One-step Synthesis of the Diterpenoid Leucothol D from Grayanotoxin-II

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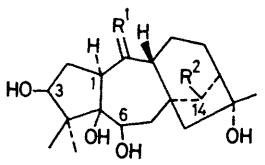
Summary Treatment of grayanotoxin-II (**1b**) with palladium acetate in methanol at room temperature gave leucothol D (**2**).

A NUMBER of toxic diterpenoids have been isolated from *Leucothoe grayana* Max. and classified into three structural groups: grayanotoxins (**1**),[1] leucothols (**2**),[2] and grayanols (**3**),[3] but they have not yet been chemically inter-related. Kakisawa and his co-workers[4] reported that the five–seven membered A–B ring system of grayanotoxin-I (**1a**), changes into a six–six membered ring system on treatment with toluene-*p*-sulphonyl chloride in pyridine. In this case,



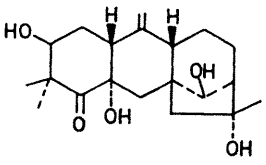
(1)

a; Grayanotoxin-I

$R^1 = \overset{OH}{\underset{Me}{\diagup\!\!\diagdown}}$, $R^2 = OAc$

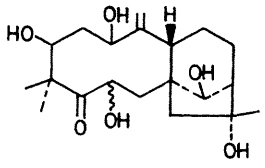
b; Grayanotoxin-II

$R^1 = CH_2$, $R^2 = OH$

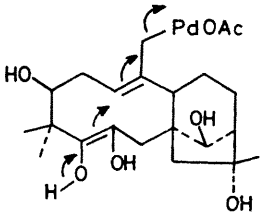


(2)

Leucothol D



(3)



(4)

however, the C-1 proton has an α orientation. We recently became interested in the reaction of grayanotoxins with organometallic compounds. Treatment of grayanotoxin-II (**1b**) with palladium acetate in methanol at room temperature gave a product, $C_{20}H_{30}O_5$, m.p. 272—274 °C. The ^{13}C n.m.r. spectrum indicated the presence of the following groups; three methyls, five methylenes, three methines, two quaternary carbons, two secondary carbinyl carbons, two tertiary carbinyl carbons, a vinylidene, and a ketone. Other spectral data (^1H n.m.r. and c.d.) were very similar to those reported for leucothol D.[2b] Comparison showed that the product was identical with an authentic specimen isolated from the plant. Hence we have achieved a one-step synthesis of leucothol D from grayanotoxin-II.

We regard the palladium compound (**4**) as a likely intermediate in the observed conversion of grayanotoxin-II into leucothol D.

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