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# NEW GUAIANOLIDES FROM *PSEUDOSTIFFTIA KINGII**

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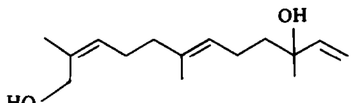
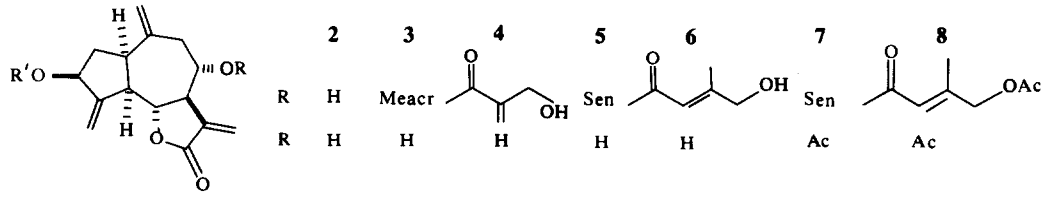
**Key Word Index**—*Pseudostifftia kingii*; Compositae; Vernonieae; sesquiterpene lactones; guaianolides.

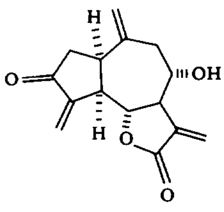
**Abstract**—*Pseudostifftia kingii* afforded several guaianolides, two of them not isolated before.

*Pseudostifftia* is a monotypic genus and the single genus in the subtribe Pseudostifftinae [1], where it has been placed with reservation as the thickened style with scabrid surface and the large non-lophorate pollen grains are unlike any other member of the Vernonieae, although it also does not fit within any other tribe. A first chemical investigation only afforded acetylenes and triterpenes [2]. We now have re-investigated the aerial parts of *Pseudostifftia kingii* H. Robins. In addition to the compounds previously isolated and 13-hydroxynerolidol (**1**) [3], minute amounts of sesquiterpene lactones were isolated, the guianolides desacylcynaropicrin (**2**) [4], arguerin B (**3**) [5], cynaropicrin (**4**) [6], 8$\alpha$-hydroxydehydrozaluzanin C (**9**) [7], the corresponding 11$\beta$,13-dihydro derivative **10** [8] as well as two further lactones, the senecioate **5** and the hydroxysenecioate **6**. The structures followed from the $^1$H NMR spectra (Table 1). The data of **5** clearly showed the presence of a zaluzanin C derivative, as most signals were similar to those of zaluzanin C. However, an additional senecioyloxy residue was present. Spin decoupling showed that this group had to be placed at C-8, while from the couplings the $\alpha$-orientation could be deduced. Acetylation afforded the acetate **7**, its $^1$H NMR spectral data further supporting the proposed structure. The $^1$H NMR spectral data of **6** indicated that a hydroxylated ester group was present, obviously the unusual 4-hydroxysenecioate. Since the signal of the olefinic methyl group was at $\delta$2.15, the

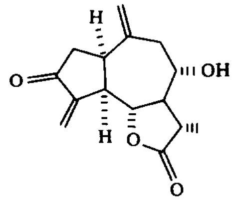


**1**





**9**



**10**

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*Part 414 in the series "Naturally Occurring Terpene Derivatives". For Part 413 see Bohlmann, F., Singh, P., Ruke, A., King, R. M. and Robinson, H. (1982) *Phytochemistry* **21** (in press).

Table 1. $^1H$ NMR spectral data of compounds **5**–**8** (400 MHz, $CDCl_3$, TMS as int. standard)

| | **5** | **6** | **7** | **8** |
|---|---|---|---|---|
| H-1 | 2.98 *dddd* | 3.02 *dddd* | 2.98 *dddd* | 3.02 *dddd* |
| H-2α | 1.74 *ddd* | 1.80 *ddd* | 1.75 *ddd* | 1.80 *ddd* |
| H-2β | 2.24 *ddd* | 2.39 *ddd* | 2.24 *ddd* | 2.38 *ddd* |
| H-3 | 4.56 *br dd* | 5.57 *dddd* | 4.55 *br dd* | 5.57 *dddd* |
| H-5 | 2.85 *br dd* | 2.85 *br dd* | 2.85 *br dd* | 2.85 *br dd* |
| H-6 | 4.22 *dd* | 4.17 *dd* | 4.22 *dd* | 4.17 *dd* |
| H-7 | 3.12 *dddd* | 3.13 *dddd* | 3.13 *dddd* | 3.15 *dddd* |
| H-8 | 5.04 *ddd* | 5.05 *ddd* | 5.06 *ddd* | 5.09 *ddd* |
| H-9α | 2.70 *dd* | 2.70 *dd* | 2.70 *dd* | 2.70 *dd* |
| H-9β | 2.36 *dd* | 2.39 *dd* | 2.37 *dd* | 2.38 *dd* |
| H-13 | 6.22 *d* | 6.23 *d* | 6.22 *d* | 6.24 *d* |
| H-13′ | 5.66 *d* | 5.67 *d* | 5.66 *d* | 5.65 *d* |
| H-14 | 5.14 *br s* | 5.13 *br s* | 5.14 *br s* | 5.14 *br s* |
| H-14′ | 4.96 *br s* | 4.98 *br s* | 4.97 *br s* | 4.99 *br s* |
| H-15 | 5.51 *ddd* | 5.53 *dd* | 5.50 *dd* | 5.54 *dd* |
| H-15′ | 5.38 *ddd* | 5.35 *dd* | 5.36 *dd* | 5.36 *dd* |
| OCOR | 5.74 *qq* | 5.74 *qq* | 6.08 *q* | 5.92 *q* |
| | 2.20 *d* | 2.20 *d* | 4.20 *br s* | 4.62 *br s* |
| | 1.95 *d* | 1.95 *d* | 2.15 *br s* | 2.20 *br s* |
| OAc | — | 2.10 *s* | — | 2.17 *s* |
| | | | | 2.11 *s* |

