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ABSOLUTE CONFIGURATION AND CHIROPTICAL PROPERTIES OF CHELIDONINE AND TETRAHYDROBERBERINE ALKALOIDS[1, 2]

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Abstract—The CD within the ^1L_b band of tetrahydroberberine alkaloids is rationalized with the aid of a rule taking into account the chirality of the second sphere, and a sector rule for third (fourth, . . .) sphere contributions. Extension to the ^1L_a band CD is proposed. On this basis the absolute configuration of mecambridine, orientalidine, and chelidonine is determined. That of chelidonine has been proven independently by the kinetic method of partial resolution during esterification with α-phenylbutyric anhydride.

WHEREAS the absolute configuration of the tetrahydroprotoberberine alkaloids is known from chemical[4] correlation or from rotational data,[5] that of chelidonine and related compounds has not been elucidated unequivocally. The relative configuration and the conformation in solution has been determined, however, by IR and NMR spectroscopy[6–9] and by chemical correlation with "didehydrochelidonine".[10] We have now proved the absolute configuration of chelidonine to be **1a** by the kinetic method of partial resolution with α-phenylbutyric anhydride[11, 12] and from its circular dichroism in the following way.

Absolute configuration at C-10 *of chelidonine.* Reaction of racemic α-phenylbutyric anhydride with (+)-chelidonine **1a** and subsequent isolation of the partially resolved acid gave in 12·3% optical yield material with a rotation $\alpha_D = +0{\cdot}17°$, which leads to the assignment of (*R*)-configuration for the chiral center C-10 in the alkaloid.[11, 12] Together with the established relative stereochemistry[6] (+)-chelidonine **1a** has, therefore, (10*R*, 11*S*, 12*R*)-configuration.

Chiroptical properties of tetrahydroberberine alkaloids. The determination of the absolute configuration from chiroptical properties uses results in the tetrahydroberberine series, which are discussed first. ORD[13–15] and CD data[15, 16] have been published and empirical correlations between these and benzylisoquinoline alkaloids and simpler model compounds lead (fortuitously!) to the correct known absolute configuration,[13] though the Cotton effect of open chain compounds and cyclic ones cannot be compared directly.[5, 15–17] Measurements with modern instrumentation

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revealed four to five CD-bands between 185 and 300 nm,[16] which is in agreement with our findings.* Thus (−)-tetrahydropalmatine (3) gives a very faint positive CD-band at 280 nm, which undoubtedly is the sum of the ^1L_b-bands of both systems, a stronger negative one at 232 nm (ET-band from oxygen lone pair electrons to the aromatic ring and/or ^1L_a of the latter), a very pronounced one, also negative, at 205 nm, assigned ^1L_a character by the French workers,[16] and a relative strong positive Cotton effect around 191 nm. These two latter bands could, however, also correspond to the two ^1B-transitions of the two aromatic chromophores, which are degenerate in simple aromatic compounds. The strongest CD-band has been compared[16] with the characteristic one of the biphenyl system of aporphine alkaloids,[18-20] which is, however, at 235 nm, due to a stronger interaction of the two aromatic chromophores.

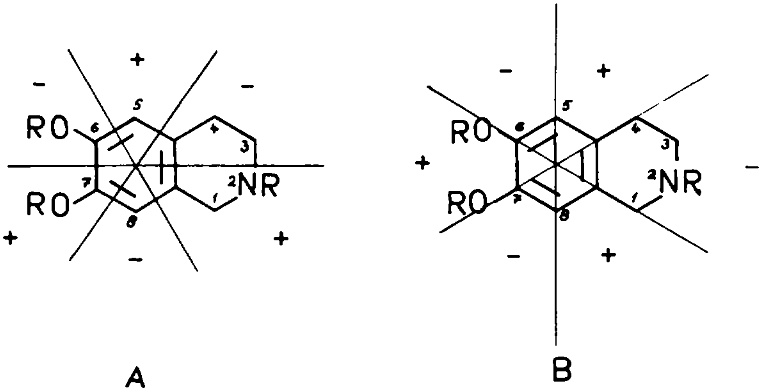

FIG 1. Sector rules for third (fourth, . . .) sphere contributions to the Cotton effect of 6,7-dioxygenated tetrahydroisoquinolines. Signs are given for upper sectors. A: ^1L_a band (signs to positive CD of L_b-band.

Recently Kuriyama *et al.*[21] and DeAngelis and Wildman[22] have proposed quadrant rules for the correlation of the CD-curves with the stereochemistry of amaryllidaceae alkaloids (mainly with tetrahydroisoquinoline chromophore). We believe, however,[23] that for third (fourth, . .) sphere effects a rule with six upper and six lower sectors is more appropriate for the benzene chromophore in general (Fig 1), and that in those cases, where the second sphere (i.e. the nonaromatic ring condensed with the benzene) is chiral, this chirality determines the sign and to a great extent even the magnitude of at least the ^1L_b-band. Newer results on simpler appropriate model compounds support this view,[3, 24] as well as data from the yohimbane series.[25] For the ^1L_b band (Fig 1B), the N atom and the C-3 are in sectors of opposite sign if we have a halfchair conformation, whereas for the ^1L_a band (Fig 1A) these signs are the same. This may be one explanation for the fact, that usually the ^1L_b band CD is much smaller than that of the ^1L_a band.

According to this treatment, a projection as given in Fig 2 leads to a positive sign for the ^1L_b band CD. In order to apply this rule, the conformation of the second

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* The CD published by Kametani and Ihara[15] differs appreciably from that found by Legrand and Viennet[16] and by us. E.g. for (−)-3, Kametani and Ihara[15] cite a small negative CD at 284 nm, a stronger one of the same sign at 234, and a strong positive one below 210 nm. The first and the third signs are, therefore, incorrect. Though for norcoralydine they reported a stronger negative CD at 279 nm, which would agree with our predictions, we do not want to use this as an argument, as long as the data are not checked.

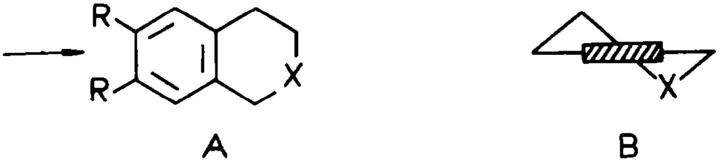

Fig 2. Second sphere contribution to the Cotton effect of dioxygenated tetralines, tetrahydroisoquinolines etc. A – shows direction of projection, B – indicates chirality which leads to positive CD of ${}^1L_b$-band.

