ULTRAVIOLET AND INFRARED SPECTRA OF ALKALOIDS WITH A CYCLOHEXADIENONE OR CYCLOHEXENONE RING

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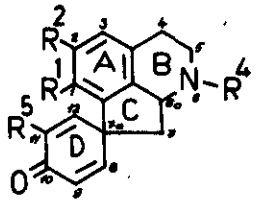
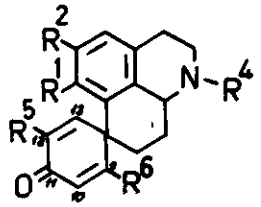
The ultraviolet and the infrared spectra (region between 1750-1600 cm^{-1}) of proaporphine/homoproaporphine and promorphinane/homopromorphinane alkaloids with a keto group on the ring D, conjugated either with two (cyclohexadienone compounds) or with one (cyclohexenone compounds) double bond, are discussed. Furthermore, the effect of the enol ether in the α-, α, α'- or β-position to the keto group and that of the electron donating substituents of the ring A on the uv and the ir spectra have been studied.

The proaporphine (Type Ia) and the promorphinane[+)] (Type IIIa) alkaloids with a cyclohexadienone ring arise on phenolic oxidation of benzyltetrahydroisoquinoline compounds and form

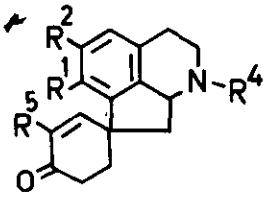
[+)] In this review, the term promorphinane compounds has been used for those bases which have no ether bridge between the rings A and D of the morphinane skeleton.



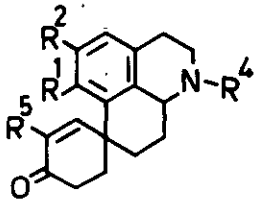
(Ia) Proaporphine Group



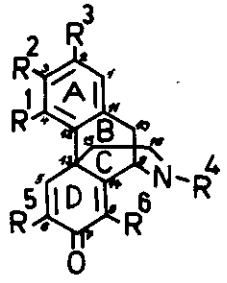
(Ib) Homoproaporphine Group



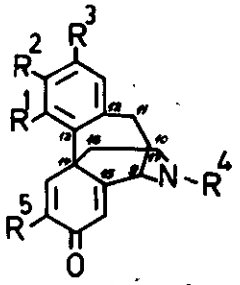
(IIa) 8,9-Dihydroproaporphine Group



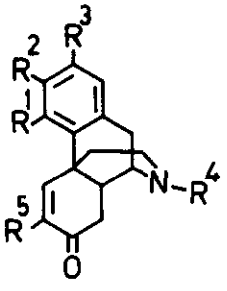
(IIb) 9,10-Dihydrohomoproaporphine Group



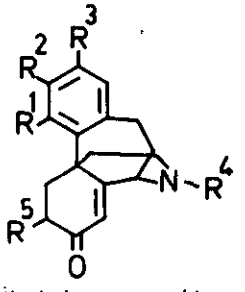
(IIIa) Promorphinane Group



(IIIb) Homopromorphinane Group



(IVa) 8,14-Dihydropromorphinane Group

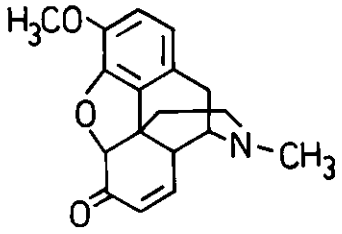


(IVb) 5,6-Dihydrohomopromorhinane Group

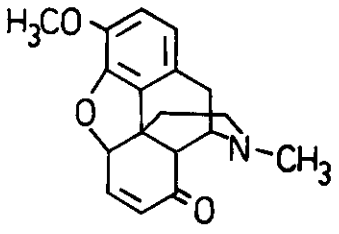
R^1, R^2, R^3 = H, OH or OCH_3; $R^1 + R^2$ or $R^2 + R^3$ = O·CH_2-O; R^4 = H or CH_3; R^5, R^6 = H or OCH_3; in the promorphinane group (IIIa), the oxygen substituents of the ring A are in the positions 2,3 or 3,4 and, in the homopromorphinane group (IIIb, IVb), in the positions 2,3,4.

intermediary steps in the biosynthesis of aporphine and morphinane alkaloids[1,2]. They occur in plants of the families Euphorbiaceae, Lauraceae, Menispermaceae, Monimiaceae, Nymphaceae, and Papaveraceae. The compounds of the homoproaporphine type (Ib) and the homopromorphinane type (IIIb) form intermediary steps in the biosynthesis of homoaporphine and homomorphinane alkaloids. They are found in the plants of the subfamily Wurmbaeoideae (family Liliaceae)[3,4]. In nature there occur or are synthetically prepared the compounds with a cyclohexadienone ring and their derivatives with one or two CH_3O groups (enol ether) in the α- or α,α'- or in the β-position vs. the keto group. In proaporphines/homoproaporphines with a cyclohexadienone ring (Types Ia, Ib), the CH_3O group of the ring D can be located in the cis- or the trans-position to the hydrogen at C-6a. Furthermore, some compounds have been found whose one double bond (Types IIa, IIb, IVa, IVb) (or both bonds) is hydrogenated or whose keto group is reduced to the secondary hydroxyl group. In the types IIa and IIb, the double bond is also in cis- or trans-position to the hydrogen at C-6a. In the promorphinanes/homopromorphinanes with a cyclohexenone ring, the double bond is located between the carbon atoms C-5 and C-6 (Type IVa) or between C-8 and C-14 (Type IVb), and the CH_3O group (enol ether) at C-6 or C-8.

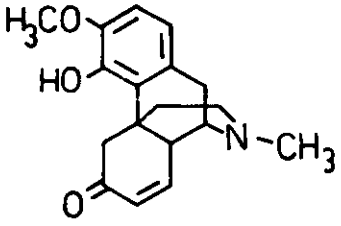
The alkaloids codeinone (Va), pseudocodeinone (Vb), thebainone (VIa), metathebainone (VIb), sinomenine (VII),



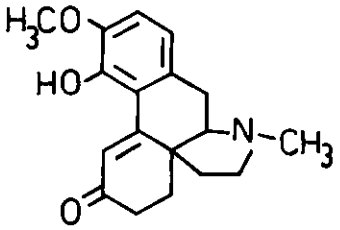
(Va) Codeinone



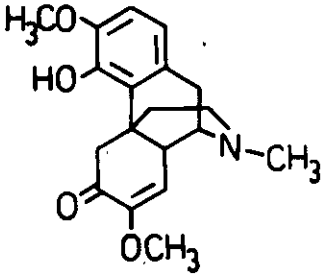
(Vb) Pseudocodeinone



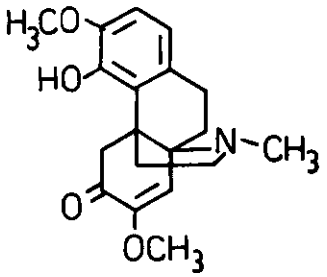
(VIa) Thebainone



(VIb) Metathebainone



(VII) Sinomenine



(VIII) Cepharamine

and the alkaloids of the hasubanane type (Menispermaceae) are closely related to the promorphinane alkaloids. Therefore the spectra of the above-mentioned alkaloids, including those of cepharamine[5,6] (VIII) and hasubanonine (IX), have also been discussed in this paper.

For the physico-chemical properties of the so-far isolated proaporphine and promorphinane alkaloids of all the above-mentioned types see the summarizing papers[4,7-10]. However, in none of them the differences between the ultraviolet and the infrared spectra have been discussed. These differences would allow to differentiate not only the cyclohexadienone from the cyclohexenone ring but also these two different rings in the compounds of the proaporphine (Ia) and promorphinane (IIIa) types or in their homoderivatives (Ib, IIIb), and in compounds where the CH_3O group is located in the α- or α,α'- or β-position vs. the keto group. In this paper, the effect of the electron donating substituents of the ring A on the uv and the ir spectra (region between 1750-1600 cm^{-1}) has also been studied.

Use was made of the values obtained from measurements of different alkaloids studied at our place[29] of work and of the data taken from the literature[4,7-10]. The uv spectra were measured in methanol or ethanol on a Unicam SP 700 (Cambridge, England) as described in the literature[11], and the ir spectra in $CHCl_3$, nujol and in KBr tablets on an Infrascan H 900 (Hilger & Watts, London, England) or on a UR-20 instrument

(Zeiss, Jena, GDR). The scale of wave number in cm^{-1} was calibrated by recording the spectra of polystyrene.

