

# Jinkoh-eremol and Jinkohol II, Two New Sesquiterpene Alcohols from Agarwood<sup>1</sup>

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From an agarwood (*Aquilaria* sp.; probably *Aquilaria malaccensis* Benth.) which is different from that obtained from *Aquilaria agallocha* Roxb., two new sesquiterpene alcohols, which we have named jinkoh-eremol (3) and jinkohol II (5), have been isolated, together with agarospirol (1), kusunol (2), and jinkohol (4), as major sesquiterpene constituents and their structures have been established.

Agarwood (Jinkoh in Japanese) is a widely used, famous incense of the Orient. About twenty years ago, Indian chemists isolated and characterized two major sesquiterpenes, agarol<sup>2</sup> and agarospirol<sup>3</sup> (1), together with six minor (–)-selinanic furanoids<sup>4,5</sup> from an agarwood (type A) originating from *Aquilaria agallocha* Roxb. Recently, we have noticed that besides the type-A wood, the other kind of agarwood (type B) is also popular in the marketplace today and from this type-B wood (*Aquilaria* sp.; probably *Aquilaria malaccensis* Benth.), collected in Indonesia and imported via Singapore, a major (+)-prezizane-type sesquiterpene alcohol, jinkohol (4) has been characterized.<sup>1</sup>

In this paper we report the results of our continuing research on major sesquiterpene components of type-B agarwood. After chromatographic and high-pressure liquid chromatography (h.p.l.c.) separation of the benzene extract of agarwood B, two new sesquiterpene alcohols, jinkoh-eremol (3) and jinkohol II (5), were isolated, together with agarospirol (1) and kusunol (2), and their structures were determined on the basis of spectroscopic and chemical evidence. The two known alcohols were also characterized.

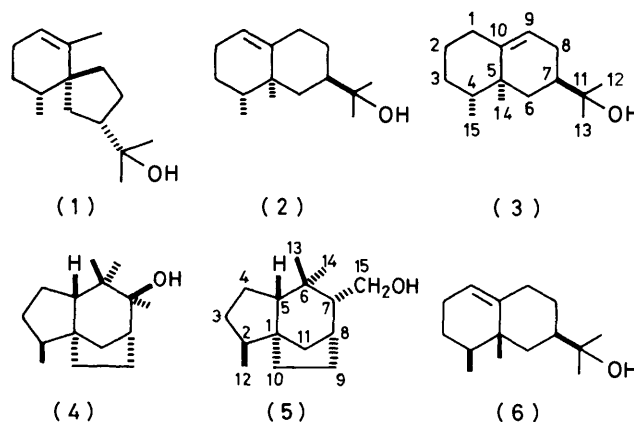
## Results and Discussion

The isolated alcohol agarospirol (1) was identified (see Experimental section) by direct comparison with an authentic sample.<sup>6</sup>

A second alcohol, C<sub>15</sub>H<sub>26</sub>O, *M*<sup>+</sup> = 222.1995, [ $\alpha$ ]<sub>D</sub> +96°, obtained from the second polar fraction, was characterized as kusunol<sup>7</sup> (valerianol<sup>8</sup>) (2) by comparison of their superimposable i.r. spectra (CCl<sub>4</sub>) and their optical rotation values. Our assignment of structure (2) was further corroborated by the <sup>1</sup>H n.m.r. data (Table 1) which are consistent with the kusunol structure (2) (possessing the chair-conformational B-ring) and are different from those of an isomer, eremoligenol<sup>9</sup> (6) (possessing the boat-conformational B-ring).

