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9-OXO-10 α H-FURANOEREMOPHILANES FROM
SENECIO CHILENSIS AND *SENECIO PATAGONICUS*¹

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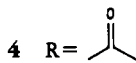
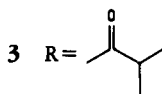
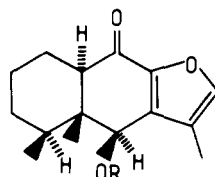
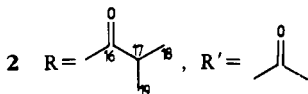
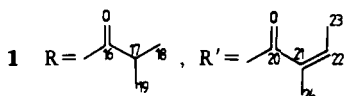
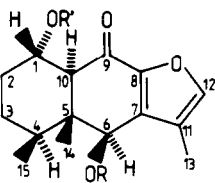
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ABSTRACT.—A new structure, 1 α -angeloxy-6 β -isobutyroxy-9-oxo-10 α H-furanoeremophilane [1] and three previously described compounds, 1 α -acetoxy-6 β -isobutyroxy-9-oxo-10 α H-furanoeremophilane [2], 6 β -isobutyroxy-9-oxo-10 α H-furanoeremophilane [3], and 6 β -acetoxy-9-oxo-10 α H-furanoeremophilane [4], were isolated from *Senecio chilensis* and *Senecio patagonicus*. ¹³C-nmr chemical shifts of structures 1–4 and double resonance and nOe experiments of structure 4 clearly confirmed a *trans*-decalin system for furanoeremophilanes.

During a search for furanoeremophilanes from the genus *Senecio* (Compositae) (1–3), three 9-oxo-10 α H-furanoeremophilanes were isolated from *Senecio chilensis* Less. A new structure, 1 α -angeloxy-6 β -isobutyroxy-9-oxo-10 α H-furanoeremophilane [1], and 1 α -acetoxy-6 β -isobutyroxy-9-oxo-10 α H-furanoeremophilane [2], and 6 β -isobutyroxy-9-oxo-10 α H-furanoeremophilane [3] previ-

cedure described elsewhere (2), in order to attempt a ¹³C-nmr chemical shift correlation. The latter was previously described with a *cis*-decalin stereochemistry (2). Careful analysis of coupling constants in ¹H-nmr spectra reported by Samek *et al.* (4) and ¹³C-nmr and nOe data included in this paper clearly showed that the stereochemistry must be corrected to a *trans*-decalin.



ously described from *Senecio umbellatus* (4) were identified. In addition, 6 β -acetoxy-9-oxo-10 α H-furanoeremophilane [4] was isolated from *Senecio patagonicus* Hook et. Arn. D.C. according to a pro-

Compound 1 was crystallized from hexane-EtOAc (9:1) as white crystals with mp 118–119°. Its uv and ir spectra were characteristic of a 9-oxo-furanoeremophilane (5). Careful analysis of a ¹H-nmr spectrum showed a great similarity with that of 1 α -acetoxy-6 β -angeloxy-9-oxo-10 α H-furanoeremophilane isolated

¹This work is dedicated to Prof. G. B. Marinetti-Bettolo on the occasion of his 75th birthday.

from *Senecio rigidus* (6). Our spectrum was missing the signal of the acetyl group, which was replaced by the typical signal of an isobutyryl group [δ 1.25 and 2.62]. This was confirmed by a double resonance experiment that collapsed the signal at δ 1.25 by irradiating the proton at δ 2.62, and by eims which showed peaks at m/z 71 [$\text{Me}_2\text{CHCO}]^+$ (79%) and m/z 43 [$\text{Me}_2\text{CH}]^+$ (100%). Further double resonance experiments showed the coupling between signals at δ 5.34 (H-1 β) and δ 2.73 (H-10 α). Use of the selective INEPT technique (7) unambiguously established the position of the isobutyryl group at C-6. When H-6 α was irradiated at δ 6.39, only the carbonyl carbon of the isobutyryl group (δ 176.6), C-7 (δ 133.7), and C-8 (δ 147.4) were enhanced in the resultant polarization transfer spectrum.

