ν_{max}^{KBr} cm^{-1}: 3490, 1752, 1660, 1640, 975, 940, 900 and 830; UV λ_{max}^{MeOH} nm: 213 (ε 12500). (Calc. for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37; O, 19.51; MW, 246.1251. Found: C, 72.58; H, 7.08; O, 19.49%; MW(MS) 246.1266).

Acetylation of 20 mg **2a** (Py–Ac_2O) furnished 20 mg **2b** identical in all respects with material isolated directly from the plant. Oxidation of 25 mg **2a** in 2 ml Me_2CO with 0.5 ml Jones' reagent for 20 min at 0° and 15 min at room temp. gave 20 mg of material, mp 198°, identical in all respects with encelin.

The lower band from PLC gave solid material (**4a**) which crystallized from $CHCl_3$–hexane as needles (0.12 g), mp 178–80°; $[\alpha]_b$ +24.5° (*c* 2.1, $CHCl_3$); IR ν_{max}^{KBr} cm^{-1}: 3575, 1765, 1649, 973, 918 and 878; UV end absorption only: MS *m/e*: 250 (M^+), 235 (M – Me), 220, 107 (base peak), 93. The substance was identical with material prepared from 3-epiisotelekin [5].

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REVISION OF THE STRUCTURES OF CALEINE A AND B, GERMACRANOLIDE SESQUITERPENES FROM *CALEA ZACATECHICHI**

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Key Word Index—*Calea zacatechichi*; Compositae; Heliantheae; new germacranolide-type sesquiterpene lactones; caleine A; caleine B.

In a previous paper [1] we assigned the structures **1a** and **1b** to caleine A and B rather than the alternative structures **2a** and **2b**. Based on chemical transformations and spectroscopical data, mainly of the ^1H NMR, structures **2a** and **2b** were discarded based on the chemical shift parameters of H-2 and H-3. Since H-2 appears as a doublet at δ 6.61 (J = 11 Hz) and H-3 as a doublet of doublets at 6.01 (J = 11 Hz, J = 12 Hz) these chemical shifts are in disagreement with common α,β-unsaturated ketones, in which the β-protons generally absorb further downfield than the α-protons.

Most recently, the isolation and structure determination of neurolenins A and B by X-ray diffraction have been reported [2]. The structure of neurolenin B (**5e**) is very similar to the alternative structures **2a** and **2b** of the caleines. Comparison of the reported ^1H NMR spectral parameters with those of the caleines indicated close similarities (Table 1). These new findings led to a re-investigation of caleine A and B. Based on the following new results, we propose the revised structures **2a** and **2b** for the caleines but without assigning the stereochemistry. Reduction of caleine with sodium borohydride gave the diol **3** which, in the ^1H NMR spectrum, lacked the C-13 α-methylene signals and showed a new secondary methyl absorption. Oxidation of the diol **3** with periodic acid produced the α,β-unsaturated aldehyde **4** which exhibited chemical shifts expected for an α,β-unsaturated aldehyde in the ^1H NMR spectrum; a doublet of doublets at δ 5.9 (J = 11 Hz, J = 7.5 Hz) and a doublet of doublets at 6.39 (J = 11.5 Hz, J = 11.5 Hz), respectively were observed. Formation of the aldehyde **4** from caleine A and B provided unambiguous evidence for their structures **2a** and **2b** but without stereochemistry. The stereochemistry of **2a** and **2b** was assigned by comparison of the ^1H NMR data of **2a** and **2b** with neurolenin B whose structure had been determined by X-ray work [2]. Based on the newly obtained chemical data and the great similarities of the ^1H NMR spectral parameters of **2a** and **2b** with neurolenin B, we propose the stereostructures **5a** and **5b** for caleine A and B, respectively.

* Contribution No. 518 from Instituto de Quimica de la UNAM, Mexico.

Table 1. ^{1}H NMR data* of caleines, neurolenin B and caleine derivatives.