(I) Ultraviolet Spectra:

The uv spectra of cyclohexadienone, cyclohexenone, and cyclohexanone compounds have already been known earlier from the studies of steroid compounds[12-15]. According to Stuart and Cava[8], the uv spectra of tetrahydroisoquinoline cyclohexadienone compounds bear resemblance to the sum of the curves of homoveratrylamine and 4-methyl-4-allyl-cyclohex--2,5-dien-1-one or of the curves of pyrocatechine ethers and cyclohexadienone[7,16] (Fig. 1). The bands at c. 215 (second primary band) and at c. 285 nm (secondary band) correspond to the absorption of the aromatic nucleus. The band at 230 nm of alkaloids with a cyclohexadienone and an aromatic ring consists of two bands, i.e. a band which is attributable to the "cross conjugated dienone system" and the first primary band+) of the aromatic nucleus with its electron donating substituents (OH, OCH_3, OCH_2O). Further on, the term "cyclohexadienone"/"cyclohexenone" band is used for that at 230 nm, and the term "aromatic" band for the secondary band at c. 285 nm. The α,β-unsaturated ketones exhibit, in addition to the already mentioned bands, a band of a shifted local extinction of the C=O group at c. 300 - 330 nm ($\log \varepsilon$ 1 - 2).

The theoretical calculations of the position of the longest

+) For the terminology of the bands see[11].

wavelength band (c. 230 nm) of cyclohexadienones and cyclohexenones of steroids were dealth with particularly by Fieser[12-14] who determined the increments of different types of substituents. According to him, the hydroxyl or the enol methyl ether group in the α- or the β-position to the keto group shifts the above-mentioned band by 35 nm or by 30 nm bathochromically. Our observations (vide infra) show, however, that in the cyclohexadienone compounds of the proaporphine and the promorphinane type, the position of the band at c. 280 nm does not change, only the extinction increases. In the cyclohexenone compounds, the introduction of a CH_3O group causes a hyperchromic and a hypsochromic shift of this band. On the contrary, substitution by a CH_3O group decreases the extinction of the band at c. 235 nm but its wavelength does not change. It might seem that the cyclohexadienone/cyclohexenone and the aryl chromophore affect each other only slightly[7,8]. This, however, is not true since the nature of the cyclohexadienone/cyclohexenone ring also affects the secondary band at c. 285 nm (vide infra).

The knowledge of the nature of the uv bands of the described compounds is important both for the determination of the constitution or the identification of the isolated compound and for the explanation of the individual Cotton bands in the ORD or the CD curves. Thus, the correct conclusion concerning the chirality[17-21] of the studied compounds can be drawn.

(A) Cyclohexadienone Compounds

(a) Proaporphine (Type Ia) and Homoproaporphine (Type Ib) Compounds

These two groups of compounds without a CH_3O group on the cyclohexadienone ring have the same type of uv curves. The proaporphine compounds exhibit an "aromatic" band at c. 285 nm (log ε 3.50) and a "cyclohexadienone" band at c. 235 nm (log ε 4.40). In homoproaporphine compounds, the absorption of these two bands is higher: the "aromatic" band by ε 820 and the "cyclohexadienone" band by ε 6,500 whereby the wavelength is maintained. The methylenedioxy group of the aromatic nucleus causes a bathochromic and a hyperchromic shift of the "aromatic" band (Fig. 2), which is a common finding in aromatic compounds[11]. The presence of a CH_3O group on the cyclohexadienone ring in α-position to the keto group produces a bathochromic shift of the "cyclohexadienone" band (Fig. 7) by c. 4 - 12 nm in both types of compounds (the decrease in the absorption of the "cyclohexadienone" band of proaporphine amounts to c. ε 7,300 - 11,000 and that of the homoproaporphine to c. ε 15,100). The "aromatic" band, whose position remains practically the same, increases in proaporphine compounds by c. ε 1,860 - 3,150, in homoproaporphine compounds only by c. ε 820. The presence of another CH_3O group in the α'-position causes[62] a further increase of the extinction of the "aromatic" band and its hypsochromic shift by c. 10 nm.

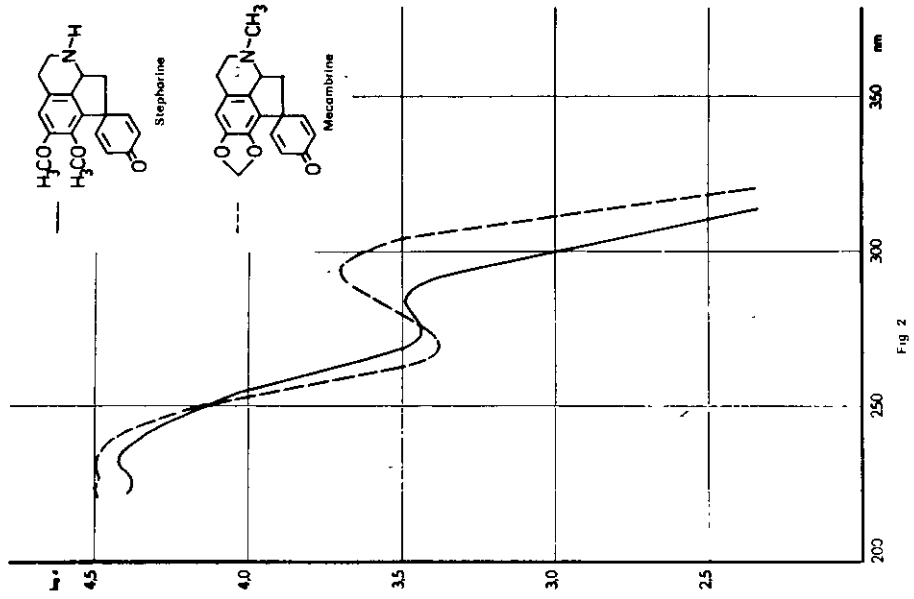

Stepharine
Mecambrine
nm
350
300
250
200
4,5
4,0
3,5
3,0
2,5

Fig 2

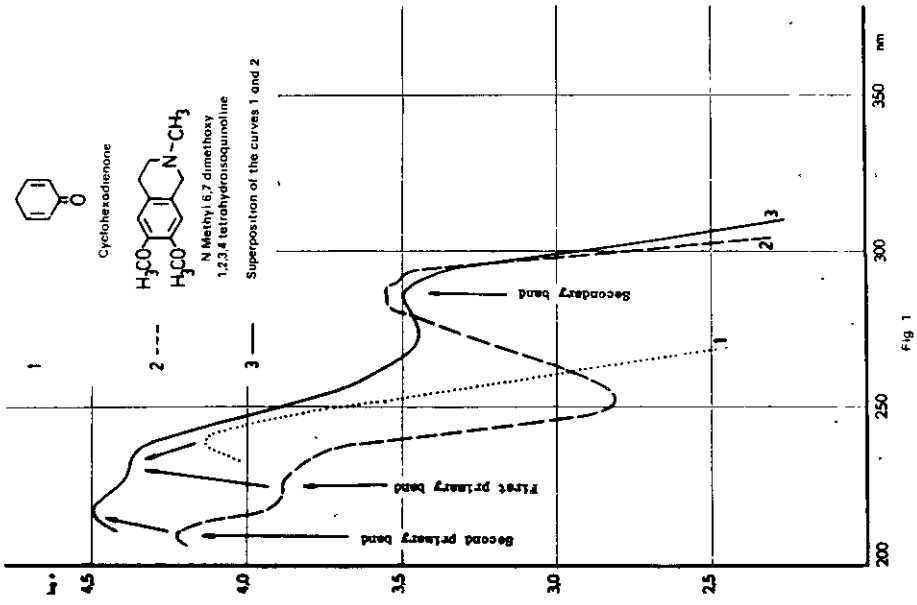

Cyclohexadienone
N Methyl 6,7 dimethoxy 1,2,3,4 tetrahydroisoquinoline
Superposition of the curves 1 and 2
Second primary band
First primary band
Secondary band
nm
350
300
250
200
4,5
4,0
3,5
3,0
2,5

Fig 1

In homoproaporphine compounds[22] with a CH_3O group in the β-position to the keto group, the position of the "cyclohexadienone" band at 235 nm is the same as that of the band exhibited by the compound without a CH_3O group on the ring D, its extinction is, however, much lower (log ε 4.19 vs. 4.53). On the contrary, the "aromatic" band at c. 285 nm shows a higher extinction (log ε 3.87 vs. 3.66). The findings made by Battersby et al.[21] as well as our own measurements show that the position of the uv bands of homoproaporphine dienones does not affect the cis- and the trans-position of the CH_3O groups of the ring D vs. the hydrogen at C-6a.