Additional proof was obtained from hydrogenation of **1**. The ^1H -nmr spectrum of hydrogenated **1** showed an up-field shift of H-1 β and maintenance of the value for the signal of H-6 α . From all the data presented it can be concluded that **1** is 1 α -angeloxy-6 β -isobutyroxy-9-oxo-10 α H-furanoeremophilane.

The ^{13}C -nmr spectra of structures **1** to **4** showed a good correlation for a series of 9-oxo-furanoeremophilanes with a *trans*-decalone system (Table 1). The stereochemistry was confirmed through careful analysis for the coupling of H-10 δ 1.86 (dd, $J_{1\alpha,10\alpha} = 3.4$ Hz and $J_{1\beta,10\alpha} = 12$ Hz) (8) of compound **4** in CDCl_3 - C_6D_6 (1:1) at 200 MHz. Additional proof was obtained from experi-

TABLE 1. ^{13}C -nmr Spectral Data of Compounds **1**–**4** (CDCl_3 ; TMS as internal standard).

Carbon	Compound			
	1	2	3	4
C-1	67.1	67.4	32.3	32.2
C-2	31.5	31.3	20.8	20.6
C-3	29.8	29.7	25.1	24.9
C-4	41.9	41.8	42.6	42.0
C-5	51.4	51.3	50.0	49.7
C-6	75.0	74.9	75.7	75.6
C-7	133.6	133.7	134.0	134.5
C-8	144.9	145.0	145.2	146.6
C-9	184.7	184.8	183.8	186.4
C-10	58.1	58.0	55.3	55.0
C-11	120.8	120.8	121.0	120.7
C-12	144.9	145.0	145.2	145.0
C-13	8.8	8.8	7.9	8.4
C-14	17.8	17.7	18.3	17.7
C-15	9.0	8.9	9.0	7.6
C-16	176.5	176.4	176.6	170.8
C-17	34.7	34.6	34.7	21.5
C-18	18.8	18.8	18.8	—
C-19	18.8	18.8	18.7	—
C-20	167.5	170.6	—	—
C-21	128.5	21.3	—	—
C-22	136.6	—	—	—
C-23	15.7	—	—	—
C-24	20.7	—	—	—

ments of double resonance and nOe in a solution of **4** (Table 2).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points were determined on a Kofler hot stage apparatus and are uncorrected. Uv spectra were recorded in *n*-hexane solution using a Carl-Zeiss DMR instrument. Ir spectra were determined in CHCl_3 solutions using a Perkin-Elmer 552 spectrometer. ^1H - and ^{13}C -nmr spectra were recorded in a Bruker WP-200F spectrometer in CDCl_3 solution with TMS as internal standard. Mass spectra were obtained at 70 eV on a Hewlett-Packard 5985-B spectrometer. Optical rota-

TABLE 2. NOe Experiments of Compound **4**.

Irradiated proton	Effect (%)
H-6 α	H-10 α (5) and H-4 α (6.5)
Hs-15	H-4 α (3) and OAc (1.4)
Hs-14	H-6 α (1.5), H-1 β (5.9), H-3 β (2.3) and H-1 α (−0.5). Small effect to OAc.
H-10 α	H-6 α (2.8) and H-1 α (0.5)
H-1 α	H-1 β (8.0), H-2 α,β (1.3) and H-10 α (1)

tions were measured with a Perkin-Elmer 241 polarimeter.

PLANT MATERIAL.—*S. patagonicus* was collected in January 1983 in Cabo Negro, Punta Arenas, Chile (71°48' W, 52°56' S). *S. chilensis* was collected in February 1987 in Osorno Vulcanano, Chile (72°30' W, 41°06' S). Voucher specimens were deposited at the Museo de Historia Natural, Santiago, Chile.

