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NEUE NORSESQUITERPENE AUS *RUDBECKIA LACINIATA* UND *SENECIO PALUDAFFINIS**

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Key Word Index—*Rudbeckia laciniata*; *Senecio paludaffinis*; Compositae; new norsesquiterpenes, new endoperoxides.

Die Wurzeln von *Rudbeckia laciniata* L. enthalten neben dem weitverbreiteten Pentainen **5** [1], den Eudesmanoliden **7** [2] und **8** [3] sowie den Sesquiterpenen **1–3** das Endoperoxid **6**, während die oberirdischen Teile neben **3**, **4**, **10–15** und **23** das Norsesquiterpen **9** liefern.

Die Konstitution von **9** folgt klar aus den ^{1}H-NMR-Daten, insbesondere, wenn man auch unter Zusatz von Eu(fod)$_3$ Doppelresonanz-Experimente durchführt. Obwohl nicht alle Signale 1. Ordnung interpretierbar sind, lassen sich so alle Signale eindeutig zuordnen (s. Tabelle 1). Zweifellos ist **9** ein Abbauprodukt von **3**. Wir möchten **9** Rudbeckianon nennen.

Die Konstitution von **6** folgt wiederum aus den NMR-Daten, die denen von Ascaridol weitgehend entsprechen. Die zusätzlichen Signale zeigen jedoch das Vorliegen einer Dimethylallyl-Seitenkette. Offenbar ist **6** ein Isomerengemisch, da einige NMR-Signale doppelt erscheinen (s. Tabelle 2). Im MS fehlt das Molekül-Ion, dafür erkennt man das Fragment $M^+ - O_2$. Mit Alanat erhält man ein Diol, das jedoch im MS ebenfalls kein Molekül-Ion zeigt. Auch unter CI-Bedingungen beobachtet man nur $M - H_2O + 1$ und $M - 2H_2O + 1$-Ionen.

Eine analoge Verbindung, mit Norsesquiterpen-Grundstruktur, haben wir aus den oberirdischen Teilen von *Senecio paludaffinis* Hilliard neben **1**, **19**, **21** und Sesamin isoliert. Die spektroskopischen Daten zeigen, daß es sich hier um das Endoperoxid von *Senedigitalen* (**21**) [6] handeln muß (**22**) (s. Tabelle 2). Wiederum beobachtet man im MS kein Molekül-Ion. Chemische Ionisation liefert jedoch das M + 1-Ion. Auch hier liegt wieder ein Isomerengemisch vor.

Tabelle 1. ^{1}H-NMR-Daten von **9**.

	$CDCl_3$	C_6D_6	Δ
1-H	*ddq* 5.27	*dd*(*br*) 4.92	0.45
2-H	*m* 2.27	*m* 2.10	0.76
3-H	*m* 2.61	*m* 2.39	1.26
5-H	*d* 5.84	*d* 5.92	1.47
6-H	*d* 6.50	*d* 6.13	0.66
7-H	*m* 1.58	*m* 1.2	~0.2
8-H	*m* 1.46		
9-H	*m* 2.02	*m* 1.78	0.23
12,13-H	*s* 1.04	*s* 0.76	0.22
14-H	*d* 1.34	*d* 1.20	0.48

J(Hz): 1, 2 = 8; 1, 14 = 1; 5, 6 = 16.

Tabelle 2. ^{1}H-NMR-Daten von **6** und **22** (270 MHz, $CDCl_3$).

	6	**22**	Ascaridol
2-H	*d* 6.48 *d* 6.49	*d* 6.49 *d* 6.48	*d* 6.51
3-H	*d* 6.41	*d* 6.42	*d* 6.42
5,6-H	A_2B_2 *m* 2.03	A_2B_2 *m* 2.02	A_2B_2 *m* 2.04
7-H	*m* 1.7	*m* 1.73	*tq* 1.93
8-H	*m* 1.55	*m* 1.55	—
9-H	*m* 2.01		
10-H	*t*(*br*) 5.09	*m* 2.01	
11-H	—	*ddt* 5.81	
12-H	*s*(*br*) 1.60	*d*(*br*) 4.94, *d*(*br*) 5.00	
13-H	*s*(*br*) 1.68		
14-H	*d* 0.99 *d* 0.98	*d* 0.97 *d* 0.98	*d* 1.01
15-H	*s* 1.37	*s* 1.37	*s* 1.38

J(Hz): 2, 3 = 8.5; 7, 14 = 7; 9, 10 bzw. 10, 11 = 7.

