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A FURTHER STEIRACTINOLIDE DERIVATIVE FROM *SPILANTHES LEIOCARPA*

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Key Word Index—*Spilanthes leiocarpa*, Compositae, sesquiterpene lactones, elemanolides, eudesmanolides

Abstract—The aerial parts of *Spilanthes leiocarpa* afforded, in addition to known compounds, a new eudesmanolide as well as two elemanolides which have both been isolated previously Careful ^1H NMR investigation showed that the configuration of one of these isomeric lactones has to be corrected

The genus *Spilanthes* (Compositae, tribe Heliantheae) is positioned in the subtribe Ecliptinae [1] So far only highly unsaturated amides have been reported as characteristic constituents of this genus [2, 3] We have now studied another species from Peru, *Spilanthes leiocarpa* DC The aerial parts gave β-isocomene, lupeyl acetate, caryophyllen-1,10-epoxide, alantolactone [4], onoseriolide [5], the isomeric elemanolides **2** [6] and **3** as well as the 11β,13-dihydro derivative callitrin [7] and the eudesmanolide **6** The spectral data of **3** are identical with those of an isomer of **2**, where, however, an 8,12-*trans*-lactone was proposed [8] Careful NOE difference spectroscopy clearly showed that the proposed configuration was incorrect and needs to be changed to that of **3** Irradiation of H-14 gave clear NOEs with H-6α, H-8, H-9α and H-2*t* A further elemanolide, named igalan [9], where no stereochemistry was proposed, may be identical with **2** or **3** However, the data were not sufficient for comparison

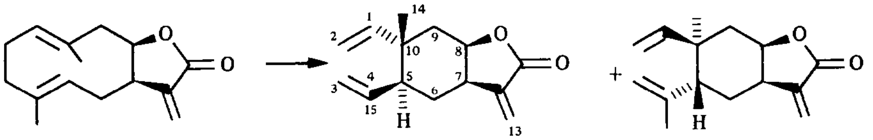
The molecular formula of **4** ($C_{15}H_{18}O_2$) indicated that an isomer of onoseriolide [5] was present Although some of the ^1H NMR signals of **4** were similar to those of the latter, it was obvious that the cyclopropane ring was missing Two pairs of double triplets indicated that this ring was replaced by an additional double bond Spin decoupling allowed the assignment of all signals (see Experimental)

Obviously all these lactones are derived from the unknown 8,12-*cis*-germacranolide **1**, which most likely would exist in two conformations If the methyls at C-4 and C-10 are both above the plane, Cope rearrangement would lead to **2**, while a conformation with both methyls below the plane would give **3** Similarly by transannular reactions alantolactone, onoseriolide or **4** may be formed

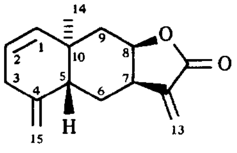
The isolation of sesquiterpene lactones, especially those with a 10α-methyl group, are of chemotaxonomic interest, as these compounds are typical for *Steiractinia* and *Wedelia* [10], which are both placed in the subtribe Ecliptinae [1]

EXPERIMENTAL

The air-dried aerial parts (150 g, voucher RMK 9089) were worked up in the usual fashion [11] The CC fractions were as follows 1 (petrol and Et_2O–petrol, 1 10), 2 (Et_2O–petrol, 1 3) and 3 (Et_2O) TLC of fraction 1 (petrol) gave 50 mg β-isocomene and 40 mg lupeyl acetate TLC of fraction 2 (Et_2O–petrol, 1 4)



1 **2** **3**



4

afforded 44 mg lupeyl acetate and 11 mg caryophyllen-1,10-epoxide, while TLC of fraction 3 (CH_2Cl_2–C_6H_6–Et_2O, 1 1 1) gave a mixture of **2**–**4** and the known compounds described in the text Separation by HPLC (RP 8, MeOH–H_2O, 3 2, flow rate *ca* 3 ml/min and 300 bar) gave a mixture of **4** and onoseriolide (I, R_t 10 1 min), a mixture of the latter, **2** and **3** (II, R_t 11 4 min) and a mixture of **2**, **3**, alantolactone and onoseriolide (III, R_t 12 2 min) TLC of I (SiO_2, $AgNO_3$-coated, Et_2O–petrol, 2 3, 2 developments) gave 4 mg of the latter and 2 5 mg **4** (R_f 0 3) TLC of II (SiO_2, $AgNO_3$-coated, Et_2O–petrol, 2 3, 2 developments) gave 2 5 mg onoseriolide, 2 1 mg **3** and 1 mg **2**, while TLC of III (SiO_2, $AgNO_3$-coated, Et_2O–petrol, 2 3, 2 developments) afforded 2 mg onoseriolide, 3 mg alantolactone and 2 5 mg **3**

