

## DIOSPYRIN: A NEW NARROW RANGE ACID-BASE INDICATOR

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Acid-base titrations can be carried out to a high degree of accuracy by the use of a suitable indicator. The precision of a titration is dependent on the pH range through which the colour change of the indicator takes place. There are a number of available indicators which can be used over the greater part of the pH scale, but most of these have the disadvantage of having a colour change over a wide pH range (1-3 pH units) [1]. The use of such indicators introduces a source of error when titrating weak acids and bases. Mixed and screened indicators which can be used to obtain sharper colour changes over a narrow pH range are less convenient to prepare [1]. Therefore, an indicator with a readily observable colour change over a narrow pH range would reduce the error in titrations where weak acids and bases are involved. In search for such an acid-base indicator diospyrin (2,6-bis-7-methyljuglone) has now been examined. It occurs naturally in some plants of family Ebanaceae. It was isolated from the dry roots bark of *Euclea natalensis* [2].

Diospyrin is an orange red crystalline solid, m.p. 258°. It gave a wine red colour with ferric chloride and pink colour with magnesium acetate. It was found to exhibit antibacterial activity against a number of gram-positive organisms [2]. The structure of diospyrin was confirmed by comparison (TLC., m.p., m.m.p., IR and NMR) with an authentic sample. Diospyrin gave a light yellow colour in acidic solution and a deep violet colour in basic medium. The obvious difference between the colours of the naphthoquinone and its anion made it worthwhile to examine its utility as a new narrow range acid-base indicator. The change in colour in the basic medium can be attributed to the following resonating structures (II  $\leftrightarrow$  III).

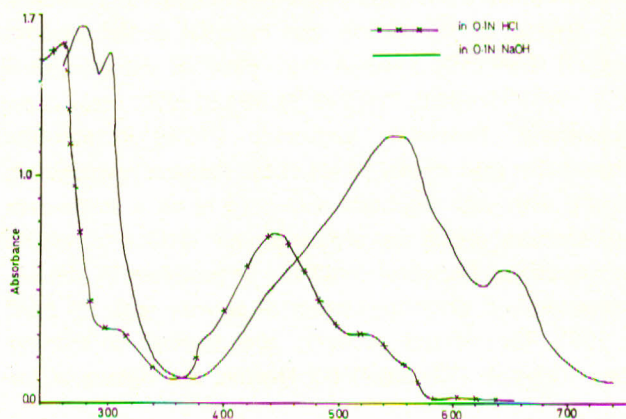
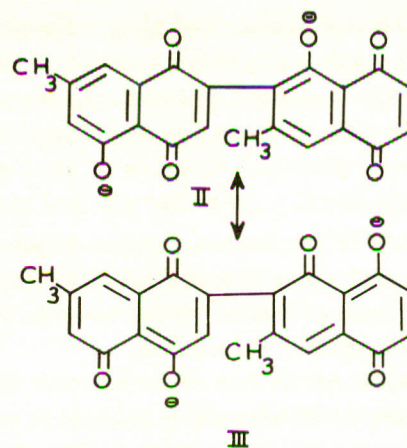
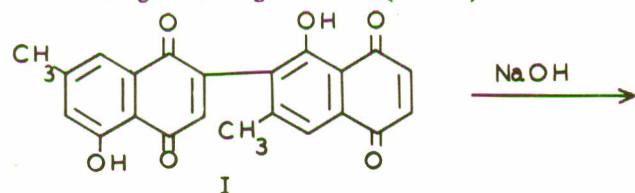


Fig. 1. Absorption spectra of the acid base forms of diospyrin

The presence of the phenolic hydroxyl groups seems to be essential for the indicator properties of diospyrin, as when these were replaced by methoxy on methylation with diazomethane, the product so obtained gave yellow solution, the colour of which was independent of the pH of the solution.

The pH transition interval was determined by adding 0.5 ml of the 0.05% stock solution of the indicator in methanol to 25 ml of a series of buffers ranging from pH 8.0 to 9.6 in increments of pH 0.2, in test tubes of equal colour and diameter. The transition interval was found to be between pH 8.4 - 9.2. The colour was assessed by looking through the solution against a white background. On going from lower to higher pH the first violet colour appeared at pH 8.4 and cease to change at pH 9.2. While in reverse direction the decrease in the intensity of colour was noticed at pH 9.2 reaching its minimum at 8.4. The pH transition interval was further checked with Metrohm Herisou E520 pH meter and electrode.

The absorption spectra (Fig. 1) of the acid and the base forms of the indicator were recorded on a Pye Unicam SP 1800 spectrophotometer, using a dilute solution (0.029 g/l) of the indicator in 0.1M HCl and NaOH, the wavelength of the maximum absorptions ( $\lambda_{\text{max}}$ ) and the molar extinction

coefficients ( $\epsilon$ ) were 438 ( $\epsilon$  9801) and 560 nm ( $\epsilon$  15217) respectively. The increase in the absorption at 560 nm is responsible for the indicator colour change in basic medium.

Detailed experiments using potentiometric titrations of strong and weak acids with strong bases gave characteristic titration curves. The indicator changing its colour from light yellow to violet at pH 8.4 and above. The addition of alternate drops of 0.1M HCl and NaOH solutions to one ml of the indicator solution showed that the colour change was reversible and that the colour was permanent at all pH levels for a long time. One part of the indicator was detectable in  $2 \times 10^5$  parts of water. The transition interval was unaffected by the presence of high concentration

of salt (10% w/v). In the stock solution no decomposition was observed after four months when checked on TLC.

In conclusion diospyrin may be used as a visual indicator in titrations of strong or weak acids with strong bases and vice-versa.

#### REFERENCES

1. E. Bishop, *Indicators* (Pergamon, Oxford, 1972), first edition, p. 65.
2. M.R. Khan, S.L. Mutasa, G. Ndaalio and H. Wevers, *Pakistan J. Sci. Ind. Res.*, **21**, 197 (1978).