C-20 Configuration in Adirubine

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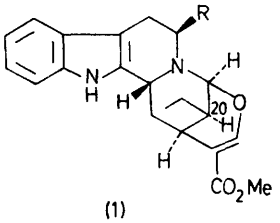
Summary Adirubine has been shown to be a member of the *allo* (3α, 15α, 20α) series (**3**) by a correlation with 5α,20α-methoxycarbonyldihydromancunine (**1b**).

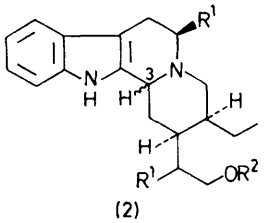
IN previous communications[1,2] we reported the isolation and structure elucidation of the novel carboxy indole alkaloid, adirubine. The absolute stereochemical relationship between H-3, H-5, and H-15 was shown to be all *cis* and α from

c.d., i.r., and n.m.r. spectra and base equilibration studies, but that at C-20 and C-16 was unknown. On equilibration in acetic acid at reflux, adirubine triacetate was largely epimerised to the 3β isomer as shown by the change in sign of Cotton effect in the c.d. spectrum. This behaviour was reminiscent of an allo–epiallo rather than a normal–pseudo relationship and strongly suggested that H-20 had an α orientation as in (**2b**,**c**).



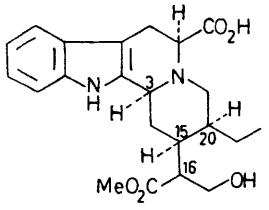
(1)

	R
a;	H
b;	CO_2Me



(2)

	H-3	R^1	R^2
a;	β	CO_2Me	H
b;	β	CH_2OAc	Ac
c;	α	CH_2OAc	Ac



(3)

Recently dihydromancunine was shown by a correlation with corynantheidine to be essentially the 20α epimer (**1a**), with only a trace of the 20β isomer detectable by n.m.r. spectra at equilibrium.[3] 5α-Methoxycarbonyldihydromancunine[2] prepared from methyl-L-tryptophanate and dihydrosecologanin in an analogous manner was also predominantly the 20α isomer (**1b**) as shown by the n.m.r. spectrum. It thus seemed feasible to establish the configuration at C-20 in adirubine by a correlation with this compound.

Reduction of (**1b**) with $NaBH_4$ in MeOH to a mixture of methoxycarbonyl dihydrositsirikine isomers, separation of the major products (**2a**), and $LiAlH_4$ reduction gave, after acetylation, a triacetate (**2b**) $[\alpha]_D^{25}$ −25° (MeOH). This proved identical with the above inversion product of adirubine triacetate. Furthermore equilibration in acetic acid at reflux afforded a trace of material corresponding to adirubine triacetate itself, which must therefore have the structure (**2c**). Hence adirubine must have 20α stereochemistry as in (**3**).†

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† Professor E. E. van Tamelen has arrived at the same conclusion after a synthesis of methyl adirubine.

[1] R. T. Brown, C. L. Chapple, and G. K. Lee, *J.C.S. Chem. Comm.*, 1972, 1007; R. T. Brown and A. A. Charalambides, *Phytochemistry*, 1975, 2527.

[2] R. T. Brown and C. L. Chapple, *J.C.S. Chem. Comm.*, 1973, 886.

[3] R. T. Brown, C. L. Chapple, R. Platt, and S. K. Sleigh, *Tetrahedron Letters*, in the press; R. T. Brown, C. L. Chapple, and A. A. Charalambides, *J.C.S. Chem. Comm.*, 1974, 756.