The Stereochemistry of Melianone and Sapelin F: Correlation with Bourjotinolone A

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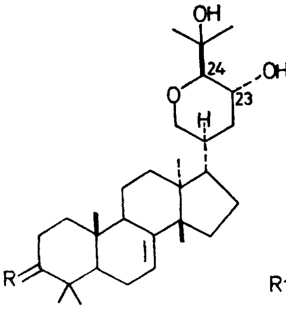
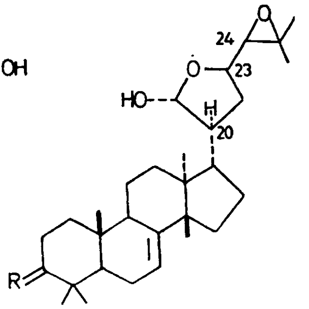
Summary Thermolysis of the epoxytriol (**9**) from melianone (**4**) gave 3-episapelin A (**2**), thus defining the stereochemistry of melianone (**4**) as 23-*R*,24-*S*; sapelin F (**16**) is shown also to have 23-*R*,24-*S* stereochemistry by correlation with melianone *via* 3-epimeliantriol (**13**).

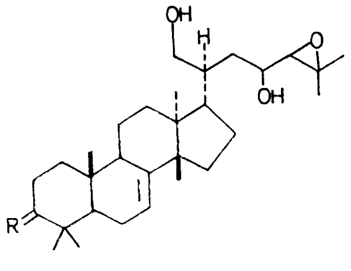
Two of the modifications of the side chain of the protolimonoids[1] (highly oxygenated triterpenes related to tirucallol) are shown in bourjotinolone A (**1**)[2] and melianone (**4**).[3] Both (**1**) and (**4**) are, in principle, derivable from the epoxydiol (**8**), bourjotinolone A presumably being formed with inversion at C(24). However, while bourjotinolone A has been shown[2] to have 23-*R*,24-*R* stereochemistry and is hence derivable from an epoxydiol (**8**) which is 23-*R*,24-*S*, melianone (**4**) has been assigned the 23-*S*,24-*R*[‡] configuration. On the assumption that (**1**) and (**4**) were derived from the same epoxydiol (**8**), and hence that the stereochemistry assigned to melianone (**4**) was wrong, we have sought a correlation between bourjotinolone A (**1**) and melianone (**4**).



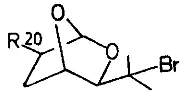
(1); R = O
(2); R = H, β-OH
(3); R = H, α-OH



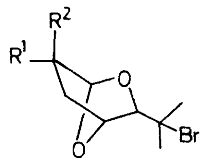
(4); R = O
(5); R = H, β-OAc
(6); R = H, α-OH
(7); R = H, α-OAc



