

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

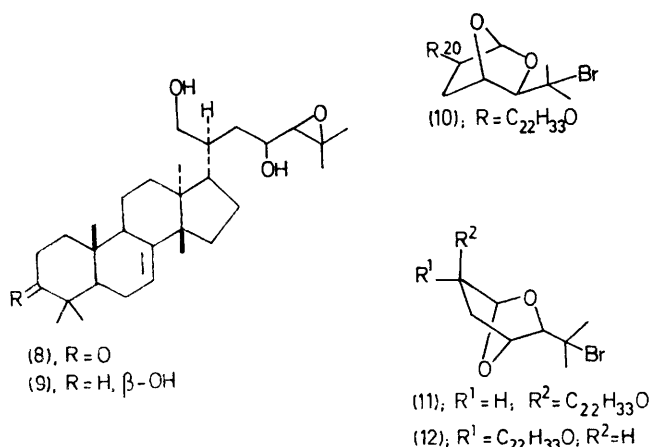
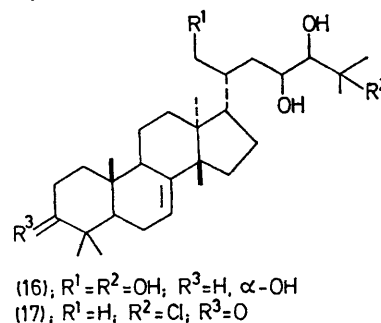
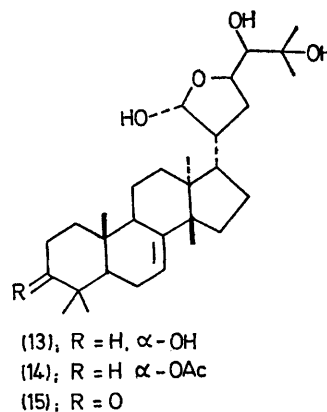
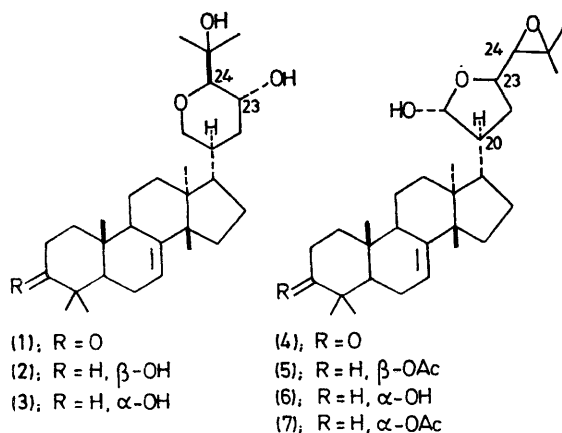
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Summary Thermolysis of the epoxytriol (9) from melianone (4) gave 3-episapelin A (2), thus defining the stereochemistry of melianone (4) as 23-*R*,24-*S*; sapelin F (16) is shown also to have 23-*R*,24-*S* stereochemistry by correlation with melianone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

Two of the modifications of the side chain of the protolimonoids¹ (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 shown² 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).



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), shown³ 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 assignment³ 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 3 β -alcohol (2) had been previously obtained² 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) (found³ 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 shown⁶ 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 deduced⁷ 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.

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