EXPERIMENTELLES

IR: Beckman IR 9, CCl_4; ^{1}H-NMR: Bruker WH 270; MS: Varian MAT 711 bzw. 311 A, 70 eV, Direkteinlaß; CI Isobutan als Stoßgas. Das lufttrocken zerkleinerte Pflanzenmaterial wurde mit Et_2O/Petrol 1:2 extrahiert. Die erhaltenen Extrakte trennte man durch SC (Si gel, Akt. St. II) und weiter durch mehrfache DC (Si gel, GF 254, Et_2O/Petrol-Gemische als Laufmittel). Bekannte Verbindungen identifizierte man durch Vergleich der IR- und NMR-Spektren mit denen authentischen Materials.

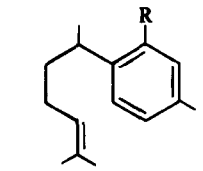
Rudbeckia laciniata *L.* (*Herbar Nr.* RMK 7147). 100 g Wurzeln ergaben 5 mg **1**, 7 mg **2**, 5 mg **3**, 3 mg **5**, 10 mg **6** (Et_2O/Petrol 1:20), 100 mg **7** sowie 50 mg **8** und 300 g oberirdische Teile 90 mg **3**, 90 mg **4**, 7 mg **9** (Et_2O/Petrol 1:10), 80 mg **10–13**, 10 mg **14**, 30 mg **15** und 10 mg **23**.

Senecio paludaffinis *Hilliard* (*Herbar Nr.* 77/131). 10 g Wurzeln lieferten 3 mg **16**, 40 mg **17**, 2 mg **18** sowie 2 mg **19** und 10 g oberirdische Teile 3 mg **1**, 2 mg **17**, 8 mg **20**, 5 mg **21**, 2 mg Sesamin und 8 mg **22** (Et_2O/Petrol 1:10).

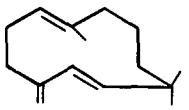
Bisabolen-1,4-endoperoxid (**6**). Farbloses Öl, CH=CH 3060, 1640; —C=CH— 880 cm^{-1}. MS: M^+ *m/e*-; $-O_2$ 204 (32%); 204 – $(CH_2)_2$ CH=CMe_2 121 (65); 121 $-H_2$ 119(100). 5 mg **6** in 2 ml absol. Et_2O versetzte man mit 10 mg $LiAlH_4$, Nach 10 min zersetzte man mit verd. H_2SO_4 und reinigte durch DC (Et_2O). Man erhielt 2 mg **6a**, farbloses Öl, MS(CI): 221 ($M^+ - H_2O + 1$) (28%), 203 ($M^+ - 2H_2O + 1$) (100%).

Rudbeckianon (**9**). Farbloses Öl, IR: C=C CO 1660 cm^{-1}. MS:

*162. Mitt. in der Serie "Natürlich vorkommende Terpen-Derivate"; 161. Mitt. Bohlmann, F., Zitzkowski, P., Suwita, A. und Fiedler, L. (1978) *Phytochemistry* (im Druck).



