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Sociedad Química de México
Distrito Federal, México

Available in: http://www.redalyc.org/articulo.oa?id=47548105
Investigación

Furanoeremophilane Derivatives from Psacalium beamanii

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Dedicated to the memory of Dr. Raymundo Cruz Almanza

Recibido el 24 de noviembre del 2003; aceptado el 26 de febrero del 2004

Abstract. The phytochemical study of Psacalium beamanii afforded the phenylethanoid 1, three sterols, the furanoeremophilane derivatives 2-10, and maturone acetate (12), which was isolated as a natural product for the first time. Its structure was established by means of spectroscopic data and confirmed by chemical correlation. The optical rotation of decompostin (4) was corrected and its identity was corroborated by the X ray analysis of its 2S-bromo derivative (11).

Keywords: Psacalium beamanii, Asteraceae, Senecioneae, Tussilaginae, furanoeremophilane derivatives.

Introduction

The genus Psacalium (Asteraceae, Senecioneae, Tussilaginae) comprises about 47 species distributed from southwestern United States to Guatemala [1]. Previous chemical studies have shown that eremophilanes are the main secondary metabolites elaborated by species of this genus [2-5]. P. decompositum, P. palmeri, P. peltatum, P. sinuatum, P. radiolifolium and Acourtia thurberi are grouped by the Tarahumara people of Mexico, in the so called Matarique complex, and used for the treatment of rheumatism and diabetes, as well as renal, hepatic and gastrointestinal ailments [6]. Ethnomedical information has motivated several research projects such as the evaluation of the antihyperglycemic activity of P. decompositum and P. peltatum extracts [4,7], and the antimicrobial activity of P. radulifolium extracts [5]. Thus, in order to continue with the phytochemical research of Mexican plants of the Senecioneae tribe [8], we studied Psacalium beamanii H. Rob. In the present study, we report the isolation of a phenylethanoid (1), three sterols, and nine furanoeremophilane derivatives (2-10). Additionally, the characterization of maturone acetate (12), isolated as a natural product, for the first time, is also described.

Results and discussion

The phytochemical study of Psacalium beamanii afforded the known compounds β-sitosterol, stigmasterol, β-sitosterol glucoside [9], the phenylethanoid icariside D2 (1) [10], the furanoeremophilane derivatives maturinone (2) [11], maturone (3) [2], decompostin (4) [12], maturinin (5) [2,13], maturin acetate (6) [2,13], cacalonol (7/8) [14] and peroxycacalonol (9/10) [14]. The steroidal compounds were identified by comparison with authentic samples, and compounds 1-10 by comparison of their physical and spectroscopic features with those described in literature.

Cacalonol and peroxycacalonol were optically inactive, suggesting the presence of 1:1 mixtures of the corresponding enantiomers (7/8 and 9/10 respectively). Compound 4, identified as decompostin by means of its mp and spectral data, showed a specific rotation ([α]D29-426°) with opposite sign to that reported in literature [12]. Its 2S-bromo derivative 11 exhibited an [α]D25-426°, which also differed from that reported for the same compound ([α]D2-41.4°) [12]. In order to clarify this ambiguity, an x-ray crystallographic analysis of the 2S-bromo derivative (Fig 1) was performed, thus confirming the struc...
Fig. 1. ORTEP projection of 11.

re and absolute configuration of decompostin (4) and showing that the reported specific rotations of 4 and 11 were mistaken.

In addition to the above mentioned, modified furanoeremophilane 12 was isolated as a crystalline yellow solid, mp 150-1º. Its molecular formula C_{16}H_{12}O_{5} deduced from HREIMS (m/z 284.068, [M]+) as well as its UV (λ_{max} 246, 293 and 350 nm) and IR (ν_{max} 1670, 1585 and 1543 cm^{-1}) spectra suggested an aromatic structure with a quinoid system. This was corroborated by the two singlet signals at δ 183.54 and 173.62 (C-6 and C-9 respectively) observed in the 13C NMR spectrum. The presence of an acetate group was deduced as an acetylation product of maturone [2]. Nevertheless, this is the first time that 12 is isolated as a natural product and fully characterized by 1H, 13C, COSY, HETCOR, and COLOC NMR spectral data.

Experimental

General Experimental Procedures

Melting points were determined on a Fisher Jones melting point apparatus and are uncorrected. Optical rotations were determined on a JASCO DIP-360 digital polarimeter. IR spectra were recorded on a Nicolet Magna-IR 750 spectrometer. EIMS data were determined on a JEOL JMS-AX505HA mass spectrometer at 70 eV. 1H NMR and 13C NMR data were obtained on a Varian Unity 300 instrument. Chemical shifts were referred to TMS (δ 0). Standard Varian programs were used for COSY spectra at 300 MHz. HETCOR experiments were obtained for J_{CH} = 140 Hz at 75 MHz. COLOC experiments were obtained for J_{CH} = 9 Hz at 75 MHz. Vacuum column chromatographies (VCCs) were performed using Sil G 60 E. Merck, 70-230 mesh.

