Enantiomeric Purity and Odor Characteristics of 2- and 3-Acetoxy-1,8-cineoles in the Rhizomes of *Alpinia galanga* Willd.

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(*S*)-(+)-*O*-methylmandelate esters of *trans*- and *cis*-1,3,3-trimethyl-2-oxabicyclo[2.2.2]octan-5- and 6-ols (2- and 3-hydroxy-1,8-cineoles) were prepared, and eight diastereomers were separated. The absolute configuration of the asymmetric carbons of the cineole moiety of each diastereomer was determined by ^{1}H NMR data according to the Mosher theory. Each mandelate was reduced with $LiAlH_4$ to obtain optically pure hydroxy-1,8-cineoles, this being followed by acetylation to afford optically pure acetoxy-1,8-cineoles. These acetates were subjected to chiral GC, using a cyclodextrin column, and the enantiomeric purity of *trans*- and *cis*-1,3,3-trimethyl-2-oxabicyclo[2.2.2]octan-5- and 6-yl acetates in the aroma concentrate from the rhizomes of *Alpinia galanga* was determined as 93.9 (5*S*), 19.4 (5*R*), 63.5 (6*R*), and 100 (6*R*) % *ee*, respectively. The aroma character of each enantiomer was also evaluated by GC-sniffing.

Keywords: *Alpinia galanga W.; rhizome; enantiomeric purity; odor; acetoxy-1,8-cineole; 1,3,3-trimethyl-2-oxabicyclo[2.2.2]octan-6-yl acetate; 1,3,3-trimethyl-2-oxabicyclo[2.2.2]octan-5-yl acetate; O-methylmandelate*

INTRODUCTION

The rhizomes of greater galangal (*Alpinia galanga* Willd.) exhibit a woody, floral, and spicy note which is different from ginger, and they are widely used as a spice throughout southeast Asia. We have described in our previous paper that four isomers, *trans*- and *cis*-2-acetoxy-1,8-cineoles ((1*SR*,4*RS*,6*SR*)- and (1*SR*,4*RS*,6*RS*)-1,3,3-trimethyl-2-oxabicyclo[2.2.2]octan-6-yl acetate, **1a** and **2a**) and *trans*- and *cis*-3-acetoxy-1,8-cineoles ((1*SR*,4*RS*,5*RS*)- and (1*SR*,4*RS*,5*SR*)-1,3,3-trimethyl-2-oxabicyclo[2.2.2]octan-5-yl acetate, **3a** and **4a**), were newly identified positively as natural aroma components from the rhizomes, and they presented individually interesting odors (Kubota et al., 1998). Although they incorporated three asymmetric carbons in the molecule, two of them were bridgehead carbons; that is, each isomer of the acetoxycineoles had two optical isomers associated with the carbon bearing the acetoxy group. It was observed by gas chromatographic analysis with a chiral column that each acetoxy-1,8-cineole in *A. galanga* could be separated into the optical isomers in a specific ratio, although the absolute configuration of each peak was not determined. It is important to investigate the enantiomeric purity of chiral aroma components, because the flavor character or biological activity of some compounds can often be different between enantiomers (Haring et al., 1972; Acree et al., 1985; Mosandl et al., 1986). Recently, the direct enantiomeric separation technique by capillary gas chromatography using some modified cyclodextrins as the chiral stationary phase has been noted to examine the enantiomeric purity of aroma constituents (König et al., 1992; Wang et al., 1996). In this study, we prepared the optically pure acetoxy-1,8-cineoles and the enantiomeric purity of *trans*- and *cis*-2- and 3-acetoxy-1,8-cineoles (**1a**−**4a**) in the rhizomes of *A. galanga* was examined by chiral GC-MS analyses. The odor characteristics of each enantiomer were also evaluated by sniffing the GC eluate.

EXPERIMENTAL PROCEDURES

Materials. The oxygenated volatile fraction of the rhizomes of *A. galanga* was prepared in the same way as that described in the previous paper (Kubota et al., 1998). *trans*- and *cis*-2-hydroxy-1,8-cineoles (**1** and **2**) and *trans*- and *cis*-3-hydroxy-1,8-cineoles (**3** and **4**) were also synthesized as described in the previous paper (Kubota et al., 1998).