EXTRACTION AND ISOLATION.—The powdered defatted sample (2.8 kg, leaves and twigs) was percolated with petroleum ether (60–80°). The extract was taken to dryness under reduced pressure. The petroleum ether extract (10 g) was chromatographed over Si gel (800 g) and eluted with petroleum ether/EtOAc mixtures to yield 32 fractions. Fractions F-5 to F-10 were stripped of solvent, leaving a white residue (1.20 g). Further purification was achieved on tlc [3 times, Si gel, hexane-EtOAc (9:1)] yielding **1** (15 mg), **2** (54 mg), and **3** (56 mg).

1 α -ANGELOXY-6 β -ISOBUTYROXY-9-OXO-10 α H-FURANOEREMOPHILANE [1].—Crystals from petroleum ether-EtOAc (9:1): mp 118–119°; $[\alpha]_D^{23}$, $[\alpha]_{589} - 35.3^\circ$, $[\alpha]_{578} - 40.6^\circ$, $[\alpha]_{546} - 52^\circ$, $[\alpha]_{436} - 156.6^\circ$, $[\alpha]_{365} - 796^\circ$ $c = 0.15$, CHCl₃; uv λ max (*n*-hexane) 269 nm ($\log \epsilon$ 4.27), sh 280 nm; ir ν max (CHCl₃) 1728, 1695, 1649, 1534 cm⁻¹; ¹H nmr δ (200 MHz, CDCl₃) 0.9 (d, 3H, $J = 7$ Hz, H-15), 1.0 (s, 3H, H-14), 1.24 (d, 3H, $J = 7$ Hz, H-18), 1.25 (d, 3H, $J = 7$ Hz, H-19), 1.42 (d, 1H, $J_{1\beta,2\beta} = 5$ Hz, H-2 β), 1.43 (d, 1H, $J_{1\beta,2\alpha} = 9$ Hz, H-2 α), 1.86 (d, 3H, $J = 1$ Hz, H-13), 1.95 (d, 1H, $J_{15,4\alpha} = 7$ Hz, H-4), 2.62 (qq, 1H, $J_{17,18}$ and $J_{17,19} = 7$ Hz, H-17), 2.73 (d, 1H, $J_{1\beta,10\alpha} = 10.5$ Hz, H-10 α), 5.34 (ddd, 1H, $J_{10\alpha,1\beta} = 10.5$ Hz, $J_{2\beta,1\beta} = 5$ Hz, H-1 β), 5.95 (qq, 1H, H-22), 6.39 (s, 1H, H-6 α), and 7.3 (q, 1H, $J_{12,13} = 1$ Hz, H-12); eims m/z [M]⁺ 416 (7.1), 83 (93.7), 71 (70), 43 (100).

HYDROGENATION OF 1.—Compound **1** (4.5

mg) was dissolved in EtOH and hydrogenated with catalytic amounts of Pd/C (5%) at 25° for 5 h. The crude product was filtered over Celite and then purified by cc [Si gel, *n*-hexane-EtOAc (1:1)]. The yield was 4 mg: ¹H nmr δ (200 MHz, CDCl₃) 0.9 (d, 3H, $J = 7$ Hz, H-15), 1.0 (s, 3H, H-14), 1.25 (d, 3H, $J = 7$ Hz, H-19), 1.24 (d, 3H, $J = 7$ Hz, H-18), 1.86 (d, 3H, $J = 1$ Hz, H-13), 2.62 (qq, 1H, $J_{17,19} = 7$ Hz, H-17), 2.70 (d, 1H, $J_{1\beta,10\alpha} = 10.5$ Hz, H-10 α), 5.32 (ddd, 1H, $J_{10\alpha,1\beta} = 10.5$ Hz, $J_{2\beta,1\beta} = 5$ Hz, H-1 β), 6.39 (s, 1H, H-6 α), 7.3 (q, 1H, $J_{12,13} = 1$ Hz, H-12).

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