

Syntheses of 2-, 3- and 4-(1, 8-Dihydroxy-3, 6-disulfo-2-naphthylazo)-mandelic Acids as New Reagents, and the Thorium Complex of the 2-Isomer*

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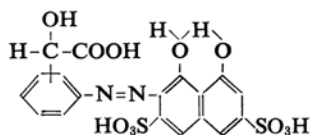
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In a series of phenylazochromotropic acid derivatives, the one with the $-\text{AsO}_3\text{H}_2$ or $-\text{OCH}_2\text{COOH}$ ¹⁾ group is an especially sensitive reagent for thorium ion.

The present paper will describe the preparation of those reagents which have the $-\text{CH}(\text{OH})\text{COOH}$ group in the ortho-, meta- or para-position to the azo group, and the determination of the acid dissociation constants of the reagents and of the constitution of the thorium complex formed with the 2-isomer.

The Syntheses of the Reagents.—The reagents, 2-, 3- and 4-(1, 8-dihydroxy-3, 6-disulfo-2-naphthylazo)mandelic acids, were obtained from the

corresponding diazotized amino mandelic acids which were coupled with chromotropic acid respectively; the structures of the reagents were as follows:



The Determination of the Acid Dissociation Constants of the Reagents.—The acid dissociation constants of the reagents have been estimated spectrophotometrically; their values are shown in Table I.

The $\text{p}K_{a3}$ value corresponds to the dissociation of the hydrogen ion from the carboxyl group of mandelic acid in the reagents, while

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1) K. Tôei, H. Miyata, T. Shibata and S. Miyamura, This Bulletin, 38, 334 (1965).

TABLE I. pK_{a3} AND pK_{a4} OF THE REAGENTS
AT 7–9°C

	pK_{a3}	pK_{a4}
2-Isomer	3.1	9.7
3-Isomer	3.4	9.7
4-Isomer	3.9	9.2

pK_{a4} corresponds to one of the hydroxy groups of chromotropic acid.

Spectral Properties of the Thorium Complex.

—Figure 1 shows the absorption spectra of the 2-isomer solution (2.5×10^{-5} mol./l.) and its thorium complex.

Figure 2 shows the determination of the mole ratio of thorium to the reagent by the

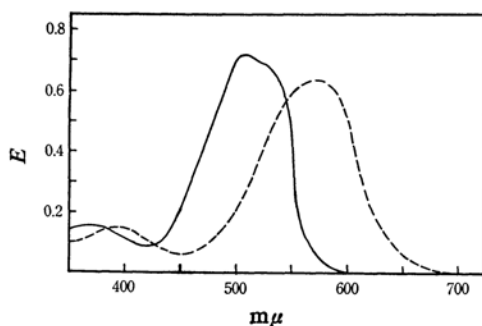


Fig. 1. Absorption spectra of the reagent and its thorium complex (broken line) at pH 2.9.
— 2.5×10^{-5} mol./l.
---- Thorium concn. to the reagent concn. = 5:1

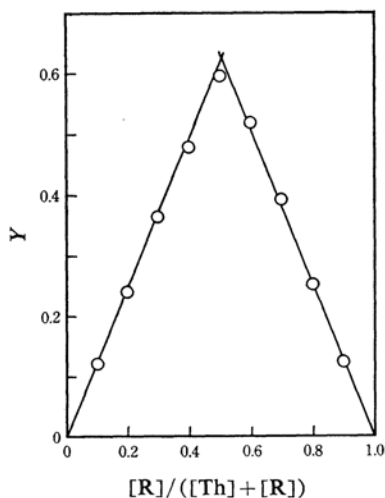


Fig. 2. Continuous variation method.
Thorium concn. + the reagent concn.
= 5.0×10^{-5} mol./l.
pH 3.1, 590 $m\mu$

continuous variation method. The result indicates the formation of a 1:1 complex.

A more detailed study of the properties of the reagents and of the thorium complexes will be reported later.

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