1 R = H 2 R = OH



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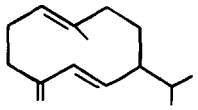

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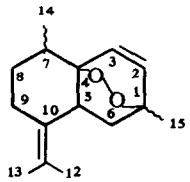
$H_3C[C{\equiv}C]_5CH{=}CH_2$

5



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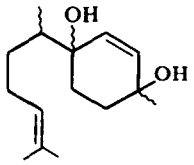
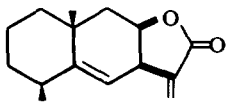


6a



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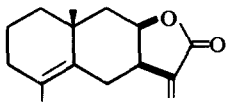

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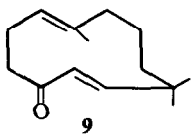

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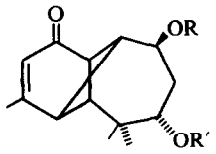
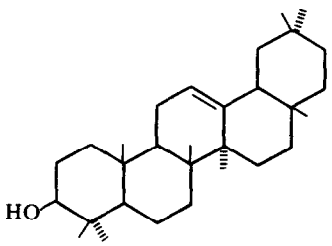


10 [4]	11 [4]	12 [4]	13 [4]
Tigl*	Ang	Meacr	Tigl
Sen	Sen	Sen	Ang



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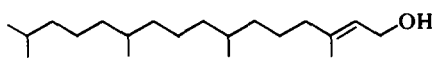

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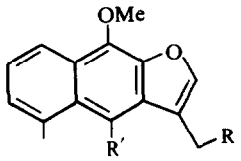
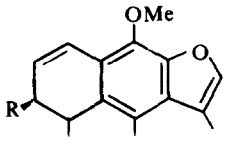
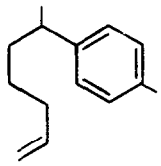


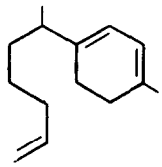
16 [5]	17 [5]
R H	OAc
R' Me	CHO



18 R = H [5]
19 R = OAc [5]

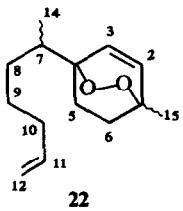


20 [6]



21 [6]

6



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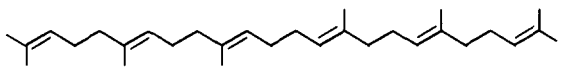

23

*Tigl = Tiglinoyl; Ang = Angeloyl; Sen = Senecioyl; Meacr = 2-Methylacryloyl; in Klammern Lit. Zitate.

M^+ *m/e* 206.167 (ber. für $C_{14}H_{22}O$ 206.167) (18%); − Me 191 (10); 191 − CO 163 (12); $C_7H_9O^+$ 109(100).

Senedigitalen-1.4-endoperoxid (**22**). Faraloses Öl, IR: CH=CH_2 3080, 1640, 910 cm^{-1}. MS: M^+ *m/e* −; $-O_2$ 190(28); $C_9H_{13}^+$ 121(100); 121 $-H_2$ 119(81); CI: M + 1 223.

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STEROIDS FROM *GRANGEA MADERASPATANA*

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Key Word Index—*Grangea maderaspatana*; Compositae; steroids; chondrillasterol; chondrillasterone.

We report the isolation and identification of the steroids chondrillasterol (**1**) and chondrillasterone (**2**) from *Grangea maderaspatana*. This is the first reported isolation of chondrillasterone.

EXPERIMENTAL

The residue from the petrol extract of the plant was separated into neutral and acidic fractions. The neutral fraction was chromatographed over a Si gel column when the following fractions were eluted: (i) Petrol, (ii) Petrol–C_6H_6 (1:1) and (iii) C_6H_6.

Fraction (iii) on rechromatography over Al_2O_3 and elution with C_6H_6–$CHCl_3$ (9:1) gave an alcohol (**1**), identified as chondrillasterol. Fraction (ii) on rechromatography over Al_2O_3 and elution with C_6H_6 gave a ketone (**2**).

