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THE CHEMISTRY OF HYDROXY-NAPHTHAQUINONES AND THE STRUCTURE AND SYNTHESIS OF SOME RELATED NATURAL COLOURING MATTERS.

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CONTENTS.

SECTION I.

SECTION II.

SECTION III.

SECTION IV. page.

SECTION V.

SECTION VI.

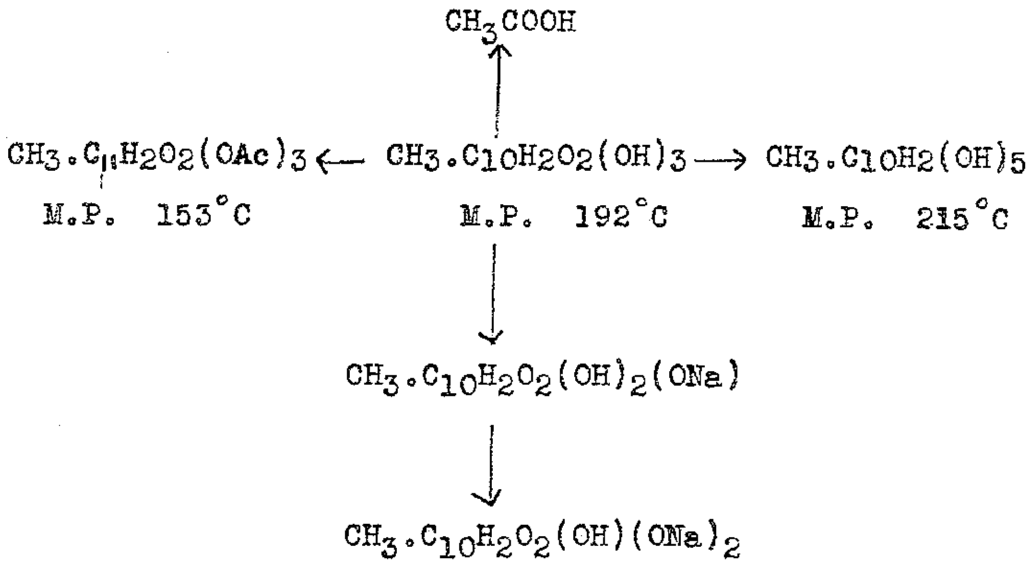
The investigation of the colouring matters occurring in the insectivorous plant Drosera Whittakeri, was first undertaken by the late Dr. E.H.Rennie, Angas Professor of Chemistry in the University of Adelaide. He published two papers on the subject - J.C.S. 1887, 51, 371, and 1893, 63, 1083, - and showed that two closely related compounds were present, but the work was never completed. The object of the present investigation was to deduce the constitution of these substances by comparing their properties and reactions with those of hydroxy quinones of known constitution; and finally to establish the structures by synthetic methods.

The plant, which is fairly widely distributed in the Mount Lofty Ranges, appears soon after the first winter rains but quickly disappears on the approach of the hot dry summer. In appearance the plant consists of a flat rosette of sticky hairy green leaves, from the centre of which, in spring, arise numerous white flowers borne on short stems. At the base of the single long root lies a round bulb about one centimetre in diameter and surrounded by several layers of black husk with flakes of colouring matter between them. The bulb itself is a soft white body filled with a reddish sap, which apparently contains very little of the dye-stuff.

Rennie's work may be summarized as follows. The bulbs were crushed, dried, and repeatedly treated with boiling alcohol until the extract was only pale red in colour. The greater part of the solvent was then distilled off and the colouring matter, together with a fat-like substance, precipitated by the addition of water. Several sublimations of the material so obtained were often necessary before the constituents could be separated by fractional crystallization from either alcohol or glacial acetic acid. The later stages of the process were greatly facilitated by acetylation of the substances as the difference in the solubilities of the acetates is more marked. When the acetates had been separated as far as possible by crystallization, a further separation was effected by fractional precipitation with water. After saponification of the acetyl derivative with caustic soda, the free colouring matter was thrown down by the addition of hydrochloric acid, and recrystallized from some suitable solvent.

EXAMINATION OF THE LESS SOLUBLE COMPOUND.

This substance crystallized from alcohol or glacial acetic acid as red plates which melted at 192 -193 °C. Combustion figures and molecular weight determinations indicated a formula $C_{11}H_8O_5$, which corresponded with that for a trihydroxy-methyl-naphthaquinone. This idea was supported by the following facts. On oxidation with chromic acid it gave almost the theoretical yield of acetic acid, indicating the presence of a methyl group attached directly to carbon. It formed a triacetate when heated with acetic anhydride and a fragment of anhydrous zinc chloride, and on reduction with alcoholic stannous chloride it gave a rather unstable yellow substance, whose combustion figures agreed with those for the corresponding hydroquinone. By boiling with a solution of sodium carbonate only a mono-sodium salt was obtained but by adding the theoretical amount of sodium hydroxide to a solution of this salt, the di-sodium derivative was formed.



$$\begin{tikzcd}
 & CH_3COOH & \\
\begin{array}{c}CH_3.C_{11}H_2O_2(OAc)_3\\ M.P.\ 153^\circ C\end{array} & \begin{array}{c}CH_3.C_{10}H_2O_2(OH)_3\\ M.P.\ 192^\circ C\end{array} \arrow[l] \arrow[r] \arrow[u] \arrow[d] & \begin{array}{c}CH_3.C_{10}H_2(OH)_5\\ M.P.\ 215^\circ C\end{array} \\
 & CH_3.C_{10}H_2O_2(OH)_2(ONa) \arrow[d] & \\
 & CH_3.C_{10}H_2O_2(OH)(ONa)_2 &
\end{tikzcd}$$

Hereafter the less soluble substance $C_{11}H_8O_5$, is referred to as the O_5 compound.