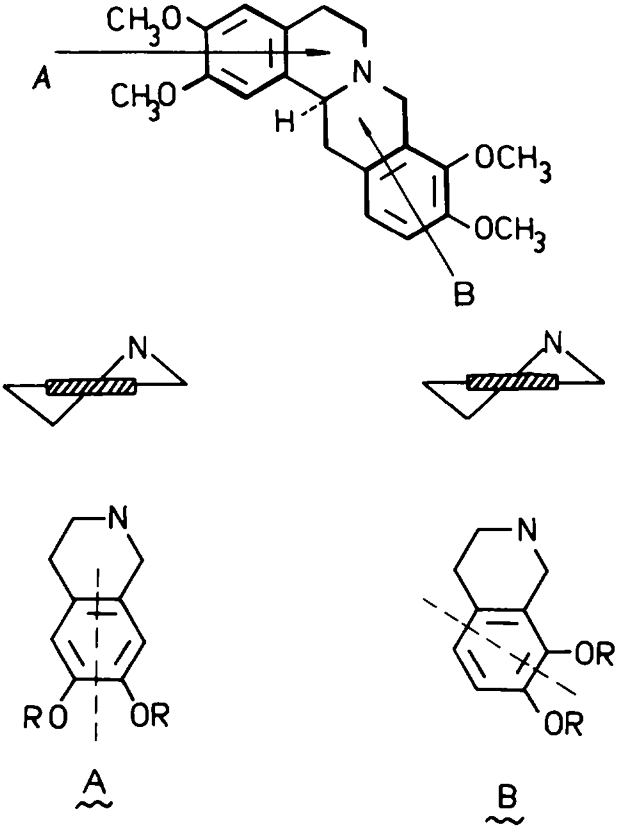

Fig 3. Projections for the two chromophores of (–)-*tetrahydropalmatine* (3). The arrows A and B in the formula indicate the direction of projection for the two chromophores A and B. ----- indicates the approximate direction of the electric transition moment vector.

sphere has to be known. X-ray data of capaurine hydrobromide (7) showed,[26] that both rings (at least in the cristalline state) adopt halfchair conformations even though the quinolizidine moiety has *cis*-configuration. Conformational analysis and NMR spectroscopy have led to the deduction that also in the *trans*-quinolizidine system both rings adopt halfchairs.[5]

Assuming the *trans*-quinolizidine stereochemistry with two halfchairs for rings B and C of (–)-tetrahydropalmatine (3), we then get the two projections of Fig 3 for the contributions of the second spheres to the CD. The chromophore of rings A/B (called "Chromophore A") should lead, according to the rule given in Fig 2, to a negative CD within the ^1L_b band. Since in the projection for the chromophore of rings C/D ("Chromophore **B**") the direction of the electric transition moment vector is rotated by approximately 60° (assuming that OR groups have a much greater influence upon it than alkyl groups), we can expect a negative contribution for this chirality of the second sphere, if we take into account the change of signs as depicted in Fig 1B. Assuming no strong coupling between the two ^1L_b transitions, the CD about 280 nm should then be approximately the sum of these two contributions. As they have opposite signs, a small value is expected, and this is in agreement with the measurements.[15, 16] Under the assumption that the preferred conformation is highly populated, we can draw the conclusion, that the magnitude of the contribution of chromophore **B** is larger than that of chromophore **A**.

An analogous treatment of the ^1L_a band leads to a sector rule as depicted in Fig 1A, but the insertion of the right signs is still difficult, as the assignment of this band in

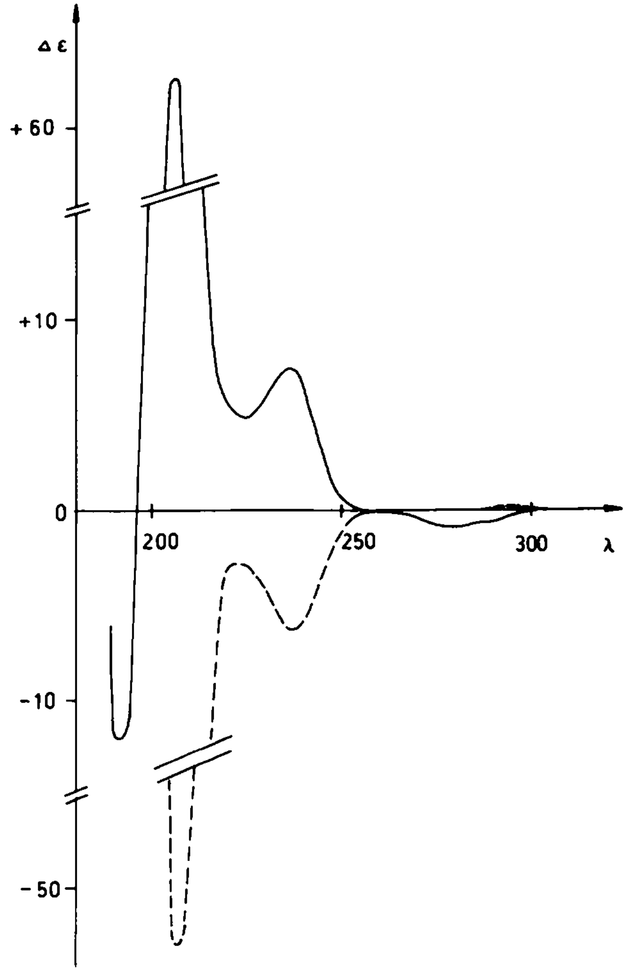

Fig 4. CD of (−)-*stylopine* (**5**) (- - - - -) and (+)-*corydaline* (**6**) (——————) in ethanol.

the CD spectra has not been done unequivocally by different workers, and changes of the magnitude and even the sign by interaction with other transitions of higher energy are possible. Furthermore, ET bands may overlap in the spectra so that the ^1L_a band may not always be identified. At present, we would, therefore, like to treat the CD within the 230 nm band merely empirically. In the model compound **8** this CD has the same sign as that in the ^1L_b band,[23] but about three to four times its intensity. Since the 230 nm CD band of **3** is negative,[16] it seems to be determined by the CD of chromophore **A** and not by that of **B**.