Compound (**1**). Needles from Me_2CO, mp 163–165° [1]. It gave a positive Liebermann–Burchard and Salkowski reactions and a yellow colour with tetranitromethane. The IR spectrum (Nujol) had ν_{max}: 3350 (—OH), 1665, 840 (trisubstituted double bond) and 970 (*trans* disubstituted double bond) cm^{-1}. The NMR spectrum (60 MHz) $CDCl_3$, TMS ($\delta = 0.00$) showed signals at δ 0.58–1.10 (Me protons), δ 3.6 ($>\underline{C}H$—OH) and δ 5.18 (3H, *m*, vinylic). The MS showed the molecular ion peak at *m/e* 412 (M^+, $C_{29}H_{48}O$). The other major peaks occur at *m/e* 394 ($M - H_2O$), 369 ($M - CHMe_2$, 19.8%), 351 ($M - H_2O + CHMe_2$, 12%), 300 M – ring A and Me, 19.8%), 273 (M – side chain, 21%), 271 (M – side chain + 2H, 100%), 255 (M – side chain + H_2O, 52.6%) and 229 (M – side chain + 42 mass units forming ring D fragment, 21%).

The acetate prepared by the Ac_2O/Py method, crystallized from Me_2CO as flakes, mp 179–81° [1], M^+ 454. The fact that the mp of the acetate is higher than that of the parent alcohol suggested the absence of a $\Delta^{5,6}$ and the presence of a $\Delta^{7,8}$ double bond [2]. Compound (**1**) on hydrogenation over PtO_2 formed a dihydro compound mp 110–112°, $[\alpha]_D^{25}$ + 19° (*c* 3.4 in $CHCl_3$). The IR spectrum (Nujol) lacked the absorption bands at 1665, 840 and 970 cm^{-1}. The NMR spectrum did not show signals due to vinylic protons indicating migration of the trisubstituted double bond from the 7,8 position to a hindered tetrasubstituted double bond which is not easily hydrogenated. The methyl resonances at C_{10} and C_{13} (δ 0.72 and 0.86) indicated $\Delta^{8,(14)}$ position (δ 0 72 and 0.84) [3].

By comparison (mp, mmp, IR and MS) with an authentic sample, (**1**) has been identified as chondrillasterol.

Compound (**2**). Needles from (Me_2CO, mp 168–70°, $[\alpha]_D^{24}$ + 17° (*c* 3.1 in $CHCl_3$), TLC (Si gel, eluent, Petrol–EtOAc (9.5:0.5), R_f 0.42. (Found: C, 84.40; H, 11.59. $C_{29}H_{46}O$ requires: C, 84.87; H, 11.21%). **2** gave positive Liebermann–Burchard and Salkowski reactions and a yellow colour with tetranitromethane. The IR spectrum (Nujol) had ν_{max}: 1720 ($>C = 0$ on a 6 membered ring), 1670, 845 (trisubstituted double bond) and 970 (*trans* di-substituted double bond) cm^{-1} The NMR spectrum (60 MHz), $CDCl_3$, TMS ($\delta = 0.00$), showed signals at: δ 0.6–1.15 (Me protons), δ 2.3 (4H, *m*, $C\underline{H}_2$—CO—$C\underline{H}_2$), δ 5.23 (3H, *m*, vinylic). The MS showed molecular ion peak at *m/e* 410 (M^+, $C_{29}H_{46}O$). The mass spectral fragmentation agrees well with that reported for stigmastane skeleton [4]. The molecular ion peak appearing at *m/e* 410 (M^+) undergoes loss of 139 mass units to give the peak at *m/e* 271 (M – side chain, 68.1%). The other peaks are at *m/e* 367 (M—$CHMe_2$, 17.54%), 298 (M – ring A and Me, 27.6%) and 229 (M-side chain + 42 mass units forming ring D fragment, 41.98%). The peak at *m/e* 269 was the base peak (100%) [5]. **2** on refluxing with NH_2OH–HCl and EtOH for 1 hr, formed an oxime which crystallized from Me_2CO as needles mp 239–41° (Found: N, 2.9, $C_{29}H_{47}NO$, requires: N, 3.27%). Reduction of **2** with $NaBH_4$ gave an alcohol identical with (**1**) (mmp, IR, NMR and MS). Ketone **2** is thus chondrillasterone.

Acknowledgements—The authors thank Dr. P. V. Bole, Head, Department of Botany, St. Xavier's College, Bombay for supplying authentic plant material and Dr. N. Vishwanathan and Dr. M. D. Nair of Ciba-Geigy Research Centre, Bombay for an authentic sample of chondrillasterol and NMR and MS.