

The high-resolution MS of (1) is consistent with the proposed structure and shows peaks which arise from the citraconic isomer as well as from (1) itself. A similar situation has been reported [5] for the MS of itaconic acid which showed fragments characteristic of mesaconic and citraconic acids. The highest ion recorded in the MS of (1) was $M^+ - H_2O - Me$. The fragment at m/e 130 was produced by a McLafferty rearrangement of (1) and this in turn formed the ion at m/e 112 by loss of H_2O . An intense peak at m/e 280 probably arose from (1) by elimination of the OH group as H_2O followed by loss of a $C_3H_4O_2$ fragment. A similar fragmentation scheme has been proposed [5] to account for the ion at m/e 58 in the MS of itaconic acid. The base peak at m/e 126 was formed from the citraconic isomer by elimination of $2H_2O$ followed by a McLafferty rearrangement of the resulting m/e 334 ion. Loss of CO from the base ion gave m/e 98. The MS of the Me ester (2) showed an M^+ at m/e 398 and a base peak at m/e 157 which was formed by simple cleavage of the allylic C—C bond. The fragment at m/e 171 was formed in a similar manner from the citraconic isomer. A McLafferty rearrangement of (2) produced the fragment at m/e 158.

EXPERIMENTAL

Extraction and isolation. A preliminary analysis (Si gel HF₂₅₄: C_6H_6 -dioxane-HOAc; 90:25:4) of a fragment of the thallus of *Usnea aliphatica* (MFK No 217 on deposit in the herbarium of the Facultad de Farmacia of this university and collected in San Eusebio, State of Merida) showed the presence of usnic, salazinic and norstictic acids as well as the aliphatic compound (1). Ground air-dried lichen (38 g) was successively extracted with C_6H_6 , Et_2O , and Me_2CO . On standing 18 hr, the C_6H_6 extract deposited a white solid which was recrystallised from HOAc- H_2O to afford (1) as colourless crystals, mp 77–79°. Found C, 68.25; H, 10.41%. Calc. for $C_{21}H_{36}O_5$: C, 68.10; H, 10.28%. γ_{max}^{KBr} (cm^{-1}): 3480, 3200–3040, 2910, 2860, 1680–1710, 1625, 1470, 1420, 1300, 1270, 1210, 1145, 1130, 1110, 1060, 1025, 1000, 970, 920, 850, 810, 755, 720, 675, 620. PMR 60 MHz (Me_2CO-d_6 , δ): 1.11 (d , $J = 6$ Hz, 3H), 1.32 (CH_2X14), 3.6 (m , 1H), 3.53 (t , 1H, $J = 7$ Hz), 5.82 (d , 1H, $J = 1$ Hz); 6.35 (d , 1H, $J = 1$ Hz). MS, m/e (rel. int.): 337 (16), 334 (9), 308 (30), 290 (17), 289 (14), 280 (36), 263 (26), 182 (18), 168 (10), 154 (8), 151 (20), 150 (16), 140 (7), 139 (10), 130 (9), 126 ($C_6H_6O_3$, 100), 123 (16), 109 (35), 107 (14), 95 (73). Concn of the C_6H_6 extract afforded usnic acid identical (PMR, mmp) with an authentic sample. Extraction with Et_2O gave norstictic acid while extraction with Me_2CO yielded salazinic acid, both compounds being identified by comparison with authentic samples.

Pyrolysis of (1). The acid (25 mg) was maintained at 140° for 1 hr in a sublimation apparatus and then distilled onto a cold finger under red. press. to give (4) as a white solid, mp 40–42°. γ_{max}^{film} (cm^{-1}): 3460, 1855, 1820, 1765, 1670, 920, 730. PMR

($CDCl_3$, δ): 1.13 (half of doublet), 1.29 (CH_2X13), 2.07 (s , 3H), 2.46 (t , 2H, $J = 7$ Hz), 3.78 (m , 1H). Found C, 71.42; H, 10.12%. Calc. for $C_{21}H_{36}O_4$: C, 71.59; H, 10.23%.

Dimethyl ester of (1). A soln of the acid (20 mg) in MeOH (2 ml) was refluxed in the presence of one drop of conc. H_2SO_4 for 6 hr. The reaction mixture was diluted with 5% $NaHCO_3$, extracted with Et_2O and the solvent evaporated to give the Me ester (2) as a colourless oil. γ_{max}^{film} (cm^{-1}): 3425, 1720, 1628, 1260, 1200, 1140, 950, 820, 720. PMR ($CDCl_3$, δ): 1.12 (half of doublet), 1.30 (CH_2X14), 3.68 (s , 3H), 3.79 (s , 3H), 5.78 (s , H), 6.38 (s , 1H), 3.80 (m , 1H), 3.53 (t , 1H, $J =$ Hz). MS (m/e): 398 (M^+), 383, 366, 351, 339, 322, 290, 263, 171, 158, 157 (100%), 149, 139, 126, 45.

