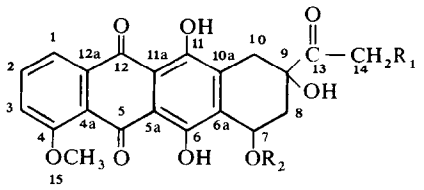

Compound	R_1	R_2
1	H	1'-α-(3-amino-2,3,6-trideoxy-L-lyxosyl)
2	OH	1'-α-(3-amino-2,3,6-trideoxy-L-lyxosyl)
3	H	H
4	OH	H

Table 1. Carbon chemical shifts, Δ (ppm) and labelling pattern found for the aliphatic sidechains of 3 and 4

Carbon No.	Daunomycinone (3) unlabelled	labelled	Adriamycinone (4) unlabelled	labelled
7	60.5		60.4	
8	35.6		36.2	
9		76.2		76.2
10	31.9		32.5	
13	211.8		213.6	
14	24.4		64.1	

Δ run in DMSO-d_6, results are reported relative to TMS using the relationship δ(TMS) = δ(DMSO-d_6) − 39.5 ppm.

one (4), respectively. The ^{13}C-NMR chemical shift assignments for the aliphatic sidechains of both aglycones are summarized in Table 1 and are based upon literature values [4].

A comparison of the intensities of the appropriate signals in spectra of the labelled and unlabelled compounds revealed that, in both cases, the quaternary aliphatic ring carbon (C-9, 76.2 ppm) was enriched *ca* 10-fold. This result constitutes direct support for the postulate that a propionate (C-15, C-14 and C-9) 'starter' is directly involved in the biosynthesis of both daunomycin and adriamycin in this organism. A similar result has been observed for the related metabolite ξ-pyrromycinone using ^{14}C-tracer studies [5].

EXPERIMENTAL

Culture. The source of *Streptomyces peucetius* var. *caesius* (IMRU No. 3920) and conditions used for its maintenance have been described [2].

Isotopic incorporation studies. Submerged production cultures of *S. peucetius* var. *caesius* were grown at 28° in 300 ml flasks containing 40 ml medium and stirred on a shaker rotating at 220 rpm with a 7 cm radius [2]. 48 hr after inoculation, 40 mg sodium propionate [1-^{13}C] (90 atoms % ^{13}C, Merck) was added to each flask. After a further 72 hr incubation the whole culture was exhaustively extracted as previously described [2]. Mild acid hydrolysis of crude 1 and 2 with 0.1 N HCl at 100° for 20 min gave a mixture of dark red coloured aglycones, 3 and 4. Each metabolite was separated and purified by repeated PLC on Si gel developed with $CHCl_3$–Me_2CO (4:1). PFT-^{13}C-NMR spectra were recorded on a Varian XL100 (25.2 MHz) spectrometer using DMSO-d_6 as solvent.

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NEUE TREMETON-DERIVATE AUS *DORINICUM MACROPHYLLUM*

FERDINAND BOHLMANN und MICHAEL GRENZ

Institut für Organsiche Chemie der Technischen Universität Berlin, Straße des 17. Juni 135, D-1000 Berlin 12, W. Germany

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Key Word Index—*Doronicum macrophyllum*; Senecioneae; Compositae; new tremetone derivatives; benzfurans.

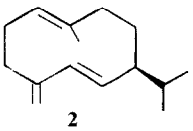
Bisher sind aus Vertretern der Gattung *Doronicum* (Tribus Senecioneae) neben dem weitverbreiteten Pentainen (**1**) [1] aus einer Art Thymol- und Tremeton-Derivate [2] isoliert worden.

Auch die Wurzeln von *Doronicum macrophyllum* enthalten neben **1–4** die Thymolderivate **9–11** und die Tremeton-Derivate **17** und **18**. Daneben isoliert man drei weitere derartige Verbindungen, denen nach den spektroskopischen Daten die Konstitutionen **15**, **16** und **21** zukommen (s. Tabelle 1).

