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SESQUITERPENE LACTONES FROM *SYNCRETOCARPUS SERICEUS**

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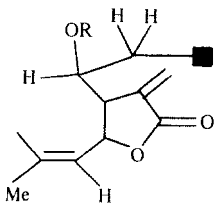
Key Word Index—*Syncretocarpus sericeus*, Compositae, Heliantheae, sesquiterpene lactones, heliangolides, carabrone; dihydrocarabrone

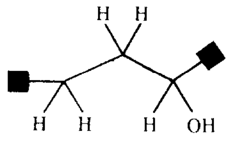
Abstract—The aerial parts of *Syncretocarpus sericeus* afforded in addition to known compounds a new heliangolide The chemistry supports the placement of this plant in the subtribe Helianthinae

Nothing is known on the chemistry of the genus *Syncretocarpus* (Compositae, tribe Heliantheae), which is placed in the subtribe Helianthinae [1] We have studied one species from Peru, *S sericeus* (DC) Blake

The aerial parts afforded germacrene D, dehydrofalcarinol (**1**) and its acetate (**2**) [2]. The polar fractions gave carabrone (**3**) [3, 4] and the corresponding carbinol, **4** [5], as well as two sesquiterpene lactones, the heliangolide, **6** [6], and the isobutyrate, **5** The latter was shown to be an isobutyrate by the typical ^{1}H NMR signals (Table 1). The IR spectrum showed the presence of a γ-lactone with a hydroxy and an ester group In the mass spectrum of **5** no molecular ion was visible. The very weak fragment at *m/z* 334 was formed by elimination of water as the fragment at *m/z* 264 ($C_{15}H_{20}O_4$) was the result of elimination of isobutyric acid Accordingly, fragments *m/z* 246 and 228 indicated a two-fold elimination of water Thus, the most likely molecular formula was $C_{19}H_{28}O_6$ The ^{1}H NMR spectrum supported this assumption as all signals could be assigned by spin decoupling. Irradiation of the signal at δ 3 35 collapsed the typical exomethylene doublets at 6 29 and 5 72 to singlets, the double doublet at 6.22 to a doublet and the signal at 5 37 to a double doublet, indicating that we were dealing with the signals of H-6–H-8 and H-13 of a germacranolide as H-6 was further coupled with a double quartet which itself was coupled with an olefinic methyl (1.72 *d*) Irradiation at δ 5 37 collapsed a pair of double doublets at 2 77 and 1 78 to doublets thus leading to sequence **A**



A



B

Irradiation of the three-fold doublet at δ 4.40 collapsed the doublet at 2 41 to a singlet, the four-fold doublet at 1 98 to a three-fold one and changed the multiplet at 1 78 As the proton which gave rise to the signal at 1 98 was further coupled with the protons which displayed three-fold doublets at 1 89 and 1 49, sequence **B** was established since, on deuterium exchange, the doublet at 2 41 disappeared and the signal at 4 40 became a double doublet Therefore, with a methyl singlet at 1 30 and a singlet at 2 11, which also disappeared by deuterium exchange, all signals were assigned The combination of these fragments led to the structure **5** as the chemical shift of the proton under the hydroxyl group required an allylic position Inspection of a model showed that the couplings observed agreed with the proposed stereochemistry Most probably the 10-hydroxyl group was hydrogen bonded leading to a stable conformation This assumption was

Table 1 ^{1}H NMR spectral data of compound **5** (400 MHz, $CDCl_3$, TMS as internal standard)

H-1α	1 89 *ddd*
H-1β	1 49 *ddd*
H-2α	1 98 *dddd*
H-2β	1 78 *m*
H-3	4 40 *ddd*
H-5	5 47 *dq*
H-6	6 22 *dd*
H-7	3 35 *dddd*
H-8	5 37 *ddd*
H-9α	2 77 *dd*
H-9β	1 78 *dd*
H-13	6 29 *d*
H-13′	5 72 *d*
H-14	1 30 *s*
H-15	1 72 *d*
O-i-Bu	2 43 *qq*, 1 05 *d*, 1 04 *d*
OH	2 41 *d*, 2 11 *s*

J (Hz) 1α, 1β = 13, 1α, 2α = 4, 1α, 2β = 9, 1β, 2α = 10, 1β, 2β = 4, 2α, 2β = 15, 2α, 3α = 5 5, 2β, 3α = 5, 3α, OH = 4, 5, 6 = 9 5, 5, 15 = 1, 6, 7 = 3 5, 7,8 = 3, 7, 13 = 2 5, 7, 13′ = 2, 8, 9α = 11, 8, 9β = 4, 9α, 9β = 15, 2′, 3′ = 2′, 4′ = 7

