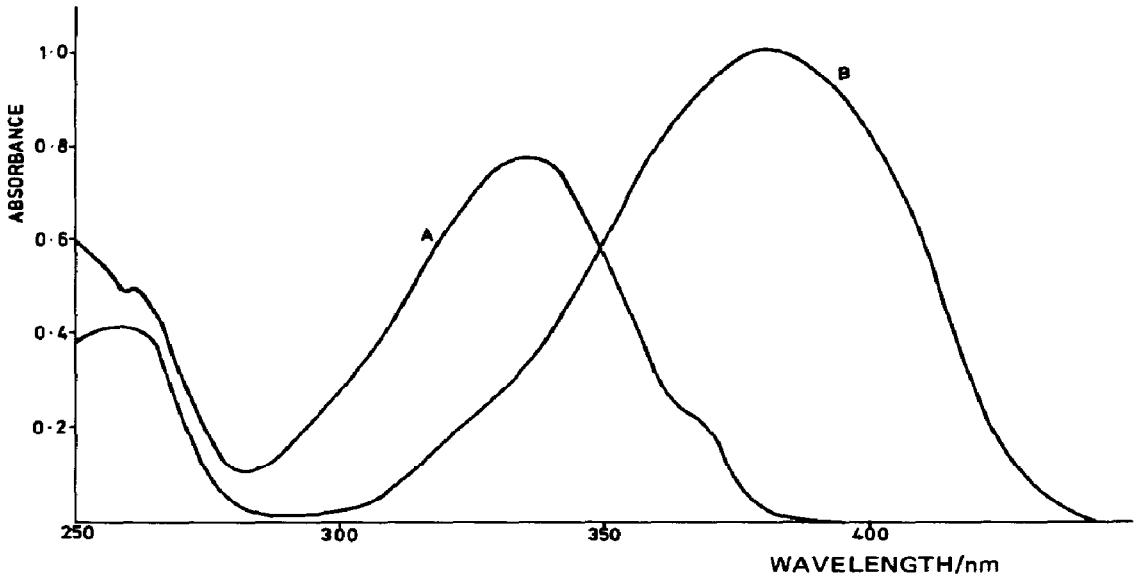


Fig. 4. Absorption spectra of harmaline in neutral (curve A) and acidic (curve B) ethanol.

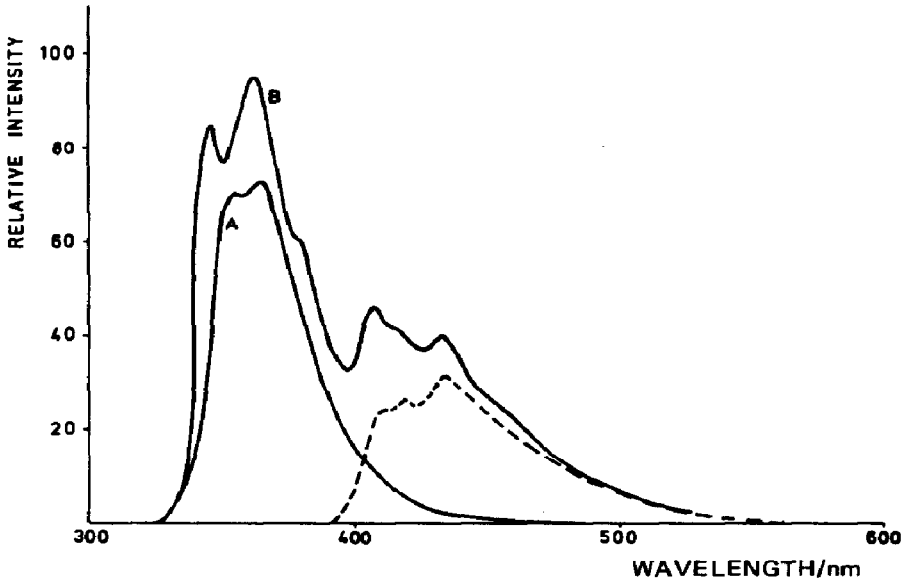


Fig. 5. Fluorescence spectrum at 298 K (curve A) and fluorescence and phosphorescence spectra at 77 K (curve B) for harmine in neutral ethanol: — — —, phosphorescence spectrum (relative intensity, 10×).

appears as an intense peak (λ_{max} = 355 nm and λ_{max} = 365 nm). The tail of this band in the visible region of the spectrum gives the β-carboline base a weak pale blue fluorescence in solution. In acidic (HCl) ethanol the intense blue–violet fluorescence of the cation (VIII) appears (λ_{max} = 412 nm) (Fig. 6). This fluorescence shows an improved resolution at 77 K (λ_{max} = 385 and λ_{max} = 400 nm) and is shifted towards the blue.

