SYNTHESES OF THE ENANTIOPURE QUINONES A AND A′ AND THEIR C-1 EPIMERS.

THIS THESIS IS PRESENTED FOR THE DEGREE OF
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BY

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I declare that this thesis is my own account of my research and contains as its main content work which has not previously been submitted for a degree at any tertiary educational institution.

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ABSTRACT

The 3,4-dihydro-1H-naphtho[2,3-*c*]pyran ring system is found in many natural products as the 5,10- or 6,9-quinones. These compounds have been synthesized by various research groups as a result of their wide range of biological activities. This thesis describes several investigations directed towards syntheses of compounds in this general area. Quinone A **(16)** and quinone A′ **(17)**, derived from the naturally occurring aphid insect pigments protoaphin-*fb* and protoaphin-*sl* respectively, were of particular interest.

The first chapter describes the previous syntheses of some naphtho[*c*]pyrans including those relating to the aphid pigment derivatives, followed by the isolation and identification of the aphid pigments. Also described was the ability of these naphthopyranquinones to act as potential bioreductive alkylating or dealkylating agents. The latter part of the chapter deals with the syntheses of the racemates of the aphid pigment derivatives quinones A and A′ and deoxyquinone as well as model studies toward the non-quinonoid cleavage product, glucoside B. The chapter concludes with the progress made towards the first asymmetric synthesis of these compounds.

Chapter 2 reports the establishment of conditions which led to *ortho* or *para* regioselectivity in the intramolecular cyclisation of tethered lactaldehydes to form benzo[*c*]pyrans. This regioselectivity depended on whether either benzyl or *t*-butyldimethylsilyl was used as protecting group. This chapter also described a model for the control of stereochemistry leading to quinone A′.

Chapter 3 describes the syntheses of naphthalenes as potential precursors to the naphthopyranquinones derived from the aphid insect pigments. This followed after problems were encountered in previous work with inappropriate protection in the oxidation of halogenated benzopyrans.

Chapter 4 develops the first successful syntheses of enantiopure quinone A and quinone A′ with the correct absolute stereochemistry. This involved the regioselective addition of 1,3-bis(trimethylsilyloxy)-1-methoxybuta-1,3-diene to

selectively halogenated benzopyranquinones. The latter were obtained through complementary series of highly diastereoselective transformations based on 2,5-dihydroxyacetophenone as starting material and (*R*)-lactate from the chiral pool as the source of asymmetry.

TABLES

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