AN ATTEMPTED SYNTHESIS OF INDOLE-2-PROPIONIC ACID

and

THE OXIDATION OF m-XYLYL BROMIDE TO m-TOLUIC ACID

A Thesis submitted

by

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C O N T E N T S

P R E F A C E

During recent years there has been a great deal of interest taken in the action of indole derivatives as plant hormones. Since, however, no intensive investigation has been made of derivatives substituted in the 2-position, the synthesis of indole-2-β-propionic acid, with which part I of this thesis deals, was undertaken with the view to having the compound tested for its possible action as a phytohormone.

Unfortunately, after some time, it was found that, due to the poor yields obtained in several of the preparations, supplies of the necessary chemicals would be sufficient for only one run. In view of the probably indefinite results to be obtained, work was begun on a second problem.

Part II of this presentation is an account of attempts to prepare m-toluic acid by the oxidation of m-xylyl bromide.

With the exception of photochemical oxidation, all previous attempts to prepare this acid by the oxidation of m-xylene have been unsuccessful, since both methyl groups attached to the benzene nucleus are attacked by oxidizing agents, resulting in the formation of isophthalic acid. However, from a con-

sideration of similar cases, it is conceivable, theoretically at least, that were a halogen such as bromine, substituted for hydrogen in one of the methyl groups in m-xylene, this group should be attacked by oxidizing agents in preference to the unsubstituted one. Thus by choice of the proper reagent and temperature conditions, it might be possible to obtain m-toluic acid. Since it involves the use of relatively inexpensive chemicals, this method, if successful, might well be of some commercial value in the manufacture of what is now a rather expensive compound.

PART I

I N T R O D U C T I O N

(a) A Survey of Indole Derivatives as Plant Hormones

Attempts to explain the various growth phenomena of plants (correlations, tropisms, bud-inhibition, etc.) have culminated in the isolation, within the last decade, of definite chemical substances, known as auxins or growth substances, which have been shown to be the cause of the afore-mentioned responses. In addition to these naturally-occuring substances, many synthetic compounds (including various indole derivatives) have also been found to be effective as phytohormones. Since the synthesis of the acid named in the title of this thesis was undertaken with the view to having its growth-promoting activity tested, a brief review of the subject of plant hormones will be given, with particular reference to derivatives of indole. A more detailed treatment, especially from the botanical point of view will be found in excellent books written by P. Boysen Jensen,[1] and by F. W. Went and K. V. Thimann[2] and also in review papers by these same authors.[3,4]

Since the early evidence for the existence and role of auxins came through the study of tropisms, it might be of interest, before continuing with a review

of the subject, to note the application of auxins to these phenomena.

It is a well-known fact that plants, when unilaterally illuminated, will grow towards the light. Many elaborate theories were evolved to account for this but the first simple one was proposed by Blaauw, whose experiments led him to state in 1918[5] that "whenever light causes a growth reaction, unequal distribution of the light will cause unequal growth, which we call phototropism" and hence that tropisms were simply a phenomenon of differential growth. The later work of Boysen Jensen and Paal further advanced this theory, giving rise to two possible explanations; first, that phototropism might be due to increased transmission of growth-promoting substance on the dark side of the plant, or second, that it might arise from decreased transmission of growth-promoting substance on the light side. That both of these occur simultaneously was finally shown by Cholodny in 1927[6] and Went in 1928.[7] From the experiments of both of these investigators was evolved the so-called Cholodny-Went theory which is now generally accepted. It may be stated as follows: "Growth curvatures whether induced by internal or by external factors, are due to an unequal distribution of auxin between the two sides of the curving organ."[2] (p.157)