Pyrolysis of norcaperatic acid. 60 mg compound prepared by hydrolysis of caperatic acid with 5% KOH, was maintained at 180° in a sublimation apparatus for 4 hr. The reaction mixture distilled at 150°/0.05 mm and the colourless liquid which condensed on the cold-finger dissolved in Et_2O . $NaHCO_3$ extraction of the soln followed by acidification gave a semi-solid which was resublimed to afford 2-methyl-3-tetradecyl-maleic anhydride, mp 27° (lit. [6] 27°). PMR ($CDCl_3$, δ): 0.88 (t , 3H), 1.29 (CH_2X12), 2.09 (s , 3H), 2.48 (t , 2H, $J = 7$ Hz).

Reduction of (1). A soln of the acid (50 mg) in HOAc (3 ml) containing Pd/C (5%; 10 mg) was hydrogenated in a Parr apparatus at room temp and 50 kg for 4 hr to give the succinic acid derivative as a white solid, mp 66–68°, γ_{max}^{KBr} (cm^{-1}): 3480, 1690, 1470, 1420, 1190, 940, 720. PMR (Me_2CO-d_6 , δ): 1.13 (d , $J = 6$ Hz, 3H), 1.33 (CH_2X14), 1.22 (d , $J = 6$ Hz, 3H), ca 2.67 (m , 2H), ca 3.65 (m , 1H).

Acetylation of (1). The acid (60 mg) was dissolved in a mixture of Py and Ac_2O (1:1, 4 ml) and maintained at room temp for 18 hr. Evaporation of the solvent afforded (3) as a colourless oil. γ_{max}^{film} (cm^{-1}): 2920, 2845, 1850, 1820, 1765, 1730, 1670, 1245, 1115, 1020, 920, 730. PMR ($CDCl_3$, δ): 1.16 (half of doublet), 1.30 (CH_2X13), 2.03 (s , 3H), 2.1 (s , 3H), 2.48 (t , $J = 7$ Hz, 2H), 2.92 (m , 1H). MS (m/e): 394 (M^+), 379, 352, 351, 350, 289, 247, 233, 219, 205, 191, 126, 87, 61, 54.

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INHALTSSTOFFE SÜDAMERIKANISCHER *SENECIO*-ARTEN*

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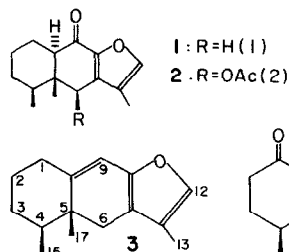
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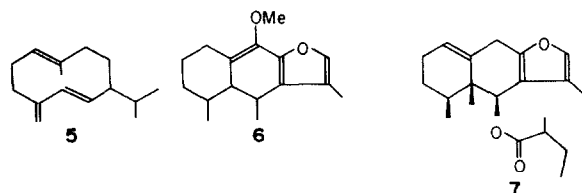
* 84. Mitt. in der Serie. "Natürlich vorkommende Terpen-Derivate" 83. Mitt.: Bohlmann, F., Czerson, H., und Schönweiß, S. (1976) *Chem. Ber.* (im Druck).

Pflanzen und Herkunft: *Senecio teretifolius* DC. und *Senecio scytophyllus* HBK. im Februar 1976 in Ecuador gesammelt (Dr. R. King, Smithsonian Institution,

Washington, Herbar Nr. 6976 und 6911). Die in Ecuador heimische *Senecio teretifolius* ist bisher noch nicht auf ihre Inhaltsstoffe untersucht worden. Die Wurzeln enthalten neben 10 α -H-Furanoeremophil-9-on (1) und dem entsprechenden Acetat 2 zwei sehr instabile Furane, deren spektroskopische Daten nur mit den Konstitutionen 3 und 4 vereinbar sind.



Verbindungen vom Typ 3 sind bisher nicht gefunden worden, während in 6-Stellung substituierte Vertreter vom Typ 4 bereits aus anderen *Senecio*-Arten isoliert wurden [3].



Die Zuordnungen wurden durch systematische Entkopplungen überprüft.

Die oberirdischen Teile enthalten ebenfalls 2.