Reagents. (*S*)-(+)-*O*-Methylmandelic acid (Sigma-Aldrich, Tokyo, Japan) and 4-(dimethylamino)-pyridine (DMAP; Merck KGaA, Darmstadt, Germany) were used.

Procedure for Preparing the *O*-Methylmandelate Esters. Oxalyl dichloride (39.7 mmol) was added to a solution of (*S*)-(+)-*O*-methylmandelic acid (1.00 g, 6.02 mmol) in dry benzene (10 mL), and the resulting mixture was stirred at room temperature for 4 h. The benzene and excess oxalyl chloride were removed in vacuo, and the obtained acid chloride was dissolved in 20 mL of dried dichloromethane. A solution of hydroxy-1,8-cineole (13.2 mmol) in dry pyridine was added, followed by the addition of DMAP (5.0 g) to give a white suspension. After being stirred overnight, the reaction mixture was diluted with 40 mL of diethyl ether, and the white precipitate was filtered off. The organic phase was successively washed with saturated aqueous cupric sulfate and water and dried over sodium sulfate, and the solvent was removed in vacuo to give a yellow oil. The oil was subjected to HPLC analysis to separate each diastereomer. *cis*-2- and *trans*-3-hydroxy-1,8-cineole were esterified as a mixture before separation into the four kinds of *O*-methylmandelate by HPLC.

Purification by HPLC. The reaction mixture of the diastereomers of (*S*)-*O*-methylmandelate from the foregoing

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Table 1. ^{1}H NMR Data for Protons of the Hydroxy-1,8-cineole Moiety of (*S*)-*O*-Methylmandelate Esters 1S,R−4S,R (600 MHz, $CDCl_3$, TMS, δ Value)[a]

H	1S	1R	2S	2R
4	1.51 (m)	1.41 (m)	1.49 (m)	1.38 (m)
5a	2.59 (m)	2.48 (m)	1.88 (m)	1.48 (m)
5b	1.31 (m)	0.93 (m)	2.12 (m)	1.93 (m)
6a	4.72 (m)	4.71 (m)		
6b			4.61 (dd, 2.9, 10.2)	4.73 (dd, 2.9, 10.0)
7a	1.65 (m)	1.75 (m)	1.69 (m)	1.73 (m)
7b	1.47 (m)	1.54 (m)	1.41 (m)	1.48 (m)
8a	1.95 (m)	1.88 (m)	1.98 (m)	1.96 (m)
8b	1.47 (m)	1.21 (m)	1.41 (m)	1.34 (m)
9Me	0.65 (s)	1.00 (s)	0.73 (s)	1.06 (s)
10Me	1.18 (s)	1.16 (s)	1.26 (s)	0.95 (s)
11Me	1.25 (s)	1.24 (s)	1.25 (s)	1.20 (s)

H	3S	3R	4S	4R
4	1.59 (m)	1.73 (m)	1.53 (m)	1.71 (ddd, 2.0, 2.0, 3.9)
5a	5.36 (m)	5.34 (m)		
5b			5.05 (ddd, 2.4, 6.0, 10.8)	5.01 (ddd, 2.0, 5.9, 10.7)
6a	2.16 (m)	2.10 (m)	1.71 (m)	1.48 (ddd, 3.4, 5.9, 14.2)
6b	1.37 (m)	1.12 (dd, 2.7, 14.9)	2.09 (dd, 10.7, 14.2)	2.03 (dd, 10.7, 14.2)
7a	1.59 (m)	1.59 (m)	1.57 (m)	1.58 (m)
7b	1.37 (m)	1.29 (m)	1.39 (m)	1.38 (m)
8a	1.59 (m)	1.78 (m)	2.00 (m)	2.06 (m)
8b	1.47 (m)	1.78 (m)	1.46 (m)	1.47 (m)
9Me	1.05 (s)	0.99 (s)	1.09 (s)	1.05 (s)
10Me	1.21 (s)	1.26 (m)	0.96 (s)	1.18 (s)
11Me	1.22 (s)	1.24 (s)	1.12 (s)	1.20 (s)