Introduction of methylenedioxy groupings instead of two OMe groups gives rise to a bathochromic shift of the UV absorption bands at 280 and 240 nm,[27] which is paralleled by similar shifts in the CD spectra.[23] Unfortunately, the CD bands of (−)-canadine (**4**) are not too well resolved, the 230 nm band appearing only as a shoulder on the very strong (negative) 205 nm band. The UV spectrum showed also the same property.[27] Obviously there is (at least) one more band present, which could correspond to the 216 nm band found for some amino substituted simpler tetrahydroberberines,[16] though it was assigned an n—σ^* transition of their amino groups. In the CD spectrum of (−)-stylopine (**5**) (Fig 4) this bathochromic shift is seen, however, clearly for the 230 nm band. As the direction of the transition moments are not changed because the substitution pattern remained unaltered by these replacements, the CD spectra of all three compounds are very similar.

(+)-Corydaline (**6**; Fig 4) has also a *trans*-quinolizidine skeleton with rings B and C in halfchair conformations; the additional Me group at C-13 is axial.[5, 28] In principle we expect, therefore, a CD spectrum which resembles that of (+)-tetrahydropalmatine with only minor quantitative changes. This is indeed the case, only the ^1L_b band CD being stronger negative, which is in best agreement with the prediction according to Fig 1B. With respect to chromophore **A** the Me group is, namely, in a lower sector of negative sign and should, therefore, give a negative contribution to the CD. With respect to chromophore **B** it is on the other hand nearly in a nodal plane, and does, therefore, not give a pronounced contribution to its CD. The rule of Kuriyama *et al.*[21] predicts on the contrary a positive contribution for both chromophores, which contradicts experiment. The rule of DeAngelis and Wildman[22] cannot be tested because according to the authors it is valid only for compounds with the chiral center next to the aromatic ring, i.e., for chromophore **A** but not for **B**.

(−)-1-Methoxy-epiophiocarpine (**9**)[5, 29, 30] gives a CD curve (Fig 5) which is very similar to that of (−)-stylopine (**5**; (Fig 4), thus showing that in this case the additional OMe group is of minor influence.

For (−)-mecambridine, the structure **10** has recently been proven by Pfeifer *et al.*[31] and by Preininger *et al.*[32, 33] This compound shows (Fig 5) a negative ^1L_b band CD, and the 230 nm band is seen only as a broadening of the strongly negative 210 nm band. The CD of this as well as the 196 nm band is nearly identical with that of **9**, thus suggesting identical chiralities for (−)-mecambridine (**10**) and (−)-1-methoxy-epiophiocarpine (**9**). The 12-hydroxymethyl group will scarcely influence the CD, but the two OMe groups are positioned at C-10 and C-11, thus building up a chromophore of type **A** also in rings C/D. A negative Cotton effect is then predicted for its ^1L_b band with the assumed absolute configuration, and this reasonably explains the sign inversion at 275 nm with respect to the CD spectrum of **9**.

(−)-Orientalidine (**11**) has the same chromophoric systems as mecambridine (**10**).

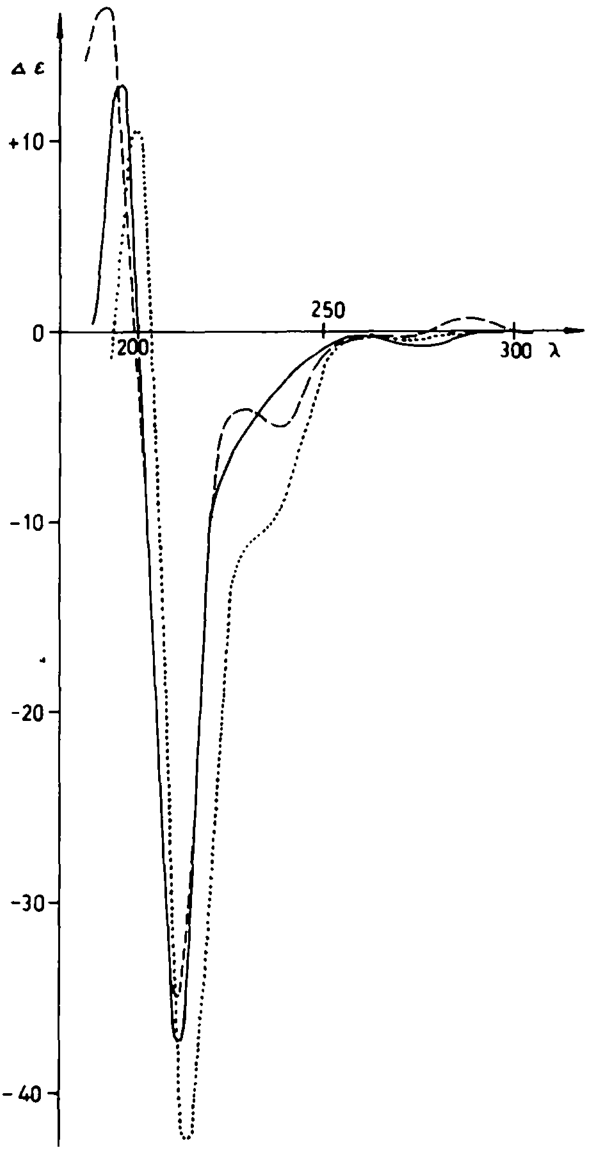

FIG 5. CD of (−)-*mecambridine* (**10**) (————), 1-*methoxyepiophiocarpine* (**9**) (– – – –) and (−)-*orientalidine* (**11**) (. . . . .) in ethanol.

as the ring closure between the CH_2OH and the OMe group does not change the substitution pattern.[32–34] Indeed the CD spectra of both alkaloids (Fig 5) are nearly identical; there appears a new shoulder in the spectrum of orientalidine (**11**) at about 233 nm, which is obviously due to a bathochromic shift owing to a more coplanar fixation of the OR group at C-11 (cf.l.c.[27]). The absolute configuration is, therefore, identical for (−)-**10** and (−)-**11**. Even though the introduction of an additional OR group complicates the picture and prevents *a priori*—predictions at the moment, the

CD of all tetrahydroberberine and tetrahydropseudoberberine alkaloids can be rationalized nicely on the basis of our rules.

The CD of some of these alkaloids has also been measured in cyclohexane solution, but there appeared only minor changes of band shapes. Even in ethanolic or methanolic HCl nearly all bands retain their original features, besides in the case of stylopine (**5**), where we found an unexpected inversion of the ^1L_b band CD.