The third polar alcohol, jinkoh-eremol, C<sub>15</sub>H<sub>26</sub>O, *M*<sup>+</sup> = 222.1991, [ $\alpha$ ]<sub>D</sub> –66°, exhibited bands for a hydroxy-group [3 620 and 3 500(w) cm<sup>-1</sup>] and a double bond (1 662 cm<sup>-1</sup>) in the i.r. spectrum. A comparison of its <sup>1</sup>H n.m.r. data (Table 1) with those of kusunol (2) suggested that jinkoh-eremol has structure (3), i.e. that it is the  $\Delta^9$ -isomer of kusunol. Both olefins (2) and (3) were hydrogenated under similar acidic conditions to yield the same epimeric mixture of dihydro-derivatives (7), C<sub>15</sub>H<sub>28</sub>O, *M*<sup>+</sup> = 224.2134; the identity of the hydrogenation products was confirmed by their superimposable <sup>1</sup>H n.m.r. (400 MHz) and mass-spectra.

The absolute configuration of compound (3) was established by comparison of its optical rotation and c.d. spectrum with those of known reference compounds as follows. (i) Rotations



of compounds (2) (+96°) and (3) (–66°) coincided in sign with those of valencene (8) (+190°) and nootkatene (9) (–194°),<sup>10</sup> respectively, and were opposite in sign to those of 1(10)-aristolene (10) (–78.5°) and 9-aristolene (11) (+80.9°),<sup>11</sup> respectively. (ii) Jinkoh-eremol (3) showed a positive c.d. Cotton effect ([ $\theta$ ] +18 000) at 200 nm, due to the isolated double bond ( $\pi \rightarrow \pi^*$  transition). In the light of the reversed octant (SW) rule,<sup>12</sup> ABP model rule,<sup>13</sup> and/or the empirical analysis method of Kirk *et al.*,<sup>14</sup> and by correlation, i.e. comparison with the c.d. signs of model compounds of known stereochemistry, viz. (2) ([ $\theta$ ] –12 700 at 199.5 nm) and (6) ([ $\theta$ ] +34 200 at 200 nm), the intense positive c.d. band of compound (3) suggests that the tertiary 5-methyl group has the  $\alpha$ -orientation in this compound.

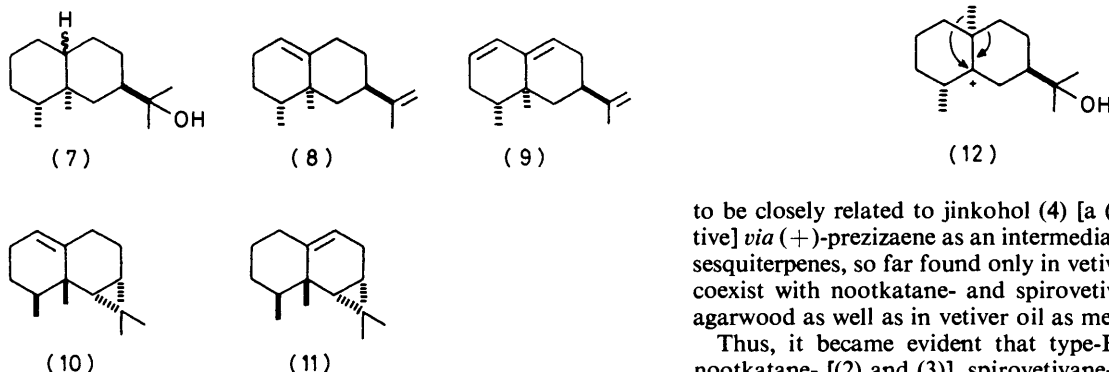
The most polar alcohol, jinkohol II,† C<sub>15</sub>H<sub>26</sub>O, m.p. 79–81 °C, possessed a primary hydroxy-group [ $\nu$  3 665(w), 3 590, and 3 440(w) cm<sup>-1</sup>;  $\delta$  3.55 (1 H, dd *J* 10.4 and 10.1 Hz) and 3.76 (1 H, dd, *J* 10.4 and 3.3 Hz)] and geminal dimethyl groups [ $\nu$  1 372 and 1 361 cm<sup>-1</sup>;  $\delta$  0.75 and 0.98 (each 3 H, s)]. Based on the detailed <sup>1</sup>H n.m.r. assignments compared with those of jinkohol (4) (Table 2), the relative structure was inferred to be that shown in formula (5), except that the configuration of the primary alcohol group at C-7 was uncertain. In order to determine the configuration of this substituent, the <sup>13</sup>C n.m.r. spectrum was investigated in detail and compared with that of jinkohol (4) (Table 3). Atoms C-5 and C-11 of compound (5), both having a 1,3-relationship to C-7, resonated at  $\delta$  59.8 and 44.0 p.p.m., respectively, downfield

