

## Conversion of a Simple Meliacin (7 $\alpha$ -Acetoxymeliaca-14,20,22-trien-3-one) into Azadirone and of Khayanthone into Khivorin

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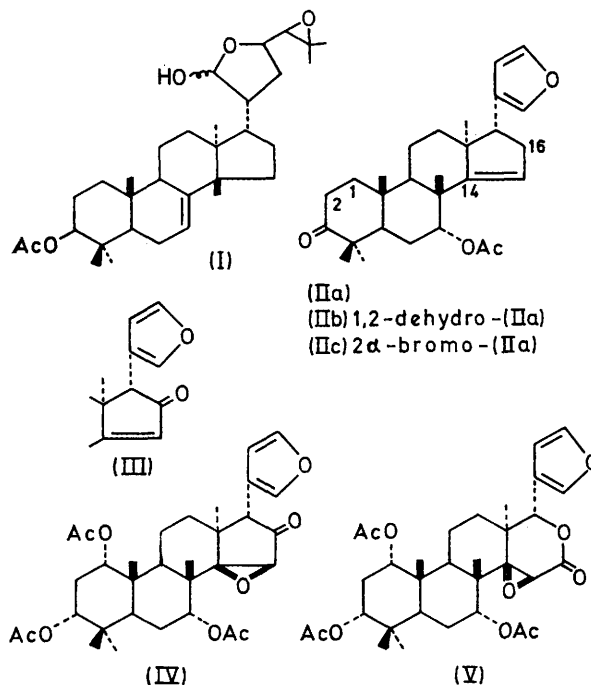
**Summary** The simple meliacin (IIa) (7 $\alpha$ -acetoxymeliaca-14,20,22-trien-3-one) has been converted into azadirone (IIb) by treatment with copper(II) bromide followed by dehydrobromination; khayanthone (IV) has been converted into khivorin (V) by oxidation with alkaline hydrogen peroxide followed by re-acetylation.

hydroxide solution was treated with hydrogen peroxide (20% of 30%) and stirred for 5 days at 40°. Re-acetylation of the resulting product yielded khivorin (V), m.p. and mixed m.p., 257–259°,  $[\alpha]_D -42^\circ$ , in 40% yield. None of the isomeric 15,16-*seco*-compound was detected.

RECENTLY<sup>1</sup> we have described the partial synthesis from turraeanthin (I) of the simple meliacin (IIa). This has now been converted into a naturally-occurring compound. Treatment of (IIa) with copper(II) bromide in tetrahydrofuran solution and dehydrobromination of the resulting bromo-ketone (IIc) with 1,5-diazabicyclo[4,3,0]non-5-ene gave in 71% overall yield azadirone (IIb),  $[\alpha]_D +24^\circ$  (lit. value<sup>2</sup>  $+26^\circ$ ) with the expected i.r., n.m.r., and mass spectral properties.

One of the characteristic features of many of the more highly oxygenated meliacins and limonoids is the ring-D  $\alpha\beta$ -epoxy- $\delta$ -lactone system exemplified by limonin,<sup>3</sup> gedunin,<sup>4</sup> and khivorin (V).<sup>5</sup> It has been suggested<sup>3</sup> that this arises biogenetically by the further oxidation of the D-ring in structures such as (IIa) and (IIb) which have been suggested as intermediates in the earlier stages of the biosynthetic pathway. Three oxidative steps are needed, allylic oxidation at C-16 [cf. (IIa) to (III)], epoxidation of the  $\Delta^{14}$ -double bond, and Baeyer-Villiger lactone formation from the 16-keto derivatives [cf. (IV) to (V)]. So far the only one of these carried out chemically has been the oxidation<sup>2</sup> of azadirone (IIb) by selenium dioxide to give the corresponding 16-ketone, azadiradione (III). This step, together with the above result represents a formal synthesis of azadiradione (III) from turraeanthin (I). A further step in the elaboration of the more highly oxygenated structures has now been accomplished: the formation of the epoxy-lactone system with the conversion of khayanthone (IV)<sup>6</sup> into khivorin (V).

Khayanthone (IV) in *t*-butyl alcohol and 7% 4N-sodium



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