Chiroptical properties of chelidonine and its derivatives. Taking the results in the field of tetrahydroprotoberberines (*vide supra*) as a basis, we can now try to determine the absolute configuration of (+)-chelidonine (**1a**). Its conformation follows from spectra data,[6–10] which indicate halfchairs for rings B and C and an axial conformation for the OH group at C-10. As the CD spectra in ethanol (Fig 6) and cyclohexane solution are very similar (besides the appearance of a small negative additional band at 229 nm in the latter solvent), we can also assume the same conformation for the application of the CD rules. Rings A/B form a chromophore of type **B** (Fig 3), and rings C/D of type **A** (C instead of N, which does, however, not change second sphere effects in principle). Assuming an absolute configuration as has been deduced from the kinetic method of partial resolution and depicted in the formula **1a**, the chiralities of these two chromophores are the opposite to that drawn in Fig 3. One expects, therefore, the same signs for all CD bands as with (+)-tetrahydropalmatine (enantiomeric to **3**), and exactly this is found. The CD of (+)-chelidonine (**1a**) proves, therefore, the absolute configuration determined by the other method.

(−)-Norchelidonine (**2**),[6, 35] which has been correlated with (−)-chelidonine (enantiomer of **1a**) gives a CD curve, which is the mirror image to that of (+)-chelidonine (**1a**), as expected. Acetylation of the OH group of chelidonine changes, however, drastically the CD (Fig 6). The ^1L_b band is now double humped with a positive lobe preponderant, the 240 nm band becomes smaller and has a negative satellite on the long wavelength side, and the two bands at short wavelengths are opposite to those of (+)-chelidonine and enhanced. The conformation of chelidonine O-acetate (**1b**) must, therefore, severely deviate from that of the parent alkaloid, in which the axial conformation of the OH group is stabilized by hydrogen bridging to the nitrogen. The same conclusion was already drawn from the IR[6] and NMR spectrum.[7–9]

Anhydrochelidonine (**12**). Dehydration of chelidonine leads to anhydrochelidonine,[36] which has structure **12** according to its NMR spectrum (Fig 7).* Integration of signals in the range between $\tau = 2{\cdot}8$–$3{\cdot}8$ indicates the presence of 5 aromatic or olefinic protons, which rules out the formula with a 9:10 double bond. Molecular models show that four conformations are possible, of which the two with equatorial N-Me groups are highly improbable because of strong steric repulsion from the hydrogens at C-5. Of the remaining two, one has ring B in a halfchair conformation, the other in the halfboat. In the first the N-Me group is in an axial disposition to both aromatic rings, in the latter only to one, so that this will be favoured (Fig 8), which is also proven by NMR.

The protons at C-1 and C-2 give rise to an AB-quartet ($\delta\sigma = 0{\cdot}5$ ppm), because the new double bond deshields appreciably the proton at C-1. In chelidonine both these protons were isochronous.[7, 8] The two singlets of the aromatic protons at C-5 and C-8 are also separated now by 0·58 ppm in contrast to chelidonine, where this difference was only about 0·1 ppm. In **12** the nitrogen is nearly coplanar with the H-C-5 bond,

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* We thank Prof. Dr. T. Reichstein, Basle, for the NMR spectra of chelidonine and anhydrochelidonine.

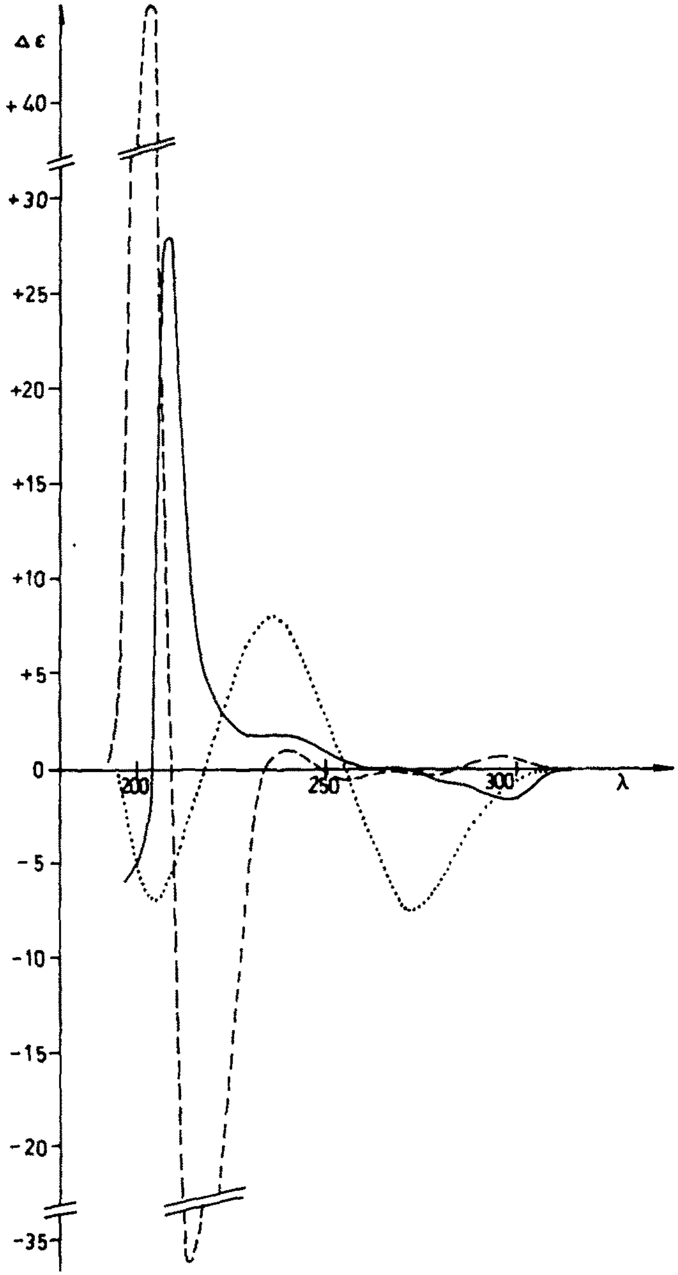


Fig 6. CD of (+)-*chelidonine* (**1a**) (———), (+)-*chelidonine acetate* (**1b**) (----) and (+)-*anhydrochelidonine* (**12**) (.........) in ethanol.

