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THIOPHENE ACETYLENES AND FLAVANOLS FROM *PTEROCAULON VIRGATUM*[*]

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So far only one species of the widespread genus *Pterocaulon* (Compositae, tribe Inuleae) has been investigated chemically; *P. sphacelatum* contains scoparon (6,7-dimethoxycoumarin) [1]. As the botanical delimination at the subtribe and even the genus level is still a problem in the tribe Inuleae [2], we have investigated a further species, *P. virgata* (L.) DC. The roots afforded humulene (**1**), thymohydroquinone dimethyl ether and a complex mixture of five thiophene acetylenes, which only could be separated by HPLC using reversed phase, two of them, the chlorohydrins **4** [3] and **6** [4], being known already. The three other compounds are also chlorohydrins. The UV and ^{1}H NMR spectra (see Table 1) clearly show that the structures **2**, **3** and **5** must be assigned to these thiophenes. The relative position of the hydroxyl and the chloro group follows from the shape of the corresponding ^{1}H NMR signals. While the H_A-signals always are very sharp, those of H_B are broadened, indicating an additional OH-coupling. In the spectrum of **5** a clear upfield shift of H_F and H_E due to the donator function of the methyl group can be observed. This can be recognized even in the spectrum of **2** if we compare the shift of H_D with that in **3**. The nature of the end group is further supported by the base peak in the mass spectra of **2**, **3** and **5** ($M - {}^{\bullet}CH_2Cl$).

The aerial parts of the plant contain squalene, thymohydroquinone dimethyl ether, taraxasterol (**9**) [5] and the corresponding acetate **8** [5] as well as the ketone **7** [5]. Furthermore, the coumarin **15** [6] is present, while the most polar fractions afforded a mixture of the two flavanols **10** and **13**. Only the latter could be isolated as its tetraacetate **14**. Also **10** was transformed to the corresponding acetates **11** and **12**. The ^{1}H NMR data of all compounds allow a clear assignment of the relative positions of the functional groups. While the free 5-OH group can be clearly recognized by the chemical shift of the corresponding protons, the position of the other free hydroxyls follow from the observed shifts, after the introduction of *O*-acetate groups (see Table 2). Furthermore, the 7-position of the prenyloxy group follows from the observed *meta*-coupling of the aromatic protons. **10**, therefore is a 7-*O*-prenyl aromadendrin [7], while **13** is a 7-*O*-prenyltaxifolin or dihydroquercetin [7].

Summarizing these results, it is obvious that *Pterocaulon* from its chemistry should be placed, as proposed, in the subtribe Inulinae [2]. Also its position in the *Sphaeranthus* group is very likely, since similar thiophene acetylenes are present there [3]. These compounds, however, are also widespread in the genus *Pluchea* [3, **8**], although here there are characteristic eudesmanes too [8, 9]. Further investigations are necessary to clarify the chemotaxonomic situation of the subtribe, since its chemistry is different from that of the other subtribes.

Table 1. ^{1}H NMR spectral data of compounds **2**–**6** (270 MHz, $CDCl_3$, TMS as internal standard)

	2	**3**	**4**	**5**	**6**
H-A	3.73 *dd*	3.74 *dd*	3.69 *dd*	3.74 *dd*	3.75 *dd*
H-A′	3.81 *dd*	3.81 *dd*	3.77 *dd*	3.82 *dd*	3.82 *dd*
H-B	4.83 *dd* (*br.*)	4.84 *dd* (*br.*)	4.76 *dd* (*br.*)	4.84 *dd* (*br.*)	4.86 *dd* (*br.*)
H-C	7.06 *d*	7.09 *d*	6.94 *d*	6.94 *d*	7.03 *d*
H-D	7.11 *d*	7.20 *d*	7.15 *d*	7.12 *d*	7.14 *d*
H-E	—	—	—	6.98 *d*	7.19 *d*
H-F	—	—	—	6.67 *d* (*br.*)	7.02 *dd*
H-G	2.05 *s*	2.66 *s*	2.08 *s*	2.48 *s* (*br.*)	—

J (Hz): A,A′ = 11; A,B = 7; A′,B = 4; C,D = E,F ~ 4; F,G = 3.

