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ON THE NATURAL OCCURRENCE OF 15α-TIGLINOYLOXY-KAUR-16-EN-19-OIC ACID

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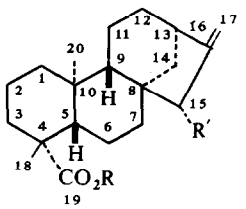
Key Word Index—*Wedelia scaberrima*; Compositae; kaur-16-en-19-oic acid; molluscicide; 15α-tiglinoyloxy-kaur-16-en-19-oic acid; miracidicide; ^{13}C NMR.

The observation that a hexane extract of *Wedelia scaberrima* Benth. showed activity against snails prompted a chemical examination in an effort to identify the active constituents. Kaur-16-en-19-oic acid **1** and 15α-tiglinoyloxy-kaur-16-en-19-oic acid **2** could be isolated. Working on *Wedelia* species, Bohlmann *et al.* [1] prepared the methyl ester of compound **2** from a complex acid mixture.

Compound **2** has a tigloyl group CH_3—CH=C(CH_3)-COO^- confirmed by MS (base peak *m/e* = 83, 100%, $C_4H_7CO^+$) and by ^{1}H NMR spectrum which exhibited signals at 6.84 (*m*, 1H) and 1.83 (*s*, 6H′ s)δ. Double resonance studies showed that irradiation of the methyl signals resulted in the collapse of the vinyl proton multiplet to a singlet and irradiation of the vinyl proton signal resulted in the opening of the singlet methyl protons to a double singlet signal. The hydrolysis product of **2** was 15α-hydroxy-kaur-16-en-19-oic acid $C_{20}H_{30}O_3$ (*m/e*, 318); mp 232–234° (lit. 228–230°) [2].



1 R = R′ = H
2 R = H; R′ = tigl. = —$O_2C^{1'}$—$C^{2'}$(H)=$C^{3'}$(CH_3)(CH_3)
3 R = H; R′ = OH
R = Me; R′ = tigl.

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Table 1. ^{13}C-NMR spectrum of **2***

C-1	40.80 *t*	C-14	37.67 *t*
C-2	18.55 *t*	C-15	83.35 *d*
C-3	37.87 *t*	C-16	156.48 *s*
C-4	43.98 *s*	C-17	110.67 *t*
C-5	56.96 *d*	C-18	29.02 *q*
C-6	20.95 *t*	C-19	185.81 *s*
C-7	35.14 *t*	C-20	15.88 *q*
C-8	48.08 *s*	C-1′	169.16 *s*
C-9	53.28 *d*	C-2′	129.80 *s*
C-10	40.09 *s*	C-3′	137.93 *d*
C-11	19.13 *t*	C-4′	14.45 *q*
C-12	32.86 *t*	C-5′	12.24 *q*
C-13	42.83 *d*		

* Run in $CDCl_3$.

The ^{13}C NMR spectrum (Table 1) of the tigloyl ester confirmed its structural identity. The absorption at 185.81 ppm as a singlet, proved the presence of the other two oxygens in the molecule in total agreement with the MS (*m/e* = 400, 7%, $C_{25}H_{36}O_4$). Treatment of **2** with diazomethane gave the methyl ester **4** whose ^{1}H NMR spectrum exhibited the signal of a methyl group at 3.64δ, confirming the presence of the carboxylic acid in **2**.

Pakraski *et al.* isolated the 15α-angeloyloxy-kaur-16-en-19-oic [3] from *Enhydra fluctuans* Lour. In an attempt to synthesize the ester, the isomeric tiglate was obtained.

Tests performed with the isolated compounds showed **1** to be molluscicidal (against *Biomphalaria glabata*) and **2** miracidicidal (against miracidia of *Schistosoma mansoni*).

EXPERIMENTAL

The leaves of *Wedelia scaberrima* Benth. (3 kg) were collected in Fortaleza, Ceará State, Brasil (May, 1977). The dry powdered plant material was exhaustively extracted with hexane to yield a green tar (165 g). Chromatography of the crude extract (50 g) on Si gel (1.5 kg) gave fraction A eluted with $CHCl_3$–EtOAc (8:2) and fraction B eluted with $CHCl_3$–EtOAc (7:3), which partly crystallized. Fraction A furnished kaur-16-en-19-oic acid **1** [4].

15α-Tiglinoyloxy-kaur-16-en-19-oic acid **2**. Fraction B (15 g) still contaminated with **1** and was therefore rechromatographed on Si gel (650 g). The fraction that eluted with hexane–$CHCl_3$ (6:4) was recrystallized in hexane–EtOAc (0.5 g) mp 173–175°, α_D^{23} − 73° (*c* 1.0; EtOH). UV λ_{max}^{EtOH} 212 nm (ε = 32000); $\nu_{max}^{CHCl_3}$ 3333–2500, 1701 (COOH); 1701, 1658, 1258, 1139, 725 (tiglate) 910(=CH_2) cm^{-1}. ^1H NMR: δ 6.84 (*m*, H-3'), 5.33 (*s br*, H-15β), 5.08 and 5.12 (*s*, H-17 and H-17'), 2.80 (*m*, H-13), 1.83 (*s*, C-4', C-5' methyls), 1.23 (*s*, C-18 methyl), 0.97 (*s*, C-20 methyl). MS showed peaks at *m/e* 400 (7%); $-C_4H_7COOH$ 300 (32%) $-CH_3$ 285 (25%); $-C_4H_7CO^+$ 83 (100%); $-C_3H_8^+$ 44 (59%). (MW calc. for $C_{25}H_{36}O_4$: C, 74.96; H, 9.06. Found: C, 75.16; H, 9.37%).