[a] **1S** (1*R*,4*R*,6*S*) isomer; **1R** (1*R*,4*S*,6*R*) isomer; **2S** (1*R*,4*S*,6*S*) isomer; **2R** (1*S*,4*R*,6*R*) isomer; **3S** (1*R*,4*S*,5*S*) isomer; **3R** (1*S*,4*R*,5*R*) isomer; **4S** (1*S*,4*R*,5*S*) isomer; **4R** (1*R*,4*S*,5*R*) isomer. The structures should be referred to Figure 2.

esterification was subjected to preparative HPLC to separate and trap each diastereomer. The HPLC conditions were as follows: instrument, Jasco 880-PU pump equipped with a Senshupak Pegasil silica 120-5 column (20 ϕ × 250 mm) and a UV-970 UV/vis detector (230 nm); eluting solvent, 1:99 2-propanol/hexane. After the solvent had been removed in vacuo, each mandelate was subjected to NMR analyses.

NMR Spectral Measurements. ^{1}H and ^{13}C NMR spectra of the *O*-methylmandelates of hydroxycineoles were recorded with a JEOL JNM A-600 spectrometer. Chemical shift data are expressed as δ values in relation to tetramethylsilane (TMS) as an internal standard. Chemical shift assignments were established through HMBC, HMQC, and NOEDF experiments.

Preparation of Acetoxy-1,8-cineoles. An optically pure alcohol was obtained by reducing the ester with $LiAlH_4$ in dry ether. Without purification, the obtained alcohol was acetylated with acetic anhydride in dry pyridine and subjected to GC-MS analysis.

Chiral GC-MS and GC-Sniffing. Using synthesized *trans*- and *cis*-2- and 3-acetoxy-1,8-cineoles (racemate), the gas chromatographic conditions were examined to separate each enantiomer clearly. The optical isomers of *trans*- and *cis*-2- and *cis*-3-acetoxy-1,8-cineoles were separated using a CP-Cyclodextrin-β-236-M-19 column (0.25 mm × 50 m; Chrompack, Middelburg, The Netherlands), and Chiraldex G-TA column (0.25 mm × 30 m; Tokyo Kasei Kogyo Co., Tokyo, Japan) gave a good separation for *trans*-3-acetoxy-1,8-cineole on GC-MS. GC-MS was recorded on a Hewlett-Packard 5972 instrument under an ionization voltage of 70 eV, and the gas chromatic conditions for both columns were as follows: Hewlett-Packard 5890 series II gas chromatograph instrument; He as the carrier gas at 0.7 mL/min; oven temperature at 130 °C; injection port and detector temperatures at 140 and 150 °C, respectively. The structure was confirmed by comparing the mass spectrum and the retention time with racemic acetoxy-1,8-cineoles synthesized. The elution order of each enantiomer on GC-MS was determined by cochromatography with synthesized optically pure acetoxycineole and the racemate. The aroma characteristics of each isomer were evaluated by sniffing the eluate from the GC column. In this case, the reaction product of each optically pure acetate already mentioned was injected into the GC instrument equipped with a DB-WAX column (0.25 mm × 60 m, J&W Scientific) held at 60 °C for 4 min and then increased at 2 °C/min to 200 °C, because the amount of sample injected was limited in cyclodextrin column. The elution time was confirmed in coincidence with that of synthesized authentic compound. The temperature of injection and detector port was 200 °C. The end of the column divided to feed the FID and ODO-1 sniffing adapter (GL Sciences, Tokyo, Japan) at 1:2.

