Synthesis of the Alkaloid, Oxogambirtannine

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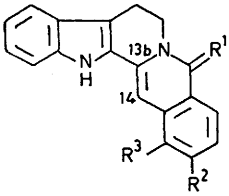
Summary The indole alkaloid oxogambirtannine (I) was synthesised *via* photo-induced rearrangement of spiro-[5′-methoxyindan-1′-one-1,2′-(1,2,3,4-tetrahydro-β-carboline)].

In an extension of photo-induced rearrangements[1] of α-aminoketones in the synthesis of indole alkaloids, we have synthesised oxogambirtannine (I),[2] which was isolated from *Uncaria gambier* Roxb. (*Rubiacea*).

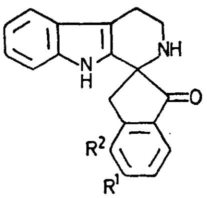
We first investigated the 1-spiro-β-carboline (II) prepared in 90% yield from tryptamine hydrochloride and the dione (III)† which was derived from 5-methoxyindan-1-one in the usual manner (α-hydroxyimination followed by acid hydrolysis). Irradiation of (II) with a high-pressure mercury lamp in benzene for 1·5 h at room temperature gave the lactam (IV) (20%) and the salt (V) (50%). Without further purification the latter was reduced with $NaBH_4$ in water to give the benz[*g*]indoloquinolizine (VI) which was identical with an authentic sample.

On this basis, we attempted the synthesis of the spiro-β-carboline (VII). Treatment of the indanone (VIII)[3] with Pb_3O_4 in AcOH–Ac_2O yielded the acetoxy-indanone (IX) (90%) which hydrolysed rapidly in refluxing MeOH–30% H_2SO_4 to give the hydroxy-ketone (X) (70%). Oxidation of (X) with Jones' reagent in acetone gave the indanedione (XI) (35%). Treatment of (XI) with tryptamine hydrochloride in EtOH gave the spiro-β-carboline (VII) (80%), m.p. 246—248 (decomp.); ν_{max} (KBr) 3325, 1710, and 1693 cm^{-1}; $\delta(CDCl_3)$ 2·84 (1H, d, *J* 6 Hz), 3·82 (1H, d, *J* 6 Hz), and 3·88 (s, OMe); M^+ 346. Irradiation of (VII) as mentioned above furnished oxogambirtannine (I) (10%), which was identical spectroscopically with the natural product. In contrast to the case of (II), the salt (XII) could not be isolated, possibly owing to its photo-sensitivity.

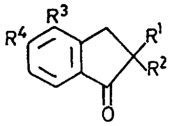
We thank Professors M. Hesse, and L. Merlini for a sample of oxogambirtannine, and Professor Kametani for a sample of (VI).



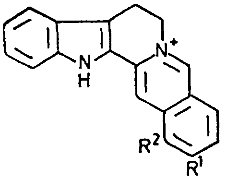
(I) R^1 = O; R^2 = H; R^3 = CO_2Me
(IV) R^1 = O; R^2 = OMe; R^3 = H
(VI) R^1 = H_2; R^2 = OMe; R^3 = H, 13b, 14-dihydro



(II) R^1 = OMe; R^2 = H
(VII) R^1 = H; R^2 = CO_2Me



(III) R^1, R^2 = O; R^3 = H; R^4 = OMe
(VIII) R^1 = R^2 = R^4 = H; R^3 = CO_2Me
(IX) R^1 = R^4 = H; R^2 = OAc, R^3 = CO_2Me
(X) R^1 = R^4 = H R^2 = OH; R^3 = CO_2Me
(XI) R^1, R^2 = O; R^3 = CO_2Me; R^4 = H



(V) R^1 = OMe; R^2 = H
(XII) R^1 = H; R^2 = CO_2Me

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† Satisfactory elemental analyses, i.r., and mass spectral data were obtained for all compounds cited.

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[3] Y. Tomita, *J. Chem. Soc. Japan*, 1961, **82**, 505.