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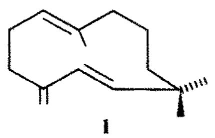
[*] Part 257 in the series "Polyacetylenic Compounds". For Part 256 see Bohlmann, F., Ziesche, J., Robinson, H. and King, R. M. (1980) *Phytochemistry* **19**, 1535.



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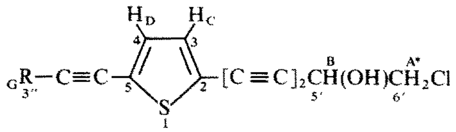
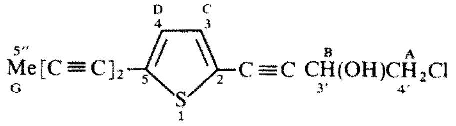


2 R = Me
3 R = H



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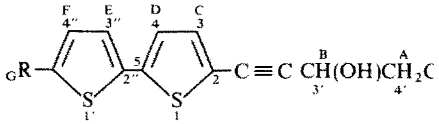
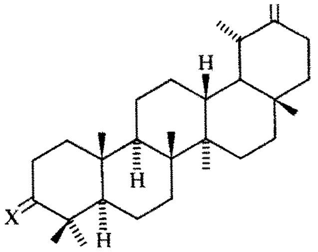
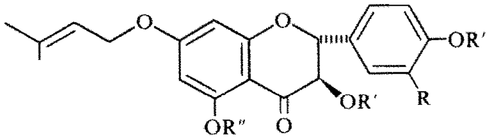


5 R = Me
6 R = H



7 X = O
8 X = *β*OAc, H
9 X = *β*OH, H



10 R = R' = R'' = H
11 R = R'' = H, R' = Ac
12 R = H, R' = R'' = Ac
13 R = OH, R' = R'' = H
14 R = OAc, R' = R'' = Ac

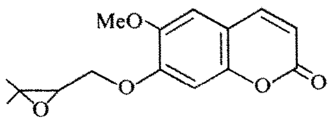


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Table 2. ^{1}H NMR spectral data of compounds **10**–**12** and **14**

	10 (CDCl$_3$)	**11**	**12**	**14**
2-H	5.03 *d*	5.37 *d*	5.38 *d*	5.37 *d*
3-H	4.56 *d*	5.78 *d*	5.67 *d*	5.36 *d*
6-H	6.13 *d*	6.12 *d*	6.39 *d*	6.40 *d*
8-H	6.06 *d*	6.06 *d*	6.31 *d*	6.32 *d*
2'-H	7.43 *d*	7.50 *d*	7.47 *d*	7.29 *d*
3'-H 5'-H	6.91 *d*	7.17 *d*	7.14 *d*	7.25 *d*
6'-H	7.43 *d*	7.50 *d*	7.47 *d*	7.38 *d*
1''-H	4.53 *d* (*br.*)	4.54 *d* (*br.*)	4.52 *d* (*br.*)	4.53 *d* (*br.*)
2''-H	5.44 *t* (*br.*)	5.44 *t* (*br.*)	5.43 *t* (*br.*)	5.43 *t* (*br.*)
4''-H	1.73 *s* (*br.*)	1.74 *s* (*br.*)	1.72 *s* (*br.*)	1.73 *s* (*br.*)
5''-H	1.80 *s* (*br.*)	1.80 *s* (*br.*)	1.79 *s* (*br.*)	1.80 *s*(*br.*)
OH	11.18 *s*	11.45 *s*	—	—
OAc	—	2.32 *s* 2.05 *s*	2.28 *s* 2.36 *s* 1.99 *s*	2.30 *s* 2.30 *s* 2.37 *s* 2.04 *s*

J (Hz): 2,3 = 11.5; 6,8 = 2.3; 2',3' = 8; 1'',2'' = 7; **14**: 2',6' = 1.5; 5',6' = 8.

