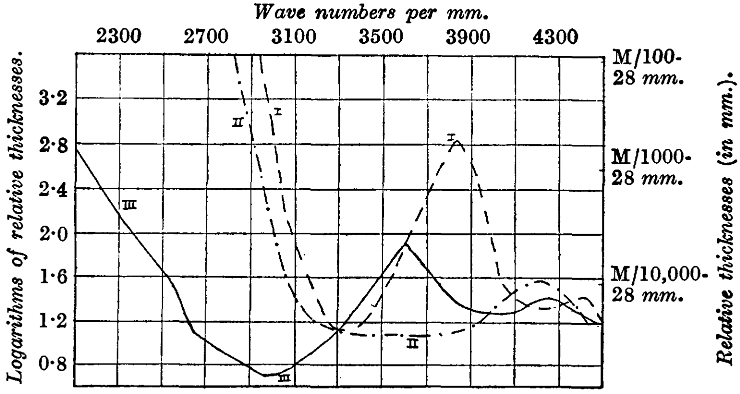
CCCLXI.—*The Absorption Spectra of Various Alkaloids and their Salicylates and of other Derivatives of Salicylic Acid.*

By John Edward Purvis.

In previous communications (J., 1925, **127**, 2771; 1926, 775; this vol., p. 780), the author has discussed the influence of the basic and acidic constituents of various salts on their absorption spectra. This communication is to describe the results of further investigations on the spectra of various alkaloids and their salicylates, and of other compounds derived from salicylic acid. The substances were dissolved in pure ethyl alcohol and a condensed cadmium spark was the source of radiant energy.

Fig. 1.



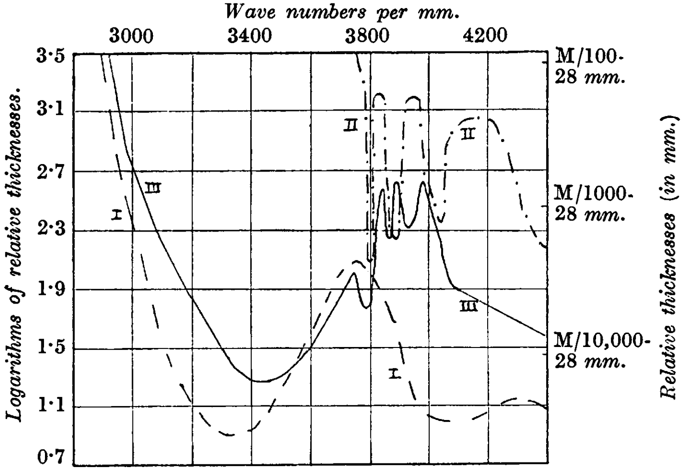
I. *Salicylamide* (— —). II. *Salicylanilide* (—·—).
III. *Benzene-5-azosalicylic acid* (——).

Salicylamide (Fig. 1, I) shows two bands. They are not unlike those of salicylic acid, but the more refrangible one is not quite so well marked as that of the acid. Hartley and Hedley (J., 1907, **91**, 319) found that the bands of benzamide and benzoic acid were comparable, except that the benzamide band was not so wide as that of the acid.

Salicylanilide has one large band (Fig. 1, II). Aniline itself has two large bands, namely, between 1/λ 3508 and 1/λ 3648 and between 1/λ 4165 and 1/λ 4309, as described by Hartley and Huntingdon (*Phil. Trans.*, 1879, **170**, 257) and by Baly and his colleagues (J., 1905, **87**, 1332; 1915, **107**, 1058). In salicylanilide, therefore, the two bands of aniline and the two bands of salicylic acid have been fused into one large band which covers the positions formerly occupied by the bands of aniline and salicylic acid. These results are comparable with those obtained with benzanilide, where the bands of benzene and of aniline are replaced by one large band (Crymble, Stewart, Wright, and Glendinning, J., 1911, **99**, 451).

Benzene-5-azosalicylic acid shows two bands (Fig. 1, III). The absorption of the less refrangible and very wide one extends into the coloured regions, the group $C_6H_5\cdot N\!:\!N\cdot$ probably accounting for the colour. The more refrangible band is weaker than the corresponding band of salicylic acid and almost disappears.

FIG. 2.



