Stereochemistry of the Blumenols : Conversion of Blumenol A into (*S*)-(+)-Abscisic Acid†

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Summary The stereochemistry of blumenols A and B at C-1′ has been established as *S* by chemical correlation with (*S*)-(+)-abscisic acid.

THE structures of blumenol A (**1**) and blumenol B (**2**), C_{13} compounds extracted from the bark of *Podocarpus blumei* Endl., were deduced[1] from spectral evidence and synthesis of the racemic compounds. The stereochemistry at C-1′ of these compounds was tentatively established by comparison of the sign of an o.r.d. spectral band with that of a band in the c.d. spectrum of (*S*)-(+)-abscisic acid (**4**). Recently[2] the stereochemistry at C-1′ of (+)-abscisic acid has been reversed and it therefore appears that the stereochemistry at C-1′ of the blumenols should also be reversed. However, such a change would not be in accord with the idea that the biosynthesis of these compounds proceeds from blumenol C (**3**) with retention of configuration. The stereochemistry of blumenols A and B has now been proved by conversion of blumenol A into (*S*)-(+)- abscisic acid.

Oxidation of blumenol A in acetone with Jones reagent under carefully controlled conditions gave the diketone (**5**) as a gum, $\lambda_{\max.}$ 238 nm (ϵ *ca.* 19,500, EtOH), $\nu_{\max.}$ 3550, 1678, and 1650 cm^{-1} (KBr), δ ($CDCl_3$) 1·05 and 1·13 (6H), 1·92 (3H, d, *J* 1·5 Hz), 2·34 (3H), 2·45 (2H, d, *J* 2 Hz), 6·00 (1H, m), and 6·50 and 6·95 (2H, q, *J* 15 Hz); *m/e* 222 (M^+); $[\phi]_{259}$ + 80,300° (peak), $[\phi]_{244}$ 0°, and $[\phi]_{228}$ −167,000° (trough) (MeOH). The o.r.d. spectral data for this compound correspond with those of (*S*)-1-hydroxy-4-oxo-α-ionone derived synthetically.[3]

Wittig reaction of (**5**) (20 mg) with ethoxycarbonylmethylenetriphenylphosphorane in toluene at 110° for 8 h and basic hydrolysis of the crude product yielded a mixture containing abscisic acid and its *trans,trans*-isomer. Abscisic acid (1·8 mg), m.p. 157—160°, $[\phi]_{287}$ + 70,000 (peak), $[\phi]_{268}$ 0°, $[\phi]_{243}$ − 211,000° (trough), was isolated by preparative t.l.c. and crystallisation; its o.r.d. and other spectral properties were similar to those reported[4] for the natural (*S*)-(+)-abscisic acid. This defines the configuration at C-1′ of blumenol A and blumenol B (obtainable from blumenol A by saturation of the side-chain double bond[1]) as in (**1**) and (**2**), the same as that recently assigned[2] to (+)-abscisic acid. Assuming a biogenetic relationship between the blumenols and (−)-theaspirone (**6**),[5–7] the configuration of the blumenols at C-2 is *S*, as indicated.

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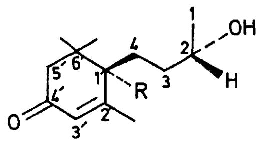
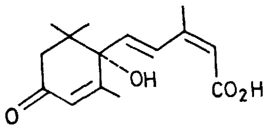


(1) R = OH, $\Delta^{3,4}$-compound
(2) R = OH
(3) R = H



(4)

The o.r.d. spectrum[7] of (−)-theaspirone bears a close resemblance to that of blumenol B acetate {$[\phi]_{269}$ − 19,700° (trough), $[\phi]_{253}$ 0°, $[\phi]_{231}$ + 58,000° (peak)}, so that it is likely that the configuration of the two compounds at C-1′ is the same (the absolute configurations shown in refs. 6 and 7 should be reversed). Surprisingly, blumenol A *gives* a spectrum {$[\phi]_{262}$ + 30,600° (peak), $[\phi]_{243}$ 0°, $[\phi]_{228}$ −37,800 (infl.)} which is the mirror-image of that of blumenol B.

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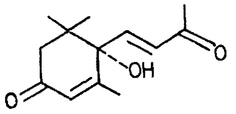
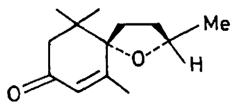


(5)



(6)

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