CCCLXVII.—*The Absorption Spectra of Phenanthripyridine Alkaloids.*

By André Girardet.

The investigation of the phenanthripyridine alkaloids pukateine, laureline, and laurepukine (*Helv. Chim. Acta*, 1931, **14**, 481) suggested a comparison of their ultra-violet absorption spectra with those of substances having the same nucleus, and the possibility of thus determining the relative positions of common natural substituents (OH, OMe, O_2CH_2). The method would have a considerable advantage over any other yet known in requiring only a minute quantity of the alkaloids.

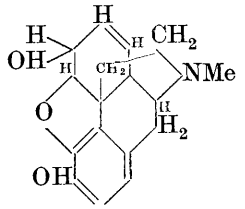
The following alkaloids have been examined: pukateine and laureline, which may be considered as epi*iso*thebaine and epimorphothebaine, if the three types of auxochrome mentioned above are regarded as equivalent; laurepukine, which was found to be either epi- or *iso*-bulbocapnine; dicentrine and its epi- or *iso*-form, domesticine, as well as glaucine, *iso*thebaine, morphothebaine, bulbocapnine, apomorphine, its epi-form, and aporphine. Further, their spectra have been compared with those of morphine and thebaine, relatively closely related, and of corydaline, belonging to a very different class of compound.

All the substances examined were analytically pure; their absorption spectra did not vary after repeated crystallisations.

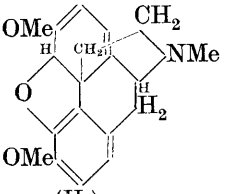
Kitasato has placed on record (*Acta Phytochimica*, Vol. III, No. 2) practically the whole of our knowledge of this type of compound

(apomorphine, bulbocapnine, dicentrine, and domesticine). He deduced very simple laws showing the relationship between these derivatives, although his experimental data were so scanty—data which the author is now able to extend.

The technique employed was similar to that of Steiner (*Bull. Soc. Chim. biol.*, 1924, 251) and Kitasato, a Baly tube being used, and a Bellingham and Stanley spectrograph giving a spectrum of 120 mm. from λ 4240 to λ 2340. The iron arc enabled the results to be directly compared with those of Kitasato. The method is not strictly quantitative, but careful study of many photographs has led to



(I.)



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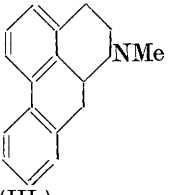
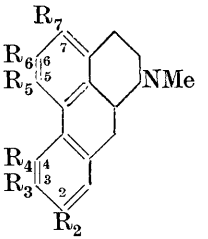
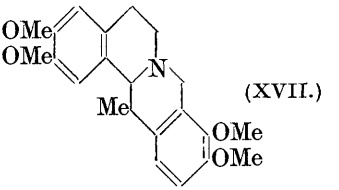


(III.)

(IV—XVI.)





(XVII.)

IV, $R_3 = R_4 = OH$. V, $R_5 = R_6 = OMe$. VI, $R_3 = OMe$; $R_4 = R_5 = OH$. VII, $R_3 = R_5 = OMe$; $R_4 = OH$. VIII, $R_4 = OH$; $R_5 + R_6 = O_2CH_2$. IX, $R_3 = OH$; $R_5 + R_6 = O_2CH_2$. X, $R_3 = R_4 = OMe$; $R_5 + R_6 = O_2CH_2$. XI, $R_3 + R_4 = O_2CH_2$; $R_5 = R_6 = OH$. XII, $R_3 = R_4 = OH$; $R_6 + R_7 = O_2CH_2$. XIII, $R_2 = R_3 = R_5 = R_6 = OMe$. XIV, $R_2 = R_3 = OMe$; $R_5 + R_6 = O_2CH_2$. XV, $R_2 + R_3 = O_2CH_2$; $R_5 = R_6 = OMe$. XVI, $R_2 = R_3 = OMe$; $R_6 + R_7 = O_2CH_2$.

comparative results which are trustworthy and appear to justify the deductions made below.

The time of exposure was 1 minute on Wellington anti-screen plates. It was found unnecessary to investigate solutions more concentrated than $N/10{,}000$ in 98% alcohol.