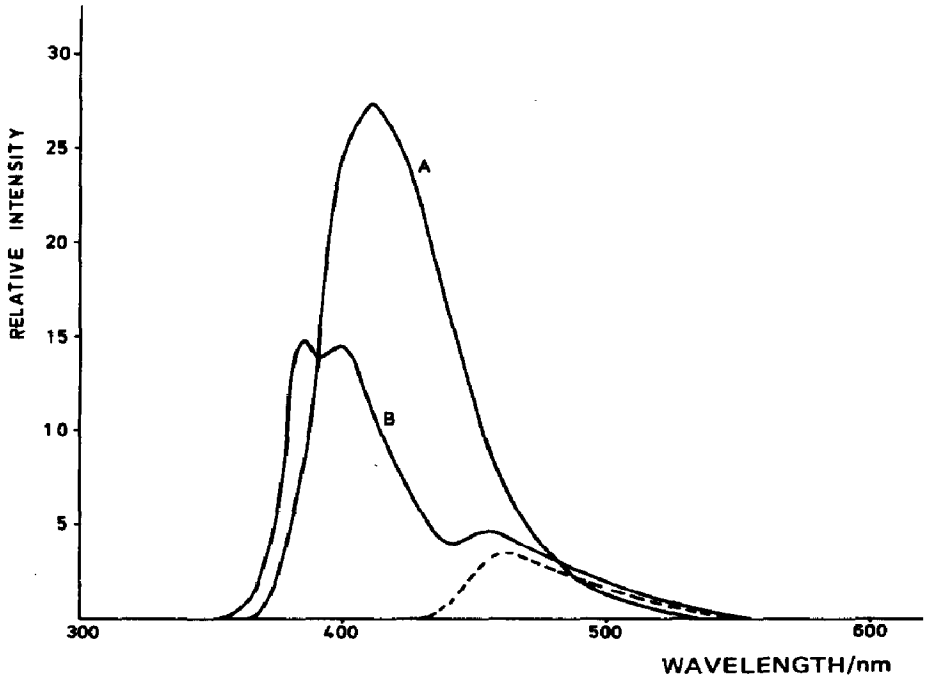


Fig. 6. Fluorescence spectrum at 298 K (curve A) and fluorescence and phosphorescence spectra at 77 K (curve B) for harmine in acidic ethanol: — — —, phosphorescence spectrum (relative intensity, 10×).

The phosphorescence spectrum of harmine (Fig. 5) displays weakly resolved bands (λ_{max} = 409 nm, λ_{max} = 419 nm and λ_{max} = 434 nm). The intensity of the phosphorescence was low. The long triplet lifetime τ_p of 2.7 s and the singlet–triplet (S–T) splitting distance of 4356 cm^{-1} are consistent with the corresponding values determined [6] for the isoelectronic carbazole nucleus (XI).

The fluorescence spectrum of harmaline in neutral ethanol at 298 K (Fig. 7 and Table 1) displays peaks at λ_{max} = 367 nm and λ_{max} = 476 nm. These bands are of comparable intensities. The peak at 476 nm is strongly intensified in acidic (HCl) ethanol and equates with a similar emission maximum from a solution of crystalline harmaline hydrochloride. The characteristic green fluorescence observed in solutions of harmaline salts corresponds to the emission at λ_{max} = 476 nm, which we attribute to the $S_0 \leftarrow S_1$ transition of the protonated species IX. The appearance of this band in the fluorescence spectrum of harmaline base in neutral ethanol solution is ascribed to protonation of the basic nitrogen atom in ring C of the β-carboline nucleus in the excited S_1 state. The addition of aqueous (NaOH) alkali to ethanolic solutions of harmaline salts quenches the green fluorescence, and the fluorescence spectrum (Table 1) shows only the shorter wavelength band (λ_{max} = 366 nm) associated with the unprotonated base. Neutral ethanolic solutions of harmaline excited (261 nm) at 77 K (Table 1) display strong fluorescence emissions from the free base (λ_{max} = 346 nm and λ_{max} =

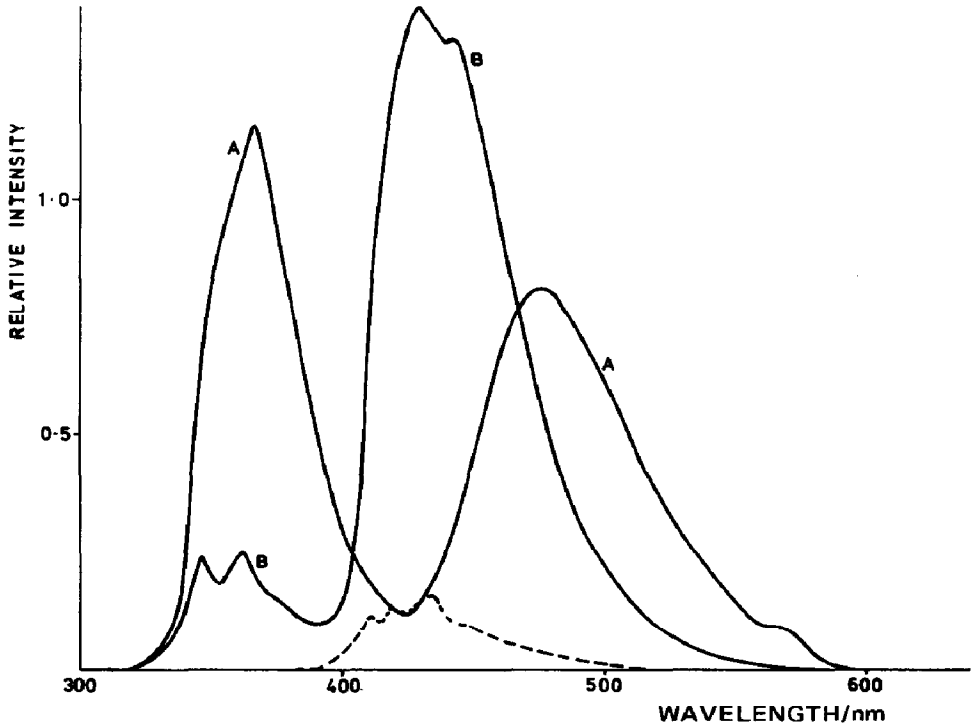


Fig. 7. Fluorescence spectrum at 298 K (curve A) and fluorescence and phosphorescence spectra at 77 K (curve B) for harmaline in neutral ethanol: — — —, phosphorescence spectrum (relative intensity, 10×).

