ling experiments and Mr. M. Nishi, Faculty of Pharmaceutical Sciences, Setsunan University, Osaka for 400 MHz (Jeol) ^{1}H NMR spectra and NOE measurements.

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EUDESMANE SESQUITERPENES FROM *EUPATORIUM QUADRANGULARE*

ANTONIO G. GONZÁLEZ, JAIME BERMEJO BARRERA, ANGEL C. YANES HERNÁNDEZ, FRANCISCO ESTÉVEZ ROSAS and XORGE A. DOMÍNGUEZ†

Instituto de Química Orgánica, Universidad de La Laguna; Instituto de Productos Naturales Orgánicos, CSIC, La Laguna, Tenerife, Canary Islands, Spain; †Departamento de Química, Instituto Tecnológico y de Estudios Superiores de Monterrey, Monterrey, Mexico

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Key Word Index—*Eupatorium quadrangulare*; Compositae; sesquiterpene lactones; eudesmanolides.

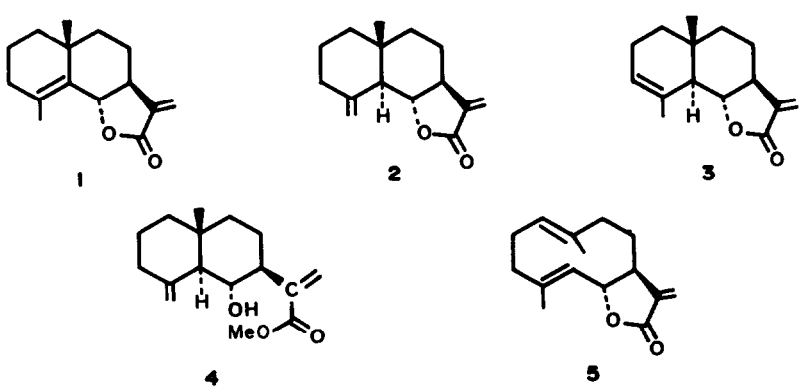
Abstract—The aerial part of *Eupatorium quadrangulare* afforded in addition to known compounds, a possible biosynthetic intermediate, quadrangulin A, of the eudesmanolides found in this species.

INTRODUCTION

As part of our research into sesquiterpene lactones from the Compositae, we have studied the composition of *Eupatorium quadrangulare*. This paper describes the isolation and structural determination of a new biosynthetic intermediate of the eudesmanolides, quadrangulin A.

RESULTS AND DISCUSSION

The aerial parts of *Eupatorium quadrangulare* afforded a complex mixture of four eudesmane sesquiterpenes, which were separated by repeated TLC. Three of these compounds are already known: arbusculin B (**1**) [1], β-cyclocostunolide (**2**) [2] and α-cyclocostunolide (**3**) [3].



Quadrangulin A (**4**), $C_{21}H_{24}O_3$ ($[M]^+$ at m/z 264), was obtained as an oil. Its IR spectrum contained bands assignable to a hydroxyl group (3580 cm^{-1}), methyl ester (1710 cm^{-1}), and a double bond (1640 cm^{-1}). An analysis of the ^1H NMR spectrum confirmed that it was the methyl ester of a sesquiterpene acid. The spectrum showed two singlets, one at δ0.80 for the C-10 methyl group, and the other at 3.74 typical of a methoxyl; four signals were at 6.28, 5.71 (2H, *br s*), 4.95 and 4.68 (2H, *br s*) due to two terminal methylene double bonds at C-15 and C-13 respectively, and a triplet at 3.92 (J = 10 Hz) for the proton attached to the carbon bearing the hydroxyl group at C-6. The last signal showed the *trans*-diaxial disposition of the protons at C-5 (α), C-6 (β) and C-7 (α) [4].

The presence of β-cyclocostunolide in the plant was thought to indicate that compound **4** was an artefact, derived by adventitious ring opening of the lactone **2** during the isolation process. This was rejected when compound **2** was refluxed with methanol and the starting material was recovered unaltered.

Since products **1**, **2** and **3** are present in *Eupatorium quadrangulare* it is very likely that costunolide is the precursor of the eudesmanolides. However, the absence of this last substance in the plant under study suggests the possibility that compound **4** or its demethylated product is the precursor of this type of lactone.

EXPERIMENTAL

^1H NMR (60 MHz): $CDCl_3$, internal standard TMS; MS: (70 eV) direct insertion; IR: $CHCl_3$. CC silica gel F-254 (0.25 mm). Spots were detected on TLC in UV light (254 nm) after spraying with oleum and then heating at 120°.

The aerial part of the plant (300 g) was collected in San Luis de Potosí, Mexico, during March 1984, and identified by Dr. Marshall Johnston. A voucher (3513) specimen is on deposit in Texas University. The plant was triturated and exhaustively extracted with hot MeOH, and worked-up in the usual manner [5]. The crude gum was pre-absorbed on 5 g of silica gel and chromatographed over 30 g of the same absorbent packed in *n*-hexane to give arbusculin B (**1**, 40 mg), β-cyclocostunolide (**2**, 20 mg), α-cyclocostunolide (**3**, 20 mg) and quadrangulin A (**4**, 30 mg).

Quadrangulin A (**4**). Colourless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580, 1710, 1640; MS m/z (rel. int.): 264 $[M]^+$ ($C_{21}H_{24}O_3$) (2.09), 249 $[M-Me]^+$ (4.03), 246 $[M-H_2O]^+$ (12.16), 233 $[M-OMe]^+$ (9.02), 205 $[M-CO_2Me]^+$ (6.93); ^1H NMR: δ0.80 (3H, *s*, C-10 Me), 3.74 (3H, *s*, OMe), 3.92 (1H, *t*, J = 10 Hz, C-6), 4.95–4.68 (2H, *br s*, C-15), 5.71 (1H, *br s*, C-13a), 6.28 (1H, *br s*, C-13b).

Synthesis of compound **4**. β-Cyclocostunolide (**2**, 100 mg) in 10 ml of MeOH containing five drops of conc. HCl was left overnight. The reactant mixture was treated in the usual manner to give an oil identical (IR, ^1H NMR) with compound **4**.

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