Phytochemistry, Vol 23, No 9, pp. 2068–2069, 1984
Printed in Great Britain

0031–9422/84 $3.00 + 0.00

SESQUITERPENOIDS IN TWO DIFFERENT KINDS OF AGARWOOD*

KAISUKE YONEDA,† ETSUKO YAMAGATA,† TSUTOMU NAKANISHI,‡¶ TSUKASA NAGASHIMA,§ ICHIRO KAWASAKI,§ TOSHIO YOSHIDA,§ HIDEO MORI|| and IWAO MIURA||

†Faculty of Pharmaceutical Sciences, Osaka University, Suita, Osaka 565, Japan; ‡Faculty of Pharmaceutical Sciences, Setsunan University, Hirakata, Osaka 573-01, Japan; §Takasago Corporation, Kamata, Ohta-ku, Tokyo 144, Japan; ||Laboratories of Natural Product Chemistry, Otsuka Pharmaceutical Co. Ltd., Kawauchi-cho, Tokushima 771-01, Japan

(*Revised received* 9 *December* 1983)

Key Word Index—*Aquilaria agallocha*; *Aquilaria* sp. (*Aquilaria malaccensis*); Thymelaeaceae; two kinds of agarwood; essential oil; sesquiterpenoids.

Abstract—Sesquiterpenoids of an agarwood originating from *Aquilaria agallocha* and of the other kind of agarwood (*Aquilaria* sp.; probably *Aquilaria malaccensis*) were investigated by a combination of GLC and GC/MS. The differences in sesquiterpene composition between the two kinds of agarwood are discussed.

INTRODUCTION

Agarwood (Jinkoh in Japanese) is a widely used, famous incense of the Orient. About 20 years ago, Indian chemists isolated and characterized two major sesquiterpenes, agarol [1] and agarospirol [2]; together with six minor (−)-selinanic furanoids, i.e. α- and β-agarofuran, dihydroagarofuran, nor-ketoagarofuran, etc. [3–5] from an agarwood (type A) originating from *Aquilaria agallocha* Roxb. Recently, we have found that besides this type A wood, the other kind of agarwood (type B) is also popular in the market-place today, and from this type B wood (*Aquilaria* sp.; probably *Aquilaria malaccensis* Benth.) eight major sesquiterpenes, i.e. jinkohol [6], agarospirol, kusunol, jinkoh-eremol, jinkohol II [7], α-agarofuran, (−)-10-epi-γ-eudesmol and oxo-agarospirol [8] have been isolated and identified. Furthermore, we have also characterized (+)-karanone [= the 1,2,9,10-tetradehydro derivative of (+)-fukinone] and (+)-dihydrokaranone (= 9,10-didehydrofukinone), together with oxo-agarospirol, from a different kind of agarwood, called Kanankoh in Japanese, which is more expensive and precious than the usual type of agarwood, i.e. Jinkoh [9]. In the present work the sesquiterpene compositions of the above-mentioned two typical kinds of agarwood, i.e. type A wood collected in Vietnam and type B wood collected in Indonesia, were analysed by means of a combination of GLC and GC/MS.

RESULTS AND DISCUSSION

The essential oil fractions from types A and B agarwood were subjected to a combination of GLC and GC/MS analyses under the conditions described for procedure I (see Experimental). Individual components were identified by means of co-GLC with authentic samples of β-agarofuran**, α-agarofuran [8], nor-ketoagarofuran**, (−)-10-epi-γ-eudesmol [8], agarospirol [2, 7], jinkohol [6], jinkoh-eremol [7], kusunol [7], dihydrokaranone [9], karanone [9], jinkohol II [7] and oxo-agarospirol [8, 9] (listed in order of increasing retention time) and by GC/MS. The sesquiterpenoid constituents identified from types A and B agarwood, together with their relative percentages from the corresponding essential oil fractions (determined by GLC), are listed in Table 1. In the analysis of type B wood using procedure I, agarospirol and jinkohol gave partially overlapping peaks. Using this procedure, only qualitative analyses of these terpenes were successful and the total content (12.4%) was also evaluated. Therefore, the individual quantitative values, i.e. 7.2% agarospirol and 5.2% jinkohol cited in Table 1, were calculated by the aid of the second set of operating conditions (procedure II), in which agarospirol and jinkohol gave their respective peaks without overlapping and the ratio of their contents was 14.7:10.6. In the

Table 1. Sesquiterpenoids of agarwood

GC peak	Compound	Type A wood	Type B wood
1	β-Agarofuran	0.6*	—
2	α-Agarofuran	—	1.3
3	Nor-ketoagarofuran	0.6	—
4	(−)-10-Epi-γ-eudesmol	—	6.2
5	Agarospirol	4.7	7.2
6	Jinkohol	—	5.2
7	Jinkoh-eremol	4.0	3.7
8	Kusunol	2.9	3.4
9	Dihydrokaranone	2.4	—
10	Jinkohol II	—	5.6
11	Oxo-agarospirol	5.8	3.1

*Percentage of essential oil.

*Part 4 in the series "Sesquiterpene Constituents in Agarwood". For Part 3 see ref. [8].

¶To whom correspondence should be addressed

**β-Agarofuran and nor-ketoagarofuran were previously isolated by us from agarwood oil and identified by comparison of their physical and spectral data with those published for the respective authentic specimens [3, 4].

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

0031–9422/84 $3 00 + 0.00

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