362 nm) and the protonated species (λ_{max} = 429 nm and λ_{max} = 442 nm), shifted normally towards the blue region.

The phosphorescence emission of harmaline in neutral ethanol (λ_{max} = 410 nm, λ_{max} = 418 nm and λ_{max} = 434 nm) is weak, with a lifetime of 3.4 s and an S–T splitting of 4207 cm^{-1} indicative of an unprotonated carboline (see ref. 6). We therefore suggest that this phosphorescence is derived from the triplet state of the unprotonated base.

It follows that the triplet state (T_1) of harmaline must possess significantly weaker basicity than the excited S_1 state. The work of Jackson and Porter [7] has shown that the acidity constants of bases are much less affected by excitation to the triplet state than to the excited singlet. By analogy with acridine and quinoline, for example, an increase of less than one p*K* unit would be indicated for triplet harmaline. On this basis harmaline in neutral solution would be virtually unprotonated in the triplet state.

3.3. Dehydroreserpines

The oxidation of reserpine (IIIa) to its 3,4-dehydro and 3,4,5,6-dehydro derivatives (Va and IVa) can be effected by a variety of reagents. In reserpine itself the hydrogen atom at position 3 has the β equatorial configuration. This equatorial hydrogen atom is resistant to dehydrogenation with mercuric acetate. In sharp contrast, the 3-isoreserpine, in which the

C(3) hydrogen atom is axial, is smoothly oxidized by mercuric acetate to 3-dehydroreserpine (Va) [8 - 11]. *Tert*-butyl hypochlorite provides a less stereospecific reagent which will attack either equatorial or axial hydrogen atoms at C(3) [12]. This reagent has been used in the yohimbine series for the oxidation of C(3) β equatorial hydrogen compounds (deserpidine and ψ-yohimbine) to their 3-dehydro derivatives. The C(3) α axial hydrogen atoms in yohimbine, corynanthine, β-yohimbine and allo-yohimbine are also easily oxidized by the hypochlorite reagent, affording the 3-dehydro derivatives in all cases.

In the reserpine–yohimbine series other reagents have been employed to effect oxidation, notably hydrogen peroxide [13], cerate [14] and lead tetraacetate [15]. These reagents tend to give rise to tetra dehydro derivatives. Photochemical oxidation is also effective. Aerobic UV irradiation of reserpine in non-ionizing media affords a mixture of 3-dehydroreserpines and 1,2,3,4-tetradehydroreserpines [16]. There is particular interest in the 3-dehydroreserpines on account of their intense green fluorescence, which can be exploited for analytical purposes. We now describe their spectra in detail.

3.4. Spectral characteristics of 3-dehydroreserpines

3.4.1. Absorption spectra

3-dehydroreserpine salts (Va) displayed well-defined absorption maxima in ethanolic solution. The data for 3-dehydroreserpic acid hydrochloride are typical (Table 2). The absorption band in the blue region (λ_{max} = 386 nm), which gives rise to the bright yellow colour of the dehydroreserpine cation, is characteristic of the chromophoric structure **XII** (Fig. 3). This chromophore is essentially that of the yellow harmalinium cation **IX**, which shows a similar absorption band (λ_{max} = 380 nm) in the visible region. While earlier papers [8] usually depict the dehydroreserpine salts in the form of the indole immonium cation **XII**, the tautomeric isoindole immonium form **XIII** (Fig. 3) cannot be excluded. Evidence for the structure **XIII** arises by analogy with 3-dehydroyohimbine chloride, the IR spectrum of which shows no characteristic N—H band at 2.9 μm [12].

When solutions of 3-dehydroreserpines are made alkaline, the yellow colour is discharged and the green fluorescence is quenched. Harmaline salts display a similar behaviour. Titration of 3-dehydroreserpic acid hydrochloride with KOH in aqueous ethanolic solution required two molar equivalents of base to the end point. The absorption spectrum was monitored throughout the titration. The spectra showed the persistence of the bands associated with the dehydroreserpine cation (**Vb**) until the end point, when an abrupt change in the spectrum is evident (Fig. 8). The final spectrum (Fig. 8, curve 2) lacks completely the peak in the visible region (λ_{max} = 390 nm) and displays a spectrum resembling that of 6-methoxyindole with peaks at λ_{max} = 267 nm, λ_{max} = 274 nm and λ_{max} = 298 nm and a further peak at λ_{max} = 330 nm. These changes in the spectrum are reversible: acidification restores the yellow colour, regenerating the original spectrum. This behaviour is characteristic of the rearrangement of a yellow immonium cation to a

