

## Structure of Effusin

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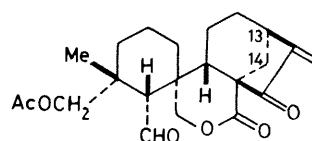
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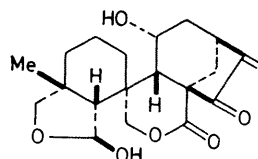
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**Summary** The structure of a new spirosecokaurene compound, effusin, isolated from *Rabdosia effusus* and possessing an insect growth inhibitor activity has been determined from spectroscopic and chemical data

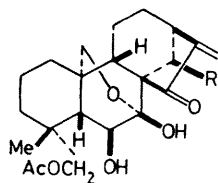
In a previous communication, we reported the isolation of a new diterpene effusin from the ether extract of dry leaves of *Rabdosia† effusus* (Labiateae)<sup>1</sup> We have now established the unique spirosecokaurene structure (1) for effusin



(1) effusin



(2) shikodonin



(3) longikaurin B, R = OH

(4) longikaurin C, R = H

Effusin (1)  $C_{22}H_{28}O_6$  (by chemical ionization m s in isobutane, and elemental analysis), m p 206—209 °C, contains an  $\alpha$ -methylenecyclopentanone moiety as shown by the following spectral data  $\lambda_{max}$  (EtOH) 234 nm ( $\epsilon$  9260),  $\nu_{max}$  (Nujol) 1705 and 1640  $cm^{-1}$ ,  $^1H$  n m r  $\delta$  5.75 and 6.25 (each 1H, br s), and  $^{13}C$  n m r  $\delta$  116.4 (t) and 147.1 (s) ( $>C=CH_2$ ) and 208.1 p p m (ketone). This moiety is a characteristic structural feature of *Rabdosia* diterpenes and is

essential for their biological activity<sup>2,3</sup> The signals appearing at  $\delta$  2.52 (1H dd  $J$  6, 12 Hz) and 2.15 (1H d  $J$  12 Hz) have been assigned to  $14\beta$ -H and  $14\alpha$ -H respectively, since  $14\beta$ -H is coupled to the isolated  $13$ -H ( $\delta$  2.44 m) which also shows allylic coupling with the aforementioned olefinic protons. The lack of coupling between  $14\alpha$ -H and  $13$ -H indicates that the dihedral angle of these two protons is roughly 90°

In addition the presence of a  $\delta$ -lactone moiety is also evident from the spectral data  $\nu_{max}$  1730  $cm^{-1}$ ,  $^1H$  n m r  $\delta$  4.16 and 4.22 (each 1H, each AB doublets,  $J$  10, 18 Hz), and  $^{13}C$  n m r  $\delta$  167.7 p p m (lactone carbonyl). The presence of an aldehyde group is shown by  $\nu_{max}$  2710 and 1710  $cm^{-1}$ ,  $^1H$  n m r  $\delta$  9.75 (1H d  $J$  5 Hz), and  $^{13}C$  n m r  $\delta$  198.7 (d) p p m. Furthermore, the signal coupled to this aldehyde proton is observed at  $\delta$  1.92 (1H, d,  $J$  5 Hz) with no further coupling. The signals of another isolated AB system at  $\delta$  3.55 and 3.77 (each 1H, each AB-doublets,  $J$  9, 15 Hz) and an acetyl group at  $\delta$  1.78 (3H, s) indicate the presence of a  $-CH_2OAc$  group. In INDOOR<sup>4</sup> experiments a nuclear Overhauser enhancement (n O e) has been observed for these AB doublets on irradiation of the tertiary methyl group at  $\delta$  1.02 (s) p p m. The  $^{13}C$  n m r spectrum further shows the presence of another five methylene groups and one methine group, together with three tetrasubstituted carbon atoms.

The spectral data and the analogy with congeners isolated so far from *Rabdosia*<sup>2,3</sup> species indicate that effusin is a shikodonin (2)<sup>5</sup>-type spirosecokaurene diterpene, with the acetoxy-group at either C-18 or C-19. Biogenetic evidence strongly suggests oxidation at C-19 as in shikodonin and longikaurin B (3),<sup>6</sup> both of which were isolated from *Rabdosia* plants. This assumption is also supported by the fact that an n O e was not observed for the  $20-H_2$  signals at  $\delta$  4.16 and 4.22 on irradiation of the C-18 methyl group. Finally, structure (1) has been confirmed by correlation with longikaurin C (4) isolated from *R. longituba*<sup>7</sup> Thus, effusin is identical in all respects with the HIO<sub>4</sub> oxidation product of (4).

Effusin exhibits growth inhibitory activity against lepidopterous larvae in feeding assays, and the  $\alpha$ -methylenecyclopentanone moiety is essential for this activity. In

† The taxon of this genus was previously recognized as *Isodon* (cf H Hata, *J Jpn Bot*, 1972, **47**, 193)

‡  $^1H$  n m r spectra were recorded in  $CDCl_3$  solution at 100 and 270 MHz.  $^{13}C$  n m r spectra were obtained in  $CDCl_3-C_2D_6N$  solution.

addition, effusin strongly inhibits the respiratory function of mitochondria isolated from the queen's ovary of an African termite, *Macrotermes subhyalinus*.§

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§ The detailed biological activity data will be published elsewhere (cf. M. Taniguchi, M. Yamaguchi, I. Kubo, and T. Kubota, *Agric. Biol. Chem.*, 1979, **43**, 71).

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