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Phytochemistry, Vol. 22, No. 12, pp. 2877–2878, 1983.
Printed in Great Britain.

0031–9422/83 $3.00 + 0.00

FLAVANONES FROM *HELICHRYSUM THAPSUS*

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(*Received* 1 *March* 1983)

Key Word Index—*Helichrysum thapsus*; Compositae; flavanones; prenylated flavanones; 3α-hydroxy-6-geranyl-pinocembrin.

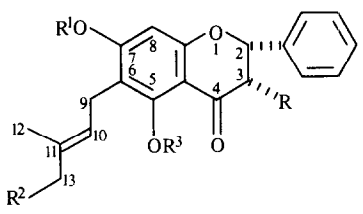
Abstract—The aerial parts of *Helichrysum thapsus* afforded three new flavanone derivatives all derived from pinocembrin.

In continuation of our studies of representatives of the large genus *Helichrysum* (Compositae, tribe Inuleae) we now have investigated *H. thapsus* (O. Kuntze) Moeser. The polar fractions contained a complex mixture of flavanones which could be separated by a combination of repeated TLC and HPLC. Finally four compounds were obtained, the known prenylated flavanone **6** [1], the 3α-hydroxy derivative **1**, the geranyl derivative **4** and the β-acetoxy flavanone **5**.

The structure of **1** followed from the molecular formula, the ^{1}H NMR spectral data (Table 1) and those of the acetates **2** and **3** obtained by acetylation **1**. The nature of the side chain could be deduced from the typical ^{1}H NMR signals which were nearly identical with those of **6** where the position of the prenyl residue was established unambiguously [1]. The signals of H-12 and H-13 collapse to a singlet if the side chain is at C-8 [1] while compounds with a prenyl group at C-6 showed separated methyl signals. The presence of a 3α-hydroxy group was deduced from the chemical shift and the coupling of the doublet at δ 4.75. The latter was shifted down field in the spectrum of the corresponding acetates **2** and **3**. As the second doublet in the spectrum of **2** was slightly broadened the signals of H-2 and H-3 could be assigned. It may be of interest to note that the chemical shifts of H-3 and H-8 differed in the spectra of **2** and **3** obviously due to the presence of a hydrogen bond in **2**.

The molecular formula of **4** was $C_{25}H_{28}O_5$ indicating that **4** may differ from **1** by an additional prenyl group. The ^{1}H NMR spectrum (Table 1), however, clearly showed that the prenyl side chain was replaced by a geranyl residue as followed from the characteristic side chain signals which were close to those of similar phenolic geranyl derivatives. The presence of a 3α-hydroxy group again could be deduced from the couplings of a pair of doublets which showed the same chemical shifts as **1**. Accordingly, **4** was closely related to **1** and most likely the side chain again was at C-6 though the position of the latter could not be established with certainty as acid catalysed cyclization failed.

The structure of **5** also followed from the molecular formula and the ^{1}H NMR spectrum (Table 1) which



	1	2	3	4	5	6
R	αOH	αOAc	αOAc	αOH	βOAc	H
R^1	H	Ac	Ac	H	H	H
R^2	H	H	H	$CH_2CH{=}CMe_2$	H	H
R^3	H	H	Ac	H	H	H

Table 1. ^{1}H NMR spectral data of compounds **1**–**5** (400 MHz, $CDCl_3$, TMS as internal standard)

	1	2	3	4	5
H-2	5.69 *br d*	5.64 *br d*	5.67 *s*	5.69 *br d*	5.37 *br d*
H-3	4.75 *d*	5.81 *d*		4.75 *d*	5.79 *d*
H-8	6.03 *s*	6.35 *s*	6.57 *s*	6.05 *s*	6.08 *s*
H-9	3.36 *br d*	3.22 *br d*	3.31 *br d*	3.39 *br d*	3.29 *br d*
H-10	5.22 *br t*	5.06 *br t*	5.09 *br t*	5.22 *br t*	5.22 *br t*
H-12	1.77 *br s*	1.68 *br s*	1.68 *br s*	2.08 *m*	1.74 *br s*
H-13	1.73 *br s*	1.67 *br s*	1.67 *br s*	1.79 *br s*	1.70 *br s*
H-14	—	—	—	2.08 *m*	—
H-15	—	—	—	5.05 *br t*	—
H-17	—	—	—	1.69 *br s*	—
H-18	—	—	—	1.62 *br s*	—
H-2′,6′	7.39 *m*	7.43 *m*	7.40 *m*	7.39 *m*	7.47 *m*
H-3′,4′,5′	7.33 *m*	7.38 *m*	7.36 *m*	7.33 *m*	7.42 *m*
OH	11.21 *s*	12.25 *s*	—	11.20 *s*	11.45 *s*
OAc	—	2.32 *s*	2.36 *s*	—	2.04 *s*
		2.01 *s*	2.32 *s*		
			1.99 *s*		

J (Hz): 9, 10 = 7; compounds **1** and **4**: 2, 3 = 4.5; compounds **2** and **3**: 2, 3 = 3.5; compound **4**: 14, 15 = 7; compound **5**: 2, 3 = 11.

showed that **5** differed in the stereochemistry at C-3 from that of **1**. The coupling $J_{2,3}$ showed that a 3β-acetoxy group was present. The chemical shifts of the signals of the olefinic methyls were close to those of **1**. Accordingly, a 6-position for the side chain was assumed. The 2*S*-configuration of the flavanones is not established. However, as **6** showed laevorotatory rotation as all other flavanones with known absolute configuration [2], the proposed one is likely.