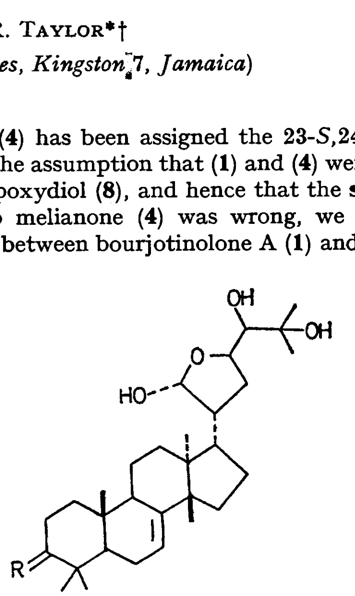
(8), R = O
(9), R = H, β-OH



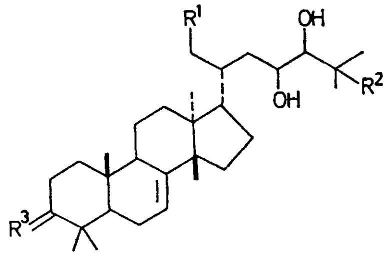
(10); R = $C_{22}H_{33}O$



(11); R^1 = H; R^2 = $C_{22}H_{33}O$
(12); R^1 = $C_{22}H_{33}O$; R^2 = H



(13); R = H, α-OH
(14); R = H α-OAc
(15); R = O



(16); R^1 = R^2 = OH; R^3 = H, α-OH
(17); R^1 = H; R^2 = Cl; R^3 = O

Thermolysis at 195° in the absence of solvent of the epoxytriol (**9**),[3] obtained by sodium borohydride reduction of melianone (**4**), gave (**2**),[§] the 3-epimer of sapelin A (**3**),[4] as the only isolable product (25% yield). (**2**) was made by sodium borohydride reduction of bourjotinolone A (**1**). This result demonstrates that melianone (**4**) is, in fact, 23-*R*,24-*S*, since the thermolysis must have involved inversion at C(24). Bevan *et al.*[5] had correctly assigned the 23-*R* configuration to turraeanthin (**5**), shown[3] to differ from melianone (**4**) only at C(3), on the basis of the molecular rotation difference of the corresponding γ-lactone and its salt, but had made no assignment at C(24).

The assignment[3] of the 23-*S*,24-*R* stereochemistry to melianone (**4**) followed from the assignment of structure (**10**) for the product of treating melianone with HBr in acetic

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[‡] In ref. 3, the deduced configurations were wrongly labelled 23-*R*,24-*R*.

[§] The 3β-alcohol (**2**) had been previously obtained[2] by catalytic hydrogenation of bourjotinolone A (**1**), but was only characterised as its acetate.

acid, assuming that no inversion had taken place at C(20), (known to be 20-*S*).[3] However, strong acids can reversibly give enols from acetals and hence C(20) must have changed from the less stable configuration in (**11**) to that in (**12**). The results of Lavie *et al.*[3] do, however, define the *threo* relationship between C(23) and C(24) in melianone (**4**) and confirm that the conversion of (**9**) to (**2**) involves S_N2 attack of the primary alcohol on the epoxide with inversion at C(24).

From Jamaican *Melia azaderach*, we have isolated, in addition to melianone (**4**) and melianodiol (**15**) (found[3] in the same plant growing elsewhere), 3-epimelianol (**6**) and 3-epimeliantriol (**13**), m.p. 200—204°.¶ The structures of (**6**) and (**13**) were deduced from their spectral data and confirmed by correlation with each other and with melianodiol (**15**). Thus, silver carbonate on celite oxidation of 3-epimeliantriol (**13**) gave, in fair yield, melianodiol (**15**), while hydrolysis of the epoxides in (**6**) and (**4**) with **1:1** 0·1N sulphuric acid–tetrahydrofuran, conditions shown[6] to give almost exclusive cleavage of epoxides *via* the more stable carbonium ion, gave cleanly 3-epimeliantriol (**13**) and melianodiol (**15**) respectively. Sodium borohydride reduction of (**13**) yielded sapelin F (**16**)[7] which is therefore 23-*R*,24-*S*. The *threo* relationship between C(23) and C(24) in (**16**) had been previously deduced[7] by the same arguments used for bourjotinolone C (**17**).[2]

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¶ The corresponding 3-acetates (**7**) and (**14**) have been isolated from *Turraeanthus africanus*, see J. G. St. C. Buchanan and T. G. Halsall, *Chem. Comm.*, 1969, 48.

[1] J. D. Connolly, K. H. Overton, and J. Polonsky, in 'Progress in Phytochemistry,' eds. L. Reinhold and Y. Liwschitz, Interscience, London, 1970, vol. 2, p. 385.
[2] G. J. W. Breen, E. Ritchie, W. T. L. Sidwell, and W. C. Taylor, *Austral. J. Chem.*, 1966, **19**, 455.
[3] D. Lavie, M. K. Jain, and I. Kirson, *J. Chem. Soc.* (*C*), 1967, 1347.
[4] W. R. Chan, D. R. Taylor, and T. Yee, *J. Chem. Soc.* (*C*), 1970, 311.
[5] C. W. L. Bevan, D. E. U. Ekong, T. G. Halsall, and P. Toft, *J. Chem. Soc.* (*C*), 1967, 820.
[6] K. Nakanishi, D. A. Schooley, M. Koreeda, and J. Dillon, *Chem. Comm.*, 1971, 1235.
[7] W. R. Chan, D. R. Taylor, and T. H. Yee, *J. Chem. Soc.* (*C*), 1971, 2662.