† The sesquiterpene corresponding to jinkohol II has also been isolated from type-B agarwood: T. Nagashima *et al.*, Takasago Perfumery Co., Ltd. (unpublished work); personal communication.

**Table 1.**  $^1\text{H}$  N.m.r. data for compounds (2) and (3).<sup>a</sup> Both compounds numbered as in structure (3)

	(2)	(3)
1-H (vinylic)	5.32, ddd, 1, $2\alpha = 5.7$ ; 1, $2\beta = 2.2$ ; 1, $9\alpha = 2.2$ <sup>b</sup>	
1 $\alpha$ -H		2.12, t (br)
1 $\beta$ -H		2.01, d (br)
2 $\alpha$ -H	1.98, m	1.44, m
2 $\beta$ -H	2.01, m	1.73, m
3 $\alpha$ -H	1.41, m	1.35, m
3 $\beta$ -H	1.41, m	1.25, m
4 $\alpha$ -Me	0.88, d, 6.2	0.85, d, 6.7
4 $\beta$ -H	1.41, m	1.26, m
5 $\alpha$ -Me	0.92, s	0.95, s
6 $\alpha$ -H	1.94, ddd, $6\alpha, 6\beta = 12.4$ ; $6\alpha, 7\alpha = 3.3$ ; $6\alpha, 8\alpha = 2.7$ <sup>c</sup>	1.84, ddd, $6\alpha, 6\beta = 12.4$ ; $6\alpha, 7\alpha = 2.2$ ; $6\alpha, 8\alpha = 2.2$ <sup>c</sup>
6 $\beta$ -H	0.81, dd, $6\beta, 6\alpha = 6\beta, 7\alpha = 12.4$	0.98, dd, $6\beta, 6\alpha = 6\beta, 7\alpha = 12.4$
7 $\alpha$ -H	1.62, dddd, $7\alpha, 6\beta = 7\alpha, 8\beta = 12.4$ ; $7\alpha, 8\alpha = 7\alpha, 6\alpha = 3.3$	1.61, dddd, $7\alpha, 6\beta = 12.4$ ; $7\alpha, 8\beta = 12.2$ ; $7\alpha, 8\alpha = 4.9$ ; $7\alpha, 6\alpha = 2.2$
8 $\alpha$ -H	1.85, ddddd, $8\alpha, 8\beta = 12.4$ ; $8\alpha, 9\beta = 4.0$ ; $8\alpha, 7\alpha = 8\alpha, 9\alpha = 3.3$ ; $8\alpha, 6\alpha = 2.7$ <sup>c</sup>	2.04, m
8 $\beta$ -H	1.01, dddd, $8\beta, 8\alpha = 8\beta, 7\alpha = 12.4$ ; $8\beta, 9\alpha = 12.4$ ; $8\beta, 9\beta = 2.7$	1.77, dddd, $8\beta, 8\alpha = 17.0$ ; $8\beta, 7\alpha = 12.2$ ; $8\beta, 9 = 2.2$ ; $8\beta, 1\alpha = 2.2$ <sup>b</sup>
9-H (vinylic)		5.30, ddd, $9, 8\alpha = 5.7$ ; $9, 1\alpha = 2.2$ <sup>b</sup> ; $9, 8\beta = 2.2$
9 $\alpha$ -H	2.27, dddd, $9\alpha, 9\beta = 13.8$ ; $9\alpha, 8\beta = 12.4$ ; $9\alpha, 8\alpha = 3.3$ ; $9\alpha, 1 = 2.2$ <sup>b</sup>	
9 $\beta$ -H	2.10, ddd, $9\beta, 9\alpha = 13.8$ ; $9\beta, 8\alpha = 4.0$ ; $9\beta, 8\beta = 2.7$	
gem. dimethyl	1.17, s (6 H)	1.18, s (3 H); 1.20, s (3 H)