TABLE 2

Compound	*Absorption*			*Fluorescence (298 K)*		*Fluorescence (77 K)*	*Phosphorescence (77 K)*	
	λ_{max} (nm)	ϵ (dm^3 mol^{-1} cm^{-1})	λ_{ex} (nm)	λ_{max}[a] (nm)	ϕ_f	λ_{max}[a] (nm)	λ_{max} (nm)	τ_p (s)
Dehydroreserpine trifluoroacetate	265 319 332 390	16309 7099 8191 14743	265 390	349, **493**, 542 **494**, 541	0.07	435, 451 436, 450	462	
Dehydroreserpine trifluoroacetate + acid	265 390	15435 18748	265 390	345, **491** 493	0.09	438, **451** 439, **450**	461	
Dehydroreserpine trifluoroacetate + alkali	267 290 319 332	21332 17219 21041 20131	267 319	351 369	5.4×10^{-3}	346, 446, 464 **351**, 444, 463	445, 509, 550 454, 507, 551	
Dehydroreserpic acid hydrochloride	264 295 386	7369 6912 5315	295 386	341 485	0.40	322 438, **451**	439 477	3.7
Dehydroreserpiline perchlorate	322 336 400	17478 18329 3244	322 336 400	476 478 483, 615		456 463 472	507, 551 505, 549	

[a]Values in bold type denote the wavelength of the peak with greatest intensity.

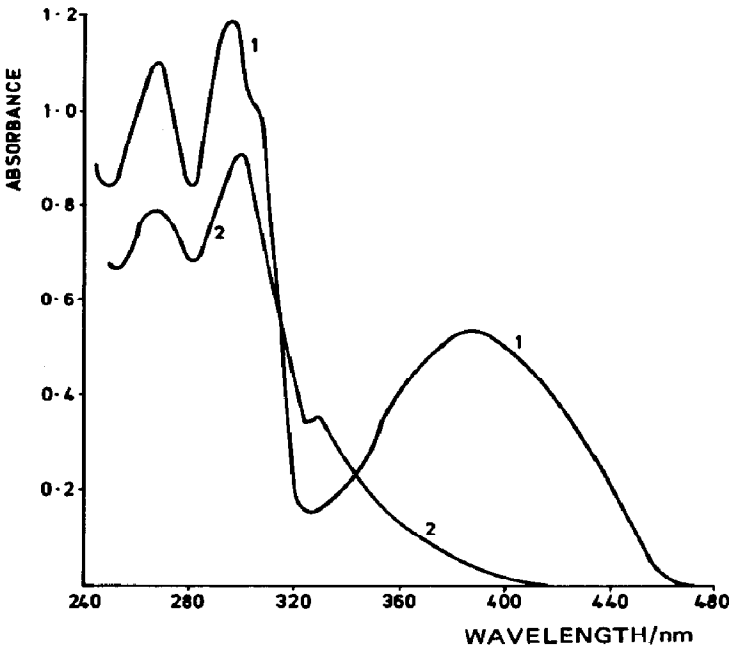


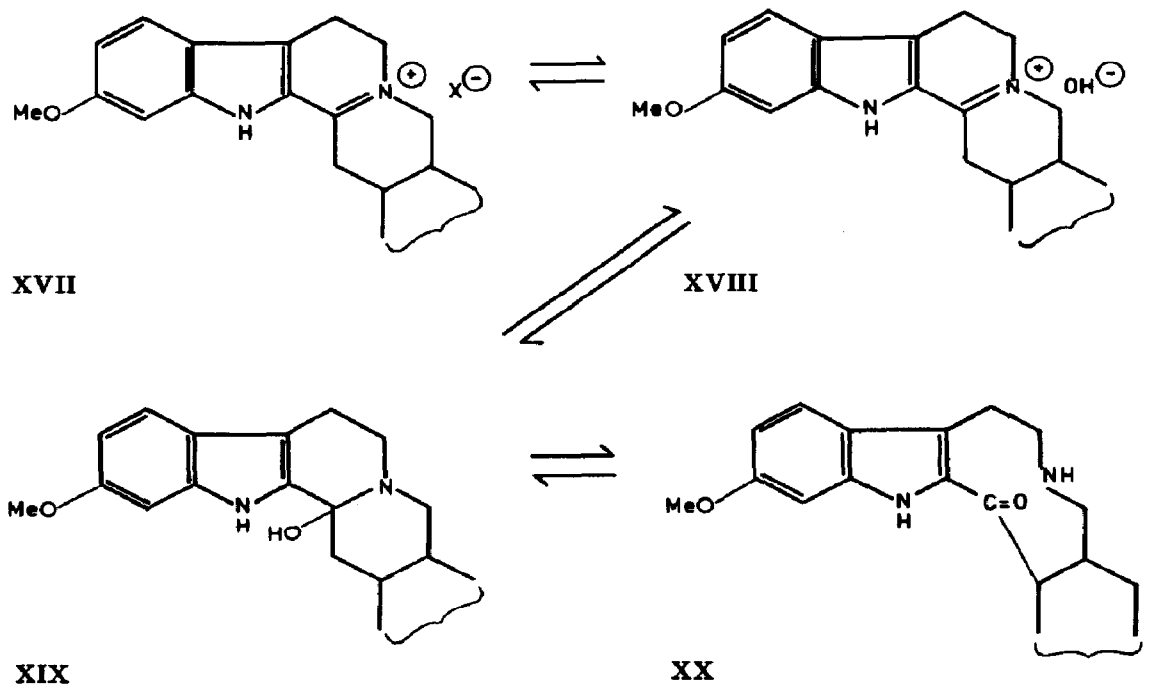
Fig. 8. Absorption spectra of 3-dehydroreserpic acid hydrochloride: curve 1, in neutral ethanol; curve 2, in ethanol with two equivalents of aqueous KOH.

