CV.—*The Absorption Spectra of Various Derivatives of Salicylic Acid.*

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THE author described (J., 1925, **127**, 2771) the absorption spectra of various compounds derived from salicylic acid in order to compare the influence of different types of nuclei. The investigation has been continued with the following coloured and colourless salts and other compounds of the acid. The substances were examined in the first instance in $M/200$-solutions, with the exceptions of 3-nitrosalicylic acid and 5-aminosulphosalicylic acid, which were not so soluble. These were examined in $M/2000$- and $M/20,000$-solutions.

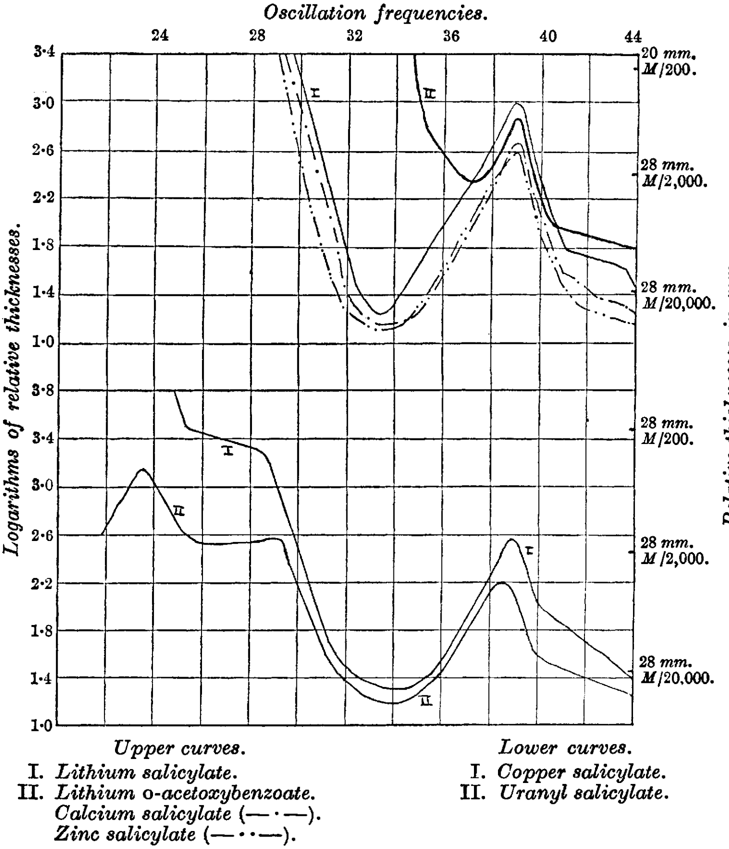
Lithium, calcium, and zinc salicylates. The curves (Fig. 1, upper curves) show in the lithium compound a band at $1/\lambda$ 3350 (λ 2984) comparable with that of salicylic acid (*loc. cit.*), but the more refrangible band between $1/\lambda$ 4120 (λ 2425) and $1/\lambda$ 4300 (λ 2320) is not so well marked as that in salicylic acid. In the calcium and zinc salts, somewhat similar phenomena were noticed; and there are differences in the positions of the bands dependent on the respective molecular weight. The less refrangible band of the monobasic lithium salt is not, of course, so strong as that of the calcium and zinc salts.

Lithium o-*acetoxybenzoate* (Fig. 1, upper curves). The replacement of the hydroxyl hydrogen atom by the acetyl group has produced a similar change to that in salicylic acid and *o*-acetoxybenzoic acid, and in theobromine salicylate and theobromine *o*-acetoxybenzoate (*loc. cit.*). The less refrangible band at $1/\lambda$ 3740 (λ 2672) is very weak and is shifted towards the more refrangible regions; and the more refrangible band is represented by a more rapid extension of the rays from about $1/\lambda$ 4020 (λ 2486). As the author has previously pointed out in the case of *o*-acetoxybenzoic acid, this has produced an absorption comparable with that of benzoic acid.

Copper salicylate (bluish-green). The curve (Fig. 1, lower curves) shows the less refrangible band of salicylic acid well developed, and the more refrangible one is nearly obliterated. There is a rapid absorption of the rays between about 1/λ 2850 (λ 3506) and 1/λ 2550 (λ 3919), extending well into the visible region.