<sup>a</sup> Spectra measured at 400 MHz in  $\text{CDCl}_3$ ; chemical shifts are in  $\delta$  values relative to internal  $\text{SiMe}_4$ , and are followed by multiplicities and  $J$  values (Hz). Assignments for both compounds were effected by double-resonance experiments. <sup>b</sup> Long-range coupling. <sup>c</sup> Long-range coupling in a periplanar W arrangement.



(by *ca.* 4–6 p.p.m.) from the corresponding signals ( $\delta$  55.7 and 38.1 p.p.m., respectively) for compound (4); this was indicative of the absence of any axial substituent at C-7 in jinkohol II. This led us to establish the relative structure (5), involving the equatorial primary alcohol group at C-7, for jinkohol II.

The lanthanide-shift experiment (Table 3), in which atoms C-8 and C-9 of compound (5) exhibited the second and third largest downfield shifts, respectively, were in favour of the established structure (5). The positive rotation,  $[\alpha]_D + 32.4^\circ$ , in conjunction with the following evidence, suggests that the absolute structure for jinkohol II should be as shown in structure (5). (i) A series of (–)-prezizane derivatives, *viz.* (–)-prezizaene ( $-47^\circ$ ), (–)-7 $\beta$ -hydroxyprezizane ( $-48.3^\circ$ ), and (–)-7 $\alpha, 15$ -dihydroxyprezizane ( $-32^\circ$ ), give negative optical rotations.<sup>15</sup> (ii) Biogenetically, jinkohol II (5) is considered

to be closely related to jinkohol (4) [a (+)-prezizane derivative] *via* (+)-prezizaene as an intermediate. (iii) (+)-Prezizane sesquiterpenes, so far found only in vetiver oil and agarwood, coexist with nootkatane- and spirovetivane-type terpenes in agarwood as well as in vetiver oil as mentioned below.

Thus, it became evident that type-B agarwood contains nootkatane- [(2) and (3)], spirovetivane- (1), and the tricyclic (+)-prezizane- [(4) and (5)] type sesquiterpenes. These structural types also occur abundantly in vetiver oil,<sup>10,16,\*</sup> which suggests a similar biosynthetic origin for the agarwood and vetiver oil sesquiterpenes. Therefore, the terpenes (1), (2), and (3) in agarwood might be synthesized *via* a common precursor ion (12) derived from a 4,10-epiudesmane, by analogy with  $\alpha$ - and  $\beta$ -vetivone biogenesis.<sup>10</sup>

Although we have assigned the configuration of the secondary methyl group (C-12) at C-2 of jinkohol II (5) as being  $\beta$  based on the  $^{13}\text{C}$ - and  $^1\text{H}$ -n.m.r. chemical shifts (Tables 2 and 3) of the related carbons (C-2 and C-12) and protons

\* A number of nootkatane- ( $\alpha$ -vetivone;  $\beta$ -vetivenene), spirovetivane- ( $\beta$ -vetivone;  $\beta$ -vetispirene), zizane- (zizaene; khusimol; zizanoic acid), and (+)-prezizane- [(+)-prezizaene] type sesquiterpenes from vetiver oil have been isolated and characterized.