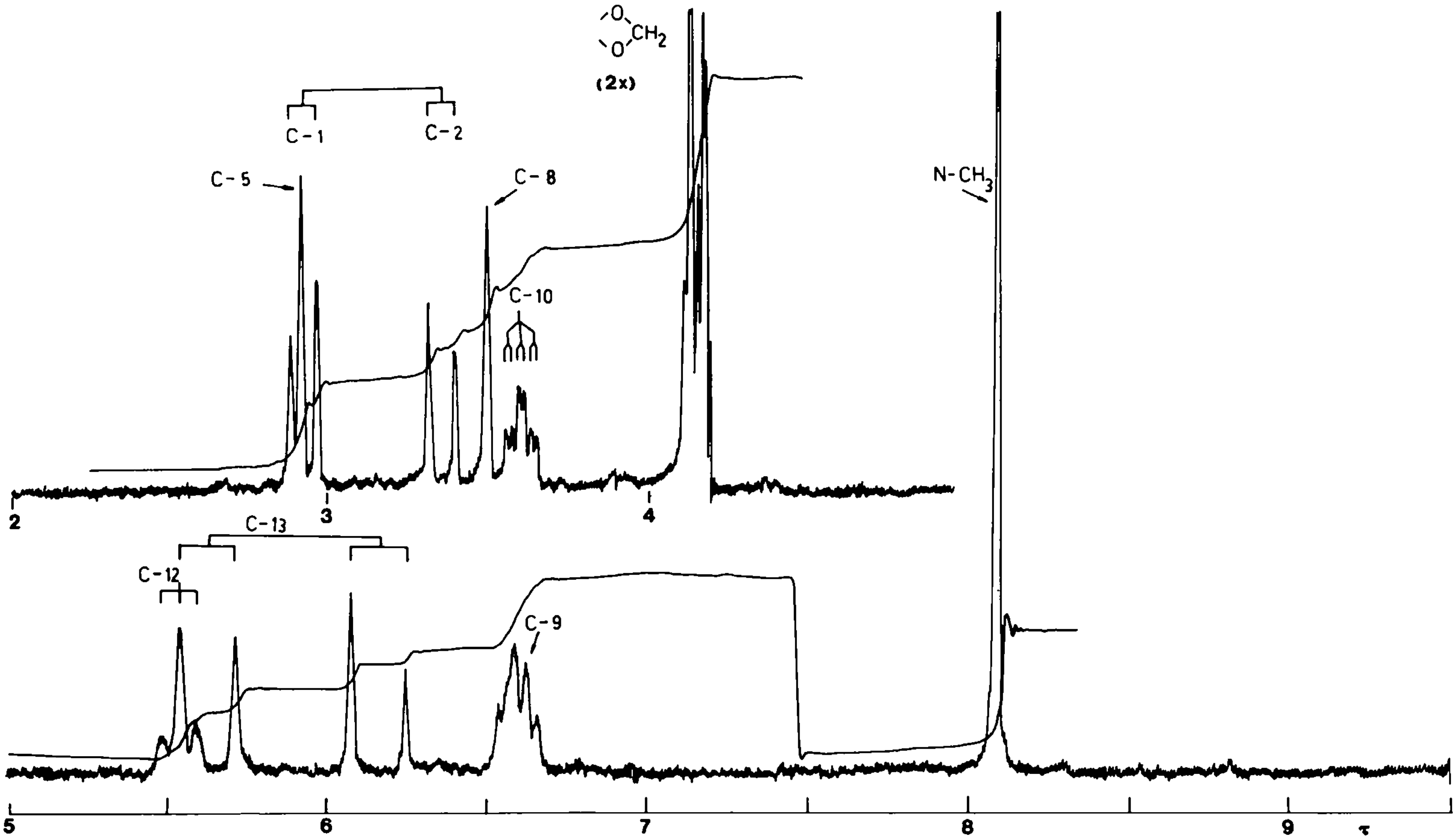


FIG. 7 NMR spectrum of *anhydrochelidonine* (**12**) in $CDCl_3$ at 100 MHz. The hydrogen atoms are numbered by the C-atom to which they are attached.

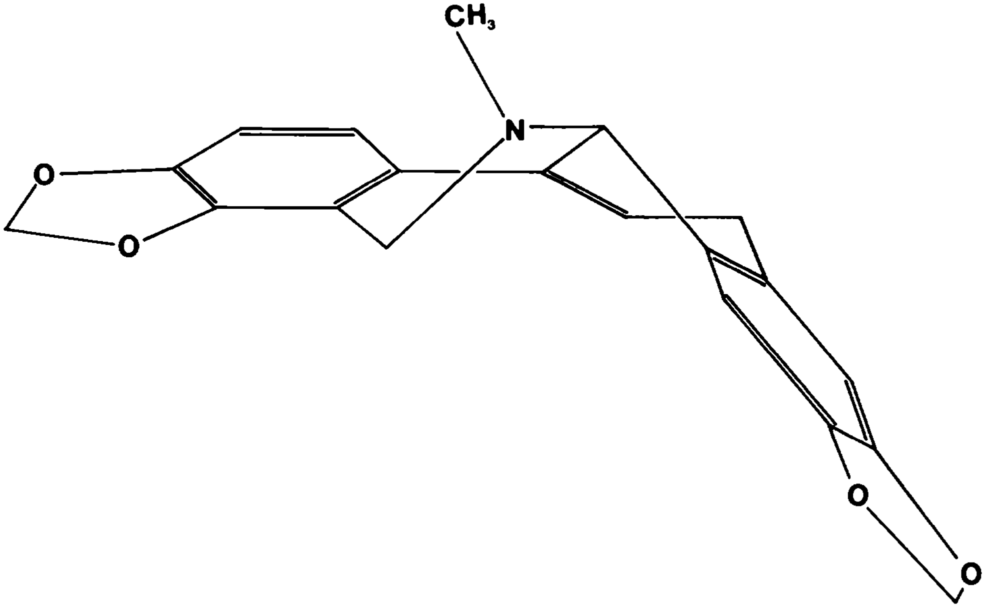


FIG 8. Conformation of (+)-*anhydrochelidonine* (12).

which leads to a stronger deshielding than in chelidonine, where it was well below this bond.[8] The two protons at C-13 give again an AB-quartet, which is shifted downfield from its position in the chelidonine spectrum. The methylene group H_2C-9 gives rise to a complex multiplet, similar to that for chelidonine, and the signal of the proton at C-12 is shifted downfield to about $\tau = 5{\cdot}57$ (from 6·55). It appears as a triplet whose inner peak overlaps with the first peak of the AB quartet of H_2C-13. The splitting is about 6 Hz, and the peaks are not sharp. This splitting can be due only to long-range coupling, and such a great coupling constant is characteristic[37] for a partial structure **13**. There is only a small difference between the *cis*- and *trans*-^5J, so that a triplet is expected. Finally, the signal of the olefinic proton is a triplet of doublets, the first splitting coming from the interaction with the methylene protons at C-9, the latter from long-range coupling with the proton at C-12. This latter coupling is not seen distinctly in the signal of the proton at C-12, which comes from the fact that there is one more long-range coupling of this with the (*pro-S*)-hydrogen at C-13, which lies nearly in the plane of ring A, and is part of an approximate "W"-path to the H at C-12. Therefore, the peaks of the lower-field doublet of the H_2C-13 quartet are smaller and broader than those of the upper-field ones.