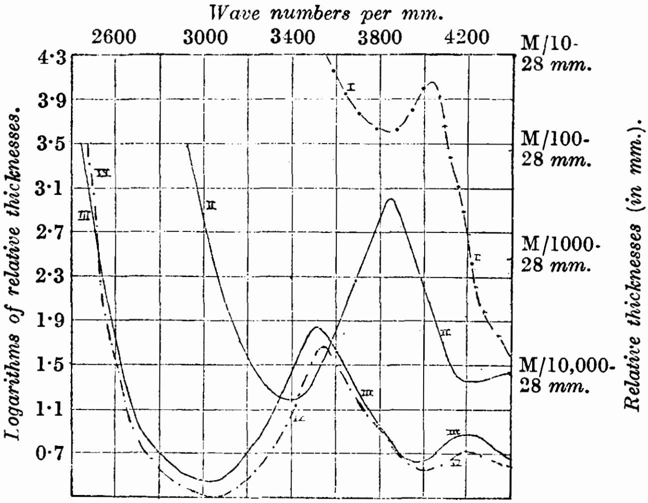
I. o-*Salicoyloxybenzoic acid* (— —). II. *Atropine* (— . —).
III. *Atropine salicylate* (——).

o-*Salicoyloxybenzoic acid* (Fig. 2, I) shows two bands not unlike those of salicylic acid in their general form, but shifted more towards the red end. It has been noticed (*loc. cit.*) that when the hydrogen of the hydroxyl group of salicylic acid is replaced by an acetyl group, as in *o*-acetoxybenzoic acid and other similar compounds, a striking change is produced and the absorption phenomena are not unlike those of benzoic acid. In *o*-salicoyloxybenzoic acid there is no such change, so that the presence of hydrogen of the hydroxyl group of $OH\cdot C_6H_4\cdot CO\cdot$ combined with the other group $-O\cdot C_6H_4\cdot CO_2H$ to produce the acid $OH\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H$ enables the compound to retain the characteristic absorption of salicylic acid itself.

Atropine and Atropine Salicylate.—Dobbie and Fox (J., 1913, **103**, 1193) describe two bands of atropine at about 1/λ 3770 and 1/λ 3880. Gompel and Henri (*Compt. rend.*, 1913, **156**, 1541) found a third, weaker, band at 1/λ 4020. The author has repeated these experiments and can confirm the presence of three bands (Fig. 2, II).

The curve of atropine salicylate (Fig. 2, III) exhibits a large band like that of salicylic acid, but not quite so strong. Besides that, there are three weak bands on the more refrangible side of this large band, and these are comparable with the three bands of atropine, but a little weaker. The more refrangible band of the acid is represented in the salt by a rapid extension of the rays between about 1/λ 4100 and 1/λ 4450. It is obvious, therefore, that the bands of both base and acid are still well marked in the salt, the chief differences being the weaker appearances of the bands of the latter. A sharper differentiation of the separate bands of the basic and acidic parts of the salt could only be made by an instrument of much greater dispersion. This remark applies to the following observations of other alkaloids and their salts.

FIG. 3.



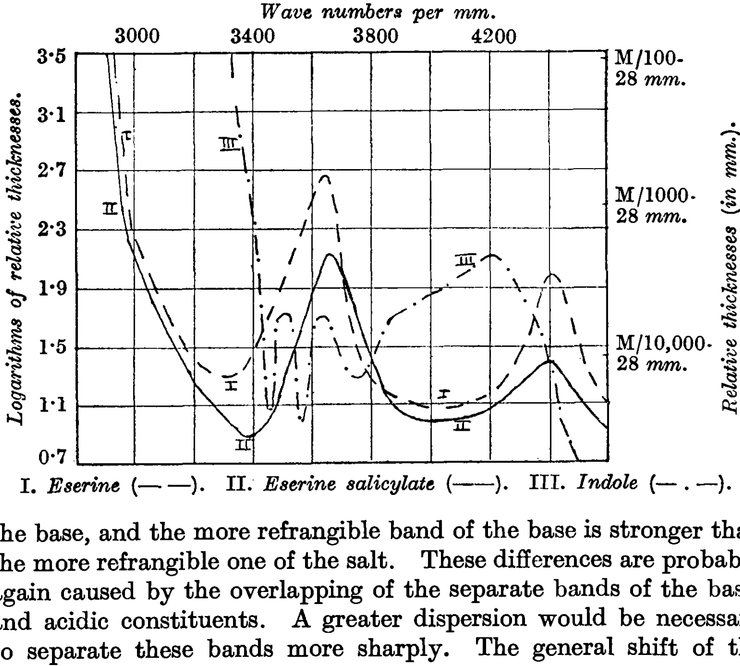
I. *Pilocarpine.* II. *Pilocarpine salicylate.* III. *Colchicine.*
IV. *Colchicine salicylate.*