**Table 2.**  $^1\text{H}$  N.m.r. data for compounds (4) and (5).<sup>a</sup> Both compounds numbered as in structure (5)

	(4)	(5)
2 $\alpha$ -H	1.80, m	1.79, m
2 $\beta$ -Me	0.84, d, 6.2	0.84, d, 6.4
3 $\alpha$ -H	1.85, m	1.81, m
3 $\beta$ -H	1.12, m	1.10, m
4-H <sub>2</sub>	1.52, m	1.49, m
5 $\beta$ -H	1.69, dd, 5, 4 $\alpha$ = 5, 4 $\beta$ = 9.8	1.49, m
6 $\alpha$ -Me	0.90, s	0.98, s <sup>b</sup>
6 $\beta$ -Me	0.91, s	0.75, s <sup>b</sup>
7 $\alpha$ -Me	1.18, s	
7 $\alpha$ -CH <sub>2</sub> OH		3.55 (15a-H), dd, 15a, 15b = 10.4; 15a, 7 $\beta$ = 10.1
		3.76 (15b-H), dd, 15a, 15b = 10.4; 15b, 7 $\beta$ = 3.3
7 $\beta$ -H		1.47, ddd, 7 $\beta$ , 8 $\beta$ = 2.4; 7 $\beta$ , 15a = 10.1; 7 $\beta$ , 15b = 3.3
8 $\beta$ -H	2.01, dd (br), 8 $\beta$ , 9 $\alpha$ = 4.9; 8 $\beta$ , 11 $\alpha$ = 4.4	2.35, ddd, 8 $\beta$ , 9 $\alpha$ = 6.4; 8 $\beta$ , 11 $\alpha$ = 5.2; 8 $\beta$ , 7 $\beta$ = 2.4
9 $\alpha$ -H	1.66, m	1.54, m
9 $\beta$ -H	1.64, m	1.67, dddd, 9 $\beta$ , 9 $\alpha$ = 13.4; 9 $\beta$ , 10 $\beta$ = 8.9; 9 $\beta$ , 10 $\alpha$ = 4.6; 9 $\beta$ , 11 $\beta$ = 2.1 <sup>c</sup>
10 $\alpha$ -H	1.25, m	1.29, ddd, 10 $\alpha$ , 10 $\beta$ = 13.4; 10 $\alpha$ , 9 $\alpha$ = 8.9; 10 $\alpha$ , 9 $\beta$ = 4.6
10 $\beta$ -H	1.26, m	1.12, dddd, 10 $\beta$ , 10 $\alpha$ = 13.4; 10 $\beta$ , 9 $\beta$ = 8.9; 10 $\beta$ , 9 $\alpha$ = 4.9; 10 $\beta$ , 11 $\beta$ = 2.1 <sup>c</sup>
11 $\alpha$ -H	1.38, dd, 11 $\alpha$ , 11 $\beta$ = 10.6; 11 $\alpha$ , 8 $\beta$ = 4.4	1.70, dd, 11 $\alpha$ , 11 $\beta$ = 10.4; 11 $\alpha$ , 8 $\beta$ = 5.2
11 $\beta$ -H	1.56, ddd, 11 $\beta$ , 11 $\alpha$ = 10.6; 11 $\beta$ , 9 $\beta$ = 11 $\beta$ , 10 $\beta$ = 1.5 <sup>c</sup>	0.99, ddd, 11 $\beta$ , 11 $\alpha$ = 10.4; 11 $\beta$ , 9 $\beta$ = 11 $\beta$ , 10 $\beta$ = 2.1 <sup>c</sup>

<sup>a</sup> Spectra measured at 400 MHz in CDCl<sub>3</sub>; chemical shifts are in  $\delta$  values relative to internal SiMe<sub>4</sub>, and are followed by multiplicities and *J* values (Hz). Assignments for both compounds were made with the aid of double-resonance experiments. <sup>b</sup> Assignments for these values may be interchanged. <sup>c</sup> Long-range couplings in a periplanar W arrangement.