This conformation is further supported by the signal of the N-Me group. In chelidonine the Me (equatorial) lies near the plane of ring D and is far away from ring A, whereas in the anhydro derivative **12** (axial) it comes already into the shielding cone of ring A and leaves the deshielding field of ring D. The signal in the spectrum of **1a** is, therefore, at lower field ($\tau = 7{\cdot}76$) than in that of **12** (8·13).

Anhydrochelidonine[36] (**12**) contains a styrene chromophore, which is twisted, on the other hand the double bond is also homoconjugated to ring D. We can expect,

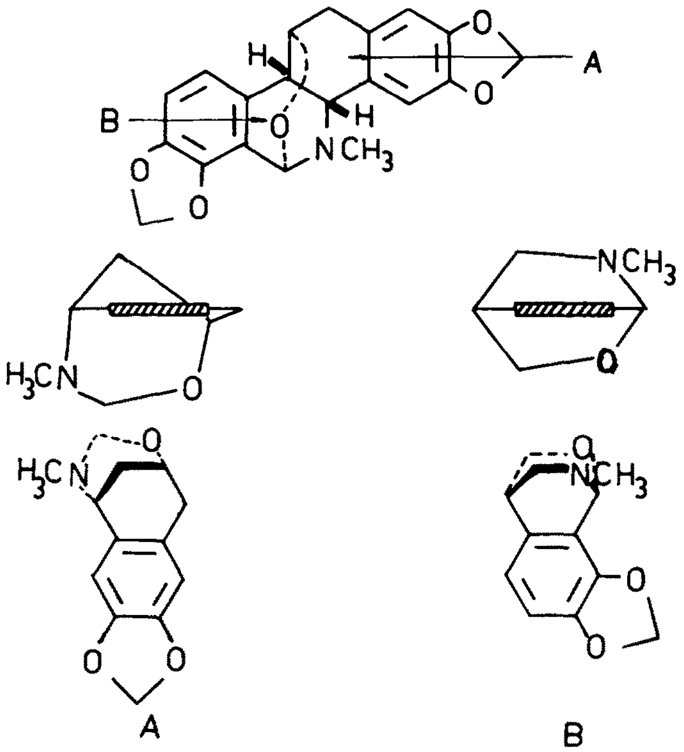


FIG 9. Projections for the two chromophores of (+)-"*didehydrochelidonine*", "neutral form" (**14a**). The arrows A and B in the formula indicate the direction of projection for the two chromophores A and B. Ring C gives a positive, the newly formed ring a negative contribution to the CD of chromophore A.

therefore, strong interaction between the two aromatic systems, and indeed the rule for the 270 nm CD band of twisted styrenes, published recently,[38] gives formally the wrong sign. It cannot be excluded, however, that the substitution with two oxygen functions is responsible for this violation of the rule.

"5,6-*Didehydrochelidonine*" contains an additional heterocyclic ring to those of chelidonine in neutral or basic solution (**14a**), whereas in acidic medium a styrene type structure **14b** has been assigned to this compound.[10] As is seen from Fig 9, both chromophores A and B are incorporated into two second spheres each, whose contributions to the CD compensate each other more or less. The molecule must be completely rigid except in the region of the N-Me group, which can adopt two conformations. Due to the balance of contributions one cannot predict the signs for the different bands. Furthermore a change of the solvent from an aprotic (cyclohexane) to a protic one (ethanol), which can form hydrogen bridges to either the O or the N atom (or to both) of rings B and C can greatly influence the Cotton effect bands. This is indeed the case as shows Fig 10, and is to our opinion not due to different solvations of the chromophores. The picture changes again drastically in acidic ethanol, which is expected because of the change of the structure from **14a** to **14b**. From molecular models it is learned that several conformations can be accepted by **14b**, so that correlations with chiroptical properties are not possible.

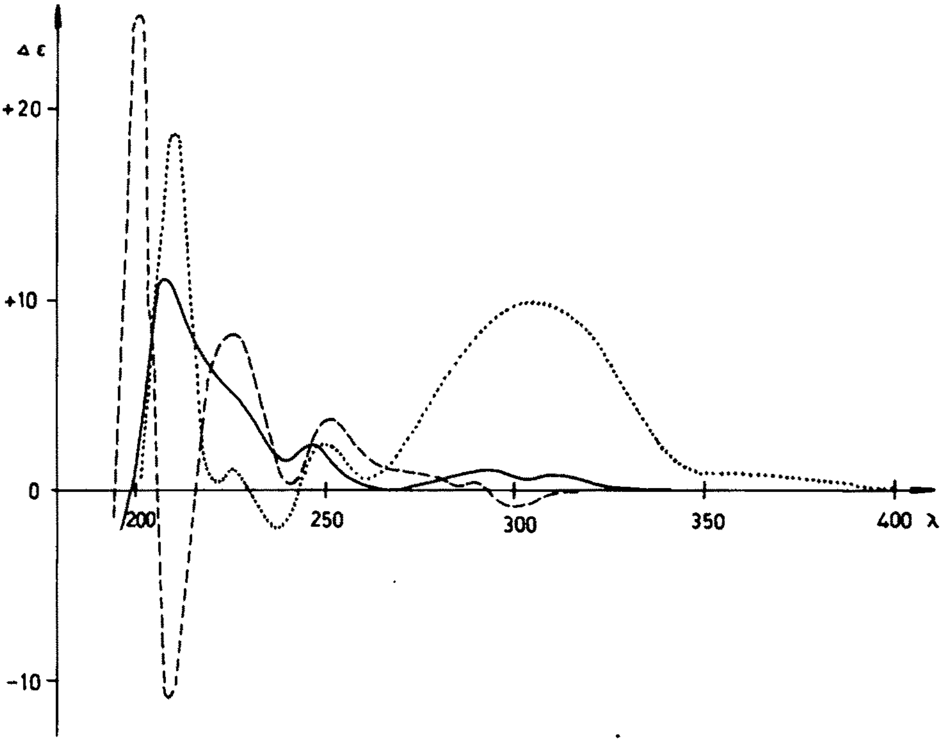
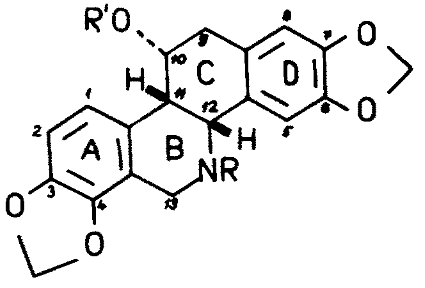
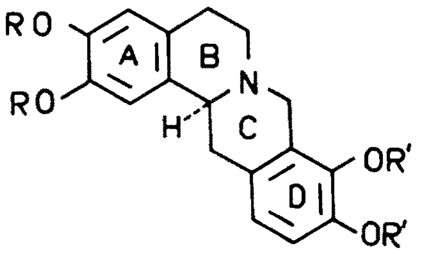


