The Structure of Trichorabdal B and its Transformation into a Novel Skeleton; *X*-Ray Crystal Structures

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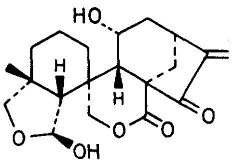
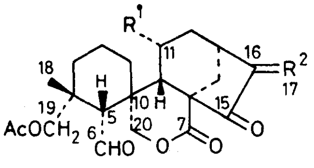
Summary The structures and stereochemistry of trichorabdal B, a new diterpene with the spirosecokaurene skeleton obtained from *Rabdosia trichocarpa*, and its novel rearrangement product have been elucidated by a combination of chemical, physical, and *X*-ray methods.

Recently, two unique diterpenes, shikodonin[1] (**1**) and effusin[2] (**2**), which have the spirosecokaurene skeleton were isolated from *Rabdosia effusus* (Labiatae). We have also isolated four new spirosecokaurene diterpenoids, trichorabdals A, B, C, and D along with longikaurin D[3] (**3**) from *R. trichocarpa* (Maxim.) Hara. Here we report the structure of trichorabdal B (**4**) and its novel skeletal rearrangement.

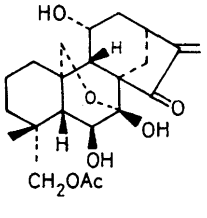
The seven oxygen atoms in trichorabdal B (**4**), $C_{22}H_{28}O_7$, m.p. 161—162 °C, $[\alpha]_D^{25}$ −120·3° (*c* 0·86, EtOH), could be assigned to an α-methylene-cyclopentanone grouping [λ_{max} (EtOH) 232 nm (ϵ 9100); ν_{max} (KBr) 1710 and 1640 cm^{-1}; ^{1}H n.m.r. ([$^2H_5$]pyridine at 60 °C) δ 5·46 br and 6·05 br (each 1H, s); ^{13}C n.m.r. 117·5 (t), 150·6 (s), and 200·4 (s) p.p.m.], a δ-lactone moiety (ν_{max} 1740 cm^{-1}), an acetoxy-group [^{1}H n.m.r. δ 2·00 (3H, s)], an aldehyde group [ν_{max} 2820 and 2720 cm^{-1}; ^{1}H n.m.r. δ 10·19 (1H, d, *J* 4 Hz); ^{13}C n.m.r. 203·0 (d) p.p.m.], and a secondary hydroxy-group [ν_{max} 3600 and 3550—3300 cm^{-1}; ^{1}H n.m.r. δ 4·50 (1H, >C*H*OH, shifted to δ 5·30 on acetylation); ^{13}C n.m.r. 65·0 (d) p.p.m.]. The structure and stereochemistry of trichorabdal B (**4**) were elucidated by showing its identity with the periodate oxidation product derived from longikaurin D (**3**) and by an *X*-ray structural analysis. The circular dichroism curve ($[\theta]_{310}$ −4570, $[\theta]_{232}$ +1440) of the dihydro-derivative (**5**) confirmed the absolute configuration of trichorabdal B to be as shown in (**4**).



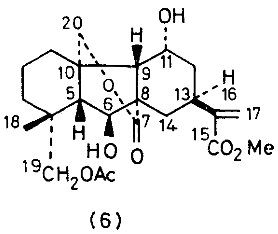
(1)



(2) R^1=H, R^2=CH_2
(4) R^1=OH, R^2=CH_2
(5) R^1=OH, R^2=α−H, β−Me



(3)



(6)

Crystal data: $C_{22}H_{28}O_7$ (**4**), space group $P2_12_12_1$ with a = 8·712(2), b = 28·973(7), c = 8·136(2) Å, U = 2053·6(8) Å^3, D_c = 1·308 g cm^{-3} for Z = 4. The structure was solved by direct methods by use of MULTAN.[4] Full-matrix least-squares refinement led to an *R* factor of 0·078 utilizing 2084 reflexions and anisotropic thermal parameters for non-hydrogen atoms.†

Trichorabdal B (**4**) on treatment with sodium hydroxide in aqueous methanol afforded a product (**6**), $C_{23}H_{32}O_8$, m.p. 214·5—217 °C, which was assigned a novel skeleton on the basis of spectral data [ν_{max} (CHCl$_3$) 3620, 3550, 1740 (sh), 1730, and 1160 cm^{-1}; ^{1}H n.m.r. ([$^2H_5$]pyridine) δ 3·58 (3H, s), and 4·81 (1H, d, *J* 6·8 Hz, C-6-H); ^{13}C n.m.r. ([$^2H_5$]-pyridine) 51·6 (q, CO$_2$*C*H$_3$), 73·8 (d, C-6), and 176·4 (s, C-15) p.p.m.]. The structure was confirmed by an *X*-ray analysis. The rearrangement (**4**) → (**6**) is formally a retro-Claisen condensation followed by an Aldol condensation.

Crystal data: $C_{23}H_{32}O_8$ (**6**), space group $P2_12_12_1$ with a = 11·198(2), b = 26·105(9), c = 7·351(3) Å, U = 2149(1) Å^3, D_c = 1·349 g cm^{-3} for Z = 4. The structure was solved by direct methods by use of MULTAN.[4] Full-matrix least-squares refinement with anisotropic thermal parameters for non-hydrogen atoms led to an R factor of 0·054 utilizing 2143 reflexions.†

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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