**Table 3.**  $^{13}\text{C}$  Chemical shifts<sup>a</sup> of compounds (4) and (5), and relative shifts<sup>b</sup> of compound (5) induced by Eu(fod)<sub>3</sub> [europium tris-(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionate)]. Both compounds numbered as in structure (5)

Carbon atom	(4)	(5)	$\Delta\delta$
1	52.5 (s) <sup>c</sup>	53.1 (s)	-1.6
2	39.2 (d)	39.4 (d)	-0.9
3	31.1 (t)	31.0 (t)	-0.7
4	21.8 (t)	21.6 (t)	-0.6
5	55.7 (d)	59.8 (d)	-1.6
6	40.0 (s) <sup>c</sup>	34.9 (s)	-1.8
7	77.1 (s)	54.4 (d)	-2.0
8	50.1 (d)	36.9 (d)	-5.4
9	26.4 (t)	24.1 (t)	-2.7
10	21.1 (t)	21.3 (t)	-0.8
11	38.1 (t)	44.0 (t)	-2.4
12	14.4 (q)	14.5 (q)	-0.7
13	27.1 (q)	33.8 (q) <sup>d</sup>	-2.6
14	21.1 (q)	18.0 (q) <sup>d</sup>	-2.5
15	24.0 (q)	62.4 (t)	-24.0

<sup>a</sup> Spectra measured with Bruker WH 400 instrument at 100.61 MHz in CDCl<sub>3</sub>; chemical shifts are in  $\delta$  (p.p.m.) relative to internal SiMe<sub>4</sub>. Signal multiplicities (in parentheses) were obtained from the off-resonance decoupled spectra. Assignments for both alcohols were made based on noise-decoupled, off-resonance decoupled, and selective proton-decoupled n.m.r. spectra, and lanthanide-shift experiments. <sup>b</sup> Induced shifts are in  $\Delta\delta$  (p.p.m.) relative to the shifts given for compound (5); minus signs represent a downfield shift. An adequate amount of Eu(fod)<sub>3</sub> was added to a solution of compound (5) whose concentration was 50 mg ml<sup>-1</sup>. <sup>c</sup> Our previous (incorrect) assignments for these two quaternary carbons (ref. 1) were the reverse of those shown here. <sup>d</sup> Assignments for these carbons may be interchanged.

(2 $\alpha$ -, 3 $\alpha$ -, and 3 $\beta$ -H, and 2 $\beta$ -Me), in agreement with those of jinkohol (4) (also possessing a 2 $\beta$ -Me group), biogenetic considerations also favour this conclusion.\*

Among the five major terpenes isolated from type-B agarwood, four, namely agarospirol (1), kusunol (2), jinkohol (4), and jinkohol II (5), possess intensive odours and appear to be a source of the fragrance of agarwood.

### Experimental

The m.p. of jinkohol II (5) was measured with a Yanagimoto micro-apparatus and is uncorrected. I.r. spectra were run with a Jasco A-202 instrument, and  $^1\text{H}$  n.m.r. spectra with Bruker WH 400 or Varian XL-200 spectrometers operating at 400 and 200 MHz, respectively, with CDCl<sub>3</sub> as solvent and tetramethylsilane as internal standard. Mass- and accurate mass-spectra were obtained from a JEOL JMS-D 300 spectrometer at 70 eV. Optical rotations were determined for solutions in chloroform on a Perkin-Elmer 141 polarimeter, and c.d. spectra for solutions in iso-octane on a Jasco J 200 spectropolarimeter with J-DP2 data processor. Analytical and preparative h.p.l.c. was performed on a Waters instrument with a M6000A pump, a UK6 septumless injector, and a series R 401 differential refractometer. A micro-bonded silica-packed column (Waters  $\mu$  Porasil; 7.8 mm i.d.  $\times$  30 cm; 8–10  $\mu$  pore diameter) was used, with an eluant flow of 3 ml min<sup>-1</sup> with n-hexane-ethyl acetate (15 : 1) as eluant. For column chromatography and thin-layer chromatography (t.l.c.), Merck Kieselgel 60 and 60 F<sub>254</sub> were used, respectively.

\* To our knowledge there is no report on the isolation of epi-prezizane- (the C-2 epimer of prezizane) type sesquiterpene, from natural sources.