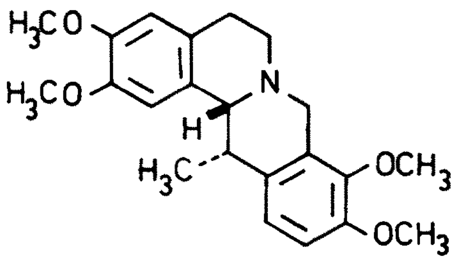
FIG 10. CD of (+)-"*didehydrochelidonine*", "neutral form" (**14a**) in ethanol (————) and cyclohexane (– – – –), and of "acidic form" (**14b**) in ethanolic HCl (. . . . .).



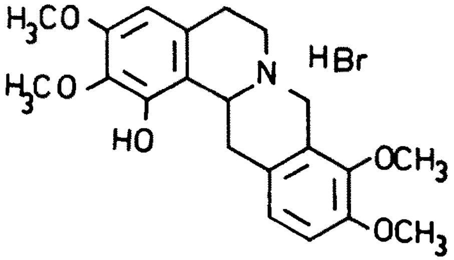
(+)-**1a**: R = CH_3, R′ = H
(+)-**1b**: R = CH_3, R′ = Ac
(+)-**2**: R = R′ = H



(−)-**3**: R = R′ = CH_3
(−)-**4**: $R_2 = CH_2$, R′ = CH_3
(−)-**5**: $R_2 = R'_2 = CH_2$



(+)-**6**



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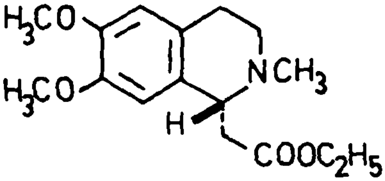
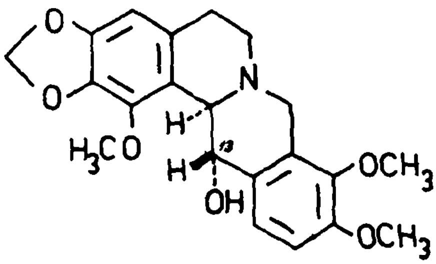
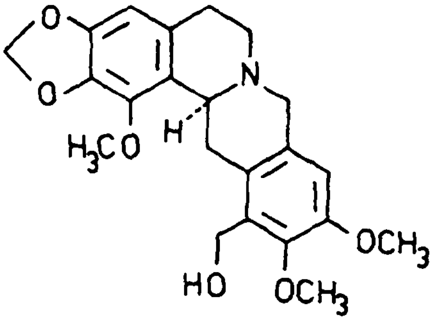


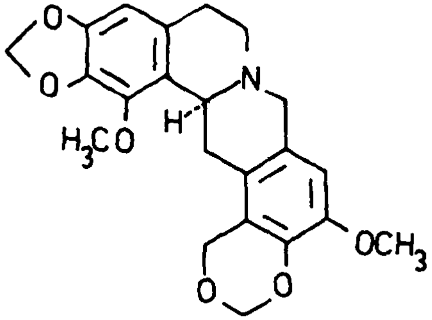
(−)-**8**



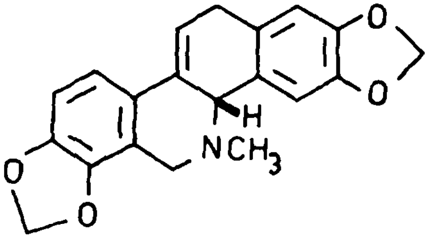
(−)-**9**



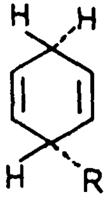
(−)-**10**



(−)-**11**



(+)-**12**



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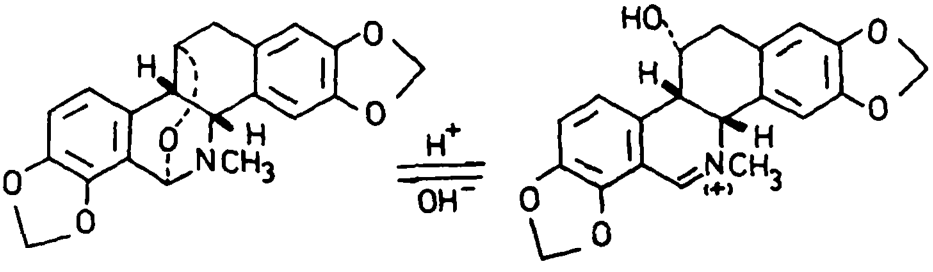

(+)-**14a**

(+)-**14b**

TABLE 1. CD DATA OF ALKALOIDS

(+)-*Chelidonine* **(1a)**: ethanol: 298 (−1·63), 284i (−0·79), 242i (+1·72), 209 (+27·8), negative at short wavelengths; ethanol + HCl[a]: 298 (−1·62), 287i (−1·27), 253 (+0·89), 227i (+2·62), 210 (+40·3), 198 (−20); cyclohexane: 299 (−1·63), 245 (+1·63), 230 (−1·06), 208 (+22·6), 196 (−6).