colourless carbinolamine (pseudobase) as observed in hydrastinine, cotarnine, berberine and certain other alkaloids [17]. For cotarnine, for example, the yellow ionic form of the salts (XIV) (Fig. 3) can assume the colourless covalent carbinolamine structure (XV) (Fig. 3) in alkaline solution, which can then ring open to the tautomeric form XVI (Fig. 3). By analogy we envisage the conversion of the yellow dehydroreserpine salt (XVII) into the hydroxide (XVIII) and the colourless carbinolamine form (XIX) which then equilibrates to the keto structure (XX) as shown in Fig. 9. The latter gives rise to the characteristic aromatic carbonyl R band $n-\pi^*$ absorption observed at λ_{max} = 330 nm.

3.4.2. Emission spectra

The fluorescence spectrum of 3-dehydroreserpine trifluoroacetate (Fig. 10 and Table 2) is typical, showing an intense peak at λ_{max} = 493 nm. It is this emission which gives rise to the characteristic green fluorescence observed in dilute solutions of 3-dehydroreserpine salts. The fluorescence maximum undergoes a normal blue shift at 77 K, and some resolution is evident (λ_{max} = 435 nm and λ_{max} = 451 nm).

The phosphorescence spectrum (Fig. 10 and Table 2) reveals a weak band at λ_{max} = 462 nm. Comparison of these spectra with the spectra of harmaline salts (Table 1) shows that the similarities which would be anticipated on the basis of the common chromophoric type XII. In alkaline solution the emission spectra of the 3-dehydroreserpine salts are completely changed. The fluorescence spectrum of 3-dehydroreserpine trifluoroacetate



XVII XVIII

XIX XX

Fig. 9. The conversion of a 3-dehydroreserpine salt (XVII) to the hydroxide (XVIII) and carbinolamine form (XIX) in equilibrium with the keto structure (XX).

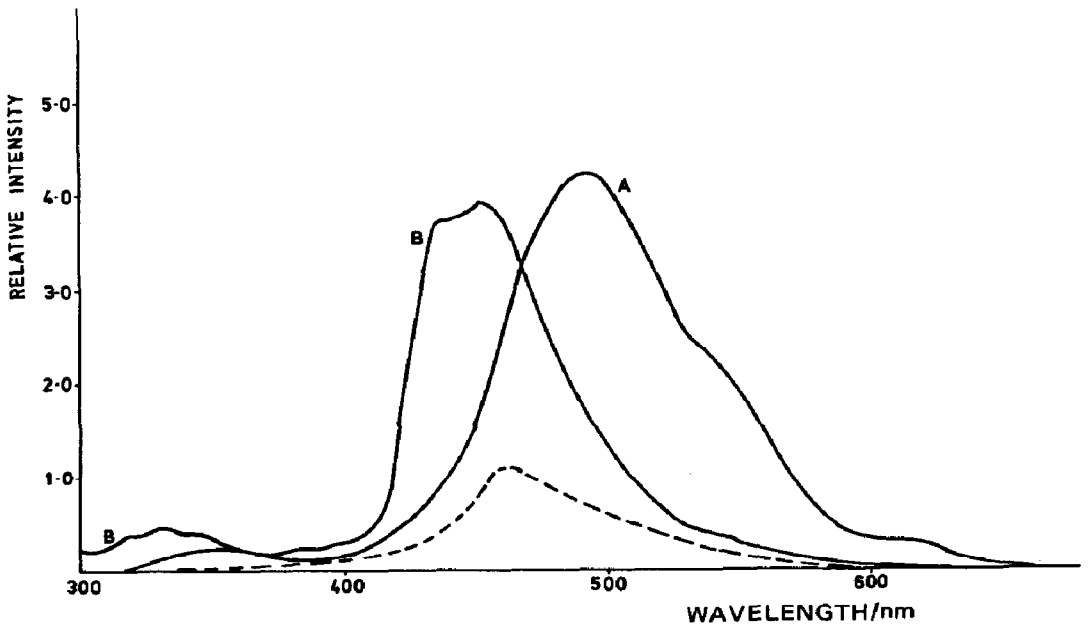


Fig. 10. Fluorescence spectrum at 298 K (curve A) and fluorescence and phosphorescence spectra at 77 K (curve B) for dehydroreserpine trifluoroacetate in neutral ethanol: — — —, phosphorescence spectrum (relative intensity, 10×).

in alkaline solution, measured at 298 K (Table 2), shows only a very weak emission at λ_{max} = 351 nm ($\phi_f = 5.4 \times 10^{-3}$).

At 77 K this fluorescence band is shifted towards the blue region and bands characteristic of the 3-dehydroreserpine cation reappear (λ_{max} = 446 nm and λ_{max} = 464 nm). The phosphorescence emission reveals a broad band at λ_{max} = 445 nm with significant new bands at λ_{max} = 509 nm and λ_{max} = 550 nm (Table 2). The latter clearly observed maxima are completely absent from the phosphorescence emission of the cation.

