

***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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TABLE OF CONTENTS

	Page
ABSTRACT	
TABLES	
ACKNOWLEDGMENTS	
CHAPTER 1 Introduction.	
1.0 General Introduction.	1
1.1 Isolation and Syntheses of Selected Naphtho[2,3- <i>c</i>]pyrans Related to the Aphid Pigment Derivatives.	5
1.2 Isolation and Structure Determination of the Aphid Pigments.	40
1.3 Naphthopyranquinones as Potential Bioreductive Alkylating or Dialkylating Agents.	47
1.4 Racemic Syntheses of Quinone A, Quinone A' and Deoxyquinone A. Synthetic Efforts Toward Glucoside B.	53
1.5 Progress Toward the Asymmetric Syntheses of Benzo[<i>c</i>]pyrans Related to Aphid Pigments.	62
1.6 Concluding Remarks.	69
CHAPTER 2 <i>Ortho vs. Para</i> Regioselectivity in the Cyclisation of Tethered Lactaldehydes to Form Benzo[<i>c</i>]pyrans.	
2.0 Introduction.	71
2.1 The Sequence Using Benzyl Protection of the Phenol.	72
2.2 The Sequence Using <i>t</i> -Butyldimethylsilyl Protection of the Phenol.	98
2.3 Concluding Remarks.	111
2.4 Experimental.	114

**CHAPTER 3 Naphthalenes as Potential Precursors to the
Naphthopyranquinones Derived From the Aphid
Insect Pigments.**

3.0	Introduction.	135
3.1	The Trimethoxynaphthol Sequence.	136
3.2	The Dibenzylloxy Methoxynaphthol Sequence.	150
3.3	Concluding Remarks.	152
3.4	Experimental.	154

**CHAPTER 4 The Syntheses of Enantiopure Quinone A and
Quinone A'.**

4.0	Introduction.	166
4.1	Choice of Appropriate Protecting Groups for the Hydroquinonoid Oxygens of the Starting Material 2,5- Dihydroxyacetophenone (322).	168
4.2	Syntheses of the Two Diastereomeric Phenolic Aldehydes (347) and (348).	173
4.3	The Synthesis of Quinone A (16) from the Phenolic Aldehyde (347).	181
4.4	The Syntheses of the C-1 Epimers (358) and (359) from Phenolic Aldehyde (348).	190
4.5	The Synthesis of Quinone A' (17) from Diol (318).	200
4.6	Concluding Remarks.	204
4.7	Future Work.	205
4.8	Experimental.	206

REFERENCES	228
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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

	Page
Table 1: Optical Rotations of the Alcohols (225) , (230) , (226) and (231)	82
Table 2: Optical Rotations of the Alcohols (256) , (258) , (257) and (259)	103
Table 3: Comparison of Chemical Shifts of Compound (240) and Compound (256a)	107
Table 4: Optical Rotations of the Alcohols (339) , (341) , (340) and (342)	177
Table 5: Comparison of Chemical Shifts for Synthesized Quinone A (16) in Methanol-d ₄ and Acetone-d ₆ with Those of the Naturally Derived Enantiomer in Dimethyl Sulfoxide-d ₆	189
Table 6: Comparison of Chemical Shifts of Naturally Derived (360) in Dimethyl Sulfoxides-d ₆ and the Synthesized Enantiomer (358) in Methanol-d ₄ and Acetone-d ₆	196
Table 7: Comparison of Chemical Shifts of Naturally Derived (361) in Dimethyl Sulfoxides-d ₆ and the Synthesized Enantiomer (359) in Methanol-d ₄ and Acetone-d ₆	199
Table 8: Comparison of Chemical Shifts for Synthesized Quinone A' (17) in Methanol-d ₄ and Acetone-d ₆ with those of the Naturally Derived Material in Dimethyl Sulfoxide-d ₆	203

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