RESULTS AND DISCUSSION

Purification and NMR Analysis of the Esters of 2- and 3-Hydroxy-1,8-cineole with (*S*)-(+)-*O*-Methylmandelic acid. The reaction mixtures of the (*S*)-*O*-methylmandelate esters from 2- and 3-hydroxy-1,8-cineoles were subjected to preparative HPLC, respectively. The ester fraction from *trans*-2-hydroxycineole gave two peaks at 17.3 and 19.0 min, and **1S** and **1R** were eluted in that order. The esters from the mixture of *cis*-2- and *trans*-3-hydroxy-1,8-cineoles were separated to four peaks at 21.0, 22.1, 23.8, and 27.7 min on HPLC. The elution order was **2S, 3R**, **3S**, and **2R**. The esters from *cis*-3-hydroxy-1,8-cineole also gave two peaks at 18.9 and 21.0 min, and **4R** and **4S** were eluted in that order. Each peak was trapped and purified by rechromatography, and each *O*-methylmandelate ester separated was subjected to NMR analyses. The signals were assigned by referring to the data of HMBC, HMQC, and NOEDF and are summarized in Tables 1 and 2. In this paper, the common names and the systematic names for hydroxy- and acetoxy-1,8-cineoles were used and the numbering of the position in the structure corresponds to the systematic name. The relationship to each other is shown in the legend of Figure 1. Trost et al. (1986) have confirmed that the model proposed by Dale and Mosher (1973) for correlating NMR shifts with absolute stereochemistry does extend to the *O*-methylmandelates. It is known that the substituent which eclipses the phenyl ring of the

Table 2. ^{13}C NMR Data for Carbons of the Hydroxy-1,8-cineole Moiety of (*S*)-*O*-Methylmandelate Esters 1S,R−4S,R (150 MHz, $CDCl_3$, TMS, δ Value)

C	1S	1R	2S	2R	3S	3R	4S	4R
1	70.8	70.7	70.8	70.6	70.3	70.4	69.9	69.9
3	73.7	73.7	73.7	73.6	73.2	73.2	72.9	72.9
4	33.7	33.6	33.2	33.0	36.9	37.1	37.4	37.5
5	32.4	32.2	32.3	31.7	70.4	70.4	73.5	73.7
6	73.3	73.5	73.9	73.5	39.7	39.7	40.1	39.9
7	25.8	26.0	29.6	29.5	30.7	30.6	30.0	30.0
8	21.9	21.7	21.7	21.7	14.4	14.8	21.0	21.0
9	23.6	24.2	22.5	23.0	26.9	26.8	26.7	26.6
10	28.8	28.8	27.9	27.5	28.6	28.7	30.1	30.4
11	28.5	28.5	28.8	28.8	28.4	28.4	30.0	30.1

[a] The structures should be referred to Figure 2.

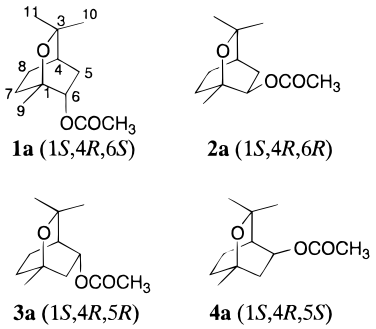

Figure 1. Structures of 2- and 3-acetoxy-1,8-cineoles. The common names and the systematic names are as follows: **1a**, *trans*-2-acetoxy-1,8-cineole (*trans*-1,3,3-trimethyl-2-oxabicyclo-[2.2.2]oct-6-yl acetate); **2a**, *cis*-2-acetoxy-1,8-cineole (*cis*-1,3,3-trimethyl-2-oxabicyclo[2.2.2]oct-6-yl acetate); **3a**, *trans*-3-acetoxy-1,8-cineole (*trans*-1,3,3-trimethyl-2-oxabicyclo[2.2.2]oct-5-yl acetate); **4a**, *cis*-3-acetoxy-1,8-cineole (*cis*-1,3,3-trimethyl-2-oxabicyclo[2.2.2]oct-5-yl acetate). Each acetoxy-1,8-cineole has two optical isomers, and one of them is shown here. The absolute configuration is indicated in parentheses. The numbering corresponds to the systematic name.

