Germacranolides of Erlangea cordifolia. Isolation and structures of cordifolia-54,-55,-P2, and-31 by spectral and X-ray methods

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Abstract:

In addition to cordifene (1) and cordifene 4β , 15-oxide (5), four new companion compounds cordifolia-54, -55, -P2, and -31 have been isolated from the insect-antifeedant plant Erlangea cordifolia. Cordifolia-54(2) is related to cordifene as the 2,3-dihydrodeoxy derivative, and cordifolia-55(3) is the acetate of a C-2,O-2-seco-cordifene resulting from a formal epoxide reduction. Cordifolia-31 is the methacrylate ester of the same sesquiterpene core as is present in cordifene 4β,15-oxide. Cordifolia-P2 has 1H and 13C n.m.r. data consistent with structure (4) but certain chemical shifts, multiplicities, and coupling constants suggest a conformation markedly different from the five other Erlangea structures. This has been confirmed by a single crystal X-ray analysis. Cordifolia-P2, in contrast to cordifene and its 4β , 15-oxide, has a negative Cotton effect near the $n \rightarrow \pi^*$ maximum in the c.d. spectrum. This is explained by McPhail's generalisation if all three compounds have the same absolute configuration, since the C(5)-C(6)–C(7)–C(8) torsion angle is significantly <120°(99°) for -P2 but significantly >120°(157°, 159°) for cordifene and its oxide. On the other hand the idealised McPhail relationship between this torsion angle and the C[double bond, length half m-dash]C-C[double bond, length half mdash]O torsion angle of the lactone is incompletely obeyed since the latter is measured as +0.7° in cordifolia-P2.