analysis of type A wood, jinkohol was not observed under either operating conditions (procedures I and II). The absence of (+)-karanone was confirmed in both kinds of wood.

The following conclusions may be drawn from the results given in Table 1: (i) agarospirol, jinkoh-eremol, kusunol and oxo-agarospirol occurred abundantly in both kinds of agarwood; (ii) type B agarwood contained a large amount of (−)-10-epi-γ-eudesmol, jinkohol and jinkohol II, whereas type A wood contained none of these sesquiterpenes; and (iii) nor-ketoagarofuran and dihydrokaranone were found only in type A agarwood. These differences in the sesquiterpene compositions of types A and B agarwood might serve to distinguish chemically the two kinds of wood and to permit identification. Furthermore, it is assumed that these differences are due to the different species of source plants. However, in order to verify this assumption, further corroborating evidence should be provided in the future.

EXPERIMENTAL

Plant material. Types A and B agarwood used in the present study were collected in Vietnam and in Indonesia (imported via Singapore), respectively. Their source plants have been identified by one of us (K.Y.) as *Aquilaria agallocha* Roxb. and the genus *Aquilaria* (probably *Aquilaria malaccensis* Benth.), respectively

Isolation of essential oils. Finely powdered wood (1 g) was extracted with C_6H_6 (70 ml) for 3 hr under reflux. The C_6H_6 extract was filtered and washed with a further 20 ml C_6H_6 and the solvent was distilled off. The residue was dissolved in an adequate amount of warm *n*-hexane and allowed to stand in a freezer for 3 hr. The insoluble resinous ppt. was filtered off and the filtrate obtained was regarded as the essential oil fraction and subjected to a combination of GLC and GC/MS analyses.

Operating conditions of GLC and GC/MS. Procedure I—analytical GLC: detector, FID; column, Carbowax 20M (25 m × 0.2 mm i.d.); He, 0.6 kg/cm^2; column temp., programmed 55–210° at 4°/min. GC/MS: column, Thermon 600T (40 m × 0.2 mm i.d.); He, 1.1 kg/cm^2; ionization energy, 20 eV; column temp., programmed 70–220° at 4°/min. Procedure II—analytical GLC: detector, FID, column, DEGS (30 m × 0.3 mm i.d.); N_2 flow rate, 50 ml/min, column temp., programmed 140–180° at 2°/min. GC/MS: column and column temp., the same as in the above GLC; He flow rate, 50 ml/min; ionization energy, 70 eV.

Mass spectra corresponding to every GC peak of more than 0.3% abundance in procedure I and of more than 1% in procedure II were obtained and the percentage compositions were recorded by a computer.

REFERENCES

1 Jain, T. C and Bhattacharyya, S. C (1959) *Tetrahedron Letters* 13.
2. Varma, K. R., Maheshwari, M. L and Bhattacharyya, S. C. (1965) *Tetrahedron* **21**, 115.
3. Maheshwari, M. L., Jain, T. C., Bates, R. B. and Bhattacharyya, S. C. (1963) *Tetrahedron* **19**, 1079.
4. Maheshwari, M. L., Varma, K R. and Bhattacharyya, S. C. (1963) *Tetrahedron* **19**, 1519.
5. Barrett, H. C. and Büchi, G. (1967) *J. Am. Chem. Soc.* **89**, 5665.
6. Nakanishi, T., Yamagata, E., Yoneda, K. and Miura, I. (1981) *Phytochemistry* **20**, 1597.
7. Nakanishi, T., Yamagata, E., Yoneda, K., Miura, I and Mori, H. (1983) *J. Chem. Soc. Perkin Trans* 1, 601.
8. Nakanishi, T., Yamagata, E., Yoneda, K., Nagashima, T., Kawasaki, I., Yoshida, T, Mori, H and Miura, I. (1984) *Phytochemistry* **23**, 2066.
9. Nagashima, T., Kawasaki, I., Yoshida, T., Nakanishi, T., Yoneda, K. and Miura, I., 9th International Congress of Essential Oils, Singapore, 13–17 March 1983.

Phytochemistry, Vol 23, No 9, pp 2069–2070, 1984
Printed in Great Britain

A FURTHER STEIRACTINOLIDE FROM *WEDELIA GRANDIFLORA*

FERDINAND BOHLMANN, WIDAYATI ANG, ROBERT M. KING* and HAROLD ROBINSON*

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, W. Germany, *Smithsonian Institution, Department of Botany, Washington, DC 20560, U S.A

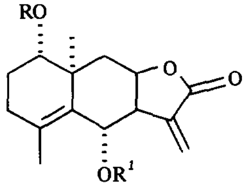
(*Received* 20 *January* 1984)

Key Word Index—*Wedelia grandiflora*; Compositae; sesquiterpene lactones, steiractinolide.