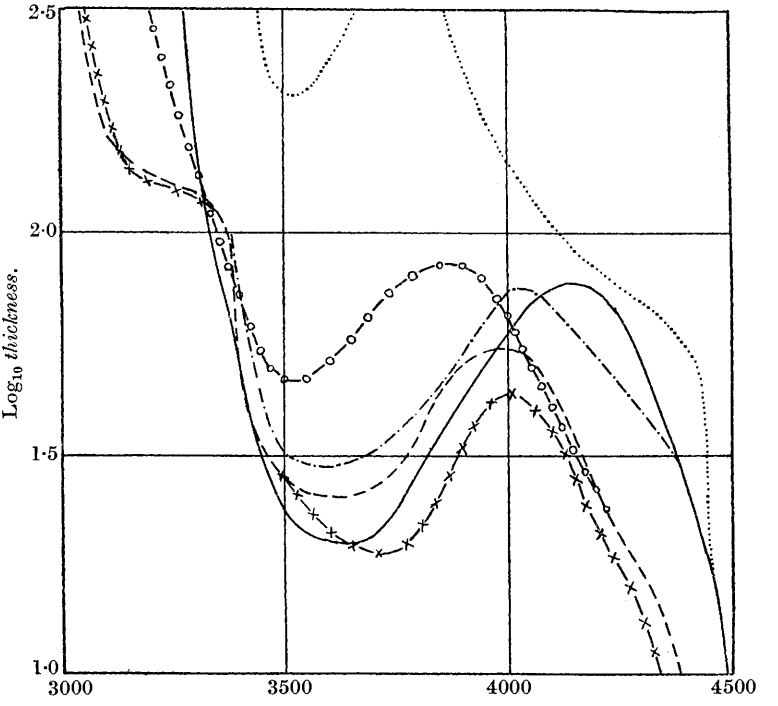
The positions of the maxima and minima of Kitasato's curves have been confirmed, but the author's bands are more distinct than his.

The identity of the absorptions of the active (*d*-) and of the racemic form of bulbocapnine (Dobbie, J., 1903, **83**, 631; Kitasato, *Acta Phytochimica, loc. cit.*, p. 241) has been confirmed.

Contrary to the statement of Dobbie (*loc. cit.*) that there is no difference between the absorptions of corybulbine and its methyl ether, the author finds that the phenolic hydroxyl has always a slight hypsochromic influence compared with methoxyl (Fig. 4).

Steiner (*loc. cit.*, p. 251) found no difference in absorption between morphine and berberine alkaloids and their respective hydro-

FIG. 1.



chlorides. The fusion of three absorption bands of papaverine into one by its transformation into the salt induced him to assign a determining importance to the *iso*quinoline nucleus in that particular compound. The author has always found a minute hyperchromic effect as the result of the conversion into the salt. The effect is, however, much larger for apomorphine with no substituents in the upper benzene ring. The presence of any auxochromes in the *iso*-quinoline nucleus may therefore be considered as inhibiting practically all the effect due to the nitrogen being tertiary or quinquevalent.

As the curves do not bring out very clearly the exact values, the frequencies for the maxima and minima are given below.

I	Morphine			3485	3770
II	Thebaine			3515	3970
III	Aporphine hydrochloride			3640	4150
IV	Apomorphine	3150	3360	3610	3985
	Apomorphine hydrochloride	3150	3360	3610	4025
V	Epiapomorphine dimethyl ether	3150	3360	3720	3990
VI	Morphothebaine hydrochloride	3220	3500	3720	3985
VII	*iso*Thebaine			3720	3985
VIII	Pukateine	3240	3520	3745	3970
	Pukateine methyl ether	3240	3520	3730	3965
IX	Laureline	3220	3500	3710	3940
X	Bulbocapnine methyl ether	3210	3350	3710	3970
XI or XII	Laurepukine	3220	3535	3750	3930
	Laurepukine dimethyl ether	3260	3540	3710	3970
XIII	Glaucine	3250	3380	3540	3935
XIV	Dicentrine	3200	3380	3540	3900
XV or XVI	Domesticine methyl ether	3200	3380	3540	3900
XVII	Corydaline			3570	3960

Morphine (I) with only four double bonds has an absorption (Fig. 1) more hypsochromic than thebaine (II) with five double bonds. The introduction of a sixth, in aporphine (III), has a similar effect, further increased by the change in fixation of the nitrogen ring and the loss of all auxochromes. At the same time, there is a marked hyperchromic effect in the last two cases.

Aporphine has only one absorption band; the presence of two auxochromes in positions 3 and 4 or 5 and 6 produces a second one, very shallow and hypochromic, at the frequency 3200 or thereabouts. At the same time, the aporphine minimum is narrowed by 165 Å. Substitution in positions 3 and 4 (apomorphine, IV) does not change the aporphine maximum appreciably, but substitution in positions 5 and 6 (epiapomorphine, V) narrows it by 80 Å.