extended Newman projection in which the intervening ester linkage is omitted is always upfield as a result of its shielding by the phenyl ring. As shown in Figure 2, with compound **1S**, this group involves the methyl protons of C-9 and methylene protons of C-7, and in the enantiomeric alcohol which corresponds to diastereomer **1R**, this group incorporates Hb of C-5, with Hb of C-8 also being shielded. In the NOEDF experiment of **1R**, the enhancement of CH of C-4 and -6 and Ha of C-5 was observed by the irradiation of methyl proton of C-10. As is shown in Table 1, the δ values of the corresponding protons are shifted to upfield which are in good agreement with this theoretical model. From these results, the absolute structures of **1S** and **1R** were determined to be those of the (*S*)-*O*-methylmandelate of (1*S*,4*R*,6*S*)- and (1*R*,4*S*,6*R*)-1,3,3-trimethyl-2-oxabicyclo[2.2.2]octan-6-ol, respectively. Similarly in **2S**, the CH_3 protons of C-9 were shielded. In **2R**, the CH_3 protons of C-10, CH of C-4, and Ha and Hb of C-5 were shielded clearly. The enhancement of Ha of C-5 and -8 and the methyne proton of C-4 in **2R** was observed by the irradiation of methyl protons of C-10 by NOEDF. These results explained that Ha of C-5 and the methyl protons of C-10 were in the same direction which lay close to phenyl ring in space and their δ values were shifted more than others in **2R**. The structures of **2S** and **2R** were thus established to be those of the (*S*)-*O*-methylmandelate of (1*R*,4*S*,6*S*)- and (1*S*,4*R*,6*R*)-1,3,3-trimethyl-2-oxabicyclo[2.2.2]octan-6-ol, respectively. The Mosher theory was also applied to the 3-hydroxy-1,8-cineole group. In **3S**, the irradiation of methyl protons

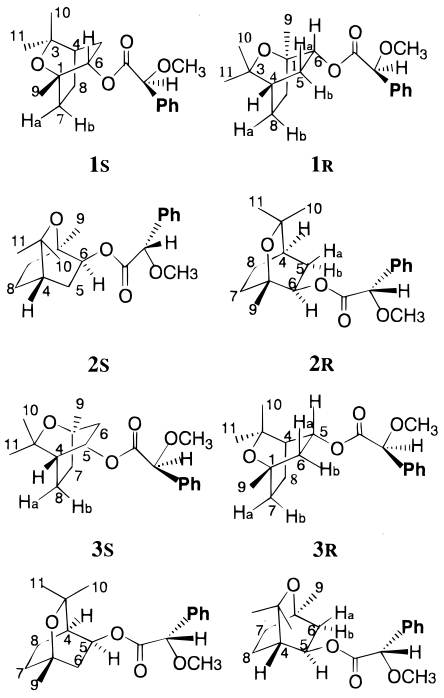

Figure 2. Structures of (*S*)-(+)-*O*-methylmandelate esters of 2- and 3-hydroxy-1,8-cineoles. For the numbering, the legend of Figure 1 should be referred to. Absolute configurations of each compound are as follows: **1S** (1*S*,4*R*,6*S*); **1R** (1*R*,4*S*,6*R*), **2S** (1*R*,4*S*,6*S*); **2R** (1*S*,4*R*,6*R*); **3S** (1*R*,4*S*,5*S*); **3R** (1*S*,4*R*,5*R*); **4S** (1*S*,4*R*,5*S*); **4R** (1*R*,4*S*,5*R*).

