Synthesis of the Diterpenoid Grayanol B from Grayanotoxin II

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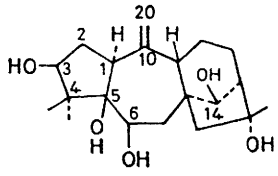
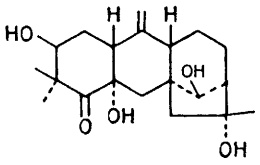
Summary Treatment of grayanotoxin II (**1**) with thallium(III) acetate in acetic acid at room temperature, followed by alkaline hydrolysis, yields grayanol B (**3b**).

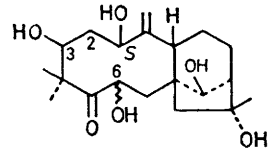
Leucothoe grayana, a well known poisonous shrub of Japan, contains three structural groups of diterpenoids: grayanotoxins (**1**), leucothols (**2**), and grayanols (**3**).[1] In the course of our study to correlate them chemically, we reported a one-step synthesis of leucothol D (**2**) from grayanotoxin II (**1**) by using palladium acetate.[1] We now describe a facile conversion of (**1**) into grayanol B (**3b**) by means of thallium(III) acetate.



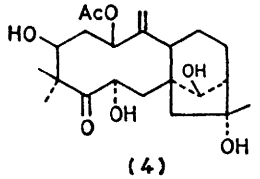
(1)
grayanotoxin II



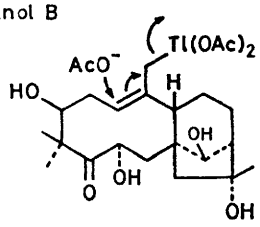
(2)
leucothol D



(3)a; 6(*S*) grayanol A
b; 6(*R*) grayanol B



(4)



(5)

Treatment of (**1**) with thallium(III) acetate in acetic acid at room temperature for two days gave a product (**4**), whose ^{1}H n.m.r. spectrum showed the presence of one secondary acetoxy-group. Its ^{13}C n.m.r. spectrum was very similar to those reported for grayanol A (**3a**) and grayanol B (**3b**) (Table).[2] Mild alkaline hydrolysis of (**4**) yielded a crystalline product, $C_{20}H_{32}O_6$, m.p. 203—204 °C, which was identical (by m.m.p., i.r. spectroscopy, and t.l.c.) with an authentic specimen of grayanol B isolated from the plant. Thus, we have been able to achieve simply the chemical conversions of grayanotoxin II (**1**) into leucothol D (**2**) and grayanol B (**3b**).

TABLE. ^{13}C N.m.r. data in C_5D_5N (δ/p.p.m.).

	(**3a**)	(**3b**)	(**4**)[a]
$-CH_3$	16·4	16·2	15·9
	24·0	23·5	23·6
	25·9	25·6	25·6
$-CH_2-$	26·6	25·6	25·9
	27·2	27·9	27·2
	35·4	38·4	35·8
	45·3	45·5	45·1
	57·8	53·5	57·7
>CH–	51·7	50·7	51·0
	53·9	53·5	53·4
>C<	53·3	53·9	53·2
	54·3	58·0	54·5
>CHOH	67·9	67·4	67·5
and	70·7	69·8	69·5
>CHOAc	79·2	73·1	74·2
	85·7	78·9	78·9
≥COH	80·4	79·9	79·9
$>C=CH_2$	115·2	111·6	113·8
	150·9	157·1	151·9
>C=O	215·6	207·7	215·2

[a] $-COCH_3$ 21·1 and 170·1 p.p.m.

A likely intermediate of this reaction is regarded as the thallium compound (**5**).

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[1] T. Kaiya, N. Shirai, and J. Sakakibara, *J. Chem. Soc., Chem. Commun.*, 1979, 431.
[2] S. Fushiya, H. Hikino, and T. Takemoto, *Tetrahedron Lett.*, 1974, 183.