15α-Hydroxy-kaur-16-en-19-oic acid **3**. **2** was hydrolysed at 90°, for 1 hr, in EtOH–KOH (5%). Work up in the usual way gave the alcohol derivative mp 232–234° [2].

Methyl 15α-tiglinoyloxy-kaur-16-en-19-oate **4**. **2** was methylated with CH_2N_2 in Et_2O, at room temp, for 15 min, yielded the ester **4**. The methyl ester, on recrystallization from petrol, melted at 111–113° [1].

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EIN UNGEWÖHNLICHES TETRAHYDROFURAN-DERIVAT AUS *HELICHRYSUM AUREO-NITENS*

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Key Word Index—*Helichrysum aureo-nitens*; Compositae; new furan derivative; unusual carbon skeleton.

Die Wurzeln von *Helichrysum aureo-nitens* Sch. Bip. enthalten neben Squalen einen optisch aktiven Alkohol, den wir Aureonitol nennen möchten, mit der Summenformel $C_{13}H_{18}O_2$, und der mit Acetanhydrid ein Acetat liefert. Alle Daten sind nur vereinbar mit der Konstitution **1**. Das ^1H-NMR-Spektrum des Acetats **2** (s. Tabelle 1) ist erst in einem Gemisch von Benzol–Chloroform erster Ordnung interpretierbar. Modell-Betrachtungen zeigen, daß die beobachteten Kopplungen nur mit einer *cis*-Stellung der Wasserstoffe an C-6 bis C-8 vereinbar sind. Die Kopplungen sind im Spektrum von **1** etwas verändert, was auf eine geringfügige Änderung der Konformation beim Übergang in das Acetat zurückzuführen sein dürfte. Die absolute Konfiguration ist unbekannt. Auch die oberirdischen Teile enthalten **1** sowie die Kohlenwasserstoffe **3**–**5**, Caryophyllenepoxid (**6**) und kleine Mengen nicht identifizierter Triterpene.

Das Kohlenstoffgerüst von **1** ist ungewöhnlich. Es könnte sich um eine Verbindung handeln, bei der auf dem Wege der Fettsäurebiogenese das Kohlenstoffatom einer Malonyleinheit erhalten geblieben ist (**8**), und daß dann reduziert worden ist. Epoxidierung der nachbarständigen Doppelbindung (**9**) könnte nach Ringöffnung des Epoxids zum Tetrahydrofuranderivat führen. Als Alternative wäre der Einbau einer Propionat-Einheit denkbar.

Tabelle 1. ^1H-NMR-Signale von **1** und **2** (270 MHz, TMS als innerer Standard)

	1 ($CDCl_3$)	**2** ($CDCl_3$)	**2** C_6D_6/$CDCl_3$ 2:1
1-H	*d(br)* 1.75	*d(br)* 1.75	*d(br)* 1.60
2-H	*dq* 5.68	*dq* 5.66	*dq* 5.52
3-H	*ddq* 6.04	*ddq* 6.01	*ddq* 5.92
4-H	*dd(br)* 6.12	*dd(br)* 6.12	*dd(br)* 6.04
5-H	*dd* 5.43	*dd* 5.47	*dd* 5.38
6β-H	*dddd* 2.85	*dddd* 2.94	*dddd* 2.81
7β-H	*dd(br)* 3.76	*dd* 4.88	*dd* 4.91
8β-H	*dd(br)* 4.14	*dd(br)* 4.34	*dd(br)* 4.35
9-H	*m* 5.74*	*m* 5.75*	*dd* 5.77
10-H	*m* 6.38*	*m* 6.30*	*ddd* 6.37
11-H	*m* 6.32*	*m* 6.25*	*ddd* 6.27
12*t*-H	*d(br)* 5.25*	*d(br)* 5.24*	*dd(br)* 5.13
12*c*-H	*d(br)* 5.13*	*d(br)* 5.13*	*dd(br)* 4.99
13-H	*dd* 4.11	*dd* 4.08	*dd* 3.94
13'-H	*dd* 3.72	*dd* 3.80	*dd* 3.69
OAc	—	*s* 2.08	*s* 1.75
OH	*s(br)* 1.56	—	—

J(Hz): 1,2 = 7; 1,3 = 1.5; 2,3 = 15; 3,4 = 10.5; 4,5 = 15; 5,6 = 8; 6,7 = 4; 6,13 = 6.5; 6,13' = 6.0; 7,8 = 4; 8,9 = 5.5; 8,10 = 1.3; 9,10 = 14.5; 10.11 = 11; 11,12*t* = 17; 11,12*c* = 10; 12*t*, 12*c* = 1.8; 13,13' = 9; bei **1**: 5,6 = 6,7 = 6, 13 = 6,13' = 13,13' = 8; 7,8 = 8,9 = 7.

* Nicht 1. Ordnung.