of C-10 and -11 enhanced Ha of C-8 and CH of C-4 and C-5 by NOEDF, which showed that Hb was eclipsed by phenyl ring more than Ha in C-8. Actually in NMR, the shielding by the phenyl ring at CH of C-4 and at Ha and Hb of C-8 was observed and the shifted value of Hb of C-8 was highest in **3S**. On the other hand, in **3R**, CH_3 of C-9 and Hb of C-6 and C-7 were shielded. Among them Hb of C-6 was shifted most to upfield, and it agreed with the result of NOESY, in which Hb was not enhanced with the irradiation of the methyne proton of C-5. The structures of **3S** and **3R** were thus established to be those of the (*S*)-*O*-methylmandelate of (1*R*,4*S*,5*S*)- and (1*S*,4*R*,5*R*)-1,3,3-trimethyl-2-oxabicyclo[2.2.2]octan-5-ol, respectively, as shown in Figure 2. Similarly, it was observed that CH of C-4 and the methyl protons of both of C-10 and -11 in **4S** and Ha of C-6 in **4R** were shielded by the phenyl ring. The NOEDF experiments supported these results well, where CH of C-4 and Ha of C-6 were enhanced by the irradiation of CH_3 of C-10 in **4S** and Ha of C-6 and CH of C-4 were enhanced by the irradiation of methyl protons of C-10 and -11 in **4R**. Therefore, **4S** and **4R** were determined to be the (*S*)-*O*-methylmandelate of (1*S*,4*R*,5*S*)- and (1*R*,4*S*,5*R*)-1,3,3-trimethyl-2-oxabicyclo[2.2.2]octan-5-ol, respectively. In the ^{13}C NMR spectra shown in Table 2, there was little variation in chemical shift between the esters of each enantiomeric alcohol, but some difference of the profile was observed between cis−trans isomers or positional isomers of the alcohol moiety.

Determination of the Enantiomeric Purity. Each mandelate ester was reduced with $LiAlH_4$ to obtain the corresponding optically pure alcohol. After extraction of the alcohol without additional purification, the alcohol was acetylated with acetic anhydride in dry pyridine and submitted to GC-MS analysis. The enantiomers

Table 3. Concentration of the Enantiomers of Acetoxy-1,8-cineoles in the Rhizomes of *A. galanga* and Their Odor Characteristics

compd[a]	configuration	GC[b] t_R (min)	peak[c] area (%)	% ee	odor impression[d]
1a	1*S*,4*R*,6*S*	21.58	18		woody (weak)
	1*R*,4*S*,6*R*	22.63	82	63.5	woody, *A. galanga*-like
2a	1*R*,4*S*,6*S*	26.26	0		fruity, sweet
	1*S*,4*R*,6*R*	25.00	100	100.0	weak
3a	1*R*,4*S*,5*S*	14.10[e]	97	93.9	sweet floral (weak)
	1*S*,4*R*,5*R*	13.80[e]	3		sweet floral (weak)
4a	1*S*,4*R*,5*S*	24.14	40		camphoraceous
	1*R*,4*S*,5*R*	23.78	60	19.4	mild woody

[a] The structures should be referred to Figure 1. The numbering of the configurations corresponds to the systematic name. [b,e]Retention times by GC-MS when using the CP-Cyclodextrin-β-236-M-19 and Chiraldex G-TA columns, respectively. The conditions are defined in the Experimental Procedures section. [c] Peak area was calculated by total ion count chromatography. [d] Evaluated by GC-sniffing.

