

STRUCTURE OF TWO EUDESMANOLIDES, MORIFOLIN A AND B

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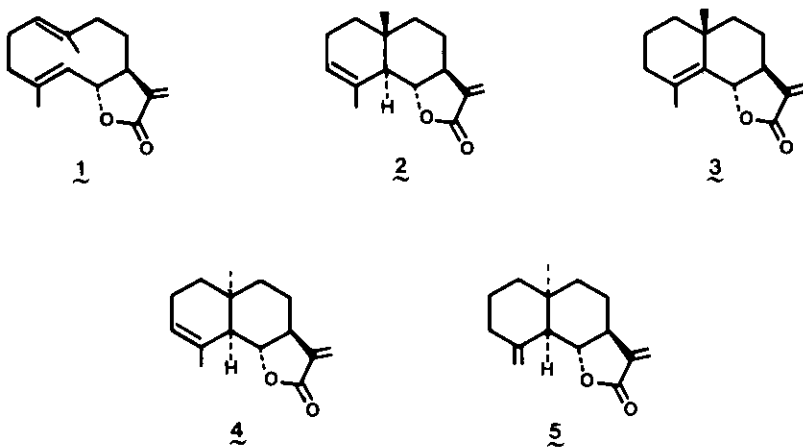
Abstract—— Two new eudesmanolides, morifolin A and B, were isolated in addition to previously known compounds from Critonia morifolia (Compositae). The structures were established by spectroscopic methods.

In the course of our studies on the constituents of Critonia morifolia (Compositae), previously known as Eupatorium morifolium Miller,¹ several sesquiterpene lactones were isolated from the methanolic extract of the dried material of this plant. We recently isolated α - (\mathcal{L}) and γ -cyclocostunolide (\mathcal{M}) from Critonia quadrangulare.² These compounds were isolated from C. morifolia together with the costunolide (\mathcal{K}) and two new eudesmanolides morifolin A (\mathcal{A}) and B (\mathcal{B}) in the ratio ca. 1:1.

Lactones (\mathcal{K}), (\mathcal{L}), and (\mathcal{M}) were identified on the basis of their physical and spectroscopical properties.^{3,4} In this communication we describe the structural determination of morifolin A and B.

Morifolin A (\mathcal{A}), C₁₅H₂₀O₂ (m/z 232), was isolated as an oil using repeated silica gel chromatography with a gradient mixture of n-hexane and ethyl acetate, and was found to contain an α -methylene- γ -butyrolactone moiety [IR (CHCl₃) 1760 cm⁻¹]; ¹H-NMR (CDCl₃): δ 5.50 (1H, d, \underline{J} = 3.2 Hz), 6.25 (1H, d, \underline{J} = 3.5 Hz) ppm. The complete structure and relative stereochemistry of \mathcal{A} were deduced mainly on the basis of its 200 MHz ¹H-NMR spectrum (CDCl₃)⁵ as described below. The spectrum of \mathcal{A} displayed signals due to a tertiary methyl group at δ 0.82 (s, H-15),

a vinylic methyl group at δ 1.81 (s, H-14), 5.38 (m, H-3), 5.50 (d, $J = 3.2$ Hz, H-13a), 6.25 (d, $J = 3.5$ Hz, H-13b), 4.58 (dd, $J = 11.2$ Hz, 11 Hz, H-6), 3.24 (m, H-7). On irradiation of this last signal the doublet of doublet signal for H-6 with $J = 11.2, 11$ Hz was changed into a doublet with $J = 10.7$ Hz. This fact indicated that the disposition of H-5, H-6 is trans-diaxial. Since the signal of the proton of the closing of the lactone is symmetric, we concluded that the disposition of H-6, H-7 is also trans-diaxial. Consequently, the structure of morifolin A is represented as 4.



Morifolin B (5) had a $^1\text{H-NMR}$ spectrum that was very similar to that of 4. Thus, it has a tertiary methyl at δ 0.75 (s, H-15), 1.63 (d, $J = 11.2$ Hz, H-5), 4.77 (dd, $J = 11.2$ Hz, 10.3 Hz, H-6), 3.24 (m, H-7). The major differences were the absence of the signal of H-3 in 4 and the appearance of two new signals at δ 4.75 (1H, d, $J = 1$ Hz) and 4.91 (1H, d, $J = 1$ Hz), both characteristic of the exo-methylene protons at C-4.

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