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* Numbering for the NMR data.

EXPERIMENTAL

The air-dried plant material, collected in north-eastern Brazil (voucher RMK 8029) was extracted with Et_2O–petrol (1:2) and the resulting extracts were separated by column chromatography (SiO_2) and further by TLC (SiO_2 GF 254). Finally the compounds **2**–**6** were separated by HPLC (reversed phase, $MeOH$–H_2O 7:3). The roots (200 g) afforded 8 mg **1**, 30 mg thymohydroquinone dimethyl ether and with Et_2O–petrol (1:1) 5 mg **2**, 0.5 mg **3**, 1 mg **4**, 1 mg **5** and 0.5 mg **6**, while the aerial parts (700 g) gave 30 mg squalene, 40 mg thymohydroquinone dimethyl ether, 10 mg **7**, 40 mg **8**, 20 mg **9**, 300 mg **10** (Et_2O), 50 mg **13** (Et_2O) and 20 mg **15**.

5-[*Prop.-1″-inylthienyl-*(1)]-*6′-chloro-5′-hydroxyhexa-3′,5-diyne* (**2**). Colourless oil, UV $\lambda_{max}^{Et_2O}$ nm: 340, 319: IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3590 (OH), 2230 (C≡C); MS *m*/*e* (rel. int.): 248 (45) (M^+, $C_{13}H_9OClS$): 199 (100) ($M - CH_2Cl$); 171 (16) ($199 - CO$).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \qquad 578 \qquad 546\,\text{nm}}{+9.3 \quad +10.0 \quad +11.6}(c = 0.44).$$

5-Ethinylthienyl-(1)]-*6′-chloro-5′-hydroxyhexa-3′,5′-diyne* (**3**). Colourless, unstable oil, UV $\lambda_{max}^{Et_2O}$ nm: 339, 322; MS *m*/*e* (rel. int.): 233,990 (26) (M^+, $C_{12}H_7OClS$); 185 (100) ($M - CH_2Cl$); 157 (8) ($185 - CO$).

5′-Methyl-2-[*4′-chloro-3′-hydroxybut-1-ynyl-*]*-dithiophene* (**5**). Colourless oil, UV $\lambda_{max}^{Et_2O}$ nm: 336; MS *m*/*e* (rel. int.) 281.993 (27) (M^+, $C_{13}H_{11}OClS_2$); 233 (100) ($M - CH_2Cl$); 205 (5) ($233 - CO$).

7-O-[*2,2-Dimethylallyl*]*-aromadendrin* (**10**). Colourless gum, UV $\lambda_{max}^{Et_2O}$ nm: 293; MS *m*/*e* (rel. int.): 356.126 (4) (M^+, $C_{20}H_{20}O_6$); 55 (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \qquad 578 \qquad 546\,\text{nm}}{+9.2 \quad +9.8 \quad +11.2}(c = 9.06,\ Me_2CO).$$

To 20 mg **10** in 2 ml $CHCl_3$ 10 mg 4-pyrrolidine and 0.1 ml Ac_2O were added. After 10 hr at room temp. usual work-up afforded by TLC (Et_2O–petrol, 3:1) 5 mg **11** and 15 mg **12**, colourless gum; ^1H NMR see Table 2.

7-O-[*2,2-Dimethylallyl*]*-taxifolintetraacetate* (**14**). Obtained by acetylation of the crude flavanol **13** (see above), colourless gum, MS *m*/*e* (rel. int.): 540.163 (1) (M^+, $C_{28}H_{28}O_{11}$); 428 (12) ($M - $ ketene); 69 (100).

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