

A NEW FURANOEREMOPHILANE FROM *SENECIO FISTULOSUS*

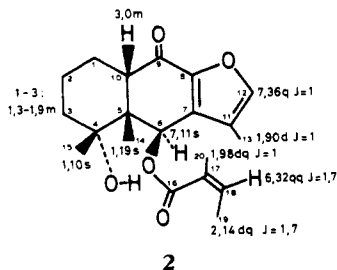
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Furanoeremophilanes are widespread in the large genus *Senecio* (1,2). In connection with a chemical study of Chilean species of that taxon, we isolated a new furanoeremophilane from the twigs and leaves of *Senecio fistulosus* Poepp ex Less: 4 α -hydroxy-6 β -angeloxy-10 β -acetoxy-9-oxofuranoeremophilane (**1**).

Compound **1** was obtained as colorless crystals that analyzed for C₂₂H₂₈O₇ (M⁺, 404.1838). Uv and ir spectra were characteristic of 9-oxofuranoeremophilane [λ max 282 (log ϵ 4.2) nm and ν max 1670 cm⁻¹] (1,3). Examination of the ¹H-nmr spectrum showed very close structural similarity to 4 α -hydroxy-6 β -angeloxy-9-oxofuranoeremophilane (**2**) (4). Signals at δ 7.14 (q) and δ 1.90 (d) indicated a furan ring with a methyl group attached to C-11.

Signals at 1.00 (s) and 1.19 (s) were assigned to methyl groups at C-4 and C-5 with stereochemistry previously reported (*cis*-decaline derivative, methyl group with β orientation at C-4) (5,6). Finally, the signal at δ 7.05 (s) was attributed to a 6 α -H geminal to an unsaturated ester group (4). ¹H-nmr and ms (m/z 83, C₄H₇CO⁺, 100%) data suggested that the ester was an angeloxy group. However, a significant difference was observed in the ¹H-nmr spectrum. The signal at δ 3.00 attributed to 10 β -H in compound **2** (4) was missing and



replaced by one at δ 2.19 (s) clearly indicating the presence of an acetoxy group. This was confirmed by the mass spectral data.

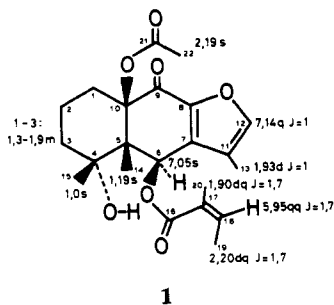
From the above spectral observations, it can be concluded that the structure of **1** is: 4 α -hydroxy-6 β -angeloxy-10 β -acetoxy-9-oxofuranoeremophilane.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Uv spectra were recorded in MeOH solutions using a Carl-Zeiss DMR Instrument. Ir spectra were determined in KBr discs using a Perkin-Elmer 735 B infrared spectrophotometer. ¹H-nmr spectra were run on a Bruker WM spectrometer at 400 MHz in CDCl₃ solutions, using TMS as internal standard. Eims spectra taken on an AEI model MS-50 mass spectrometer at 70 eV. Mps were determined on a Köfler hot stage apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 241 polarimeter.

PLANT MATERIAL.—The plant was collected in December (Summer) 1983, in Cajón del Maipo, Santiago, Región Metropolitana, Chile. A specimen sample is deposited at the Museo de Historia Natural, Santiago, Chile.

EXTRACTION AND FRACTIONATION.—The powdered, defatted sample (280 g, leaves and twigs) was extracted with petroleum ether (60-80°) in a Soxhlet apparatus. The extract was taken to dryness under reduced pressure; 4 g of the residue was applied to a prepacked column of Lichroprep Si 60 Merck (63-125 μ m, pressurized to 2 bars) and developed with petroleum ether-EtOAc (3:1); 210 fractions of 20 ml were collected. Tubes 20-40 were taken to dryness and crystallization of the residue afforded needles of **1**.



4 α -HYDROXY-6 β -ANGELOXY-10 β -ACETOXY-9-OXOFURANOEREMOPHILANE (1).—Crystals from EtOAc (mp 174-175°); uv λ max (MeOH) 282 (log ϵ 4.2), 219 (log ϵ 4.15) nm; ir λ max (KBr) 3400, 1740, 1710, 1670, 1630, and 1520 cm^{-1} ; $^1\text{H-nmr}$ δ (400 MHz, CDCl_3) 1.00 (s, 3H, H-15), 1.19 (s, 3H, H-14), 1.3-1.9 (m, 6H, H-1, H-2 and H-3), 1.90 (dq, 3H, $J=1$ Hz, $J=1$ Hz, H-20), 1.93 (d, 3H, $J=1$ Hz, H-13), 2.19 (s, 3H, H-22), 2.20 (dq, 3H, $J=7$ Hz, $J=1$ Hz, H-19), 5.95 (qq, 1H, $J=7$ Hz, $J=1$ Hz, H-18), 7.05 (s, 1H, H-6) and 7.14 (q, 1H, $J=1$ Hz, H-12); eims m/z 404.1838 (M^+ , $\text{C}_{22}\text{H}_{28}\text{O}_7$), 344.1624 (M^+ -AcOH, $\text{C}_{20}\text{H}_{24}\text{O}_5$, 29.5), 83.0480 ($\text{C}_5\text{H}_7\text{O}$, 100); $[\alpha]_D^{23}$

589	578	546	436	365
-46.6°	-48.3°	-54.4°	-82.7°	-45.5°

nm (c 0.18, CHCl_3).

ACKNOWLEDGMENTS

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