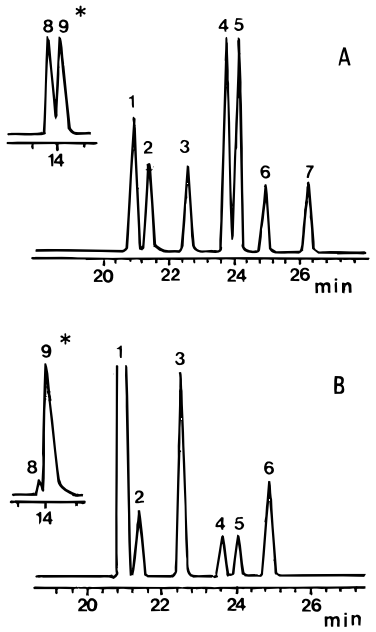

Figure 3. TIC chromatograms of synthesized 2- and 3-acetoxy-1,8-cineoles (A) and acetoxy-1,8-cineoles in oxygenated volatile fraction from the rhizomes of *A. galanga* (B) using CP-Cyclodextrin-β-236-M-19 and Chiraldex G-TA* columns. See Experimental Procedures for the conditions. Key: 1, **3a** (racemate); 2, **1a** (1*S*,4*R*,6*S*); 3, **1a** (1*R*,4*S*,6*R*); 4, **4a** (1*R*,4*S*,5*R*); 5, **4a** (1*S*,4*R*,5*S*); 6, **2a** (1*S*,4*R*,6*R*); 7, **2a** (1*R*,4*S*,6*S*); 8, **3a** (1*S*,4*R*,5*R*); 9, **3a** (1*R*,4*S*,5*S*). The structures of each compound should be referred to Figure 1.

could be clearly separated using the modified β-cyclodextrin column (CP-Cyclodextrin-β-236-M-19), except for *trans*-3-acetoxy-1,8-cineole (**3a**) which was separated using another cyclodextrin column (γ-cyclodextrin column, Chiraldex G-TA) as shown in Figure 3. An optically pure acetate was used to determine the relationship between the stereostructure and elution order by GC-MS as shown in Table 3. Similarly, the enantiomeric ratio of the acetoxy-1,8-cineoles in an oxygenated compound fraction of the volatile concentrate from the rhizomes of *A. galanga* (Kubota et al., 1998) was investigated under the same conditions by using the two kinds of cyclodextrin columns just described. The total ion current (TIC) chromatograms by GC-MS are shown in Figure 3, and the results are summarized in Table 3. It was found in this research that *cis*-2-acetoxy-1,8-cineole (**2a**) was optically active for the (1*S*,4*R*,6*R*) isomer, while *trans*-3 (**3a**), which produced the largest peak by GC-MS among the four acetates, was also almost optically active for the (1*R*,4*S*,5*S*) isomer in the rhizomes. In *trans*-2 (**1a**), the (1*R*,4*S*,6*R*) isomer was present in a much larger amount than the enantiomer at 63.5% ee. On the other hand, *cis*-3 (**4a**) was present as almost a racemate at 19.4% ee.

It was noted that **1a** and **3a** were the main components of the aroma concentrate and that one of their enantiomers was in large excess in the rhizomes, whereas **2a** and **4a** were each present in very small amounts.

Odor Characteristics and Contribution of Acetoxy-1,8-cineoles to the Odor of *A. galanga*. Since there was so little of the acetate isolated from the reaction mixture, the odor was evaluated by sniffing the GC column eluate. As shown in Table 3, it was observed that each enantiomer presented a different odor from the other except for the **3a** pair. Mariani et al. (1995) have synthesized a series of alkyl esters of hydroxy-1,8-cineoles and described the odorous note of *trans*-2-acetoxy-1,8-cineole to be woody, pine oillike, and violetlike. However, they did not mention anything about the optical isomers. In the case of **1a**, the (1*R*,4*S*,6*R*) isomer presented a woody and *A. galanga*-like odor, which was stronger than that of the enantiomer. In addition, the amount of the stronger enantiomer in the rhizomes was about four times more than the other (1*S*,4*R*,6*S*) isomer as already described. In the case of **2a**, the (1*R*,4*S*,6*S*) isomer, which was not found in the rhizomes, showed a fruity and sweet odorous note, while the odor of the enantiomer was weak. So **2a** seems not to have had a large effect on the odor of greater galangal. **3a** was almost optically active in the rhizomes, but the odors of both enantiomers were too weak to evaluate. Although it has been selected from an aroma extract dilution analysis as one of the potent odorants because its concentration in the aroma concentrate was highest among **1a**−**4a** (Mori et al., 1995), **3a** seems not to have had much of a qualitative effect on the characteristic flavor. **4a** presented a different odor between each enantiomer, although it might have very little effect on the odor of *A. galanga* because of the low concentration. It was thus concluded from these results that, among the acetoxy-1,8-cineoles, *trans*-2-acetoxy-1,8-cineole (**1a**) was the most potent odorant in the rhizomes of *A. galanga* both quantitatively and qualitatively.

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