Die oberirdischen Teile, aus denen bereits das Pyrrolizidin-Alkaloid Doronin isoliert wurde [3], ergeben neben **1**, **2–8**, **12** und **16–18** zwei weitere Tremeton-Derivate, denen die Konstitutionen **19** und **20** zukommen (s. Tabelle 1). Die Stellung der phenolischen OH-Gruppe ergibt sich aus der Lage und der Kopplung der aromatischen Protonen-Signale.

Die vorliegenden Ergebnisse geben keine neuen Anhaltspunkte über eine mögliche Umgruppierung dieser Gattung in eine andere Tribus. Ähnliche Tremeton-

1



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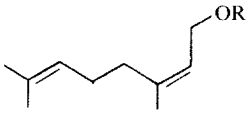
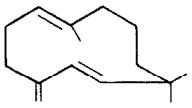


3 R = iBu [4]
4 R = Mebu [4]



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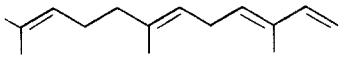

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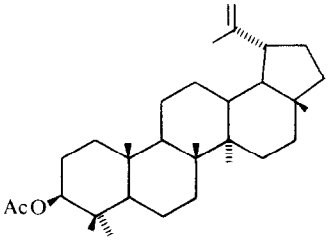

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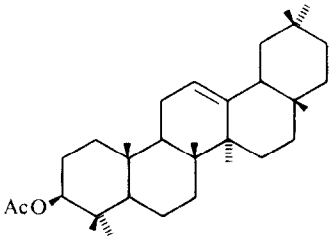

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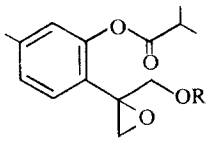
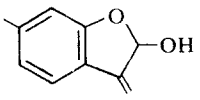


9 R = Ac [5]
10 R = iBu [6]
11 R = Mebu [7]



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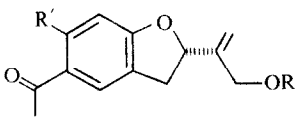
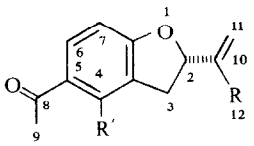


	13 [2]	**14** [2]	**15**
R	iBu	Mebu	Mebu
R′	H	H	OH



	16	**17** [2]	**18** [2]	**19**	**20**	**21**
R	CH_2OH	CH_2OiBu	CH_2OMebu	CH_2OAc	CHO	CHO
R′	OH	OH	OH	OH	OH	H

Tabelle 1. ^{1}H-NMR-Spektren von **15**, **16**, und **19**–**21** (270 MHz, $CDCl_3$, TMS als innerer Standard)

	15	**16**	**19**	**20**	**21**
2-H	*dd(br)* 5.37	*dd(br)* 5.48	*dd* 5.44	*dd(br)* 5.68	*dd(br)* 5.64
3-H	*dd* 3.28	*dd* 3.41	—	*dd* 3.60	*dd* 3.68
3′-H	*dd* 3.11	*dd* 3.10	—	*dd* 2.88	*dd* 2.94
4-H	*t* 7.51	—	—	—	*dt* 7.82
6-H	—	*d* 7.61	*d* 7.62	*d* 7.64	*dd* 7.84
7-H	*s* 6.38	*d* 6.41	*d* 6.50	*d* 6.47	*d* 6.90
9-H	*s* 2.55	*s* 2.56	*s* 2.57	*s* 2.57	*s* 2.55
11-H	*s(br)* 5.34	*s(br)* 5.28	*s(br)* 5.36	*d* 6.52	*d* 6.56
11′-H	*s(br)* 5.28		*s(br)* 5.30	*d* 6.18	*d* 6.19
12-H	*d* 4.71 *d* 4.64	ABq 4.27	*s* 4.70	*s* 9.66	*s* 9.66
OH	*s* 12.97	*s* 12.74	*s* 12.75	*s* 12.70	—
OCOR	*tq* 2.39	—	*s* 2.06	—	—
	dq 1.67	—			
	dq 1.48	—			
	t 0.90	—			
	d 1.15	—			

