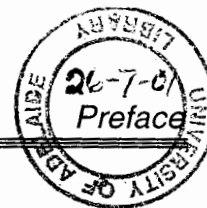


K415



thesis titled:

**“Investigations into the Synthesis of Dendralene
Precursors and Epicatechins.”**

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by

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Abstract

Two heterocyclic chemistry projects were investigated to establish whether new methods for the synthesis of substituted dendralene precursors and green tea catechins were viable.

The synthesis of a number of unique, substituted dendralene precursors was achieved in excellent yield using Stille coupling reactions with palladium catalysis between two different substituted vinyl triflates. Some of these precursors were oxidised using either OXONE or OXONE derivatives, to give sulfolene molecules or 'masked dendralenes' in high yields. The extrusion of sulfur dioxide from these unique substituted molecules using many different techniques proved to be extremely difficult compared to simple non-substituted sulfolenes. It was concluded that the combination of the two particular substituents acted to increase the stability of the sulfolene.

The second project investigated potentially new syntheses of the four main green tea catechins. Readily available, natural (+)-catechin (**1**) was transformed into epicatechin (**32**) and epicatechin gallate (**33**) derivatives by oxidation of the alcohol group at position-3 to the corresponding ketone. Of the many oxidising reagents investigated the Dess-Martin periodinane reagent provided the best yield of 38%. Reduction of the ketone using sodium borohydride and incorporating the use of stereoselective additives such as CeCl_3 afforded the epicatechin derivative (**32**). Esterification of the alcohol at position-3 of the epicatechin derivative (**32**) with 3,4,5-trimethoxybenzoic acid and DCC gave the epicatechin gallate derivative (**33**). Direct synthesis using allylation and acylation reactions were employed in an attempt to synthesise the other required catechin derivatives, epigallocatechin (**3**) and epigallocatechin gallate (**5**). Instead of providing the epicatechin molecules, the allylation reactions afforded a diallylated phloroglucinol species (**70**). The acylation

reaction of 1,3,5-trimethoxybenzene and a mixed anhydride formed from trifluoroacetic anhydride and a propiolic acid derivative furnished the novel chalcones such as (95) in one step, *via* acylation then Michael addition of 1,3,5-trimethoxybenzene to the β -position of the triple bond. The acylation reaction between 1,3,5-tribenzyloxybenzene and a substituted propioloxy chloride catalysed by a Lewis acid gave the aurone (104) in good yield when the Lewis acid was ferric chloride. A number of substituted acetylenic ketones and/or the corresponding hydrogen chloride adducts, were obtained in good yield when the Lewis acid was zinc chloride. The acetylenic ketones and the adducts had one of the benzyl group adjacent to the acyl substituent removed *in situ* for which a mechanism is proposed, leaving these products perfectly set up for cyclisation. The cyclisation reactions of both the alkyne and hydrogen chloride-adducts using a broad range of reagents and conditions, gave aurones in excellent yields. In no case was the desired flavone observed indicating that the cyclisation of these species was not as simple as has been suggested in the literature.