(b) Promorphinane (Type IIIa) and Homopromorphinane (Type IIIb) Compounds

These two types of compounds without a CH_3O group on the cyclohexadienone ring have not been available to us. We have studied only the compounds with one CH_3O group on the cyclohexadienone ring and with two or three oxygen electron donating substituents on the ring A. The promorphinane compounds have the substituents on the ring A in the positions 2,3 or 3,4, whereas the homopromorphinane compounds in the positions 2,3 or 2,3,4.

The uv spectra of these two types of compounds also show two bands, i.e. the "aromatic" band at c. 280 nm and the "cyclohexadienone" band at c. 240 nm. The substituents in the positions 2,3 cause a bathochromic shift of the "aromatic"

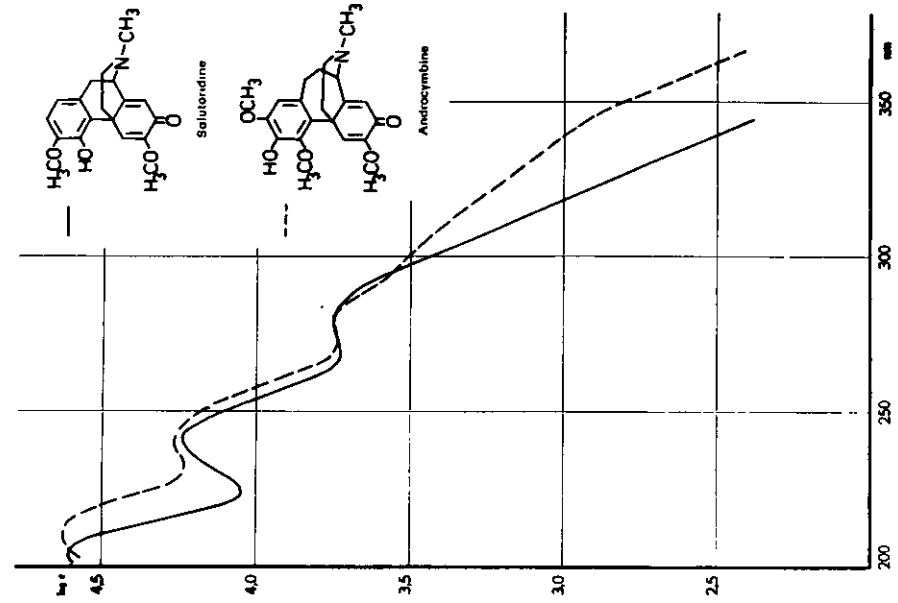

Salutaridine
Androcymbine
4.5
4.0
3.5
3.0
2.5
200
250
300
350
nm

Fig 4

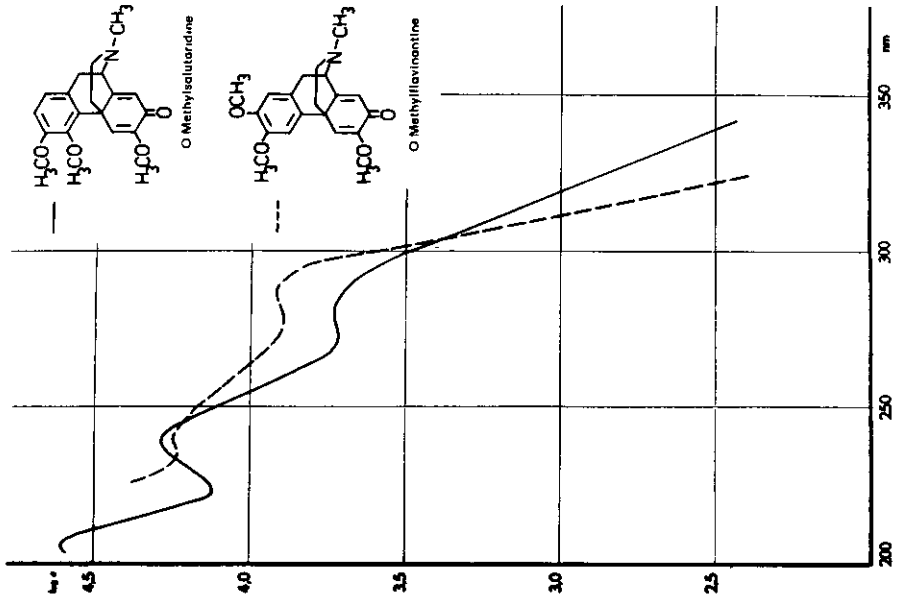

O Methylsalutaridine
O Methylflavinantine
4.5
4.0
3.5
3.0
2.5
200
250
300
350
nm

Fig 3

band by c. 6 - 9 nm, which is consistent with the literature[8], and a hyperchromic shift by c. ε 3,290 if compared with the position of this band in compounds with substituents in the positions 3,4 (Fig. 3). Thus, the uv spectra of compounds with substituents in the positions 3,4 greatly resemble those of the proaporphine alkaloids (Fig. 5) or even more closely those of the homopromorphinane alkaloids where the electron donating substituents are located in the positions 2,3,4. The spectra of the homopromorphinanes differ from those of the promorphinanes with substituents in the positions 3,4 only by the presence of a slight shoulder at c. 315 nm (log ε 3.42) (Fig. 4). The methylenedioxy group of the ring A in the positions 2,3 (the compound with this group in the positions 3,4 was not available) causes a bathochromic and a hyperchromic shift of the "aromatic" band even in the spectra of the promorphinanes.

If we assume that the absorption of the "aromatic" band of the promorphinanes and homopromorphinanes without substituents on the cyclohexadienone ring is similar to that of the proaporphines and homoproaporphines (log ε 3.5), then, in promorphinanes substituted in the positions 3,4, the substitution of the cyclohexadienone ring by a CH_3O group will increase the intensity of this band by c. ε 2,470, and in those substituted in the positions 2,3 by c. ε 4,790.

We also studied two promorphinane compounds without methoxyl groups on the aromatic ring A but one CH_3O group