Bulbocapnine methyl ether (Fig. 2) has the same absorption maximum at the frequency 3720 as epiapomorphine; its first band, however, is hypochromic and more accentuated than that of the latter.

Formula (XI) for laurepukine accords with Kitasato's observation (*loc. cit.*, p. 237) that a change from a methylenedioxy-group to two vicinal methoxyls has a hypsochromic influence equivalent to 50 Å. This, however, only affects the first band.

Corydaline (XVII), which possesses a nucleus quite different from that of the phenanthripyridines, has an absorption spectrum not to be mistaken.

Dicentrine (XIV) (Fig. 3) differs from glaucine (XIII) in having a methylenedioxy-group instead of two methoxyls; the deviation is 50 Å. The second maxima coincide, but the second minimum of glaucine is moved towards the ultra-violet by 35 Å and is strongly hypochromic.

The first half of the curve of domesticine (XV or XVI) is identical with that of dicentrine, but the other part is hypochromic. The replacement of a methylenedioxy-group by two methoxyls is without

FIG. 2.

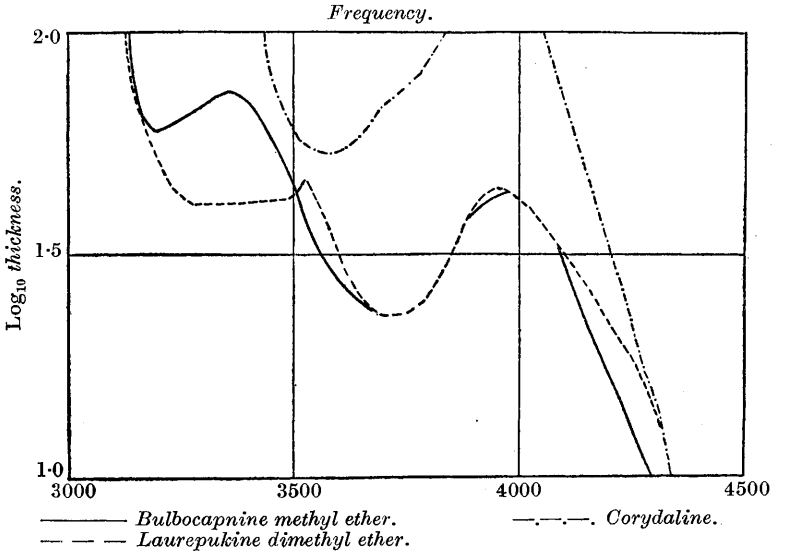
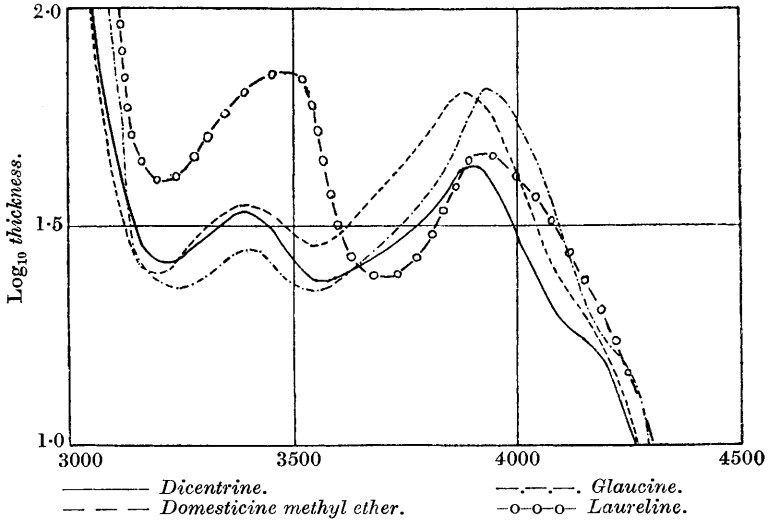


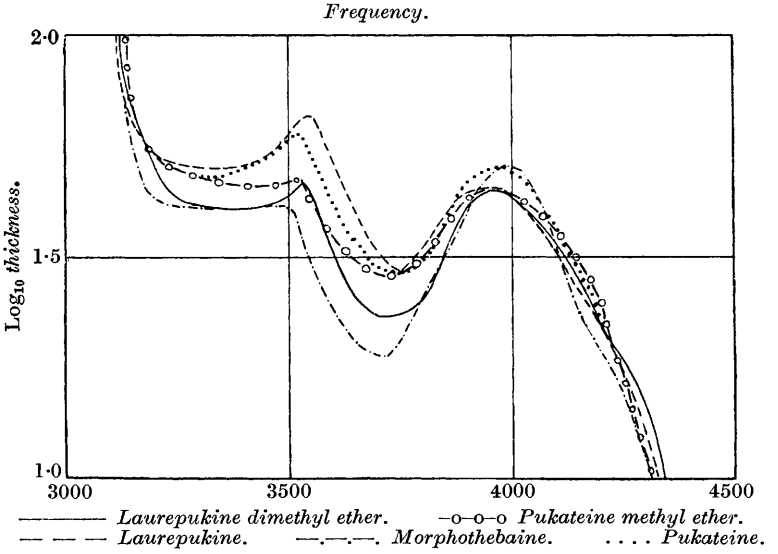
FIG. 3.