These results are consistent with the cation–carbinol base equilibria depicted in Fig. 9. In line with this scheme conversion of the yellow dehydroreserpine cation **XVII** to the colourless keto form **XX**, via the carbinol base **XIX**, gives rise to an emission spectrum which is highly characteristic of the aromatic carbonyl group. Aromatic carbonyl compounds tend to show only weak or no fluorescence from singlet states, but they display fairly intense phosphorescence emission at long wavelengths in many cases from T_{π,π^*} states. The naphthalene aldehydes provide a useful analogy with the isoelectronic indole carbonyl system **XX**. The phosphorescence spectrum of naphthalene 1-aldehyde, for example, [18] displays prominent bands at λ_{max} = 500 nm and λ_{max} = 550 nm, which closely parallel the bands in the triplet emission which we have attributed to the equilibrium form **XX**. As for the naphthalene aldehydes the phosphorescent state is probably π–π^* in character.

The fluorescence spectra observed in alkaline solutions of dehydroreserpinium salts at 77 K require further comment. It is evident (Table 2) that the effect of cooling these solutions from 298 to 77 K is to displace the equilibria back in favour of the dehydroreserpinium cation, the characteristic fluorescence bands of which reappear (λ_{max} = 446 nm and λ_{max} = 464 nm). This tendency to revert to the ionic form of the base would be favoured by the increase in the dielectric constant D of the medium at 77 K. Calculations using the relationship $D = a \exp(-bT)$ [19] show that the increase in D is very large. For the 95% ethanol employed here, the value of D rises from 23 to 101 as the temperature of the medium falls from 298 to 77 K.

3.5. Oxidation of reserpines by molecular oxygen

Reserpine and its derivatives are very susceptible to aerial oxidation in acidic media, yielding 3-dehydroreserpines. The conversion goes well in glacial acetic acid solution in the presence of trifluoroacetic acid as a catalyst in a stream of oxygen. The progress of the reaction may be monitored by determining the concentration of the yellow dehydroreserpinium cation spectrophotometrically (Fig. 11). In this way 3-dehydroreserpines may be conveniently prepared and isolated from the reaction product in the form of their trifluoroacetate or perchlorate salts. Reserpiline (**VI**) is rapidly oxidized to the 3-dehydro derivative (**VII**) using the foregoing method. 3-dehydroreserpilinium perchlorate [20] forms golden leaflets which reveal characteristic absorption and emission bands associated with the 10,11-dimethoxy-substituted 3-dehydro cation (**VII**) (Table 2). The perchlorate possesses a

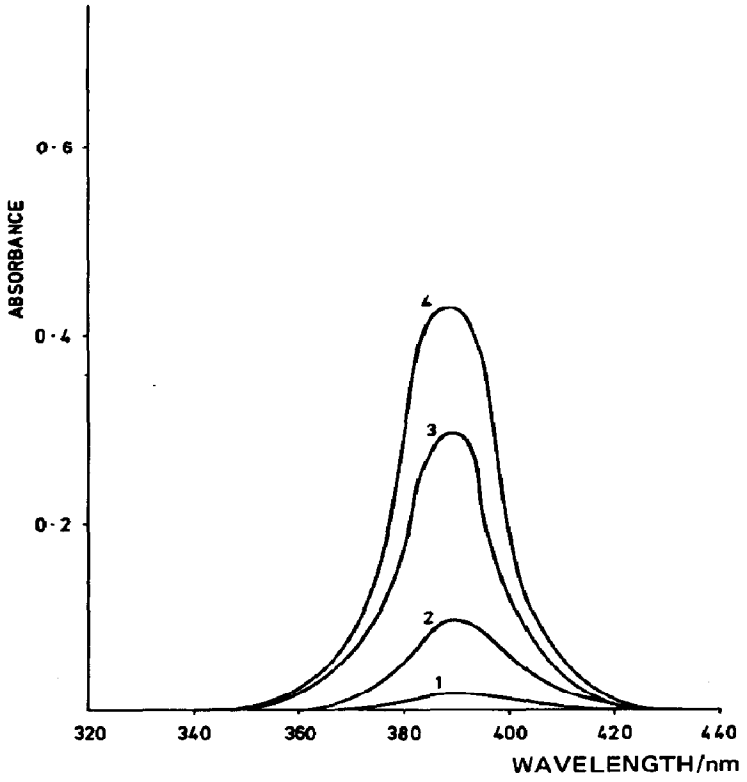
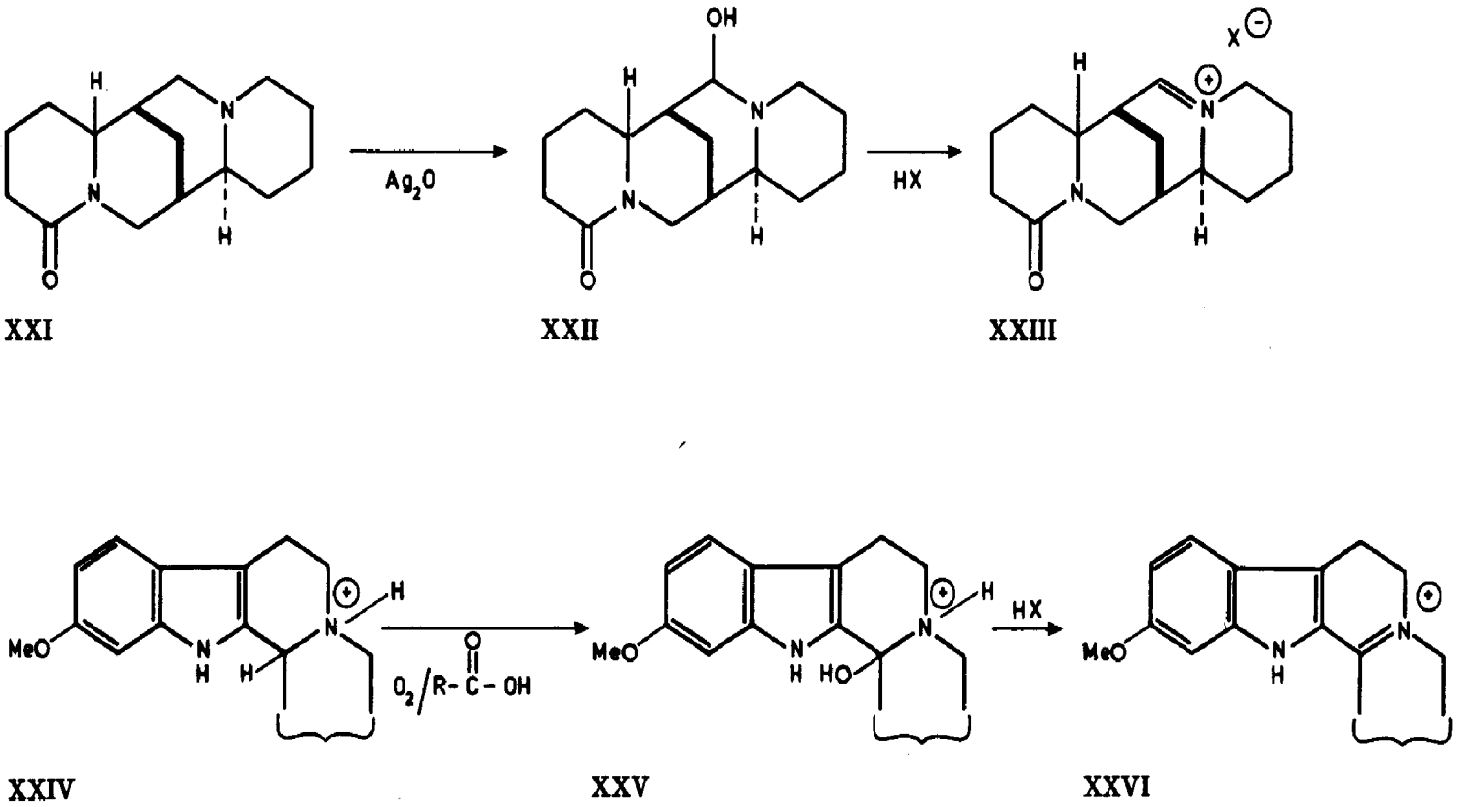


