CXIII. THE ABSORPTION SPECTRA OF KYNURENIC ACID AND SOME RELATED QUINOLINE COMPOUNDS.

By FRED WILBERT WARD.

From the Biochemical Laboratory, Cambridge.

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THE absorption spectra of the following compounds were measured in the course of an investigation into the intermediary metabolism of indolepropionic acid [Ward, 1923, 2]. The injection of indolepropionic acid into the animal organism produces a body in the urine which is very unstable towards heat and is very difficult to isolate. It is the precursor of a bright cherry red pigment. The formation of kynurenic acid from tryptophan [Ellinger, 1904] and indolepyruvic acid [Ellinger and Matsuoka, 1920] suggested the possibility that a similar body might be formed from indolepropionic acid. The plan was to measure the absorption of the precursor of the pigment separated as completely as possible from other compounds found in the urine and to compare this absorption spectrum with the absorption spectra of known quinoline derivatives.

EXPERIMENTAL.

The apparatus and method employed were the same as that described by the present writer in a paper on the absorption spectra of some indole compounds [1923, 1].

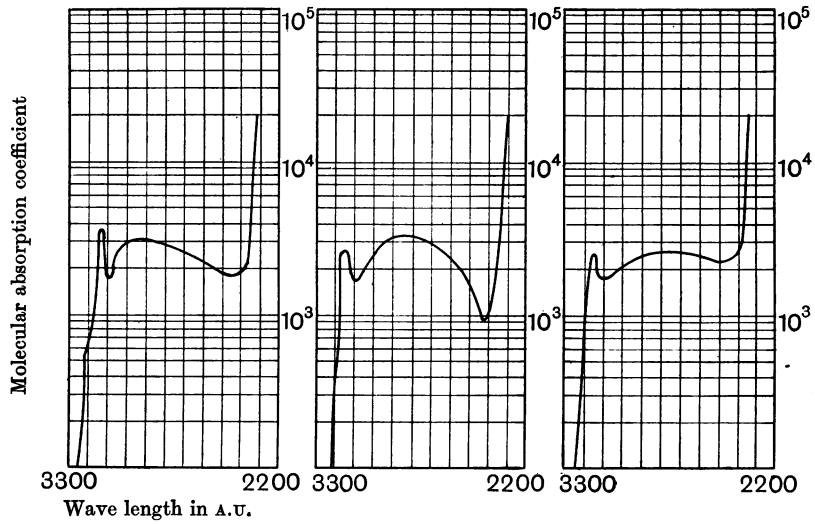
Seven different compounds of the quinoline series were investigated. These were as follows: quinoline, quinaldine, lepidine, quinaldinic acid, quinolylacetaldehyde, 2:6-dimethylquinoline and kynurenic acid.

The quinoline and quinaldine were purchased from British Drug Houses. The lepidine, quinaldinic acid, quinolylacetaldehyde and 2:6-dimethylquinoline were obtained from various sources in very small quantities of about two-tenths of a gram.

The kynurenic acid was prepared by feeding 20 g. of tryptophan to a dog at the rate of 4 g. per day. The kynurenic acid was first isolated in a crude state by acidifying the urine with hydrochloric acid and allowing to stand overnight. After filtering off the precipitated crude kynurenic acid and washing with water, it was dissolved in dilute ammonia and reprecipitated with dilute hydrochloric acid. By repeating this several times some of the urinary pigments were removed. It was then boiled up with 95 % alcohol and allowed to

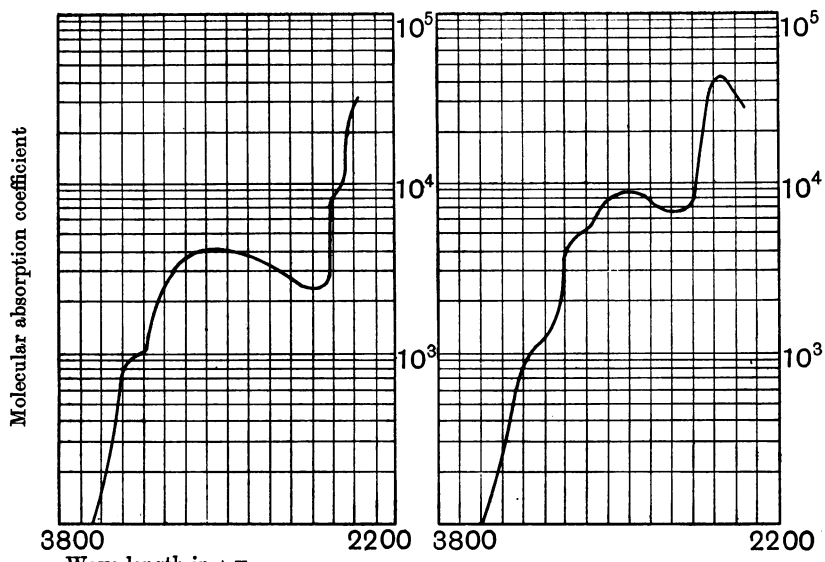
cool and then filtered. This removed some more of the pigment. It was finally recrystallised several times from 40 % acetic acid [Homer, 1914]. The final traces of pigment were removed by boiling in 40 % acid solution with animal charcoal before a final recrystallisation. This gave a white crystalline product.

