Configuration of Aglaiol, a (24*S*)-24,25-Epoxy-triterpene

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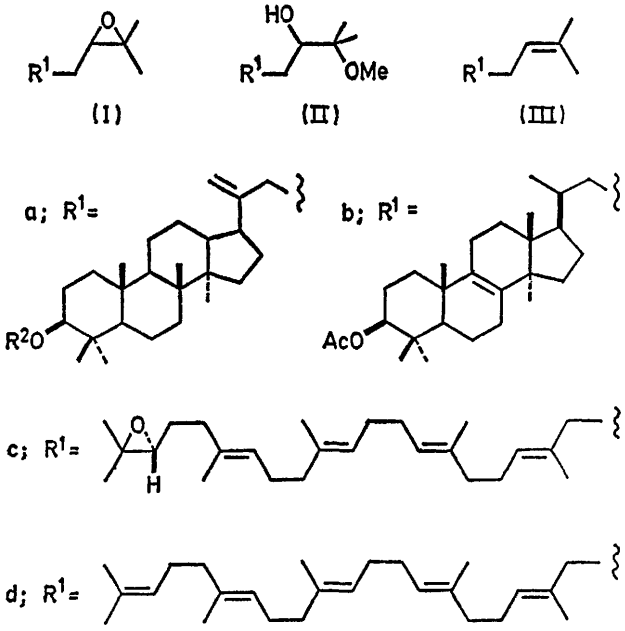
Summary A convenient method for determining the configuration of epoxides is described; biogenetic implications of the (24*S*)-configuration of aglaiol are outlined.

AGLAIOL, a major triterpene of *Aglaia odorata*, has been shown to be 24ξ,25-epoxy-5α-dammar-20-en-3β-ol (Ia; R^2 = H).[1] We have now established that the configuration of epoxides such as (I) can be conveniently determined by acid-catalysed methanolysis followed by application of Horeau's method[2] to the resulting methoxy-alcohol (II). Thus, the known[3] (24*R*)- and (24*S*)-24,25-epoxy-5α-lanost-8-en-3β-yl acetates (Ib) with methanol and perchloric acid afforded the stereochemically pure (by t.l.c.) methoxy-alcohols (IIb)† which with (±)-α-phenylbutyric anhydride gave, as required, an excess of (+)- and (−)-α-phenylbutyric acid (optical yields 32·3 and 20·2%) respectively. Similarly, aglaiol acetate gave the methoxy-alcohol (IIa; R^2 = Ac), m.p. 141—144°, $[\alpha]_D$ + 38·2°, which subsequently yielded (−)-α-phenylbutyric acid (optical yield 37·4%). Aglaiol therefore has the (24*S*)-configuration. This assignment is supported by molecular rotation data.

A similar approach, but involving hydrolysis to a glycol, has been independently developed for determining the absolute configuration of the epoxide function of *Cecropia*



juvenile hormone.[4] Our method using methanolysis has the advantage of obviating the need to check the direction of opening of the epoxide ring.

Whilst the role of 2,3-epoxysqualene in the biosynthesis of 3-oxygenated triterpenes is well established,[5] the widespread assumption[6] that it is only the (3*S*)-isomer that is involved has received no experimental support. The biosynthesis of aglaiol must involve either (24*S*)-24,25-epoxidation of 5α-dammara-20,24-dien-3β-ol (IIIa; R^2 = H) or, more likely,[7] (22*S*)-22,23-epoxidation and subsequent cyclisation of (3*S*)-2,3-epoxysqualene (IIIc), both processes which are comparable to the conversion of squalene (IIId) into (3*S*)-2,3-epoxysqualene. The demonstration of the (24*S*)-configuration of aglaiol thus provides preliminary evidence for the existence of an enzyme system capable of performing this type of transformation. Squalene epoxidase is already known to be non-specific to the extent that it will form both the 2,3-epoxide and 2,3;22,23-diepoxide of 10,11-dihydrosqualene.[8]

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† All new compounds gave satisfactory analytical and spectroscopic data.

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