**Plant Material.**—The agarwood used in this study was collected in Indonesia and imported via Singapore. The source plant belongs to the genus *Aquilaria* and has been tentatively identified by one of us (K. Y.) as *Aquilaria malaccensis* Benth. from morphological and chemotaxonomical considerations. The exact identification seems to be very difficult but will be the subject of a future publication.

**Extraction and Purification.**—Crushed wood (1.3 kg) was extracted with benzene (total 6 l) three times for 3 h under reflux. The combined benzene extracts were concentrated under reduced pressure to give an oily residue (130 g), a portion (117 g) of which was fractionated on a silica-gel (70–230 mesh; 1 kg) column with benzene as eluant to afford a fraction (5.9 g) containing the four major alcohols (1), (2), (3), and (5). A part (5.0 g) of the fraction was further purified on a silica-gel (230–400 mesh; 400 g) column with n-hexane-diethyl ether (15 : 2) as eluant and then by preparative h.p.l.c. Agarospirol (620 mg), jinkoh-eremol (300 mg), kusunol (260 mg), and jinkohol II (380 mg) were eluted in that order. Every alcohol obtained was further purified by repeated h.p.l.c. separation.

Agarospirol (1), an oil,  $[\alpha]_D -23.5^\circ$  (c, 0.43 in  $\text{CHCl}_3$ ) (lit.,<sup>3</sup>  $[\alpha]_D -5.7^\circ$ ; lit.,<sup>17</sup>  $[\alpha]_D -10^\circ$ ) [Found:  $M^+$ , 222.1985 (8.2 %). Calc. for  $\text{C}_{15}\text{H}_{26}\text{O}$ :  $M$ , 222.1984] was identified by comparison with an authentic synthetic racemate<sup>6</sup> [i.r. ( $\text{CCl}_4$ ),  $^1\text{H}$  n.m.r. (200 MHz), and mass-spectra and retention times (h.p.l.c.)]. As a matter of course, the isolated alcohol (1) was shown to be distinguishable from natural hinesol in all respects [i.r. ( $\text{CCl}_4$ ),  $^1\text{H}$  n.m.r. (200 MHz), and mass-spectra and retention times (h.p.l.c.)]. In our previous work<sup>1</sup> we failed to confirm the occurrence of agarospirol in type-B wood because of the co-existence of other sesquiterpenes showing similar chromatographic behaviour [(2), (3), etc.] and also we cited an incorrect structural formula for agarospirol.

Kusunol (2), an oil,  $[\alpha]_D +96^\circ$  (c, 0.31 in  $\text{CHCl}_3$ ) (lit.,<sup>7</sup>  $[\alpha]_D +111.5^\circ$ ; lit.,<sup>8</sup>  $[\alpha]_D +134^\circ$ ); c.d. (c, 0.907 mg  $\text{ml}^{-1}$  in iso-octane)  $[\theta]_{210} 0$ ,  $[\theta]_{199.5} -12\ 700$ ,  $[\theta]_{192} 0$ ;  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 3 620, 3 500(w), 1 662(sh), and 1 642  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. data are given in Table 1 [Found:  $M^+$ , 222.1995 (7.3%). Calc. for  $\text{C}_{15}\text{H}_{26}\text{O}$ :  $M$ , 222.1984]. The i.r. ( $\text{CCl}_4$ ) spectra of the isolated compound (2) and of authentic natural kusunol were identical. As a matter of course, the isolated alcohol (2) was shown to be distinguishable from natural eremoligenol (6) [c.d. (c, 0.988 mg  $\text{ml}^{-1}$  in iso-octane)  $[\theta]_{200} 0$ ,  $[\theta]_{220} +34\ 200$ ,  $[\theta]_{191} 0$ ] by i.r. ( $\text{CCl}_4$ ),  $^1\text{H}$  n.m.r., c.d., and mass-spectra, and retention times (h.p.l.c.).