effect (contrast bulbocapnine–laurepukine). This is not conclusive evidence for formula (XV), which Kitasato informs the author he now favours, and formula (XVI) must still receive consideration. A decision cannot, however, be made on these lines, as the absorption spectrum of a phenanthripyridine substituted in positions 6 and 7 is not available for comparison.

The second maxima of the ethers of laurepukine and pukateine (VIII) (Fig. 4) are slightly bathochromic, compared with those of the non-methylated natural substances. Apart from this small difference, the curves for pukateine and its ether are very similar; but those for laurepukine and its ether are different. This is

FIG. 4.



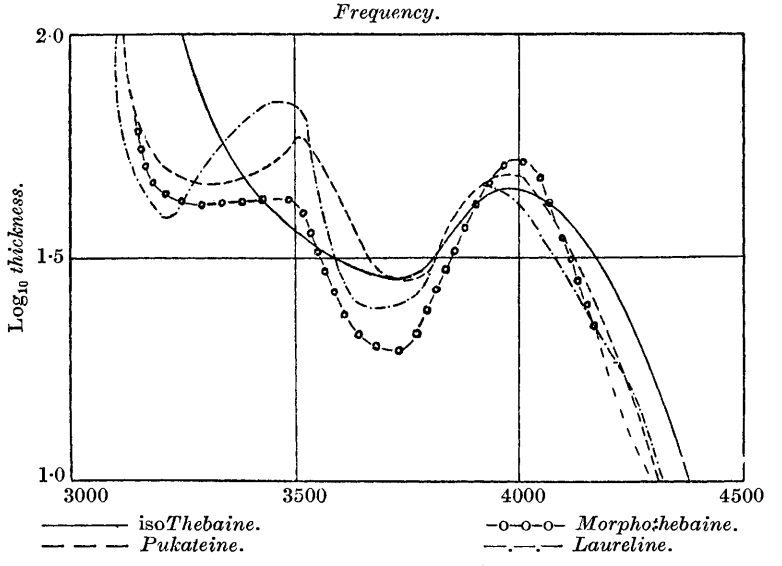
evidence in favour of the betaine structure for the phenolic compound (*Helv. Chim. Acta*, 1931, **14**, 481).

The comparison of these ethers shows the great similarity of the effects produced by substitution in position 4 only and in positions 3 and 4. It also appears that this type of substitution inhibits the hypsochromic effect inherent in the change from a methylenedioxy-group to two methoxyls.

Morphothebaine (VI) has its first curve displaced towards the visible end of the spectrum to the extent of 40 Å, compared with laurepukine dimethyl ether; its second curve is widened by 15 Å. both at its maximum and at its minimum (effect of substitution in position 6 compared with positions 5 and 6). Such substitution does not modify the second band of epiapomorphine.

Substitution in positions 3, 4, and 5 (*iso*thebaine; VII) (Fig. 5) produces the same second band (shallow) as substitution in positions 5 and 6 alone or in 3, 4, and 6, but prevents the formation of the first band; it strikes a mean between the absorption of aporphine and epiapomorphine. Substitution in positions 3, 5, and 6 (laureline; IX) instead of 3, 4, 5, and 6 narrows the second band minimum by 30 Å; the first minimum is very hypochromic. The first maximum and the second minimum of laureline practically coincide with those of glaucine, dicentrine and domesticine (compare Fig. 3), but its first band is wider and the second narrower. Laureline is therefore more nearly related to the compounds sub-

FIG. 5.



stituted in positions 3, 4, 5, and 6 than to those substituted in positions 2, 3, 5, and 6.

As regards the hyperchromic influence of substituents on the first band, two of them, either in positions 3 and 4 or in 5 and 6, produce the same small effect, but substitution in positions 3, 4, 5, and 6 increases it considerably; the effect is greater in the case of substitution in positions 3, 4, and 6 and still more so with substituents in positions 2, 3, 5, and 6.

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