(2 ml/min) and UV detection (A_{270}). R_ts for **3** (total yield 7 3 mg) and **2** (total yield 1.2 mg) were 8 min and 9 min, respectively.

MS analysis. EI spectra (including HRMS) showed the following important ions for the alkaloids isolated. *8-oxo-erythraline m/z* (rel. int.): 311 $[M]^+$ (100), 296 $[M-15]^+$ (50), 280 $[M-31]^+$ (65), 279 (33), 278 (76), 268 (15), 266 (15), 250 (30). HRMS $[M]^+$ 311.1163, $C_{18}H_{17}NO_4$ (calc. 311 1157). *Crystamidine m/z* (rel. int.). 309 $[M]^+$ (85), 294 $[M-15]^+$ (28); 278 $[M-31]^+$ (60), 277 (65), 276 (100), 266 (35), 250 (20). HRMS $[M]^+$ 309.0997, $C_{18}H_{15}NO_4$ (calc. 309 1000).

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THREE PRENYLATED FLAVANOIDS FROM *HELICHRYSUM ATHRIXIIFOLIUM*

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Key Word Index—*Helichrysum athrixiifolium*; Compositae; flavanones, chalcones; prenylated flavanoids.

Abstract—*Helichrysum athrixiifolium* afforded in addition to known ones three new prenylated flavanoids, one chalcone and two flavanones.

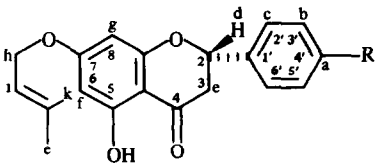
In continuation of our chemical investigation of the genus *Helichrysum* [1] we now have studied the constituents of *H. athrixiifolium* (Kuntze) Moeser. The aerial parts afforded the flavanoids **1**, **2**, **3** [2], **4** [3], **5** [4] and **6**. The structure of **1**, molecular formula $C_{20}H_{20}O_4$, followed from the ^1H NMR spectrum (Table 1) especially when compared with those of similar prenylated compounds. The presence of an *O*-prenyl derivative could be deduced from the mass spectrum, which showed a strong fragment formed by loss of isoprene, and from the typical broadened doublet at δ 4.52 in the ^1H NMR spectrum of **1**. The position of the free hydroxyl group followed from the low field singlet at δ 10.26 and from the IR spectrum, which showed the presence of a hydrogen bonded aromatic ketone (3500–2700, 1650 cm^{-1}). Since a *meta*-coupling was visible, the second oxygen function could be assigned to C-7. The ^1H NMR spectrum of **2** (Table 1) was close to that of **1** However, an additional hydroxyl group at C-4′ was indicated by the typical doublets of H-2′, H-3′, H-5′ and H-6′. If the chemical shifts of the aromatic protons were compared with those of similar flavanones, the relative positions of the free hydroxyl groups again were clear. This was supported further by the observed fragments in the mass spectrum of **2**.

The molecular formula of **6** was the same as that of **2**. However, the ^1H NMR spectrum (Table 1) clearly showed that a chalcone was present. Accordingly, the spectral data were close to those of the known compound **5**. Again the presence of a free *para* hydroxyl group followed from the chemical shifts of the corresponding aromatic signals.

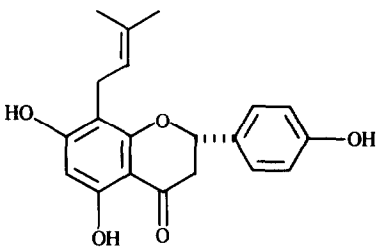
The roots afforded **1** and **5** only. The chemistry of this species is similar to that of a group of *Helichrysum* species, which also contains prenylated flavanoids [1, 4, 5]. However, some prenylated flavanones also have been isolated from Compositae belonging to *Marshallia* [2, 6], *Flourensia* [7] and *Wyethia* [8].

EXPERIMENTAL

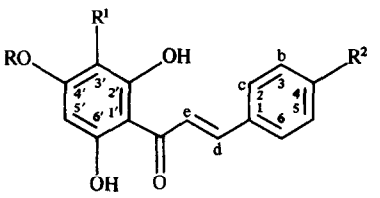
The air dried plant material (collected in February 1981 in Transvaal, voucher 81/98, deposited in the Botanic Research Institute, Pretoria) was extracted with Et_2O–petrol, 1:2, and the resulting extracts were separated first by CC (silica gel) and further by TLC (silica gel PF 254, detection by UV light). The CC fraction (Et_2O–petrol, 1 1) of the roots (20 g) gave by TLC (silica gel, solvent Et_2O–petrol, 1·1) 7 mg **1** (R_f 0.43) and 4 mg **5** (R_f 0.38). The CC fractions (Et_2O–petrol, 1:1 and Et_2O) of the aerial parts (180 g) were combined and separated by repeated