Pilocarpine and Pilocarpine Salicylate.—In Jowett's investigation of pilocarpine (J., 1903, **83**, 438), Dobbie describes a weak band of pilocarpine nitrate at about 1/λ 3350. The author has repeated the observations with an alcoholic solution of the base itself and finds a weak band at about 1/λ 3800 (Fig. 3, I).

Pilocarpine salicylate shows two bands of salicylic acid (Fig. 3, II). As the thickness of the solution increases, the less refrangible band of the salt appears to be slightly wider than that of the acid; and this is probably caused by the latter impinging on the weak band of the base and covering it up; the absorptive power of the base only becomes visible as the thickness of the solution increases. A saturated solution of pilocarpine salicylate was also examined, but there was no appearance of a separate band of pilocarpine, showing that the bands of the acidic constituent covered up that of the basic part. The more refrangible band of the salt is not so well marked as that of the acid itself.

Colchicine and Colchicine Salicylate.—The curves show (Fig. 3, III and IV) that each substance has two bands. The less refrangible band of the salt is wider on the more refrangible side than that of the base, and the more refrangible band of the base is stronger than the more refrangible one of the salt. These differences are probably again caused by the overlapping of the separate bands of the basic and acidic constituents. A greater dispersion would be necessary to separate these bands more sharply. The general shift of the absorption towards the red end explains the slight yellow colour of both these substances.

FIG. 4.



I. *Eserine* (— —). II. *Eserine salicylate* (——). III. *Indole* (— . —).

Eserine (*Physostigmine*) *and Eserine Salicylate.*—The absorption curves (Fig. 4, I and II) show that each substance has two large bands, and, as in colchicine and its salicylate, the differences are the result of the bands of the acid and basic constituents partly overlapping each other. It was suggested by Stedman and Barger and experimentally confirmed by Späth and Brunner (*Ber.*, 1925, **58**, 518) that physostigmine is a substituted indoline. The author has investigated the absorption of indole and the curve is compared with that of eserine (Fig. 4, III). This exhibits several bands at 1/λ 3460, 1/λ 3560, and a weaker wider one at 1/λ 3750. There is also a rapid extension of the line of absorption to about 1/λ 4200, and this probably indicates other weaker bands. All the bands of indole disappear in eserine.

These results are to be compared with those described in the previous investigations (*loc. cit.*). In camphor salicylate, for example, the weak band of camphor at 1/λ 3480 would appear to be covered up by the less refrangible strong band of salicylic acid, which widens out with increased thickness of the solution, to 1/λ 3600. Camphor salicylate has again been studied in $M/10$-solutions, and these are stronger than those of the earlier observations, and through thicknesses of from 2 mm. to 28 mm. No camphor band appeared, whereas in camphor itself the band is perfectly clear in such strengths. Similar explanations account for the differences in theobromine and caffeine and their salicylates (*loc. cit.*). In the salicylates of phenazone and quinine (*loc. cit.*), the differences in the absorption are more clearly marked because the specific bands of the bases themselves are fairly strong, and they are not hidden by the bands of the acid nuclei.

The specific absorptive capacity of these compounds, therefore, appears to depend upon the more or less intimate chemical combination of the various centres, as well as upon their chemical type. Where the chemical combination is not so close, as in the salicylates of the alkaloids, both the basic and the acid nuclei largely retain their own specific absorption. On the other hand, where there is a closer chemical combination of the absorbing centres, as, for example, in salicylanilide or benzene-5-azosalicylic acid, the specific absorption of each centre is not so sharply defined. Each centre is influenced by the other centres to a much larger extent than in the salicylates of the alkaloids and other organic bases.

PUBLIC HEALTH CHEMICAL LABORATORY,
CAMBRIDGE.
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