Table 1. $^1\text{H-NMR}$ -Daten von 3 und 4 (δ -Werte, TMS als innerer Standard, 270 MHz)

	3(C_6D_6)	$J(\text{Hz})$	4(CDCl_3)	$J(\text{Hz})$
1 α -H	<i>d</i> (br) 2,05	1,1 = 15	—	—
2 β -H	<i>dddd</i> 2,16	1 β , 2 α = 10	—	—
2 α -H	<i>m</i> 1,56	1 β , 2 β = 4	<i>dd</i> (br) 2,43	1 α , 2 β = 16
2 β -H	<i>m</i> 1,3	1 β , 9 = 2	<i>ddd</i> 2,60	2 α , 3 α = 10 2 α , 2 β = 2
3 α -H	<i>m</i> 1,3	3 α , 3 β = 11	<i>m</i> 1,77	2 β , 3 β =
3 β -H	<i>ddd</i> 1,21	3 β , 4 α = 11	<i>m</i> 1,77	2 β , 2 β = 4
4 α -H	<i>ddq</i> 1,47	3 α , 4 α = 3	<i>ddq</i> 1,98	3 α , 4 α = 3
6 α -H	<i>d</i> 2,35	4 α , 15 = 7	<i>d</i> 2,53	3 β , 4 α = 11
6 β -H	<i>d</i> 2,58	6 α , 6 β = 16	<i>d</i> 2,74	4 α , 15 = 7
9-H	<i>d</i> 6,06	12, 13 = 1	<i>s</i> 7,31	
12-H	<i>s</i> (br) 6,95		<i>s</i> (br) 7,24	
13-H	<i>d</i> 1,80		<i>s</i> (br) 1,99	
14-H	<i>s</i> 0,88		<i>s</i> 0,99	
15-H	<i>d</i> 0,78		<i>d</i> 1,04	

Die Wurzeln von *Senecio scytophyllus* liefern neben Germacren D (5) die Furan-Derivate 6 [4] und 7 [4], die ebenfalls schon aus anderen *Senecio*-Arten isoliert wurden. Die oberirdischen Teile enthalten keine Furan-sesquiterpene. Nur Germacren D läßt sich eindeutig identifizieren. Weitere Untersuchungen müssen zeigen, wie weit die Inhaltsstoffe für die Unterteilung der großen Gattung *Senecio* von Bedeutung sind. Die bisherigen Ergebnisse lassen vermuten, daß eine Reihe von charakteristischen Verbindungen hier gute Dienste leisten könnten [3, 5].

EXPERIMENTIELLES

IR. Beckman IR 9 in CCl_4 ; $^1\text{H-NMR}$: Bruker WH 270, δ -Werte, TMS als innerer Standard; MS: Varian MAT 711 mit Datenverarbeitung, 70 eV, Direkteinlaß. Die lufttrockenen Pflanzenteile extrahierte man mit Ether-Petrol (1:2) und trennte die erhaltenen Extrakte zunächst grob durch Säulen-chromatographie (Si gel, Akt. St. II) und anschließend weiter durch DC (Si gel, GF 254). Als Laufmittel dienten Ether-Petrol (br 30–60°)-Gemische (= E-PE).

Isolierung der Inhaltsstoffe aus *Senecio teretifolius*. 71 g Wurzeln ergaben 80 mg 3 (E-PE 1:30), 20 mg 4 (E-PE 1:10), 15 mg 1 und 10 mg 2. 60 g oberirdischer Teile lieferten 40 mg 2.

Isolierung der Inhaltsstoffe aus *Senecio scytophyllus*. 88 g Wurzeln ergaben 50 mg 5, 5 mg 6 und 5 mg 7. 72 g oberirdischer Teile lieferten 50 mg 5.

9, 10-Dehydrofuraneremophilan (3). Farbloses, schnell dunkel werdendes Öl, $\text{Sdp}_{0,1}$ 130° C (Kugelrohr). IR: 1615 ($\text{C}=\text{C}$) cm^{-1} . UV (Ether): λ_{max} = (313), 297,290 nm (ϵ = 6300, 10500, 10400). MS: M^+ m/e 216.151 (100%) (ber. für $\text{C}_{15}\text{H}_{20}\text{O}_2$ 216,151); —Me 201 (31); — C_4H_9 159 (76); — C_5H_{11} 145 (68)

$$[\alpha]_{24}^{20} = \frac{589 \cdot 578 \cdot 546 \text{ nm}}{+ 145 + 152 + 173^\circ} (c = 1,21, \text{CHCl}_3)$$

9, 10-Dehydrofuraneremophil-1-on (4). Gelbgefärbtes Öl, IR: 1675, 1570, 1530 cm^{-1} (konj. Furanketon). UV (Ether): λ_{max} = 350 nm. MS: M^+ m/e 230.131 (91%) (ber. für $\text{C}_{15}\text{H}_{18}\text{O}_2$ 230,131); —Me 215 (100); —Me — $\text{CH}_2\text{-CH}_2\text{CH}$ (Me). 159 (60).

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EIN NEUES GUAJANOLID AUS *MATRICARIA ZUURBERGENSIS*

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Univ. of Natal, Herbar ebenda.

Die Einordnung der südafrikanischen *Matricaria*-