*J*(Hz): 1,2α = 11; 1,2β = 1,5 = 8; 2α,2β = 13; 2α,3 = 2β,3 = 8; 3,15 = 5,15 = 1.5; 5,6 = 10.5; 6,7 = 9; 7,8 = 10; 7,13 = 3.5; 7,13′ = 3; 8,9α = 5; 8,9β = 4; 9α,9β = 15.

stereochemistry was also clear. All other signals were similar to those of **5**. Acetylation afforded the diacetate **8**, its $^1H$ NMR spectrum further establishing the structure. Finally a trace of a further lactone was isolated, which obviously was a furanoheliangolide with an angelate residue, deduced from the typical $^1H$ NMR signals of H-2, H-5, H-14, H-15 and angelate. However, the amount of material was not sufficient to establish the structure.

These additional results on the chemistry of *Pseudostifftia* support the placement of this genus in the Vernonieae, since guaianolides and lupanes are widespread in the tribe.

## EXPERIMENTAL

The air dried aerial parts (100 g), collected in north-eastern Brazil, voucher RMK 8666, deposited in the U.S. National Herbarium, Washington, was extracted with $Et_2O$–petrol, 1:2 and the resulting extract was separated by CC (Si gel) and further by repeated TLC (Si gel). Known compounds were identified by comparing the $^1H$ NMR spectra with those of authentic material. In addition to compounds isolated before, 2 mg **1**, 5 mg **2**, 1.5 mg **3**, 4 mg **4**, 2 mg **5** ($Et_2O$–petrol, 3:1), 2.5 mg **6** ($Et_2O$), 5 mg **9** and 0.5 mg **10** were obtained.

*8α-Senecioyloxy dehydrozaluzanin C* (**5**). Colourless gum, not free from **3**, IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 3600 (OH), 1775 (γ-lactone), 1720 ($C{=}CCO_2R$); MS *m*/*z* (rel. int.): 344.164 $[M]^+$ (1) ($C_{20}H_{24}O_5$), 244 $[M - HO_2CR]^+$ (23), 226 $[244 - H_2O]^+$ (12), 83$[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (40).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+32 \quad +33 \quad +37 \quad +68} (CHCl_3;\ c\ 0.2).$$

Acetylation (1 hr, $Ac_2O$, 70°) afforded **7**, a colourless gum; $^1H$ NMR see Table 1.

*8α-(4′-Hydroxysenecioyloxy)-dehydrozaluzanin C* (**6**). Colourless gum, which was purified as its acetate **8** also a colourless gum, IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 3605 (OH), 1780 (γ-lactone), 1740 (OAc), 1720 ($C{=}CCO_2R$); MS *m*/*z* (rel. int.): 444 $[M]^+$ (0.1), 286 $[M - HO_2CR]^+$ (0.2), 226.099 $[286 - HOAc]^+$ (9) $C_{15}H_{14}O_2$), 211 $[226 - Me]^+$ (1), 198 $[226 - CO]^+$ (3), 141 $[RCO]^+$ (7), 99 $[C_4H_6(OH)CO]^+$ (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+22 \quad +24 \quad +36 \quad +98} (CHCl_3;\ c\ 0.25).$$

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## REFERENCES

1. Robinson, H., Bohlmann, F. and King, R. M. (1980) *Phytologia* **46**, 421.
2. Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1980) *Phytochemistry* **19**, 2669.
3. Bohlmann, F. and Zdero, C. (1980) *Phytochemistry* **19**, 587.
4. Gonzales, A. G., Bermejo, J., Massanet, G. M. and Perez, J. (1973) *An. Quim.* 1333.
5. Gonzales, A. G., Bermejo, J., Cabrera, I., Massanet, G. M., Mansilla, H. and Galindo, A. (1978) *Phytochemistry* **17**, 955.
6. Suchy, M., Herout, V. and Sorm, F. (1959) *Collect. Czech. Chem. Commun.* **24**, 1542.
7. Bohlmann, F., Singh, P., Borthakur, N. and Jakupovic, J. (1981) *Phytochemistry* **20**, 2379.
8. Bohlmann, F., Brindöpke, G. and Rastogi, R. C. (1978) *Phytochemistry* **17**, 475.