J(Hz): 2,3 = 9.5; 2,3′ = 7.5; 3,4 = 1; 4,6 = 1.5; 6,7 = 8; bei **15**: 12,12′ = 12.5; 2′,3′$_1$ = 2,3′$_2$ = 2′,5′ = 7; 3′$_1$,3′$_2$ = 14; 3′,4′ = 7; bei **20**/**21**: 2,11 = 1.5; 2,11′ = 1.

Derivate findet man auch in mehreren *Senecio*-Arten, so daß zusammen mit dem Vorkommen von Pyrrolizidinalkaloiden die Eingruppierung in die Tribus Senecioneae gerechtfertigt ist.

EXPERIMENTELLES

IR: Beckman IR 9, CCl_4; ^{1}H-NMR: Bruker WH 270; MS: Varian MAT 711, 70 eV. Direkteinlaß. Die frisch zerkleinerten Pflanzenteile (angezogen aus Samen vom Botanischen Garten Nijmegen) wurden mit Ether/Petrol 1:2 extrahiert und die erhaltenen Extrakte zunächst durch SC (Si gel Akt. St. II) und weiter durch mehrfache DC (Si gel GF 254) aufgetrennt. Als Laufmittel dienten Et_2O/Petrol-Gemische. Bereits bekannte Substanzen identifizierte man durch Vergleich der IR- und ^{1}H-NMR-Spektren mit denen authentischer Verbindungen.

1 kg Wurzeln ergaben 5 mg **1**, 15 mg **2**, 50 mg **3** und **4** (*ca* 3:1), 38 mg **10** und **11** (*ca* 4:1), 20 mg **9**, 12 mg **15** (Et_2O/Petrol 1:1), 23 mg **21** (Et_2O/Petrol 1:1) 13 mg **16** (Et_2O/Petrol 1:1) und 150 mg **17** und **18** (*ca* 5:1). 3 kg oberirdische Teile lieferten 1 mg **1**, 20 mg **2**, 45 mg **5**, 50 mg **6**, 17 mg **3** und **4** (*ca* 3:1), 19 mg **12**, 5 mg **19** (Et_2O/Petrol 1:1), 10 mg **20** (Et_2O/Petrol 1:1), 20 mg **17** und **18** (*ca* 4:1), 5 mg **16** und 280 mg **7** und **8** (*ca* 1:1).

6,12-*Dihydroxytremeton*-12-*O*-[2-*methylbutyrat*] (**15**). Farbloses Öl, IR: CO_2R 1740; PhCO (brückengebunden) 1640 cm^{-1}. MS: M^+ *m/e* 318.147 (6%) (ber. für $C_{18}H_{22}O_5$ 318.147); $-C_4H_9CO_2H$ 216 (26); $C_4H_9CO^+$ 85 (50); 85 $-$ CO 57 (100).

4,12-*Dihydroxytremeton* (**16**). Farbloses Öl, IR: OH 3620; PhCO (brückengebunden) 1645 cm^{-1}, MS: M^+ *m/e* 234.089 (56%) (ber. für $C_{13}H_{14}O_4$ 234.089); $-H_2O$ 216 (35); 216 $-$ $^{\cdot}$Me 201 (26); $C_3H_7^+$ 43 (100).

4-*Hydroxy*-12-*acetoxytremeton* (**19**). Farbloses Öl, IR: OAc 1750, 1230; PhCO (brückengebunden) 1645 cm^{-1}. MS: M^+ *m/e* 276.100 (5%) (ber. für $C_{15}H_{16}O_5$ 276.100); $-$ AcOH 216 (38): 216 $-$ $^{\cdot}$Me 201 (13); $MeCO^+$ 43 (100).

