ABSTRACT

Thesis Title : Ring A Modification of 20-Hydroxyecdysone

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Reaction of 20-hydroxyecdysone 20,22-acetonide (**49**) with triphenylphosphine-diethyl azodicarboxylate in the presence of formic acid yielded 2-dehydro-3-deoxy-20-hydroxyecdysone 20,22-acetonide (**50**) as the major product and a mixture of 20-hydroxyecdysone 2-formate 20,22-acetonide (**51**) and 20-hydroxyecdysone 3-formate 20,22-acetonide (**52**) as the minor products. The acetonide protecting group in **50** was removed by treatment with 70% acetic acid to give 2-dehydro-3-deoxy-20-hydroxyecdysone (**53**). Reduction of the 2-dehydro product **50** with sodium borohydride afforded 2-epi-3-deoxy-20-hydroxyecdysone 20,22-acetonide (**54**) and 3-deoxy-20-hydroxyecdysone 20,22-acetonide (**55**) in a ratio of 3:1. These two compounds were separately treated with 70% acetic acid to yield 2-epi-3-deoxy-20-hydroxyecdysone (**56**) and 3-deoxy-20-hydroxyecdysone (**57**). The moulting hormone activity of the compound **53**

in *Musca* bioassay was moderately active, as compared with that of 20-hydroxyecdysone (**3**). The corresponding alcohol **57** was more active than **53**. However its C-2 epimer, the compound **56**, was much less active than **57**.

Oxidation of 20-hydroxyecdysone 2-acetate 20,22-acetonide (**12**) with chromium trioxide-pyridine gave 3-dehydro-20-hydroxyecdysone 2-acetate 20,22-acetonide (**13**) and 20-hydroxyecdysone 2-acetate 3α,9α-epoxide 20,22-acetonide (**60**), the latter of which was supposed to derive from the former by allylic oxidation at the 9-position followed by intramolecular hemiketal formation. After column chromatography of the crude products consisted of **13** and **60**, the compound 2-dehydro-3-epi-20-hydroxyecdysone 3-acetate 20,22-acetonide (**53**) was additionally obtained, presumably by enolization followed by C-2 to C-3 acetyl migration and C-3 epimerization. Acetonide deprotection of **60** followed by deacetylation yielded 20-hydroxyecdysone 3α,9α-epoxide (**62**). Reduction of **13** with sodium borohydride gave 3-epi-20-hydroxyecdysone 2-acetate 20,22-acetonide (**63**), an inseparable mixture of 20-hydroxyecdysone 2-acetate 20,22-acetonide (**12**) and 20-hydroxyecdysone 3-acetate 20,22-acetonide (**64**), together with a small quantity of 3-epi-20-hydroxyecdysone 20,22-acetonide (**65**). Compound **64** derived from C-2 to C-3 acetyl migration of **12** and compound **65** was supposed to be the deacetylation product of **63** occurring in silica column. Sodium borohydride reduction of **59** furnished 2,3-epi-20-hydroxyecdysone 3-acetate 20,22-acetonide (**66**) and its isomer

2,3-epi-20-hydroxyecdysone 2-acetate 20,22-acetonide (**67**). Compound **67** was supposed to derive from **66** by C-3 to C-2 acetyl migration. Acetylation of **66** and **67** gave the same diacetate, 2,3-epi-20-hydroxyecdysone 2,3-diacetate 20,22-acetonide (**68**). When **66** and **67** were separately subjected to deacetylation with guanidine hydrochloride-potassium hydrogen carbonate the same product, 2,3-epi-20-hydroxyecdysone 20,22-acetonide (**69**), was resulted. With potassium carbonate as the base, both compounds **66** and **67** were converted to 2,3,5-epi-20-hydroxyecdysone 20,22-acetonide (**70**), which was then epimerized at C-5 to compound **70**. Compound **62** was inactive in the *Musca* bioassay. The result was in agreement with of 9,20-dihydroxyecdysone (**72**) and it was thus concluded that a substituent at C-9 position brought about to complete loss of moulting hormone activity in this bioassay.