Plant Material

Psacalium beamanii H. Rob. was collected in Ixtlán, Oaxaca, México, June 1997. A voucher specimen (MEXU 775149) was deposited at the Herbario Nacional, Instituto de Biología, UNAM, México.

Extraction and Isolation

Dried and ground roots (129 g) were extracted successively with hexane and MeOH at room temperature. Hexane extract (4.47 g) was analyzed by VCC eluting with an hexane/EtOAc gradient system. Fractions eluted with hexane were combined and purified by means of VCC (hexane/EtOAc 99:1) to yield maturone (2, 11.1 mg) [11], mp 169-72º. Fractions eluted with hexane/EtOAc 90:10 afforded maturone acetate (12, 44 mg) [2], mp 150-1º. The mother liquors of the last compound and fractions eluted with hexane/EtOAc 85:15 were combined and submitted to VCC (hexane/EtOAc 95:5) to yield decompostin (4, 49.4 mg) [12], mp 195-6º, [α]_{D}^{20} -68º (c 0.456, CHCl_{3}). 12 (37.9 mg). Decompostin (4, 19 mg) was transformed into 25-bromodecompostin (11, 6 mg) as already described [12], mp 188-192º dec, [α]_{D}^{20} -426º (c 0.2, CHCl_{3}). MeOH extract (28 g) was purified by VCC eluting with an hexane/Me_{2}CO gradient system. Fractions eluted with hexane were analyzed by VCC (hexane/EtOAc 99:1) affording maturinin (5, 18.1 mg) [2, 13], mp 94-96º, [α]_{D}^{20} (c 4.4 mg) and a mixture of β-sitosterol/stigmasterol (25 mg), mp 134-6º. Fractions eluted with hexane/Me_{2}CO 90:10 were submitted to VCC (hexane/EtOAc 95:5) to yield 4 (123.6 mg) and maturin acetate (6, 125.5 mg) [2, 13], mp 84-85º. Fractions eluted with hexane/Me_{2}CO 80:20 were purified by VCC (hexane/EtOAc 85:15) affording caecalol (7/8, 11.4 mg) [14], mp 205-7º, [α]_{D}^{20} 0º (c 0.26, CHCl_{2}) and maturon (3, 3 mg) [2], mp 164-70º. Dried and ground aerial parts (476.2 g) were extracted with hexane and MeOH. Hexane extract (12.7 g) was submitted to VCC eluting with an hexane/Me_{2}CO gradient system. Fractions eluted with hexane/Me_{2}CO 95:5 afforded a mixture of β-sitosterol/stigmasterol (25 mg). Fractions eluted with hexane/Me_{2}CO 90:10 yielded 7/8 (33.4 mg) and peroxycacalol (9/10, 34.7 mg) [14], mp 204-6º dec, [α]_{D}^{20} 0º (c 0.185, CHCl_{3}). The MeOH extract (100 g) was analyzed by VCC eluting with an hexane/Me_{2}CO gradient system. Fractions eluted with hexane/Me_{2}CO 95:5 were purified by VCC (hexane/EtOAc 90:10) yielding a mixture of β-sitosterol/stigmasterol (28 mg), and 12 (10.6 mg). Fractions eluted with hexane/Me_{2}CO 90:10 and 85:15 were combined and purified by VCC (hexane/EtOAc 85:15) affording 12 (2.1 mg), 7/8 (31.6 mg) and 12 (10.6 mg).