R
1 H
2 OH



3



4 R = R²=H, R¹ = CH₂CH=CMe₂
5 R = CH₂CH=CMe₂, R¹=R²=H
6 R = CH₂CH=CMe₂, R¹=H, R²=OH

TLC (silica gel, solvent Et_2O–petrol, 2.1) affording 40 mg **1** (R_f 0.58), 16 mg **2** (R_f 0.55), 7 mg **3** (R_f 0.5), 150 mg **4** (R_f 0.42), 100 mg **5** (R_f 0.40) and 24 mg **6** (R_f 0.38). Quantities were determined by weighing. Compounds **1** and **6** were homogeneous by TLC (on silica gel solvents: Et_2O–petrol, 2·1, and $CHCl_3$–C_6H_6, 1:1) but could not be induced to crystallize. Known compounds were identified by comparing the UV, mass and ^1H NMR spectra with those of authentic materials.

5-Hydroxy-7-prenyloxyflavanone (**1**). Colourless gum, UV (nm) MeOH: 285; $AlCl_3$ 360, 312; NaOEt 295, IR $\nu_{max}^{CCl_4}$ cm^{-1}. 3500–2700, 1650 (H-bonded PhCO); MS *m/z* (rel. int.): 324 136 $[M]^+$ (42) ($C_{20}H_{20}O_4$), 256 $[M-\text{isoprene}]^+$ (82), 255 $[M-C_5H_9]^+$ (68), 179 $[256-C_6H_5]^+$ (96), 152 $[256-H_2C{=}CHPh]^+$ (66), 69 $[C_5H_9]^+$ (100).

4',5-Dihydroxy-7-prenyloxyflavanone (**2**). Colourless crystals, mp 69°, UV (nm) MeOH 286, $AlCl_3$ 360, 310; NaOEt 295; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 3500–2700, 1630 (H-bonded PhCO); MS *m/z* (rel. int.): 340 131 $[M]^+$ (36) ($C_{20}H_{20}O_5$), 272 $[M-\text{isoprene}]^+$ (36), $[M-C_5H_9]^+$ (40), 120 $[HOC_6H_4CH{=}CH_2]^+$ (18), 70 $[C_5H_{10}]^+$ (100).

Table 1. ^1H NMR spectral data of compounds **1**, **2** and **6** (400 MHz, $CDCl_3$, TMS as internal standard)

	1	2	6
a			
b	7.45 *m*	6.88 *d*	6.89 *d*
c		7.33 *d*	7.55 *d*
d	5.42 *dd*	5.35 *dd*	7.90 *d*
e	3.09 *dd*	3.08 *dd*	7.80 *d*
e'	2.83 *dd*	2.78 *dd*	
f	6.07 *d*	6.04 *d*	5.98 *s*
g	6.09 *d*	6.08 *d*	5.98 *s*
h	4.52 *br d*	4.51 *br d*	4.52 *br d*
i	5.45 *tq*	5.45 *tq*	5.48 *tq*
k	1.82 *br s*	1.78 *br s*	1.80 *br s*
l	1.76 *br s*	1.71 *br s*	1.74 *br s*
OH	10.26 *s*	12.00 *s*	9.4 *br s*

J (Hz): d, e = 13; d, e' = 3; e, e' = 17; g, f = 2; h, i = 6.5; i, k = 1.5 compound **2**: b, c = 8.5; compound **6**: d, e = 15

$$[\alpha]_{24^\circ}^{\lambda} = \underset{-23}{589}\ \underset{-24}{578}\ \underset{-27}{546}\ \underset{-30}{436\ \text{nm}}\ CHCl_3;\ c\ 1.6.$$

2',4,6'-Trihydroxy-4'-prenyloxychalcone (**6**) Yellow coloured gum, UV (nm) Et_2O 347; NaOEt 425; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2700, 1650 (H-bonded PhCO); MS *m/z* (rel. int.): 340.131 $[M]^+$ (43) ($C_{20}H_{20}O_5$), 272 $[M-\text{isoprene}]^+$ (60), 271 $[M-C_5H_9]^+$ (56), 153 $[272-CH{=}CHC_6H_4OH]^+$ (60), 120 $(CH_2{=}CHC_6H_4OH]^+$ (40), 69 $[C_5H_9]^+$ (100).

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