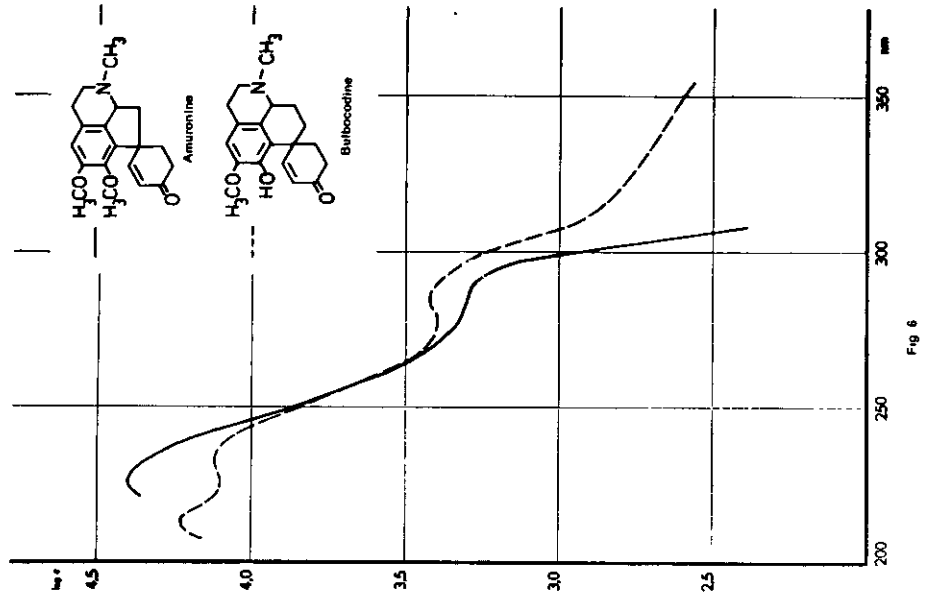

Amuronine
Bulbocodine
hν
4.5
4.0
3.5
3.0
2.5
200
250
300
350
nm

Fig 6

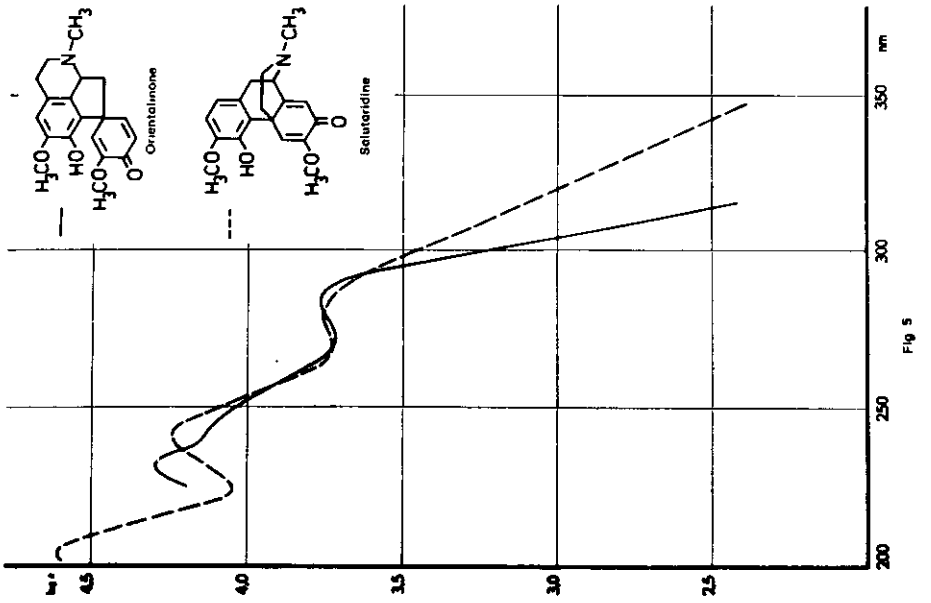

Orientaline
Salutaridine
hν
4.5
4.0
3.5
3.0
2.5
200
250
300
350
nm

Fig 5

in the position α, or two CH_3O groups in the positions α, α' of the cyclohexadienone ring. The first compound produces only a band at 246 nm (log ε 4.14), which represents the coalesced "aromatic" and the "cyclohexadienone" band. This band of the second compound undergoes a bathochromic shift by 30 nm and a hypochromic shift by ε 2,600.

From the cyclohexadienone group of substances, we can easily differentiate the cyclohexadienole base where the keto group is reduced to the secondary hydroxyl group. Such compounds exhibit a strong minimum between the first and the second band (nudaurine: $\lambda_{max}^{ethanol}$ nm (log ε) 237sh (3.73), 293 (3.82); λ_{min} 258 (2.98), ref.[10]).

(B) Cyclohexenone Compounds

(a) Proaporphine (Type IIa) and Homoproaporphine (Type IIb) Compounds

The proaporphine compounds (Type IIa) without a CH_3O group on the cyclohexenone ring (Figs 6,7) show a "cyclohexenone" band at c. 225 nm (log ε 4.3) and a "aromatic" band at c. 288 nm (log ε 3.3) which is attributable to the aromatic ring substituted with two electron donating substituents. In these compounds, the methylenedioxy group of the ring A also causes a bathochromic and a hyperchromic shift of the "aromatic" band. The proaporphine compounds with a CH_3O group in the α-position on the double bond of the cyclohexenone ring were not available to us.

The homoproaporphine compounds (Type IIb) (Figs 6,7)

behave in a similar manner except that the band of the cyclohexenone chromophore is shifted bathochromically by c. 8 nm, if compared with the bands of the proaporphine compounds, and the absorption is by about ε 7,400 lower. The band of the aromatic chromophore also appears at 285 nm and its absorption is by about ε 820 higher. The CH_3O group on the double bond of the cyclohexenone ring causes a considerable increase in the absorption of the "aromatic" band which is shifted hypsochromically by c. 20 nm, and a decrease in the absorption of the "cyclohexenone" band. These changes are greater than in the cyclohexadienone compounds. This is to be seen in luteidine[23] where the intensity of the "aromatic" band is even higher than that of the "cyclohexenone" band (Fig. 7).

(b) Promorphinane (Type IVa) and Homopromorphinane (Type IVb) Compounds

There were available to us only three of these compounds with a cyclohexenone ring (double bond between C-5 and C-6). The promorphinane base carries a CH_3O group in the α-position (C-6) to the keto group on the double bond, the two homopromorphinane compounds have a CH_3O group at the same carbon atom and a double bond on the opposite side of the ring. The "aromatic" band of the promorphinane bases (Type IVa) is shifted hypsochromically and hyperchromically due to a CH_3O group on the double bond on the ring D, whereas the band of the cyclohexenone ring hypochromically contrary to the bands of the proaporphines (Type IIa) and the homopro-

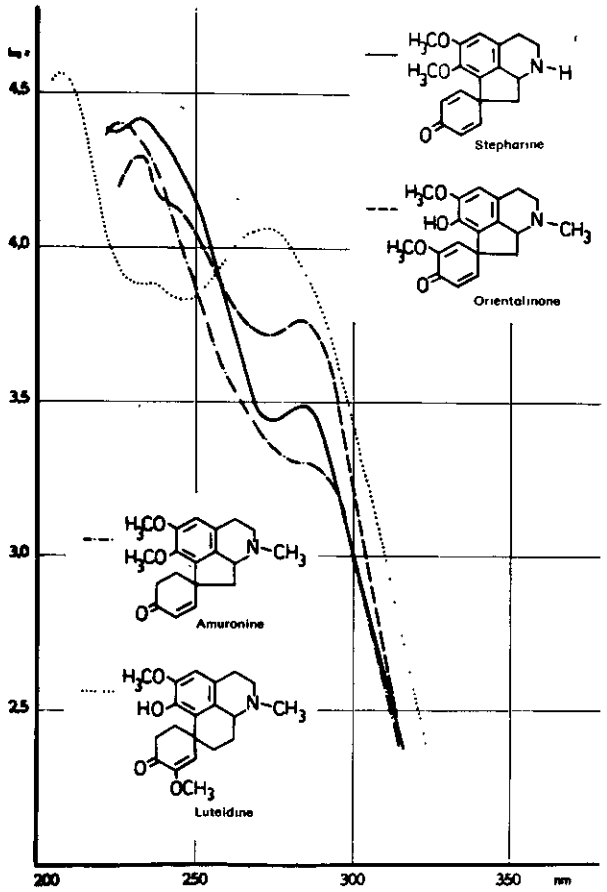

Stepharine
Orientalinone
Amuronine
Luteidine
4,5
4,0
3,5
3,0
2,5
200
250
300
350
nm

Fig 7

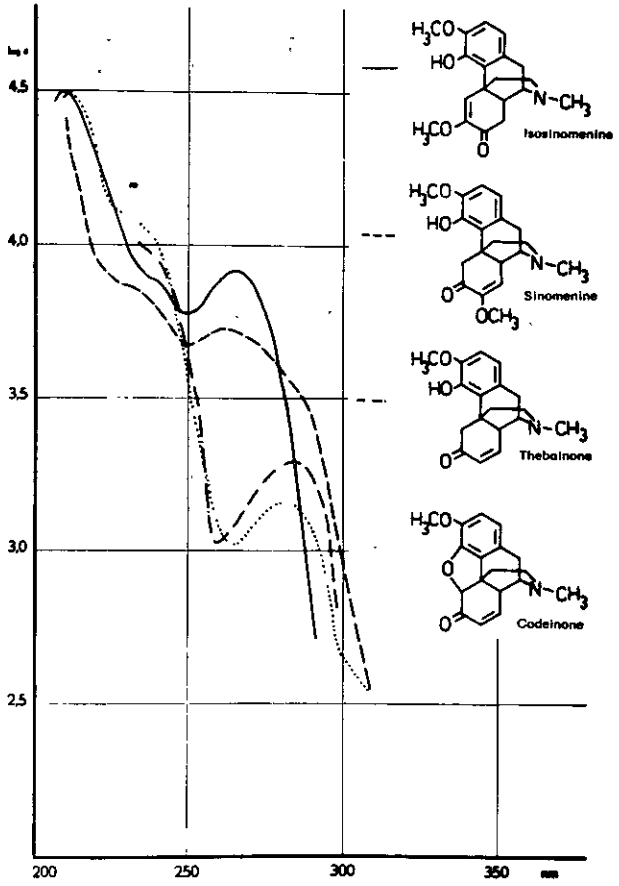

Isosinomenine
Sinomenine
Thebainone
Codeinone
4,5
4,0
3,5
3,0
2,5
200
250
300
350
nm

Fig. 8

aporphines (Type IIb) with a cyclohexenone ring without a CH_3O group.

The promorphinane compounds with a cyclohexenone ring D and a double bond between the carbon atoms C-7 and C-8 or C-6 and C-7 (codeinone, thebainone and pseudocodeinone) exhibit similar uv curves as for example the cyclohexenone compounds of the proaporphine type IIa, except that the absorption of the "cyclohexenone" band is c. ε 10,000. The compounds with the CH_3O group in the α-position (C-7) to the keto group have the "aromatic" band shifted hypsochromically and hyperchromically. The "cyclohexenone" band does not change its wavelength but its absorption is lower (Fig. 8). This phenomenon is also observed in proaporphine compounds with a cyclohexenone ring (Fig. 7). The uv curve of sinomenine (VII) (shoulder at 295 nm) does not differ greatly from the curve of cepharamine (VIII). The curve of isosinomenine is similar to that of sinomenine as far as the position and the intensity of these two bands are concerned. In isosinomenine, the shoulder at 295 nm is, however, missing. The "aromatic" band of hasubanonine (IX) (with both hydrogens of the double bond in the ring D substituted with CH_3O groups) undergoes a hyperchromic and a bathochromic shift (10 nm).