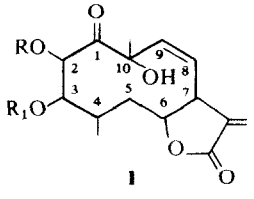
Compound	Caleines (**5a**, **5b**)	Neurolenin B (**5e**)	3†	4
1-H			4.30 *dd* (3, 1)	10.03 *d* (7.5)
2-H	6.61 *d* (12)	6.62 *d* (11)	5.14 *dd* (12, 3)	5.90 *dd* (11, 7.5)
3-H	6.01 *dd* (12, 11)	6.02 *d* (11)‡	4.90 *dd* (12, 10)	6.39 *dd* (11, 11)
4-H	3.13 *m*	3.12 *m*	3.58 *m*	3.50 *m*
5-H	ob	ob	1.48, 1.20 *m*	ob
6-H	4.59 *dd* (11, 5)	4.57 *dd* (11, 5)	4.70 *dd* (9, 6)	4.7 *m*
7-H	2.65 *brs*	2.63 *s*	4.20 *brd*(9)	2.65 *m*
8-H	5.70 *dd* (10, 2)§	5.57 *s*	5.71 *dd* (9, 1.5)	5.57 *t* (4.5)
9-H	5.58 *d* (10)§	5.57 *s*	5.54 *d* (9)	5.14 *d* (4.5)
13-H	6.31 *d* (1.5)	6.31 *d* (2)	1.16 *d* (7)	1.27 *d* (7)
13′-H	5.83 *d* (1.5)	5.82 *d* (2)		
14-H	1.34 *s*	1.34 *s*	1.1 *s*	2.22 or 2.17 *s*
15-H	1.12 *d* (6.5)	1.13 *d* (7)	0.84 *d* (7)	1.15 *d* (7)
3′-H	6.04 *qq* (7.5, 1.5)	ob	ob	6.22 *qq* (7)
4′-H	1.92 *qd* (7.5, 1.5)	0.86 *d* (7)	2.00 *dq* (7, 1.5)	2.01 *dq* (7, 1.5)
5′-H	1.74 *q* (1.5)	0.86 *d* (7)	1.92 *q* (1.5)	1.86 *q* (1.5)
OAc	2.01 *s*	2.09 *s*	1.75 *s*	2.22 or 2.17 *s*

* Run at 100 MHz in $CDCl_3$ with TMS as internal standard. Values are in ppm (δ). Values in parentheses are coupling constants in Hz. ob is obscured signal.

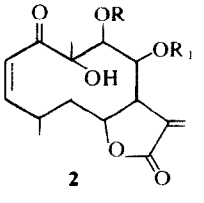
† Run in benzene-d_6.

‡ Reported as a doublet, but actually is a triplet or doublet of doublets.

§ AB pattern, no first order.



1



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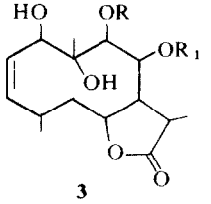

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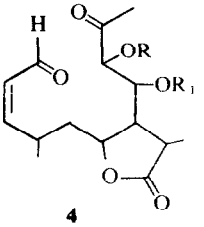

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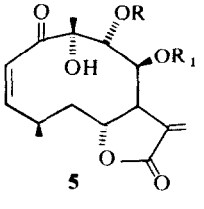

5

	R	R_1
a	Ac	Angelate
b	Angelate	Ac
c	Ac	Methacrylate
d	Methacrylate	Ac
e	Ac	*i*-Valerate

A later fraction, obtained during the isolation of caleine A and B, showed in the ^{1}H NMR spectrum signals typical for the methacrylate moiety with signals at δ 5.54 and 6.05 for the vinylic protons and an absorption at 1.82 due to the vinyl methyl group, the rest of the signals were the same as in caleines A and B. We named these new compounds caleines C (**5c**) and D (**5d**).

EXPERIMENTAL

Reduction of caleine (**5a**, **5b**) *with* $NaBH_4$. To a soln of caleine (50 mg) in 5 ml MeOH was added 50 mg $NaBH_4$ and the mixture allowed to react for 15 min. After dilution with H_2O and acidification with 5% aq. HCl, the aq. phase was extracted with EtOAc then washed with H_2O and dried. Evapn provided 45 mg of **3** as a gum. IR ν_{max}^{film} cm^{-1}: 3450, 1765, 1750, 1730, 1715,

1640. MS *m/e* (rel. int.): 424 (12.4, M^+) ($C_{22}H_{32}O_8$); 406 (0.6, M − 18), 364 (0.6, M − 60); 341 (1.3, M − 83); 325 (2.8, M − 99); 324 (2.8, M − 100); 282 (28.2, M − 142); 264 (9.1, M − 160); 83 (100.0, C_5H_7O); 55 (18.8, C_4H_7); 43 (14.4, C_2H_3O).

Oxidation of **3** *with periodic acid.* To a soln of the diol **3** in 15 ml Et_2O was added a saturated soln of periodic acid in Et_2O (10 ml). After 15 min the reaction mixture was washed with H_2O and dried. Evapn provided the α,β-unsaturated aldehyde **4**. UV λ_{max}^{MeOH} nm: 220 (ε = 8700); IR ν_{max}^{film} cm^{-1}: 1760, 1750, 1730, 1720, 1690. MS, *m/e* (rel. int.): 422 (2.7, M^+): 380 (1.8, M − 42); 362 (1.6, M − 60); 363 (1.5, M − 59); 339 (7.9, M − 83); 323 (73.2, M − 99); 83 (100.0, C_5H_7O); 55 (28.1; C_4H_7); 43 (41.5, C_2H_3O).