Jinkoh-eremol (3), an oil,  $[\alpha]_D -66^\circ$  (c, 0.13 in  $\text{CHCl}_3$ ); c.d. (c, 0.986 mg  $\text{ml}^{-1}$  in iso-octane)  $[\theta]_{214} 0$ ,  $[\theta]_{200} +18\ 000$ ,  $[\theta]_{191} 0$ ;  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 3 620, 3 500(w), and 1662  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. data are listed in Table 1 [Found:  $M^+$ , 222.1991 (2.1%) and ( $M - \text{H}_2\text{O}$ )<sup>+</sup>, 204.1873 (74.3%).  $\text{C}_{15}\text{H}_{26}\text{O}$  and  $\text{C}_{15}\text{H}_{24}$  require  $M$ , 222.1984 and ( $M - \text{H}_2\text{O}$ ), 204.1876, respectively].

Jinkohol II (5), crystals from chloroform, m.p. 79–81 °C;  $[\alpha]_D +32.4^\circ$  (c, 0.26 in  $\text{CHCl}_3$ );  $\nu_{\text{max}}$  ( $\text{CHCl}_3$ ) 3 665(w), 3 590, 3 440(w), 1 372, and 1 361  $\text{cm}^{-1}$ ;  $^1\text{H}$ , and  $^{13}\text{C}$  n.m.r. data are given in Tables 2 and 3, respectively [Found:  $M^+$ , 222.1980 (58.7%), ( $M - \text{Me}$ )<sup>+</sup>, 207.1739 (24.9%), and ( $M - \text{H}_2\text{O}$ )<sup>+</sup>, 204.1869 (7.3%).  $\text{C}_{15}\text{H}_{26}\text{O}$ ,  $\text{C}_{14}\text{H}_{23}\text{O}$ , and  $\text{C}_{15}\text{H}_{24}$  require  $M$ , 222.1984, ( $M - \text{Me}$ ), 207.1746, and ( $M - \text{H}_2\text{O}$ ), 204.1876, respectively].

**Hydrogenation of Kusunol and Jinkoh-eremol.**—(a) Kusunol (2) (20 mg) was stirred (5 d) with Adams catalyst (250 mg) in ethanol (5 ml) and acetic acid (0.5 ml) under hydrogen. T.l.c. [silica gel impregnated with silver nitrate; benzene-ethyl acetate (20 : 3) as developer] showed complete transformation into the desired hydrogenated product. The catalyst was re-

moved by filtration and the ethanol was evaporated off under reduced pressure. The residual acetic acid was, after the addition of an adequate amount of benzene, removed azeotropically under reduced pressure to leave the corresponding epimeric mixture of dihydro-compounds (7) (18 mg) as needles from ethanol [Found:  $M^+$ , 224.2134 (0.2%), ( $M - \text{Me}$ )<sup>+</sup>, 209.1919 (1.7%), ( $M - \text{H}_2\text{O}$ )<sup>+</sup>, 206.2018 (3.3%), and ( $M - \text{C}_3\text{H}_6\text{O}$ )<sup>+</sup>, 166.1709 (60.5%).  $\text{C}_{15}\text{H}_{28}\text{O}$ ,  $\text{C}_{14}\text{H}_{25}\text{O}$ ,  $\text{C}_{15}\text{H}_{26}$ , and  $\text{C}_{12}\text{H}_{22}$  require  $M$ , 224.2137, ( $M - \text{Me}$ ), 209.1904, ( $M - \text{H}_2\text{O}$ ), 206.2033, and ( $M - \text{C}_3\text{H}_6\text{O}$ ), 166.1719, respectively]. The  $^1\text{H}$  n.m.r. (400 MHz) spectrum showed that this hydrogenated product (7) was an epimeric mixture at C-10.

(b) A solution of jinkoh-eremol (3) (20 mg) in ethanol (7 ml) and acetic acid (0.7 ml) was hydrogenated (6 d; t.l.c. monitoring) with Adams catalyst (350 mg) in a similar manner to that described in (a). The same product (7) (19 mg) as in (a) was obtained and its identity was confirmed by  $^1\text{H}$  n.m.r. (400 MHz) and mass-spectra, and t.l.c.

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