Fig. 11. Absorption spectra of the oxidation product of reserpine in an acetic acid–trifluoroacetic acid mixture at 368 K after various time intervals (reserpine concentration, 1×10^{-2} M; trifluoroacetic acid concentration, 0.12 M): curve 1, 0 min; curve 2, 5 min; curve 3, 10 min; curve 4, 15 min.

distinctive yellow fluorescence with a long wavelength emission at λ_{max} = 615 nm.

The oxidation of reserpines to their 3-dehydro derivatives is essentially a dehydrogenation process in which a hydrogen atom attached to carbon adjacent to a bridging heterocyclic nitrogen is removed to give the immonium cation XII. The reaction closely resembles certain quinolizidine oxidations [21 - 23] notably that of lupanine (Fig. 12, XXI). This alkaloid is oxidized by silver oxide [23] to the carbinol base 17-hydroxylupanine (XXII) which affords the immonium salt (XXIII) in acid solution. Oxidations by silver oxide often effectively achieved in trifluoroacetic acid medium [24] probably involve the participation of activated (singlet) oxygen. The role of $Ag-O_2$ complexes in silver-catalysed oxidations [25] is closely related. The significant factor in these reactions is evidently the activation of molecular oxygen by catalytically induced breakdown of spin conservation in the ground state (triplet) oxygen molecule. More generally hydroxylation of aromatic systems can be effected by molecular oxygen in the presence of hydrogen fluoride [26] and trifluoroacetic acid catalysed by metal acetates [27 - 29]. The indole nucleus is easily hydroxylated to



XXI XXII XXIII

XXIV XXV XXVI

Fig. 12. Reaction scheme of the oxidation of lupanine (**XXI**) by silver oxide to 17-hydroxylupanine (**XXII**) giving an immonium salt (**XXIII**) in acid solution and the formation of a 3-dehydroreserpine salt (**XXVI**) via the 3-hydroxy intermediate (**XXV**).

indoxyl and its red condensation products in trifluoroacetic acid solution [30, 31].

In the light of the foregoing discussion we suggest that the dehydrogenation of the reserpine derivatives in trifluoroacetic acid medium involves the participation of oxygen activated by association with trifluoroacetic acid. As a result hydroxylation takes place at C(3) in structure **XXIV** (Fig. 12) to give the 3-hydroxy intermediate **XXV** from which the dehydro reserpinium salt is formed by elimination of water. The observed inhibition of the dehydrogenation by the efficient singlet oxygen quencher α-tocopherol [32, 33] would indicate that spin uncoupling to give the reactive singlet state of the oxygen molecule occurs, probably involving percarboxylic intermediates.