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SENOXYDEN, EIN NEUER SESQUITERPEN-KOHLENWASSERSTOFF AUS *SENECIO OXYODONTUS**

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Key Word Index—*Senecio oxyodontus*; Compositae; new sesquiterpene hydrocarbon; new carbon skeleton.

Kürzlich haben wir neben anderen Verbindungen aus den Wurzeln von *S. oxyodontus* einen Kohlenwasserstoff isoliert, dessen Konstitution nicht endgültig geklärt werden konnte [1]. Eingehende ^{1}H-NMR-spektroskopische Untersuchungen führen zu der Konstitution **3**, insbesondere, wenn man die Daten des aus **3** erhaltenen Epoxids **4** berücksichtigt (s. Tabelle 1). Doppelresonanz-Experimente bei **3** zeigen, daß die allylischen Protonen an C-1 jeweils mit einer Methylgruppe und zwei weiteren Protonen koppeln. Die Signallagen der Kopplungspartner zeigen klar, daß nur die Gruppierung A mit diesen Befunden vereinbar ist (s. Schema). Ungewöhnlich ist lediglich, daß auch eine Kopplung zwischen H_C und H_E vorhanden ist, während das Fehlen einer Kopplung zwischen H_C und H_D auf einen Winkel von *ca* 90° zwischen den beiden Wasserstoffen zurückgeführt werden kann, wie aus Modellbetrachtungen zu sehen ist. Da die Signale für H_A und H_C keine weiteren Kopplungen zeigen, müssen beide von quartären C-Atomen flankiert sein, während die Grösse der Kopplungskonstanten für $J_{A,B}$ und $J_{A',B}$ das Vorliegen eines Fünfringes erfordert. Diese Kopplungen sind im entsprechenden Epoxyd so klein, daß nur noch ein verbreitertes Singulett für H_B zu beobachten ist.

Die gleiche Situation liegt jedoch z.B. beim Estafiatin (**5**) vor [2] und auch hier beobachtet man keine vicinalen Kopplungen. Da beim Olefin das Kopplungsmuster nur mit der Gruppierung A gedeutet werden kann, muß beim Epoxid die Gruppierung B vorliegen. Systematische Doppelresonanz-Experimente beim Epoxid nach Zusatz von Eu(fod)$_3$ erlauben die Erweiterung der Partialstruktur **B** zur Konstitution **4**, wobei die Stellung der sekundären Methylgruppe aus den relativen Verschiebungen der entsprechenden Signale folgt. Die absolute Konfiguration kann jedoch nicht angegeben werden. In der Pflanze wird **3** evt. aus Humulen über **2** gebildet (s. Schema). Das Kohlenstoffgerüst ist bisher nicht

Tabelle 1. ^{1}H-NMR-Daten von **3** und **4** (270 MHz, TMS als innerer Standard)

	3 (C_6D_6)	($CDCl_3$)	**4** ($CDCl_3$)	+ Eu(fod)$_3$
1-H	*ddq* 2.62	*d(br)* 2.55	*d(br)* 1.57	*d(br)* 3.78
1′-H	*ddq* 2.55	*d(br)* 2.48	*d(br)* 1.40	*d(br)* 3.05
2-H	*ddq* 5.09	*s(br)* 5.13	*s(br)* 3.16	*s(br)* 8.69
4-H	*dddq* 2.40	*m* 2.32	*dd* 1.88	*dd* 6.14
5-H	*dd* 2.35		*m* 1.96	*dd* 4.14
5′-H	*m* 1.88	*m* 1.9		*dd* 3.98
7-H	*dd* 1.75	*dd* 1.78	*dd* 1.70	*dd* 2.80
9-H	*dq* 1.88	*dq* 1.98	*dq* 2.05	*dq* 4.40
10-H	*m* 1.45	*m* 1.66		
10′-H	*dd* 1.15	*dd* 1.20	*dd* 1.18	*m* 3.17
11-H	*m* 1.45	*m* 1.66		*dd* 2.11 *m* 2.41
12-H	*s* 1.08	*s* 1.08	*s* 1.11	*s* 1.86
13-H	*s* 1.21	*s* 1.17	*s* 1.19	*s* 2.14
14-H	*d* 0.98	*d* 0.84	*d* 1.07	*d* 4.08
15-H	*ddd* 1.61	*ddd* 1.60	*s* 1.32	*s* 4.06

J (Hz): bei **3**: 1,1′ = 13; 1,2 = 1,2′ = 1,15 = 1′,15 ~ 2; 1,4 = 1′,4 = 1; 4,5 = 8; 4,5′ = 2; 4,15 = 1; 5,5′ = 11.5; 7,11 = 7,11′ = 3; 9,10 = 10,12 = 7; 10,10′ = 13; bei **4**: 1,1′ = 13; 4,5 = 8; 7,11 = 7,11′ = 3; 9,10 = 10,12 = 7; 10,11 = 7; 11,11′ = 14.

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