The results are given in Figs. 1–3.



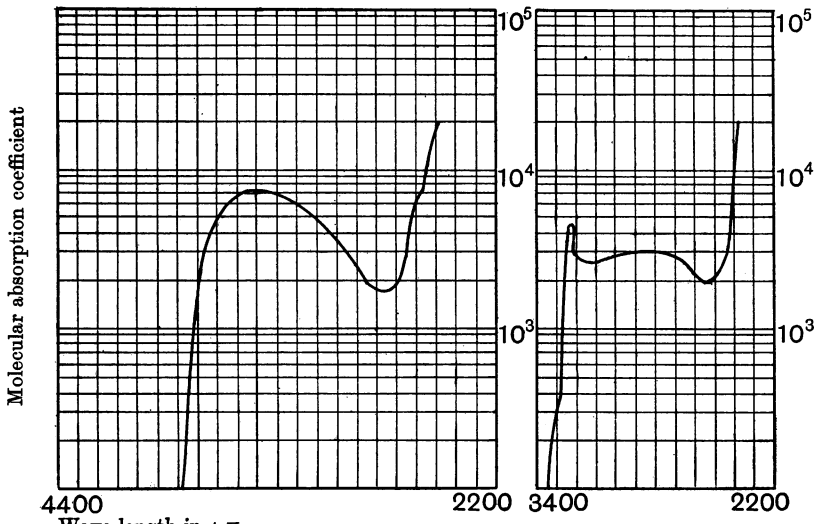
(*a*) Quinoline. (*b*) Lepidine. (*c*) Quinaldine.

Fig. 1.



(*a*) Quinaldinic acid. (*b*) Quinolylacetaldehyde (so-called).

Fig. 2.



(*a*) Kynurenic acid. (*b*) 2:6-Dimethylquinoline.

Fig. 3

Discussion.

From the absorption spectra of the three compounds quinoline, lepidine and quinaldine may be observed the difference of effect in the absorption spectra produced in one case by substituting in the α-position and in the other case in the γ-position. Substitution in the α-position produces a shift towards the red end of the spectrum without any increase in the intensity of the absorption. Substitution in the γ-position produces an increase in intensity of the absorption without producing any shift of the absorption band towards the red end of the spectrum.

Quinaldinic acid is quinoline substituted in the α-position by a carboxyl group. This brings about a well-marked change in the absorption as compared with quinaldine. There is a shift towards the red end of the spectrum of about 400 A.U. and there is also an increase in intensity.

Quinolylacetaldehyde is the name under which the compound whose absorption spectrum is given in Fig. 2 *b* is described in the literature [Einhorn, 1885, 1886; Carlier and Einhorn, 1890; Einhorn and Sherman, 1895]. It gives the correct elementary analysis for this constitution but it does not behave in its reactions as such a compound. It gives a hydrazone with great difficulty and in very poor yield. The absorption spectrum is not such as would be expected of such a compound.

2:6-Dimethylquinoline is a compound with a methyl group substituted in both rings. It retains a strong resemblance to quinaldine and quinoline. The effect of the double substitution is to increase the intensity of the absorption and to shift the absorption band towards the red end of the spectrum.

In kynurenic acid there is substitution in the α-position by a carboxyl group and in the γ-position by a hydroxyl group [Homer, 1913]. The presence of the carboxyl group in the α-position brings about a shift towards the red end of the spectrum with an increase in intensity. The presence of the hydroxyl in the γ-position brings about an increase in intensity. The effect of the two substitutions is to give a big shift towards the red end of the spectrum and greatly to intensify the absorption.

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