

## ABSTRACT

Thesis Title : Reactions of 20-Hydroxyecdysone with Acids and Bases

Student's Name : Miss Penpan Ganpinyo

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Advisory Committee :

1. Assoc. Prof. Dr. Apichart Suksamrarn Chairperson
2. Assoc. Prof. Dr. Mayuree Chuankamnerdkarn

Treatment of 20-hydroxyecdysone (**1**) with 0.2 N hydrochloric acid yielded stachysterone B (**34**), a minor naturally occurring ecdysteroid, and a number of unstable products. On the other hand, upon treatment of 20-hydroxyecdysone 2,3,22-triacetate (**35**) with 0.05 N hydrochloric acid selective deacetylation took place to give 20-hydroxyecdysone 2,22-diacetate (**36**), 20-hydroxyecdysone 3,22-diacetate (**37**), 20-hydroxyecdysone 2-acetate (**38**) and 20-hydroxyecdysone 22-acetate (**39**). Calonysterone (**40**), a rare and unusually modified ecdysteroid, and 9,20-dihydroxyecdysone (**41**) were synthesized by reaction of **1** with oxygen in the presence of 0.5 N sodium hydroxide. This base catalyzed autoxidation reaction was also applied to the synthesis of calonysterone 20,22-acetonide (**44**) and 9-hydroxystachysterone B 20,22-acetonide (**45**) from 20-hydroxyecdysone 20,22-acetonide (**43**). Reactions of **1** with formic acid and potassium carbonate gave similar

results but the reactions proceeded much slower than those of hydrochloric acid and sodium hydroxide.

Stachysterone B (34) was found to be less active than 20-hydroxyecdysone (1) in the *Musca* bioassay for moulting hormone activity, indicating that the 14 $\alpha$ -hydroxyl group was important for high biological activity in this assay. The compound 39 was as active as compound 1, suggesting that the hydroxyl group at the 2-position was not essential for high moulting hormone activity in this assay. However, a *ca* 8:1 mixture of compound 36 and 37 exhibited lower activity than that of 1 probably because the hydroxyl group at the 22-position (and partly the 3-position) was acetylated. The complete loss of activity in calonysterone (40) resulted from lack of the 6-keto-7-ene system, a *cis*-fused A/B ring junction and probably a 14 $\alpha$ -hydroxyl group. The extra hydroxyl group at the 9-position in case of compound 41 brought about a complete loss, or almost complete loss, of moulting hormone activity in the *Musca* bioassay.