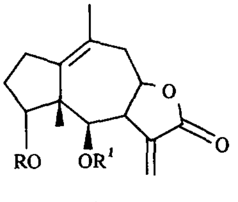
Abstract—A reinvestigation of the aerial parts of *Wedelia grandiflora* showed that the described lactones also are steiractinolides. 6α-Angeloyloxy-1α-hydroxysteiractinolide has not been isolated previously.

Several *Wedelia* species have yielded eudesmanolides with a 10α-methyl group ("steiractinolides") [1–3]. We have therefore reinvestigated *Wedelia grandiflora* where we proposed earlier that the lactones were pseudoguaianolides [4].

In addition to the *ent*-kaurene derivatives obtained previously [4], three steiractinolides, the tiglate **1** identical with a lactone from a *Steiractinia* species [1], the angelate **2** and the methacrylate **3** were obtained. The spectrum of **3** was identical with that of the methacrylate obtained previously [4]. Therefore its structure as well as those of the corresponding esters has to be corrected to **3**–**7**. The



	1	2	3	4	5	6	7
R	H	H	H	Ac	Ac	Ac	Ac
R	Tigl	Ang	Meacr	Meacr	Tigl	iBu	iVal



8

^{1}H NMR spectrum (see Experimental) of **2** clearly showed that it is a steiractinolide with an angelate residue. All signals were close to those of **1** and **3** except those of the ester moiety. NOE difference spectra again showed that an eudesmanolide with a 10α-methyl group was present. A clear differentiation between steiractinolides of types **1**–**7** and the structures proposed previously (**8**) [4] can be made by the NOE difference spectra [2, 3] whereas the chemical shifts and the sequences obtained by spin decoupling do not give such clear indications.

EXPERIMENTAL

The aerial parts (260 g) (voucher RMK 9088, collected in January 1983 in Peru) were extracted with Et_2O–petrol–MeOH, 1:1:1, and worked-up in the usual fashion [5]. The polar CC fractions (Et_2O–MeOH, 10:1) gave by TLC (SiO_2, PF 254, CH_2Cl_2–C_6H_6–Et_2O, 1:1:1, two developments) a mixture of **1**–**3** (R_f 0.3) which was separated by HPLC (RP 8, MeOH–H_2O, 3:2, flow rate 330, *ca* 100 bar) affording 18 mg **3** (R_t 11.0 min), 46 mg **1** (R_t 15 min) and 9 mg **2** (R_t 17.5 min). The 400 MHz ^{1}H NMR spectra of **1** and **3** were identical with those of authentic material.

6α-Angeloyloxy-1α-hydroxy-steiractinolide (**2**). Colourless oil, homogeneous by TLC (Et_2O or CH_2Cl_2–C_6H_6–Et_2O, 1:1:1) and HPLC (RP, MeOH–H_2O, 3:2); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone), 1720, 1650 (C=CCO_2R); MS *m/z* (rel. int.): 247.133 $[M-OCOR]^+$ (21) (calc. for $C_{15}H_{19}O_3$: 247.133), 246 $[M-RCO_2H]^+$ (0.5), 228 $[246-H_2O]^+$ (6), 203 $[247-CO_2]^+$ (24), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (61); CD (MeCN): $\Delta\varepsilon_{277} = -0.44$; ^{1}H NMR (400 MHz, TMS as internal standard, $CDCl_3$): 3.77 (*dd*, H-1), 5.89 (*d*, H-6), 3.45 (*br d*, H-7), 4.86 (*ddd*, H-8), 2.55 (*dd*, H-9), 1.91 (*dd*, H-9′), 6.35 (*d*, H-13), 5.91 (*d*, H-13′), 1.10 (*s*, H-14), 1.67 (*br s*, H-15), 6.16 (*qq*, H-3′), 2.04 (*dq*, H-4′), 1.93 (*dq*, H-5′); *J* (Hz): 1, 2 = 11.5; 1, 2′ = 6; 6, 7 = 2; 7, 8 = 8; 7, 13 = 2.5; 7, 13′ = 2; 8, 9 = 4; 8, 9′ = 3; 9, 9′ = 15; 3′, 4′ = 7; 3′, 5′ = 4′, 5′ = 1.

REFERENCES

1. Bohlmann, F., Knoll, K.-H., Robinson, H. and King, R. M. (1980) *Phytochemistry* **19**, 971.
2. Bohlmann, F., Jakupovic, J., Ates (Gören), N., Schuster, A., Pickardt, J., King, R. M. and Robinson, H. (1983) *Liebigs Ann. Chem.* 962.
3. Bohlmann, F., Zdero, C., Jakupovic, J., Ates (Gören), N., King, R. M. and Robinson, H. (1983) *Liebigs Ann. Chem.* 1257.
4. Bohlmann, F., Rosenberg, E., Robinson, H. and King, R. M. (1980) *Phytochemistry* **19**, 2041.
5. Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1984) *Phytochemistry* **23**, 1979.