(+)-*Chelidonine acetate* **(1b)**: ethanol: 295 (+0·56), 276 (−0·39), 257 (−0·53), 240 (+0·99), 214 (−36·2), 204 (+45); cyclohexane: 295 (+0·50), 278 (−0·27), 255 (−1·17), 248i (−0·38), 238 (+0·83), 214 (−42·5), 203 (+62·6); acetonitril: 296 (+0·78), 279 (−0·64), 251 (−0·91), 238 (+0·51), 214 (−42), 202 (+97).

(−)-*Norchelidonine* **(2)**: ethanol: 297 (+1·08), 286i (+0·76), 240 (−1·96), negative at shorter wavelengths; methanol + HCl[b]: 298 (+0·61), 229 (−2·98), 208 (−57).

(+)-*Tetrahydropalmatine* (enantiomer to formula **3**): ethanol: 280 (−0·22), 233 (+6·71), 205 (+45·0), negative at shorter wavelengths; ethanol + HCl[a]: 277 (+0·3), 242 (−0·74), 229 (+5·61), 206 (+36·6), negative at shorter wavelengths; cyclohexane: 279 (−0·58), 238 (+9·19), 206 (+38·3), 191 (−19·6).

(−)-*Canadine* **(4)**: ethanol: 281 (+0·16), 230 (−5·3), 205 (−65·6); cyclohexane: 279 (+0·28), 240i (−2·45), 223i (−6·03), 206 (−22·9).

(−)-*Stylopine* **(5)**: ethanol: 293 (+0·17), 237 (−6·31), 207 (−53); methanol + HCl[b]: 255 (−1·29), 240 (−4·20), 208 (−41); cyclohexane: 290 (+0·75), 236i (−8·43), 223i (−10·53), 207 (−29·3).

(+)-*Corydaline* **(6)**: ethanol: 291i (−0·44), 280 (−0·78), 236 (+7·54), 206 (+62·5), 192 (−12).

(−)-1-*Methoxy-epiophiocarpine* **(9)**: ethanol: 288 (+0·73), 266 (−0·20), 238 (−4·91), 210 (−35), 192 (+17).

(−)-*Mecambridine* **(10)**: ethanol: 275 (−0·62), 211 (−37·2), 196 (+13); cyclohexane: 296 (−0·02), 281 (+0·01), 270 (−0·04), 215 (−39·4).

(−)-*Orientalidine* **(11)**: ethanol: 274 (−0·40), 233i (−10·58), 213 (−42·6), 200 (+10·6); ethanol + HCl[a]: 278 (−0·77), 233 (−11·8), 215 (−42·7), 201 (+21); cyclohexane: 273 (−0·23), 230i (−14·9), 215 (−43·5), 200 (+19·6).

(+)-*Anhydrochelidonine* **(12)**: ethanol: 310i (−0·98), 274 (−6·85), 236 (+8·26), 205 (−6); ethanol + HCl[a]: 307i (−1·75), 274 (−6·83), 233 (+10·57), 213 (−11·5), 200 (+16·2).

(+)-"5,6-*Didehydrochelidonine*" **(14)**: ethanol: 310 (+0·79), 293 (+1·12), 247 (+2·48), 224i (+5·54), 208 (+11·1); ethanol + HCl[a]: 365i (+0·81), 305 (+9·85), 250 (+2·44), 238 (−1·99), 225 (+1·1), 210 (+18·7); cyclohexane: 300 (−0·83), 289 (+0·49), 280 (+0·71), 252 (+3·79), 225 (+8·27), 209 (−11·1), 201 (+25·0).

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[a] Ethanol + 1% HCl conc.

[b] N/2 HCl in methanol.

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EXPERIMENTAL

The purity of the studied compounds was checked by m.p., UV and IR spectra. UV spectra were measured in ethanolic soln with a UNICAM model SP 700 spectrophotometer. The CD was measured with the Roussel-Jouan dichrograph, model 185, in concentrations between 0·1 and 1 mg/ml at 20° in cells of path lengths 0·01–2·0 cm.

TABLE 2. UV ABSORPTION SPECTRA

All values are in ethanol and are presented as λ (max or min) in nm with log ε in parentheses

Compound	Formula	Max	Max (Sh.)	Min	Max	Min	Max	Max (Sh.)	Min	Max	Max	Max
(+)-*Chelidonine*	**1a**	206 (4·85)	—	228 (3·92)	238 (3·96)	257 (2·98)	289 (3·90)					
(+)-*Chelidonine acetate*	**1b**	205 (4·78)	232 (3·93)	—	—	260 (3·10)	290 (3·90)					
(−)-*Norchelidonine*	**2**	—	?	230 (3·83)	239 (3·86)	257 (2·95)	288 (3·91)					
(+)-*Tetrahydropalmatine*	enantiomer to formula **3**	205 (4·81)	224 (4·24)	—	—	252 (2·90)	282 (3·71)	290 (3·55)				
(−)-*Canadine*	**4**	214 (4·29)	224 (4·17)	—	—	255 (2·88)	287 (3·77)					
(−)-*Stylopine*	**5**	205 (4·84)	—	233 (4·01)	236 (4·02)	257 (3·00)	290 (3·97)					
(+)-*Corydaline*	**6**	204 (4·83)	227 (4·28)	—	—	254 (2·94)	283 (3·75)	291 (3·63)				
(−)-1-*Methoxy-epiophiocarpine*	**9**	207 (4·78)	229 (4·27)	—	—	257 (3·10)	282 (3·52)					
(−)-*Mecambridine*	**10**	209 (4·82)	229 (4·28)	—	—	255 (2·98)	288 (3·74)					
(−)-*Orientalidine*	**11**	209 (4·84)	229 (4·27)	—	—	255 (2·91)	287 (3·71)					
(+)-*Anhydrochelidonine*	**12**	204 (4·70)	217 (4·56)	—	—	250 (3·87)	282 (4·19)					
(+)-"5,6-*Didehydrochelidonine*" in ethanol	**14a**	206 (4·72)	227 (4·22)	—	—	260 (3·64)	291 (4·05)	—	315 (3·51)	325 (3·52)	350 (3·42)	364 (3·28)
(+)-"5,6-*Didehydrochelidonine*" in ethanolic HCl	**14b**	206 (4·66)	—	221 (4·21)	238 (4·28)	262 (3·85)	295 (4·23)	339 (3·62)	349 (3·50)	356 (3·53)	366 (3·42)[a]	399 (3·48)

[a] Minimum.

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