An exception is the spectrum of metathebainone (VI) where the double bond of the ring D is conjugated both with the keto group and the aromatic system of the ring A. Thus, the uv spectrum of this compound resembles that of the derivatives

of cinnamic acid where the aromatic nucleus is substituted by electron donating groups in the positions 2,3.

(C) Cyclohexanone Compounds

The unsubstituted cyclohexanone exhibits[24] a band at 285 nm with an ε value of only 14. The uv spectra of proaporphine or promorphinane compounds, whose two double bonds of the cyclohexadienone nucleus are hydrogenated, are overlapping the band of the tetrahydroisoquinoline chromophore[7,8] with two electron donating substituents.

(II) Infrared Spectra:

The ir spectroscopy was used[15,25] for the first time to study the cyclohexadienone structure of derivatives with a sterane A-ring. These compounds exhibit three bands: 1672-1650 cm^{-1} (ν C=O), 1647-1630 cm^{-1} (ν -$\underset{H}{C}$=$\underset{H}{C}$-), and 1618-1605 cm^{-1} (ν >C=C<). After the elucidation of the cyclohexadienone structure of alkaloids of the proaporphine and the promorphinane type, the experiences made with the ir spectroscopy of this "cross conjugated dienone" system were also applied to this group of natural substances[8].

The cyclohexenone structure of the steroid substances was originally also studied by Jones et al.[26]. It is known[5,27] that the CH_3O group on the double bond of the cyclohexenone ring, conjugated with the keto group, shifts the band of this double bond (designated as the "enolic double bond") from 1620 cm^{-1} to 1630-1640 cm^{-1} and leads to a simultaneous increase of its intensity.

(A) Cyclohexadienone Compounds (Types Ia, Ib, IIIa, IIIb)

The proaporphine and homoproaporphine compounds show a weak band at c. 1610-1600 cm^{-1} which is attributable to the π-electron system of the aromatic nucleus (Fig. 9a). There also appears a band at 1620 cm^{-1} of medium intensity, which corresponds to the double bonds of the cyclohexadienone ring, and a high intensity band of the carbonyl group at c. 1660 cm^{-1}. When the whole system is carrying a methylenedioxy group on the ring A instead of two methoxyl groups, then the spectra exhibit a well separated median band in all the media ($CHCl_3$, KBr, nujol) at 1640 cm^{-1}. This band corresponds to the planar skeletal vibrations of the $\rangle C=C\langle$ bonds of the aromatic nucleus whose π-electron system is influenced by the attached methylenedioxy group+) (Figs 9,10).

+) In the region of c. 1640 cm^{-1}, the compounds with a methylenedioxy group show a low intensity band which, for example in the spectra of stylopine, can be identified only with difficulty. The spectra of simple compounds, whose five-membered isocyclic or heterocyclic ring is attached to the benzene nucleus (indane, phthalide, methylenedioxybenzene, 2,2-dimethyl-4,5-benzo-1,3-dioxolan), also exhibit a median band (1620-1650 cm^{-1}). The methylenedioxybenzene shows even two weak bands at 1776 and 1626 cm^{-1}. Therefore we assume that the vibrations of the band at c. 1640 cm^{-1} ($CHCl_3$, KBr, nujol) are produced by the tension of the aromatic nucleus, which is caused by the attached five-membered ring.

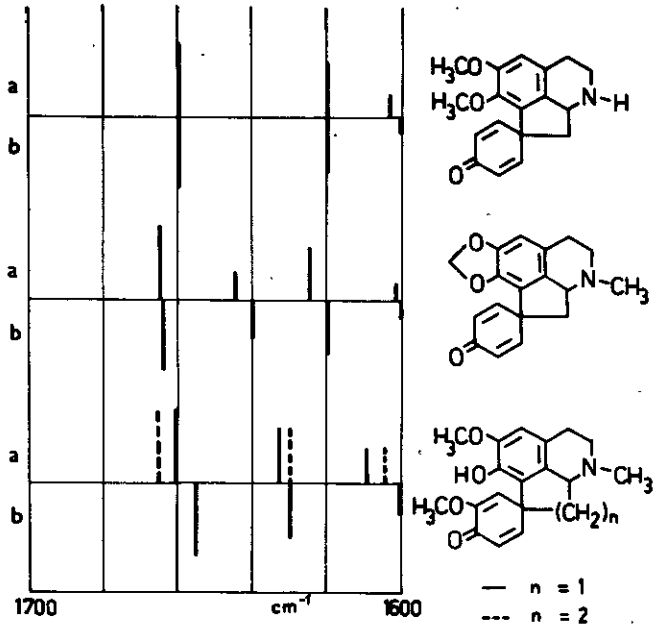

a
b
a
b
a
b
1700
cm⁻¹
1600
H3CO
H3CO
N-H
O
O
O
N-CH3
H3CO
HO
(CH2)n
— n = 1
--- n = 2
a CHCl3
b Nujol

Fig. 9a

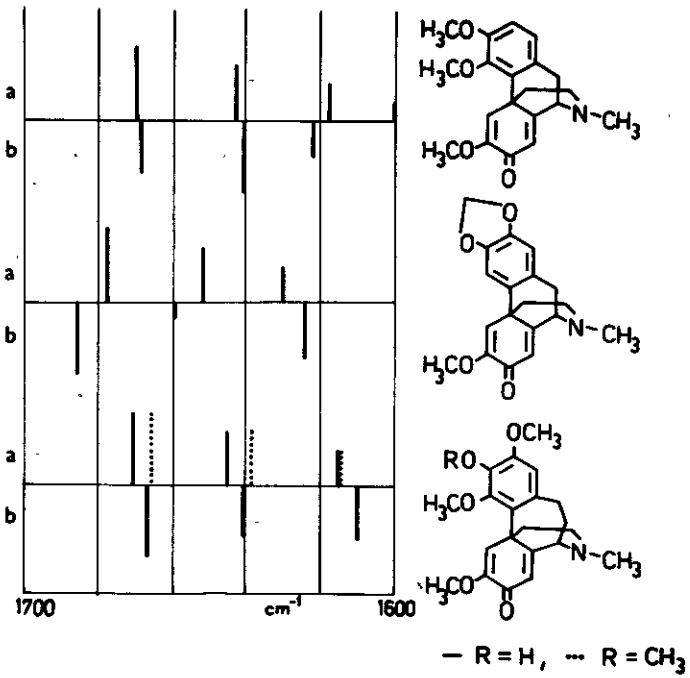

a
b
a
b
a
b
1700
cm⁻¹
1600
H3CO
H3CO
N-CH3
H3CO
O
O
O
N-CH3
H3CO
OCH3
RO
H3CO
N-CH3
H3CO
— R = H, ··· R = CH3

Fig. 9b

The band of the carbonyl group is shifted by c. 5-10 cm^{-1} to higher values. The proaporphine system (Ia) with a CH_3O group on one of the double bonds in the α-position to the keto group produces bands at c. 1665, 1630 and 1605 cm^{-1} ($CHCl_3$). The ir spectrum of the cyclohexadienone compound of the homoproaporphine type with a CH_3O group in the β-position[22] shows only two bands at 1650 and 1605 cm^{-1} ($CHCl_3$).

The promorphinane alkaloids (IIIa) available to us were only the bases with a CH_3O group on the cyclohexadienone ring. The compounds with methoxyl groups in the positions 2,3 on the ring A showed bands at 1670, 1640 and 1620 cm^{-1} ($CHCl_3$). The compound with a methylenedioxy group in the positions 2,3 exhibited a band of the carbonyl group at 1678 cm^{-1} ($CHCl_3$). The promorphinanes with methoxyl groups in the positions 3,4 show practically the same values at c. 1670, 1640, 1620 and 1600 cm^{-1} in all the systems (Fig. 9b). The band of the double bond at 1640 cm^{-1} is overlapping the corresponding band of the methylenedioxy group in those compounds where this electron donating group is present.

The above mentioned bands are often split into several bands or there appear at least indications of shoulders. When each of the measurements is carried out in at least two systems ($CHCl_3$, KBr or $CHCl_3$, nujol) then the intensity and the position of the individual bands can orientatively

indicate what type of compound is dealt with in the analyzed case.

On reduction of the keto group, when only the two double bonds of the ring D remain, the ir spectrum exhibits weak intensity bands at 1680, 1625 and 1605 cm^{-1}, or the first two bands coalesce into one broad band.