The mother liquors of the last compound and fractions eluted with hexane/EtOAc 85:15 were combined and submitted to VCC (hexane/EtOAc 95:5) to yield decompostin (4, 49.4 mg) [12], mp 195-6º, [α]_{D}^{20} -68º (c 0.456, CHCl_{3}). 12 (37.9 mg). Decompostin (4, 19 mg) was transformed into 25-bromodecompostin (11, 6 mg) as already described [12], mp 188-192º dec, [α]_{D}^{20} -426º (c 0.2, CHCl_{3}). MeOH extract (28 g) was purified by VCC eluting with an hexane/Me_{2}CO gradient system. Fractions eluted with hexane were analyzed by VCC (hexane/EtOAc 99:1) affording maturinin (5, 18.1 mg) [2, 13], mp 94-96º, [α]_{D}^{20} (c 4.4 mg) and a mixture of β-sitosterol/stigmasterol (25 mg), mp 134-6º. Fractions eluted with hexane/Me_{2}CO 90:10 were submitted to VCC (hexane/EtOAc 95:5) to yield 4 (123.6 mg) and maturin acetate (6, 125.5 mg) [2, 13], mp 84-85º. Fractions eluted with hexane/Me_{2}CO 80:20 were purified by VCC (hexane/EtOAc 85:15) affording caecalol (7/8, 11.4 mg) [14], mp 205-7º, [α]_{D}^{20} 0º (c 0.26, CHCl_{2}) and maturon (3, 3 mg) [2], mp 164-70º. Dried and ground aerial parts (476.2 g) were extracted with hexane and MeOH. Hexane extract (12.7 g) was submitted to VCC eluting with an hexane/Me_{2}CO gradient system. Fractions eluted with hexane/Me_{2}CO 95:5 afforded a mixture of β-sitosterol/stigmasterol (25 mg). Fractions eluted with hexane/Me_{2}CO 90:10 yielded 7/8 (33.4 mg) and peroxycacalol (9/10, 34.7 mg) [14], mp 204-6º dec, [α]_{D}^{20} 0º (c 0.185, CHCl_{3}). The MeOH extract (100 g) was analyzed by VCC eluting with an hexane/Me_{2}CO gradient system. Fractions eluted with hexane/Me_{2}CO 95:5 were purified by VCC (hexane/EtOAc 90:10) yielding a mixture of β-sitosterol/stigmasterol (28 mg), and 12 (10.6 mg). Fractions eluted with hexane/Me_{2}CO 90:10 and 85:15 were combined and purified by VCC (hexane/EtOAc 85:15) affording 12 (2.1 mg), 7/8 (31.6 mg) and 12 (10.6 mg).
Furanoeremophilane derivatives from *Psacalium beamanii* 23 mg), and 3 (17.5 mg). Fractions eluted with hexane/Me₂CO 50:50 and 40:50 were combined and analyzed by VCC (CHCl₃/MeOH 95:5) to give β-sitosterol glucopyranoside (75.6 mg) [9], mp 285-90°. Fractions eluted with hexane/Me₂CO 30:70 were treated with charcoal/MeOH and submitted to VCC (CHCl₃/MeOH 80:20) to yield icariside D₂ (1, 148.3 mg) [10], mp 153-5°.


1'H-NMR (300 MHz, CDCl₃): δ 8.17 (1H, br d, J = 6.6 Hz, H-1), 7.61 (1H, t, J = 7.5 Hz, H-2), 7.54 (1H, br d, J = 7.2 Hz, H-3), 7.76 (1H, s, H-12), 5.38 (2H, s, H-13), 2.81 (3H, s, H-15), 1.24 (3H, s, Ac). 13C-NMR (75 MHz, CDCl₃): δ 125.99 (C-1), 132.94 (C-2), 138.49 (C-3), 142.29 (C-4), 130.55 (C-5), 183.54 (C-6), 128.70 (C-7), 152.17 (C-8), 173.62 (C-9), 134.05 (C-10), 121.61 (C-11), 147.10 (C-12), 56.47 (C-13), 23.12 (C-15), 170.56 (C=O, Ac), 20.85 (CH₃, Ac).

**Oxidation of maturin acetate (6).** A solution of 6 (27.8 mg) in Me₂CO (2 ml) at 3° was oxidized with Jones reactive in the usual manner. The residue purified by VCC (hexane/EtOAc 80:20) gave maturone acetate (12). mp 153-5°.

**X-ray crystallographic data of 11.** Colorless crystal obtained from CHCl₃/EtOH; crystal size 0.206 × 0.144 × 0.052 mm; crystal data: C₁₅H₂₉BrO₄, mol. wt = 387.4, monoclinic, space group P2₁, a = 7.242 (1) Å, b = 8.321 (1) Å, c = 14.131 (1) Å, β = 93.535 (2)°, V = 827.9 (2) Å³, Z = 2, Dc = 1.473 Mg/m³, F (000) = 376, T = 293 (2) K, μ = 2.497 mm⁻¹, λ (Mo Kα) = 0.71073 Å, 6805 measured intensities (2.86 < θ < 25.03°), -8 ≤ h ≤ 8, -9 ≤ k ≤ 9, -16 ≤ l ≤ 16, collected Bruker Smart Apex CCD diffractometer. Refinement by the full matrix-least squares on F² method was performed using 2907 reflections (＞ 2σ (I)) with 203 parameters. The largest difference peak was 0.497. The final R-factor was 4.04 % and wR² was 5.6 %.

Flack’s parameter = -0.05 (1). Crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC 232110), 12 Union Road, Cambridge, CB2 1EZ, UK.

**Acknowledgement**

We are indebted to Rubén Toscano, Rubén Gaviño, María Isabel Chávez, Héctor Ríos, Angeles Peña, Rocío Patiño, Luis Velasco, Javier Pérez, and Gabriela Salcedo for technical assistance.

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