

ABSTRACT

The Δ^7 tirucallenes comprise a group of triterpenes which has been proposed as the biogenetic precursors of the tetranortriterpenes or limonoids. These proposals have been substantiated, by the synthesis of limonoids from these triterpenes in experiments which parallel the biogenetic proposals, and by the isolation of key intermediates in the proposed biogenesis, the apotirucallenes, as natural products. These biogenetic proposals are discussed in Part I of this thesis which also contains a review of the triterpenes isolated from Meliaceae and Rutaceae.

One phenomenon especially attractive in the light of the above proposals, is the co-occurrence of the Δ^7 tirucallenes, apotirucallenes and limonoids in, not only the same plant families (the botanically related Meliaceae and Rutaceae mentioned above), but also in the same plants. Entandrophragma cylindricum is such a plant which contains Δ^7 tirucallenes, apotirucallenes and limonoids. The isolation of six triterpenes, sapelins A, B, C, D, E, and F, and three limonoids designated A, B, and C, is described in Part II.

Part III describes the structural elucidation of the six triterpenes isolated, and constitute the

the major portion of this thesis. Sapelins A, B, and F are shown to be derivatives of Δ^7 tirucallol and sapelins C, D, and E-derivatives of 7 α -hydroxy-apotirucall-14-ene. The isolation of sapelins C, D, and E augment the small number of 7 α -hydroxy-apotirucall-14-enes isolated as natural products.

In Part IV is described the structural studies on the limonoids of E. cylindricum. The major compound, limonoid A, has been found to be identical with utilin. The structure of utilin, recently established by X-ray, satisfactorily explains the chemistry of limonoid A.

The surprising dehydrogenation of the Δ^7 tirucallene nucleus to the 7,9(11) diene by periodic acid led to a brief study of the scope and mechanism of this reaction. This is described in Part V.