(B) Cyclohexenone Compounds (Types IIa, IIb, IVa, IVb)

A comparison of the ir spectra of the above-mentioned cyclohexadienone compounds with those of the cyclohexenone compounds (Fig. 10a) shows that the first group has well formed bands at c. 1670-1660, (1640), 1610 and 1600 cm^{-1}, whereas the second group at c. 1690-1670, 1620 and 1600 cm^{-1}. The band in the region between 1690-1670 cm^{-1} often decomposes into two bands at c. 1690 and 1670 cm^{-1}. The band of the carbonyl group of these compounds has never been found to be located at a lower value than 1670 cm^{-1}. Roemeronine, whose nucleus A carries a methylenedioxy group, has again a band at 1644 cm^{-1} which is similar to that of the mecambrine or the amurine type.

There were available to us only two substances of the homopromorphinane compounds with double bonds between the carbon atoms C-8 and C-15. The ir spectra of these compounds also show bands only at c. 1680 and 1620 cm^{-1} ($CHCl_3$, KBr).

When one of the double bonds of the cyclohexenone ring carries a CH_3O group in the α-position to the keto group, the original band of the double bond at c. 1620 cm^{-1} becomes

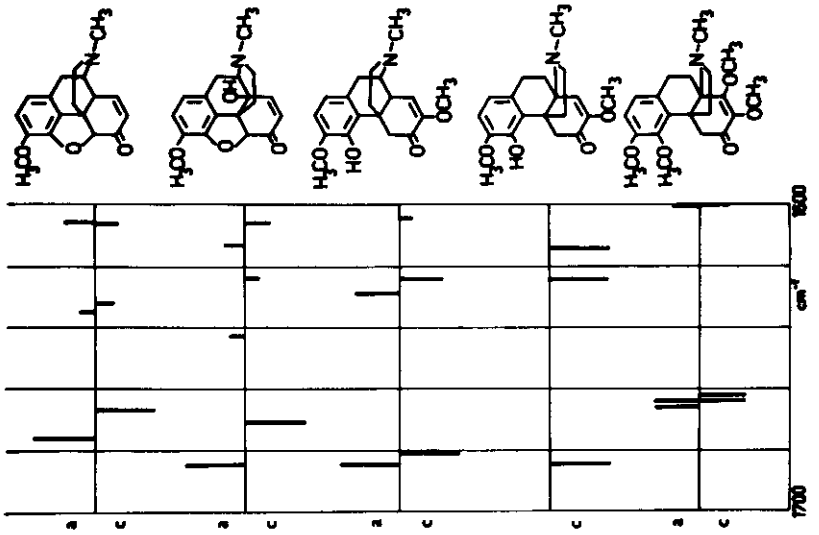


Fig. 10b

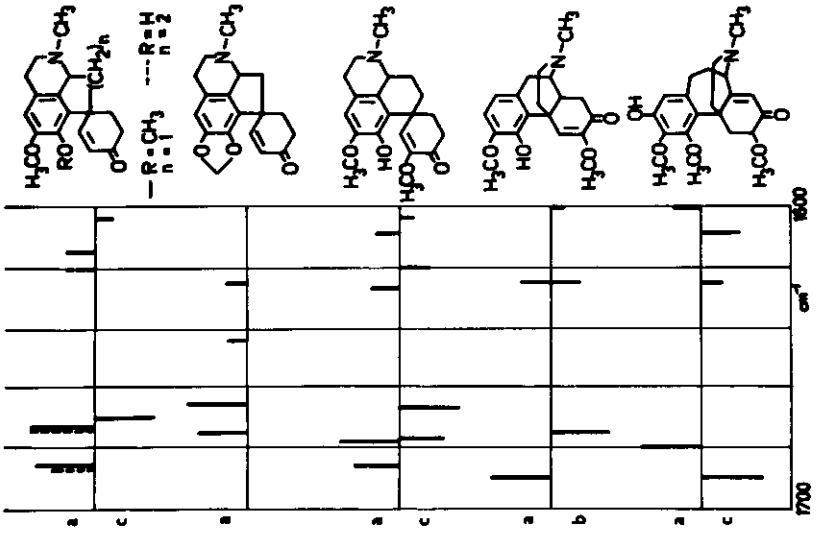


Fig. 10a

still more pronounced (increase in intensity) and is shifted to c. 1640-1625 cm^{-1}. Further measurements have shown, however, that the position of this band may differ considerably (see luteidine) in dependence on the concentration and the medium.

A different location of the cyclohexenone ring is observed in codeinone and ψ-codeinone where, moreover, this ring is connected by an oxygen bridge with the ring A. The ir spectra of all these compounds exhibit an intense band at c. 1667 cm^{-1} and two low intensity bands at c. 1632 and at 1606 cm^{-1} (KBr) (Fig. 10b). The first band (1667 cm^{-1}) is attributable (vide supra) to the keto group conjugated with a double bond which does not carry any other substituents than hydrogens. The somewhat lower value of this band can be accounted for by the deformation of the ring D due to the oxygen bridge between the rings A and D. Metathebainone (VI) exhibits a marked band (doublet) at 1653 cm^{-1} which does not correspond to that of cyclohexadienone. A similar band is produced by 2-hydroxy-trans-cinnamic acid (1665, 1618, 1603 cm^{-1} - KBr) or its aldehyde which has the hydroxyl group in the ortho-position. In the ir spectra of hydroxycodeinone, the bands in the region between 1700-1600 cm^{-1} are by c. 9 cm^{-1} higher than those of codeinone.

In the ir spectra of sinomenine (VII) whose CH_3O group is located on the double bond in the α-position to the keto group, the band of this oxo-group appears at 1682 cm^{-1} (KBr),

that is by about 20 cm^{-1} higher than that of codeinone and ψ-codeinone. In cepharamine (VIII), the band of the oxo--group is also located at c. 1680 cm^{-1} due to the presence of the CH_3O group of the ring D. Moreover there also appear two intense bands at 1625 and 1615 cm^{-1} ($CHCl_3$). The spectrum of hasubanonine (IX), whose double bond carries two CH_3O groups, shows only a strong band at 1665 cm^{-1} and a median band at 1600 cm^{-1} in $CHCl_3$, KBr, and in nujol; a band of $-\overset{H}{C}=\overset{H}{C}-$ is not found present.

(C) Cyclohexanone Compounds

The compounds derived from benzyl- or phenethyltetrahydroisoquinoline, carrying only a keto group on the saturated ring D, exhibit a band of this group at c. 1720 cm^{-1} and a frequency of the π-electron system of the ring A at c. 1610 cm^{-1} (KBr).

(III) Conclusion:

There have been studied the uv and the ir spectra of cyclohexadienone and cyclohexenone compounds of the proaporphine/homoproaporphine and the promorphinane/homopromorphinane types, codeinone, sinomenine, and of compounds of the hasubanane type.

The alkaloids of the proaporphine/homoproaporphine and the promorphinane/homopromorphinane types with a cyclohexadienone ring (Types Ia, Ib, IIIa, IIIb) and with oxygen electron donating substituents on the ring A exhibit three

bands at c. 285 nm (secondary band of the aromatic nucleus - - "aromatic" band), at c. 235 nm (a band of the cyclohexadienone ring which is overlapping with the first primary band of the aromatic chromophore - "cyclohexadienone" band) and a band at c. 215 nm (second primary band of the aromatic chromophore). The cyclohexenone bases (Types IIa, IIb, IVa, IVb) behave in a similar manner.

The absorption and the position of the "aromatic" band at c. 285 nm is affected by the electron donating substituents and, furthermore, by the cyclohexadienone or the cyclohexenone ring and its electron donating substituents. Substitution of the hydrogen of the cyclohexadienone ring with a CH_3O group in the α-, α,α'- or β-position vs. the keto group increases the absorption of the "aromatic" band by about ε 2,330-3,970 and decreases the absorption of the band at c. 230 nm of the cyclohexadienone and the cyclohexenone compounds. Moreover, the "aromatic" band of all the cyclohexenone compounds with a CH_3O group in the α-position is shifted hyperchromically and hypsochromically (c. 260 nm).

In the promorphinane/homopromorphinane compounds, the absorption of the "aromatic" band is also affected by that whether the electron donating substituents of the aromatic nucleus are in the positions 2,3 or 3,4. The uv bands of the proaporphine alkaloids with oxygen electron donating substituents in the positions 1,2,11 are similar to those of promorphinane compounds with substituents in the positions

3,4,6 (Fig. 7). There is practically no difference between the uv band of the 3,4-dimethoxy-promorphinane and that of the 2,3,4-trimethoxy-homopromorphinane alkaloid (Fig. 4). When one of the methoxyl groups on the ring A is replaced by a hydroxyl group, this does not manifest itself in the shape and the intensity of the bands. In all these compounds, the presence of a methylenedioxy group on the ring A (instead of two methoxyl groups) produces a hyperchromic and a bathochromic shift of the "aromatic" band.