The photochemical oxidation of reserpine to its dehydro derivatives referred to earlier [16] represents the analogous reaction involving singlet oxygen excited by UV irradiation.

4. Conclusion

The absorption and emission spectra of harmine and harmaline free bases show profound changes in acidic solution as a result of protonation of the tertiary heterocyclic nitrogen in ring C. The fluorescence characteristics of these systems are essentially those of the parent β-carbolines.

The 3-dehydroreserpines show similar characteristics to harmaline in acid solution owing to the presence of the same cationic chromophore. In alkaline solution, however, they behave quite differently. Unlike harmaline salts which merely deprotonate to the free base, 3-dehydroreserpines undergo a carbinol–base rearrangement to a keto–indole form. This is a reversible ring-opening involving equilibria which are strongly dependent on changes in dielectric constant and excited state basicity at 77 K.

Dehydroreserpine salts are formed when reserpines are oxygenated in trifluoroacetic acid medium. This reaction appears to involve spin uncoupling of oxygen to yield the reactive singlet form. As such the process provides a ground state analogue of the dehydrogenation of reserpines by molecular oxygen excited to the singlet state by UV light.

References

1 B. Savory and J. H. Turnbull, *J. Photochem., 23* (1983) 171.
2 Z. Jung and M. Jungova, *Cesk. Farm., 22* (1973) 195.
3 I. M. Jakoljevic, J. M. Fose and N. R. Kuzel, *Anal. Chem., 34* (1962) 410.
4 J. Hetherington, B. Savory and J. H. Turnbull, *J. Photochem., 20* (1982) 367.
5 F. Pruckner and B. Witkop, *Justus Liebigs Ann. Chem., 554* (1943) 127.
6 V. L. Ermolaev, *Opt. Spectrosc. (U.S.S.R.), 11* (1961) 266.
7 G. Jackson and G. Porter, *Proc. R. Soc. London, Ser. A, 260* (1961) 13.
8 F. L. Weisenborn and P. A. Diassi, *J. Am. Chem. Soc., 78* (1956) 2022.
9 C. Djerassi, J. Fishman, M. Gorman, J. P. Kutney and S. C. Pakrashi, *J. Am. Chem. Soc., 79* (1957) 1218.

10 E. Wenkert and D. K. Roychaudhuri, *J. Org. Chem., 21* (1956) 1315.
11 M. W. Klohs, F. Keller, R. E. Williams and G. W. Kusserow, *J. Am. Chem. Soc., 79* (1957) 3763.
12 W. O. Godtfredsen and S. Vangedal, *Acta Chem. Scand., 10* (1956) 1414.
13 H. Auterhoff and F. Moll, *Arch. Pharm. (Weinheim, Ger.), 292* (1959) 540.
14 J. A. Gordon and D. J. Campbell, *Anal. Chem., 29* (1957) 488.
15 M.-M. Janot, R. Goutarel, A. Le Hir, M. Amin and V. Prelog, *Bull. Soc. Chim. Fr.,* (1952) 1089.
16 G. E. Wright and T. Y. Tang, *J. Pharm. Sci., 61* (1972) 299.
17 D. Beke, *Adv. Heterocycl. Chem., 1* (1963) 167.
18 R. Shimada and L. Goodman, *J. Chem. Phys., 43* (1965) 2030.
19 G. Akerlöf, *J. Am. Chem. Soc., 54* (1932) 4125.
20 J. Poisson, R. Bergoeing, N. Chauveau, M. Shamma and R. Goutarel, *Bull. Soc. Chim. Fr.,* (1964) 2853.
21 N. J. Leonard, W. J. Middleton, P. D. Thomas and D. Chaudhury, *J. Org. Chem., 21* (1956) 344.
22 N. J. Leonard, P. D. Thomas and V. W. Gash, *J. Am. Chem. Soc., 77* (1955) 1552.
23 O. E. Edwards, F. H. Clarke and B. Douglas, *Can. J. Chem., 32* (1954) 235.
24 M. A. Schwartz, B. F. Rose, R. A. Holton, S. W. Scott and B. Vishnuvajjala, *J. Am. Chem. Soc., 99* (1977) 2571.
25 P. A. Kitty and W. M. H. Sachtler, *Catal. Rev., 10* (1974) 1.
26 J. H. Simons and D. S. McArthur, *Ind. Eng. Chem., 39* (1947) 364.
27 J. Hanotier, H. Hanotier-Bridoux and P. de Radzitzky, *J. Chem. Soc., Perkin Trans. II,* (1973) 381, 1035.
28 R. T. Tang and J. K. Kochi, *J. Inorg. Nucl. Chem., 35* (1973) 3845.
29 R. O. C. Norman, C. B. Thomas and P. J. Ward, *J. Chem. Soc., Perkin Trans. I,* (1974) 2197.
30 J. H. Turnbull, unpublished work, 1982.
31 B. Witkop and J. B. Patrick, *J. Am. Chem. Soc., 73* (1951) 713.
32 R. H. Young, D. Brewer and R. A. Keller, *J. Am. Chem. Soc., 95* (1973) 375.
33 C. S. Foote and R. W. Denny, *J. Am. Chem. Soc., 90* (1968) 6233.