Thus the chemistry of *H. thapsus* shows relationships to some South African species: *H. hypocephalum* [1], *H. tenuiculum* [3], *H. umbraculigerum* [4] and *H. polycladum* [5], which also contain prenyl or geranyl flavanones. However, there are many other *Helichrysum* species which contain all kinds of aromatics with these side chains.

EXPERIMENTAL

The air dried aerial parts (300 g) (voucher 81/277, deposited in the Botanic Research Institute, Pretoria) were extracted with Et_2O–petrol, 1:2, and the extract was worked-up in the usual fashion. The polar CC^{l_4} fractions (Et_2O–petrol, 1:1, and Et_2O) were separated by TLC (silica gel, Et_2O–petrol, 3:1) followed by HPLC (RP 8, MeOH–H_2O, 4:1) affording 10 mg **1**, a mixture of **5** and **6** as well as 10 mg **4**. **5** and **6** were separated by TLC (Et_2O–petrol, 1:1) affording 4 mg **5** and 2 mg **6**, its ^{1}H NMR spectrum being identical with that of an authentic sample [1]. **1**, **4** and **5** were viscous oils which were homogeneous by TLC in different solvent mixtures and showed no impurities in the 400 MHz ^{1}H NMR spectra.

3α-*Hydroxy*-6-[3′,3′-*dimethylallyl*]*pinocembrin* (**1**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2600, 1650, 1605 (hydrogen bonded PhCO); MS *m/z* (rel. int.): 340.131 $[M]^+$ (92) ($C_{20}H_{20}O_5$), 272 [M − isoprene]$^+$ (9), 270 $[M-C_5H_{10}]^+$ (27), 165 $[C_8H_5O_4]^+$ (100). 5 mg **1** were heated with 0.1 ml Ac_2O for 2 hr at 70°. TLC (Et_2O–petrol, 1:1) afforded 2 mg **2** and 4 mg **3**.

2: IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (PhOAc), 1665, 1600 (PhCO, hydrogen bonded); MS *m/z* (rel. int.): 424.152 $[M]^+$ (68) ($C_{24}H_{24}O_7$), 382 [M − ketene]$^+$ (22), 381 [M − MeCO]$^+$ (48), 364 [M − HOAc]$^+$ (22), 349 [364 − Me]$^+$ (21), 321 [381 − HOAc]$^+$ (54), 276 (24), 234 (82), 219 (68), 91 $[C_7H_7]^+$ (100).

3: IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1785, 1775 (PhOAc), 1715, 1610 (PhCO); MS *m/z* (rel. int.): 466.169 $[M]^+$ (3) ($C_{26}H_{26}O_8$), 424 [M − ketene]$^+$ (75), 423 [M − MeCO]$^+$ (100), 381 [423 − ketene]$^+$ (64), 364 [424 − HOAc]$^+$ (28), 321 [381 − HOAc]$^+$ (51), 234 (57), 219 (56), 177 (62), 165 (72), 91 (76).

3α-*Hydroxy*-6-*geranylpinocembrin* (**4**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2600, 1650, 1605 (hydrogen bonded PhCO); MS *m/z* (rel. int.): 408.194 $[M]^+$ (12) ($C_{25}H_{28}O_5$), 285 $[M-C_9H_{15}]^+$ (62), 219 (100), 165 (40), 91 (43); $\alpha_D = -38.5$ ($CHCl_3$; *c* 1.15).

3β-*Acetoxy*-6-[3′,3′-*dimethylallyl*]*pinocembrin* (**5**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2600, 1650, 1610 (hydrogen bonded PhCO), 1770 (OAc); MS *m/z* (rel. int.): 382.142 $[M]^+$ (100) ($C_{22}H_{22}O_6$), 322 [M − HOAc]$^+$ (30), 307 [322 − Me]$^+$ (51), 234 (64), 205 (77), 177 (92), 165 (87), 91 (79); $\alpha_D = +8$ ($CHCl_3$; *c* 0.3).

Acknowledgements—We thank Dr. B. de Winter and Miss M. Welman, Botanic Research Institute, Pretoria, for their help during plant collection and identification of the material and the Deutsche Forschungsgemeinschaft for financial support.

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