The cyclohexenone bases exhibit the lowest absorption of the "aromatic" band (c. ε 2,000), somewhat higher is that of the cyclohexadienone base (c. ε 3,162), the 11-methoxy--cyclohexadienone (i.e. that of proaporphine, 3,4-dimethoxy--promorphinane or 2,3,4-trimethoxy-homopromorphinane) (c. ε 5,012), and that of 11-methoxy-cyclohexadienone (i.e. that of 2,3-dimethoxy-promorphinane) (c. ε 7,943). The highest absorption is exhibited by the homoproaporphine bases with a CH_3O group on the cyclohexenone ring (luteidine) (c. ε 12,600). The bases with an unsubstituted cyclohexenone ring also show an absorption (first primary band) already at 225 nm, whereas the other compounds at c. 235 nm (Figs 7,8). The behaviour of the bases of codeinone, sinomenine and cepharamine is similar to that of the other promorphinane bases; thus the position of the cyclohexenone ring does not significantly influence the position and the absorption of the uv bands. The "aromatic" band of hasubanonine undergoes a hyperchromic and a bathochromic shift.

On the basis of the described positions of the bands and particularly of the position and the intensity of the "aromatic" band, the described groups of alkaloids can be differentiated (Types I and III; II, IV, V, VII, and IX; with or without a CH_3O group on the ring D - Tables and Figs 3,7,8).

In spite of the fact that the cyclohexadienone proaporphine/homoproaporphine and promorphinane/homopromorphinane alkaloids have many common characteristic properties in the range between 1700-1600 cm^{-1}, there can be pointed out some differences: the proaporphine alkaloids, whose ring A carries a methylenedioxy group instead of a couple of methoxyl groups, have a characteristic band at c. 1640 cm^{-1} which in $CHCl_3$, KBr and nujol is lower than the two vicinal bands (at c. 1665 and 1622 cm^{-1}). This phenomenon is also observed in the promorphinane alkaloids with a methylenedioxy group in the positions 2,3. In the ir spectra of this type of compounds, the strongest bands usually appear at c. 1660 cm^{-1} ("cross conjugated dienone" system), at c. 1620 cm^{-1} (double bonds of this system), and at c. 1605 cm^{-1} (aromatic system).

The cyclohexenone alkaloids behave in a similar manner: their double bonds show, however, low bands only at 1620 and 1603 cm^{-1} and a significant band of the keto group in the region between 1690-1675 cm^{-1}. The cyclohexadienone as well as the cyclohexenone compounds with a CH_3O group on the

double bond in the α-position to the keto group, shift and intensify the original band at 1620 cm^{-1} to c. 1635 cm^{-1}; the position of this band is dependent on the medium and the concentration of the analyzed substances.

TABLES. Ultraviolet and infrared data of the studied compounds

(A) Cyclohexadienone Compounds

Proaporphine Derivatives (Type Ia)

Glaziovine[10,16,28] (1-OH, 2-OCH_3, 6-CH_3): uv 234 nm (log ε 4.42), 288 (3.58); ir ($CHCl_3$) 1659, 1619 cm^{-1}; ir (nujol) 1658, 1618 cm^{-1}.

Crotonosine[10,29,30] (1-OCH_3, 2-OH, 6-H): uv 235 nm (log ε 4.39), 283 (3.51)sh, 289 (3.52); ir (nujol) 1661, 1621, 1600 cm^{-1}.

N-Methylcrotonosine[30,31] (1-OCH_3, 2-OH, 6-CH_3): uv 228 nm (log ε 4.29), 282 (3.18), 288 (3.19); ir (nujol) 1664, 1625 cm^{-1}.

Pronuciferine[30,32] (1,2-$(OCH_3)_2$, 6-CH_3): uv 227 nm (log ε 4.40), 230 (4.41), 280 (3.55), 285 (3.55); ir ($CHCl_3$) 1656, 1618 cm^{-1}; ir (KBr) 1656, 1634, 1613 cm^{-1}; ir (nujol) 1658, 1618, 1605 cm^{-1}.

Stepharine[10,33] (1,2-$(OCH_3)_2$, 6-H): uv 231 nm (log ε 4.42), 284 (3.49); ir ($CHCl_3$) 1660, 1620, 1603 cm^{-1}; ir (nujol) 1660, 1620, 1600 cm^{-1}.

Mecambrine[10,29,34] (1,2-OCH_2O-, 6-CH_3): uv 217 nm (log ε 4.44)sh, 231 (4.42), 296 (3.58); ir ($CHCl_3$) 1665, 1644, 1625, 1602 cm^{-1}; ir (KBr) 1665, 1642, 1622, 1598 cm^{-1}; ir (nujol) 1664, 1640, 1620, 1597 cm^{-1}.

Orientalinone[35,36] (1-OH, 2,11-$(OCH_3)_2$, 6-CH_3): uv 231 nm (log ε 4.30), 242 (4.14)sh, 284 (3.77); ir ($CHCl_3$) 1665, 1630, 1605 cm^{-1}; ir (KBr) 1667, 1640, 1610 cm^{-1}.

Homoproaporphine Derivatives (Type Ib)

1-Hydroxy-2-methoxyhomoproaporphine[37] (1-OH, 2-OCH_3, 6-CH_3): uv 235 nm (log ε 4.53), 290 (3.66); ir (KBr) 1657, 1619, 1600 cm^{-1}.

Kreysiginone[21,29,38,39] (1-OH, 2,12-$(OCH_3)_2$, 6-CH_3): uv 212 nm (log ε 4.50), 242 (4.08)sh, 287 (3.73); ir ($CHCl_3$) 1660, 1635, 1608 cm^{-1}; ir (KBr) 1655, 1648sh, 1629, 1600 cm^{-1}; ir (nujol) 1664sh, 1655, 1630, 1600 cm^{-1}.

1-Hydroxy-2,9-dimethoxyhomoproaporphine[22] (1-OH, 2,9-$(OCH_3)_2$, 6-CH_3): uv 235 nm (log ε 4.19), 285 (3.87); ir ($CHCl_3$) 1650, 1605 cm^{-1}.

1-Hydroxy-2,10,12-trimethoxyhomoproaporphine[21,62] (1-OH, 2,10,12-$(OCH_3)_3$, 6-CH_3): uv 217 nm (log ε 4.61), 232 (4.06), 275 (4.14); ir ($CHCl_3$) 1660, 1650, 1620 cm^{-1}.

Promorphinane Derivatives (Type IIIa)

Flavinantine[40] (2,6-$(OCH_3)_2$, 3-OH, 17-CH_3): uv 239 nm (log ε 4.17), 286 (3.85); ir ($CHCl_3$) 1667, 1639, 1626 cm^{-1}.

O-Methylflavinantine[41-44] (2,3,6-$(OCH_3)_3$, 17-CH_3): uv 239 nm (log ε 4.25), 285 (3.92); ir ($CHCl_3$) 1670, 1640, 1620 cm^{-1}.

Flavinine[40] (2,6-$(OCH_3)_2$, 3-OH, 17-H): uv 238 nm (log ε 4.12), 285 (3.91); ir ($CHCl_3$) 1667, 1639, 1629 cm^{-1}.

Isosalutaridine (Pallidine)[44,45] (2-OH, 3,6-$(OCH_3)_2$, 17-CH_3): uv 235 nm (log ε 4.08), 283 (3.81); ir ($CHCl_3$) 1666, 1643, 1624 cm^{-1}.

Amurine[10,29,46] (2,3-OCH_2O-, 6-OCH_3, 17-CH_3): uv 243 nm (log ε 4.11), 290 (4.05); ir ($CHCl_3$) 1678, 1652, 1630 cm^{-1}; ir (KBr) 1669, 1646, 1615 cm^{-1}; ir (nujol) 1685, 1660, 1624 cm^{-1}.

Sinoacutine[10,47,48] (3,6-$(OCH_3)_2$, 4-OH, 17-CH_3): uv 242 nm (log ε 4.31), 278 (3.75); ir ($CHCl_3$) 1669, 1640, 1620 cm^{-1}; ir (nujol) 1670, 1640, 1610 cm^{-1}.

Norsinoacutine[10,40] (3,6-$(OCH_3)_2$, 4-OH, 17-H): uv 242 nm (log ε 4.30), 275 (3.94)sh; ir (nujol) 1672, 1643, 1623 cm^{-1}.

Salutaridine[10,29,48] (3,6-$(OCH_3)_2$, 4-OH, 17-CH_3): uv 242 nm (log ε 4.25), 279 (3.75); ir ($CHCl_3$) 1670, 1642, 1623 cm^{-1}; ir (KBr) 1668, 1642, 1616 cm^{-1}; ir (nujol) 1670, 1641, 1612 cm^{-1}.