4-*Hydroxy*-12-*oxotremeton* (**20**). Farblose-Kristalle, Schmp. 80° (Petrol) IR: C=CCHO 2740, 2700, 1695, 1620; PhCO (brückengebunden) 1650 cm^{-1} MS: M^+ *m/e* 232.074 (100%) (ber. für $C_{13}H_{12}O_4$ 232.074); $-$ $^{\cdot}$Me 217 (25); $-$CO 204 (27); 176 $-$ $^{\cdot}$Me 161 (79).

12-*Oxotremeton* (**21**). Farbloses Öl, IR: CHO 2700, 1695; PhCO 1685, 1600 cm^{-1}, MS: *m/e* 216.079 (100%) (ber. für $C_{13}H_{12}O_3$ 216.079); $-$ $^{\cdot}$Me 201 (92); 201 $-$ CO 173 (21); 173 $-$ CO 145 (82).

Anerkennung—Der Deutschen Forschungsgemeinschaft danken wir für die Förderung dieser Arbeit.

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A NEW CHROMONE GLUCOSIDE FROM *TECOMELLA UNDULATA*

V. K. GUJRAL, S. R. GUPTA* and K. S. VERMA
Department of Chemistry, University of Delhi, Delhi-110007, India

(*Received* 23 *June* 1978)

Key Word Index—*Tecomella undulata*; Bignoniaceae; 2-methyl-5,7-dihydroxychromone 7-*O*-β-D-glucopyranoside.

Previous investigations [1–4] of the genus *Tecomella* have revealed the presence of lapachol, dehydrotectol, *n*-hentriacontanol, *n*-heptacosane, *n*-nonacosane, tecomin and tecomelloside. We now report the isolation and structure determination of a new chromone glucoside from the bark of *T. undulata*.

EtOAc insoluble portion of the alcoholic extract of the bark (2 kg) was dissolved in a minimum amount of MeOH and dry ether was added with constant shaking. The precipitate thus obtained on column chromatography over Si gel using ($CHCl_3$–MeOH, 4:1) as eluent yielded the new compound as an amorphous powder, 500 mg; mp 235–37°; $[\alpha]_D^{27}$ −169.0 (*c*, 0.71, MeOH) (Found: C, 51.4; H, 5.1. $C_{16}H_{18}O_9 . H_2O$ requires: C, 51.6; H, 5.4%); R_f: 0.54 (EMW, 100:16.5:13.5); 0.39 ($CHCl_3$–MeOH, 9:1); 0.5 (EtOAc–EtCOMe–HCO_2H–H_2O, 5:3:3:1); 0.33 (EtOAc–MeOH, 5:1). It gave brown ferric reaction and positive Molisch's test. IR(KBr) showed strong absorptions at 1660 cm^{-1} (chelated >C=O) and 3450 cm^{-1}. MS exhibited M^+ 354 and an aglycone peak formed by the loss of a six carbon sugar. These observations coupled with UV spectrum (λ_{max}^{MeOH} (log ε) 255(4.15), 285(3.85), 315(3.6); $AlCl_3$, 255(sh), 302, 362; $AlCl_3$–HCl, 255(sh), 302, 362; NaOAc, 255(sh), 341 nm) indicated it to be a chromone glycoside. It formed a pentaacetate, mp 129–30° (Py/Ac_2O); $[\alpha]_D^{22}$ −100.2 (*c*, 0.2, $CHCl_3$). NMR (60 MHz, δ) ($CDCl_3$) 2.05(*b*, 12H, four alcoholic acetoxyls), 2.32(*s*, 3H, phenolic acetoxyl), 2.43(*s*, $C\underline{H}_3$ at C-2), 6.84(*d*, J = 2.5 Hz, 1H at C-8), 6.71(*d*, J = 2.5 Hz, 1H at C-6), 6.12(*s*, 1H at C-3), 4.9–5.6(sugar protons).

Acid hydrolysis gave an aglycone, mp 280–81°, M^+ 192, $C_{10}H_8O_4$ and a sugar unit identified as glucose

*To whom correspondence should be addressed.