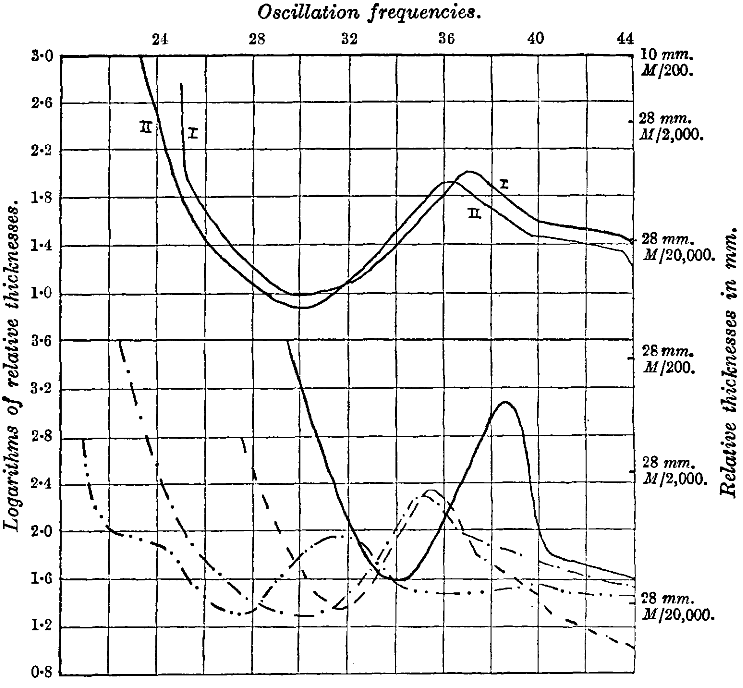
Uranyl salicylate (reddish-brown). The curve (Fig. 1, lower curves) has a somewhat similar form to that of copper salicylate, but the band between 1/λ 2940 (λ 3400) and 1/λ 2520 (λ 3967) is better marked, and there is another band on the less refrangible visible parts at about 1/λ 2200 (λ 4544). The band at 1/λ 3400 (λ 2940) is wider than the corresponding band of the copper salt.

Fig. 1.



3-*Nitrosalicylic acid* (yellow), 3 : 5-*dinitrosalicylic acid* (yellow). In each of these substances there is a large band extending into the visible region (Fig. 2, upper curves), and it is much wider than the corresponding bands of the substances described above. The more refrangible band is merely indicated by the more rapid extension of the rays from 1/λ 4000 (λ 2498) to 1/λ 4400 (λ 2271) in the nitro-compound, and from 1/λ 3920 (λ 2550) to 1/λ 4350 (λ 2298) in the dinitro-compound. These results are not unlike those described by the author (J., 1915, **107**, 966) in the case of some nitro-compounds of benzoic and cinnamic acids.

FIG. 2.



Upper curves.
I. 3-*Nitrosalicylic acid.*
II. 3 : 5-*Dinitrosalicylic acid.*

Lower curves.
5-*Sulphosalicylic acid* (——).
5-*Aminosulphosalicylic acid* (— —).
5-*Nitrosulphosalicylic acid* (— · — · —).
Sodium salt of 3-*nitro*-5-*aminosalicylic acid* (— · · —).

5-*Sulphosalicylic acid*, 5-*aminosulphosalicylic acid.* These two substances show (Fig. 2, lower curves) that the more refrangible band of salicylic acid is not so definite, but in each case the less refrangible one is well marked. In the amino-compound this band is not quite so strong as it is in the sulpho-compound, and there are differences in the persistency.

5-*Nitrosulphosalicylic acid* (yellow). There is a wide band

(Fig. 2, lower curves) at 1/λ 3000 (λ 3344) not unlike that of the other nitro-compounds, and extending into the visible region. The more refrangible one almost disappears.

Sodium 3-nitro-5-aminosalicylate (reddish-brown). This substance (Fig. 2, lower curves) exhibits a large band at 1/λ 2750 (λ 3633) which extends rapidly into the visible regions. This band may be compared with that of the other nitro-compounds. There is also a shallow band from about 1/λ 3400 (λ 2939) to 1/λ 3930 (λ 2543).

Hexamethylenetetramine, Hexamethylenetetramine salicylate. Through 56 mm. thickness of a *M*/200-solution hexamethylenetetramine exhibited no band; and the rays were transmitted to λ 2150. Its salicylate, on the other hand, exhibited an absorption band comparable with that of salicylic acid. Paraldehyde shows no specific absorption (J., 1925, **127**, 9); and it is suggested that, like paraldehyde, the condensation of formaldehyde with ammonia in the production of hexamethylenetetramine neutralises the free valencies of the aldehydic oxygen which produce a band in formaldehyde itself.

Results.—Considering these results with those of salicylic acid and its various salts (*loc. cit.*), it appears that the specific absorption of the substances depends on the nature of the basic and of the acid radicals. Changes in the nature of the one or the other produce changes in the position and intensity of the bands characteristic of each. The author has already shown, in a study of the absorption spectra of some organic and inorganic salts of didymium (*Proc. Camb. Phil. Soc.*, 1923, **21**, 781), that the bands of didymium in the visible regions were modified in intensity according to the type of the negative radical united with this base.

As regards the other derivatives of salicylic acid, the influence of the nitro-group in the benzene radical powerfully intensifies and shifts the less refrangible band of the acid, but appears to lessen that of the more refrangible one. Also the replacement of the hydrogen atom of the hydroxyl group by a radical, as in lithium salicylate and lithium *o*-acetoxybenzoate, changes the absorption capacity of the other parts of the molecule; and this is comparable with the phenomena of *o*-acetoxybenzoic acid, and of the *o*-acetoxybenzoates of theobromine and quinine.

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