1,2,4,15-*Tetradehydro*-4,5-*dihydrosteiractinolide* (**4**) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1770 (γ-lactone), MS m/z (rel int) 230 146 $[M]^+$ (5) (calc for $C_{15}H_{18}O_2$ 230 146), 215 $[M-Me]^+$ (2 5), 173 $[215-C_3H_6]^+$ (100), ^{1}H NMR ($CDCl_3$, 400 MHz, TMS as internal standard) δ5 39 *dt* (H-1), 5 52 *dt* (H-2), 2 89 *br d* and 2 74 *br dd* (H-3), 2 10 *br d* (H-5), 2 10 *br dd* (H-6), 1 93 *ddd* (H-6′), 3 33 *m* (H-7), 4 80 *ddd* (H-8), 2 15 *br d* (H-9), 1 33 *dd* (H-9′), 6 32 *d* and 5 54 *d* (H-13), 0 80 *s* (H-14), 4 93 and 4 71 *br s* (H-15), [J (Hz) 1, 2 = 10, 1, 3 = 2, 2, 3 = 3 5, 5, 6′ = 6, 6′ = 6′, 7 = 12, 5, 6 = 6, 7, 8 = 7, 3, 17 = 3 5, 7, 13′ = 3, 8, 9 ~ 7, 8, 9′ = 11, 9, 9′ = 13]

Callitrin [7] ^{1}H NMR ($CDCl_3$, 400 MHz) δ5 75 *dd* (H-1), 4 93 *dd* (H-2*c*), 4 89 *dd* (H-2*t*), 4 89 *dq* (H-3), 4 64 *br s* (H-3′), 1 67 *br d* (H-5), 2 06 *m* (H-6), 2 30 *m* (H-7), 4 60 *ddd* (H-8), 1 90 *dd* (H-9), 1 40 *dd* (H-9′), 2 56 *dq* (H-11), 1 20 *d* (H-13), 1 00 *s* (H-14), 1 72 *br s* (H-15), [J (Hz) 1, 2*c* = 10, 1, 2*t* = 17, 2*c*, 2*t* = 1, 3, 5 = 3, 15 = 1 5, 5, 6 = 12, 7, 8 = 8, 7, 11 = 12, 8, 9 = 6, 8, 9′ = 11, 9, 9′ = 14, 11, 13 = 7]

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FURTHER CADINENE DERIVATIVES FROM *HETEROTHECA LATIFOLIA*

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Key Word Index—*Heterotheca latifolia*, Compositae, sesquiterpenes, cadinene derivatives

Abstract—A reinvestigation of the aerial parts of *Heterotheca latifolia* afforded four new cadinene derivatives

So far the chemical investigations of *Heterotheca* species have shown that cadinene derivatives are characteristic for this genus [1, 2] A reinvestigation of the aerial parts of *H latifolia* Buckley afforded in addition to compounds isolated previously [1] the cadinene derivatives **1**–**4** which were isolated as their methyl esters (**1a**–**4a**) The structures of **1a** and **2a** could be deduced from the ^{1}H NMR spectral data (Table 1) which were close to those of the corresponding esters of **1a** [1] Also the ^{13}C NMR spectrum (see Experimental) supported the structure of **1a** which finally was established by saponification of the corresponding acetate [1] After addition of diazomethane, a methyl ester was obtained which was identical with **1a** The structures of **3a** and **4a** also could be deduced from the ^{1}H NMR spectra (Table 1) The presence of hydroperoxides followed from the low-field broadened singlets at δ7 45 and 7 28, respectively, while several signals were close to those of methyl-13-hydroxy-δ-cadinen-15-oate [1] However, in the spectrum of **3a** the Δ^9 bond was replaced by a 9,14-double bond, which followed from the typical signals of exocyclic olefinic protons Their chemical shifts already indicated that the hydroperoxy group