O-Methylsalutaridine[29] (3,4,6-$(OCH_3)_3$, 17-CH_3): uv 239 nm (log ε 4.29), 279 (3.73); ir ($CHCl_3$) 1670, 1643, 1618, 1600 cm^{-1}; ir (KBr) 1668, 1640, 1622, 1597 cm^{-1}; ir (nujol) 1668, 1640, 1622, 1594 cm^{-1}.

2,3,4,6-Tetramethoxypromorphinandienone[49] (2,3,4,6-$(OCH_3)_4$, 17-CH_3): uv 234 nm, 276; ir ($CHCl_3$) 1665, 1641, 1617 cm^{-1}.

6-Methoxypromorphinandienone[42] (6-OCH_3, 17-CH_3): uv 208 nm (log ε 4.30), 246 (4.14); ir ($CHCl_3$) 1665, 1640, 1620 cm^{-1}.

6,8-Dimethoxypromorphinandienone[42] (6,8-$(OCH_3)_2$, 17-CH_3): uv 208 nm (log ε 4.27), 263 (4.05).

Homopromorphinane Derivatives (Type IIIb)

4-Demethoxy-O-methylandrocymbine[50] (4-H, 2,3,6-$(OCH_3)_3$, 18-CH_3): uv 240 nm (log ε 4.16), 280 (3.76); ir ($CHCl_3$) 1667, 1640, 1615 cm^{-1}.

Androcymbine[29] (3-OH, 2,4,6-$(OCH_3)_3$, 18-CH_3): uv 211 nm (log ε 4.63), 241 (4.27), 280 (3.75), 303 (3.48)sh; ir ($CHCl_3$) 1670, 1645, 1615 cm^{-1}; ir (nujol) 1665, 1640, 1610 cm^{-1}.

2-Hydroxy-3,6-dimethoxyhomopromorphinandienone[51] (2-OH, 3,6-$(OCH_3)_2$, 18-CH_3): uv 241 nm (log ε 4.22), 282 (3.85); ir ($CHCl_3$) 1664, 1642, 1620 cm^{-1}.

2,3,6-Trimethoxy-4-hydroxyhomopromorphinandienone[52] (2,3,6-$(OCH_3)_3$, 4-OH, 18-CH_3): ir ($CHCl_3$) 1663, 1638, 1613 cm^{-1}.

O-Methylandrocymbine[29] (2,3,4,6-$(OCH_3)_4$, 18-CH_3): uv 211 nm (log ε 4.62), 233 (4.22)sh, 277 (3.66)sh, 305 (3.42)sh; ir ($CHCl_3$) 1665, 1638sh, 1633, 1615 cm^{-1}.

2,3-Methylenedioxy-4,6-dimethoxyhomopromorphinandienone (Alkaloid CC-20)[29,53] (2,3-OCH_2O-, 4,6-$(OCH_3)_2$, 18-CH_3): uv 211 nm (log ε 4.60), 241 (4.24), 280 (3.70), 305 (3.42)sh; ir ($CHCl_3$) 1674, 1644, 1615 cm^{-1}.

2-Hydroxy-3,4,6-trimethoxyhomopromorphinandienone (Alkaloid CC-10)[29,53] (2-OH, 3,4,6-$(OCH_3)_3$, 18-CH_3): uv 240 nm (log ε 4.26), 280 (3.65), 305 (3.42)sh; ir ($CHCl_3$) 1665, 1635sh, 1630, 1615 cm^{-1}.

(B) Cyclohexenone Compounds

Proaporphine Derivatives (Type IIa)

Linearisine[10,29,30] (1-OCH_3, 2-OH, 6-CH_3): uv 227 nm (log ε 4.40), 282 (3.45), 287 (3.44); ir (KBr) 1671, 1610 cm^{-1}; ir (nujol) 1670, 1612, 1604 cm^{-1}.

Amuronine[10,54] (1,2-$(OCH_3)_2$, 6-CH_3): uv 225 nm (log ε 4.41), 285 (3.30)sh; ir ($CHCl_3$) 1685, 1673, 1615 cm^{-1}.

Roemeronine[55] (1,2-OCH_2O-, 6-CH_3): uv 220 nm (log ε 4.24), 294 (3.32); ir ($CHCl_3$) 1675sh, 1666, 1644, 1625 cm^{-1}.

Dihydroorientalinone[56] (1-OH, 2,11-$(OCH_3)_2$, 6-CH_3): ir ($CHCl_3$) 1680, 1625 cm^{-1}.

Homoproaporphine Derivatives (Type IIb)

Bulbocodine[29] (1-OH, 2-OCH_3, 6-CH_3): uv 232 nm (log ε 4.12), 285 (3.42); ir ($CHCl_3$) 1688sh, 1674, 1620 cm^{-1}; ir (KBr) 1645, 1603 cm^{-1}.

Dihydrokreysiginone (Luteidine)[23,29,38,57,58] (1-OH, 2,12-$(OCH_3)_2$, 6-CH_3): uv 208 nm (log ε 4.56), 234 (3.88)sh, 272 (4.07); ir ($CHCl_3$) 1685sh, 1678, 1627, 1608 cm^{-1}; ir (KBr) 1677, 1667, 1620, 1604 cm^{-1}.

Promorphinane Derivatives (Type IVa)

8,14-Dihydronorsalutaridine[59] (3,6-$(OCH_3)_2$, 4-OH, 17-H):

uv 206 nm (log ε 4.55), 235 (3.93), 261 (3.95); ir (nujol) 1670, 1625, 1600 cm^{-1}.

8,14-Dihydrosalutaridine[59] (3,6-$(OCH_3)_2$, 4-OH, 17-CH_3): uv 206 nm (log ε 4.51), 238 (3.84), 265 (3.88); ir (nujol) 1675, 1613, 1575 cm^{-1}.

Isosinomenine[60] (3,6-$(OCH_3)_2$, 4-OH, 17-CH_3): uv 208 nm (log ε 4.50), 238 (3.89), 265 (3.92); ir ($CHCl_3$) 1690, 1625 cm^{-1}.

Homopromorphinane Derivatives (Type IVb)

2-Hydroxy-3,4,6-trimethoxyhomopromorphinanenone (Alkaloid oxo-CC-3b)[29,53] (2-OH, 3,4,6-$(OCH_3)_3$, 18-CH_3): uv 237 nm (log ε 4.19), 280 (3.34); ir ($CHCl_3$) 1680, 1600 cm^{-1}; ir (KBr) 1690, 1625, 1609 cm^{-1}.

2,3-Methylenedioxy-4,6-dimethoxyhomopromorphinanenone (Alkaloid oxo-CC-2)[53] (2,3-OCH_2O-, 4,6-$(OCH_3)_2$, 18-CH_3): uv 238 nm (log ε 4.06), 281 (3.37); ir ($CHCl_3$) 1690, 1620 cm^{-1}.

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Codeinone[29] (Va): uv 210 nm (log ε 4.48), 229 (4.09), 281 (3.15); ir ($CHCl_3$) 1676, 1635, 1606 cm^{-1}; ir (KBr) 1667, 1632, 1605 cm^{-1}; ir (nujol) 1670, 1634, 1611 cm^{-1}.

Pseudocodeinone[29] (Vb): uv 207 nm (log ε 4.62), 231 (3.92)sh, 282 (3.19); ir (KBr) 1669, 1631, 1601 cm^{-1}.

Thebainone[61] (VIa): uv 236 nm (log ε 4.00)sh, 285 (3.29).

Metathebainone[29] (VIb): uv 206 nm (log ε 4.29), 229 (4.09)sh,

298 (4.11), 338 (3.55)sh; ir ($CHCl_3$) 1655, 1650, 1626, 1606 cm^{-1}; ir (KBr) 1655, 1643, 1622, 1600 cm^{-1}; ir (nujol) 1655sh, 1642, 1600 cm^{-1}.

Sinomenine[29] (VII): uv 231 nm (log ε 3.86)sh, 261 (3.73); ir ($CHCl_3$) 1685, 1640sh, 1630, 1586 cm^{-1}; ir (KBr) 1684, 1625, 1605sh cm^{-1}; ir (nujol) 1689, 1630, 1604 cm^{-1}.

Cepharamine[29] (VIII): uv 229 nm (log ε 3.94)sh, 259 (3.82); ir (KBr) 1685, 1625, 1615 cm^{-1}.

Hasubanonine[29] (8-methoxycepharamine) (IX): uv 228 nm (log ε 3.94)sh, 268 (3.98); ir ($CHCl_3$) 1665, 1658sh, 1604 cm^{-1}; ir (KBr) 1662, 1656sh, 1596 cm^{-1}; ir (nujol) 1667, 1601 cm^{-1}.

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Received, 9th April, 1975