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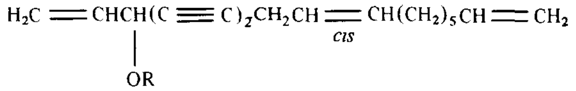
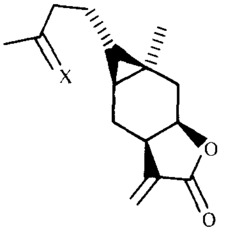
*Part 471 in the series "Naturally Occurring Terpene Derivatives" For Part 470 see Bohlmann, F, Ludwig, G-W, Jakupovic, J, King, R M and Robinson, H (1983) *Phytochemistry* **22**, 983



$$H_2C{=}CHCH(OR)(C{\equiv}C)_2CH_2CH\underset{cis}{=}CH(CH_2)_5CH{=}CH_2$$

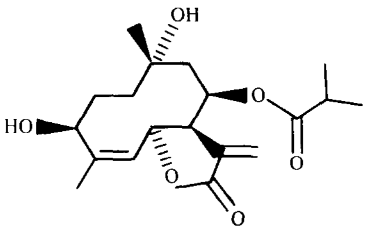
1 R = H

2 R = Ac

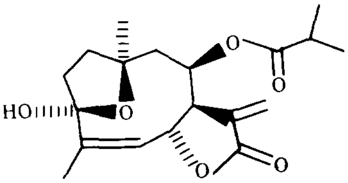


3 X = O

4 X = H,OH



5



6

supported by the IR spectrum (OH 3580 and CO_2R 1725 cm^{-1}). The ^1H NMR spectral data were close to those of the corresponding angelate which has been reported from *Helianthus maximiliani* [7]. Oxidation of **5** with manganese dioxide gave **6**.

The chemistry of the *Syncretocarpus* species agrees with that of the other genera in the subtribe Helianthinae where heliangolides are widespread (*Helianthus* [7–15], *Tithonia* [6, 8, 16–18] and *Viguiera* [2, 19–23]). Also dehydrofalcarinone-like acetylenes are present in nearly all genera of this subtribe so far investigated (*Helianthus*, *Hymenostephium*, *Lagascea*, *Simsia*, *Tithonia* and *Viguiera* [24]). However, a xanthanolide, has so far only been reported from a *Lagascea* species [25] in which diterpenes, that are widespread in the other genera of this subtribe [2, 12, 25–31], were absent.

EXPERIMENTAL

The air-dried aerial parts (260 g), collected in January 1982 in Peru (voucher RMK 9014, deposited in the U.S. National Herbarium, Washington) were extracted with Et_2O–petrol (1:2) and the extract obtained was treated with MeOH to remove saturated long chain hydrocarbons. After evaporation of the MeOH the residue was separated by CC (Si gel) and further by TLC (Si gel). Known compounds were identified by comparing the 400 MHz ^1H NMR spectra with those of authentic material. The less polar fractions afforded 5 mg germacrene D, 40 mg **1** and 40 mg **2**. The polar fractions gave 5 mg **3**, 8 mg **4**, 2 mg **6** and 30 mg **5** (Et_2O), colourless crystals, mp 164° (Et_2O), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580, 3400 (OH), 1760 (γ-lactone), 1725 (CO_2R, hydrogen bonded), MS m/z (rel. int.): 334 $[M-H_2O]^+$ (0.5), 264.136 $[M-RCO_2H]^+$ (8) ($C_{15}H_{20}O_4$), 246 $[264-H_2O]^+$ (13), 228 $[246-H_2O]^+$ (9), 213 $[228-Me]^+$ (7), 71 $[C_3H_7CO]^+$ (100).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-107 \quad -112 \quad -128 \quad -224}\ (CHCl_3;\ c\ 0.71)$$

Compound **5** (5 mg) was stirred for 1 hr with the MnO_2 in Et_2O. TLC afforded 3 mg **6**.

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TWO EUDESMANOLIDES FROM *SONCHUS MACROCARPUS**

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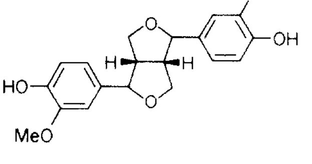
Key Word Index—*Sonchus macrocarpus*, Compositae, sesquiterpene lactones, eudesmanolides

Abstract—The aerial parts of *Sonchus macrocarpus* afforded, in addition to known triterpenes, two new eudesmanolides

Sonchus macrocarpus Boulos et Jeffrey so far has not been investigated chemically. The aerial parts afforded lupeyl acetate and its Δ^{12} isomer, β-amyrin and its acetate, lupeol, sitosterol and its glucoside, pinoresinol (**1**) and two sesquiterpene lactones, molecular formulae $C_{15}H_{20}O_4$ and $C_{15}H_{22}O_4$, which could not be separated. The ^{1}H NMR spectral data (Table 1), especially in deuteriobenzene, showed that the eudesmanolides **2** and **3** were present. The main compound, **2**, was obviously a methylene lactone because of the typical lowfield doublets at δ 5.97 and 4 83. Spin decoupling, starting with these two signals, allowed the assignment of all other signals. The presence of an aldehyde group at C-4 could be deduced from the doublet at 9.51 which was slightly shifted in the spectrum of **3**. The stereochemistry followed from the couplings observed Though the signals of the minor



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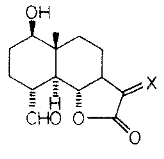

2 X = CH$_2$
3 X = α-Me,H

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*Part 480 in the series "Naturally Occurring Terpene Derivatives" For Part 479 see Bohlmann, F, Ates (Goren), N, King, R M and Robinson, H (1983) *Phytochemistry* **22** (in press).