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Identification of Dihydrogalangal Acetate in Galangal [*Alpinia galangal* (L.) Swartz] Extracts

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Dihydrogalangal acetate has been discovered for the first time in galangal roots [*Alpinia galangal* (L.) Swartz]. The compound has a taste sensation similar to galangal acetate—the pungent principle of galangal—but it is more stable in food and beverage applications. Therefore, dihydrogalangal acetate provides many advantages as a flavor ingredient for alcohol enhancement and taste modification. Dihydrogalangal acetate is present in approximately 0.0005% of fresh roots and in about 0.004% of dried roots. (*S*)-Dihydrogalangal acetate is found as the main optical isomer in galangal roots (98%), while its minor (*R*)-isomer is less abundant (2%). Enantiomers of galangal acetate and dihydrogalangal acetate were separated and evaluated by sensory analysis. (*R*)-Galangal acetate has a very faint woody and sweet aroma, and (*R*)-dihydrogalangal acetate is almost odorless, while (*S*)-galangal acetate has strong and (*S*)-dihydrogalangal acetate has weak pungent and woody notes. Although the aroma characters of these optical isomers are different, taste sensations were found to have no significant differences among galangal acetate, dihydrogalangal acetate, and their optical isomers.

KEYWORDS: Dihydrogalangal acetate; galangal acetate; galangal; *Alpinia galanga; Alpinia galangal* (L.) Swartz; 1′-acetoxydihydrochavicol acetate; 1′-acetoxychavicol acetate

INTRODUCTION

Galangal [*Alpinia galangal* (L.) Swartz] is a popular spice in Thailand and eastern Asia. Galangal acetate (1′-acetoxychavicol acetate, **Figure 1**) has been identified as the pungent principle of galangal (*1*, *2*). Because of its mild and clean pungent taste, galangal acetate has found many applications in food, beverages, and personal care products as an alcohol enhancer, cooling enhancer, flavor modifier, and pungent impact (*3*). However, because of the 1,5-oxadiene system, galangal acetate easily undergoes hydrolysis and isomerization in aqueous media and loses its desirable taste sensations. The instability limits the applications of galangal acetate in food and beverages. Studies on the structure and taste relationship led to the discovery of a series of stable galangal acetate derivatives (*2*). It was concluded that the double bond of the vinyl group, which causes the instability in food applications, is not necessary for the pungency of galangal acetate. Therefore, a straightforward approach to stabilize galangal acetate is to hydrogenate the double bond, yielding dihydrogalangal acetate (1′-acetoxydihydrochavicol acetate, **Figure 1**). The stability of dihydrogalangal acetate is excellent in food and beverage applications, while the clean pungency of galangal acetate is preserved. Recently, dihydrogalangal acetate has been granted GRAS (generally regarded as safe) status (FEMA #4555) as a flavor ingredient.

The presence of dihydrogalangal acetate in plants has not been reported in literature. During our study on galangal extracts, we found an unknown trace peak close to galangal acetate in the gas chromatography (GC) chromatogram. This trace compound has been isolated and identified as dihydrogalangal acetate by chromatographic techniques and spectroscopic methods. The discovery will enable development of this compound as a natural ingredient for food flavors. In this paper, we report the discovery and the characterization of its optical isomers.

MATERIALS AND METHODS

Materials. Fresh galangal roots were obtained from a local market in Cincinnati, OH. Dried galangal roots were obtained from Haldin International (Closter, NJ).Galangal oleoresin was obtained by ethanol extraction (product of Givaudan Flavors, Cincinnati, OH). All synthetic reagents were obtained from Aldrich (Milwaukee, WI).

Synthesis of Galangal Acetate (Racemic). A solution of 30.5 g (0.25 mol) of 4-hydroxybenzaldehyde in 150 mL of tetrahydrofuran (THF) was added dropwise to a vigorously stirred and chilled solution of vinylmagnesium bromide (0.8 mol) in THF (800 mL). The mixture was stirred at room temperature under a nitrogen atmosphere for 5 h before the reaction was quenched by carefully adding, under ice cooling, a solution of 100 g of NH_4Cl in 350 mL of water. Additional water was introduced as necessary, and stirring was continued until all solids had dissolved. Extraction with 1000 mL of methyl *tert*-butyl ether (MTBE), washing of the organic layer with water (2 × 1000 mL),

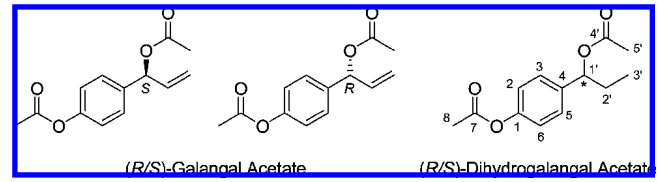

Figure 1. Structures of galangal acetate and dihydrogalangal acetate.

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drying over $MgSO_4$, filtration, and solvent removal yielded 35 g of 4-(1-hydroxy-2-propenyl)phenol as a viscous oil, which was acetylated without further purification.

To the stirred and chilled solution of the crude 4-(1-hydroxy-2-propenyl)phenol in 100 mL of acetic anhydride, 100 mL of anhydrous pyridine followed by 0.2 g of solid dimethylaminopyridine were added dropwise. The clear mixture was agitated at room temperature overnight before excess reagent was removed by repeated evaporation with toluene (rotary evaporator). A solution of the resulting oily residue in 1000 mL of MTBE was then extracted sequentially with 10% aqueous sodium metabisulfite (2 × 500 mL) and water (2 × 500 mL). Drying over $MgSO_4$, filtration, and solvent removal yielded 38 g of crude galangal acetate as a pale-yellow oil.

Purification by silica gel chromatography (heptane:ethyl acetate in a ratio of 3:1) and fractional distillation eventually furnished 30 g of pure [>95% by GC−flame ionization detection (FID)] racemic galangal acetate as a colorless oil (bp 102−105 °C at 0.05 mmHg) that slowly solidified with time.

Synthesis of Dihydrogalangal Acetate (Racemic). To a vigorously stirred and chilled solution of ethylmagnesium chloride (1 mol) in THF (750 mL), a solution of 61 g (0.5 mol) of 4-hydroxybenzaldehyde in 750 mL of THF was added dropwise. The mixture was agitated at room temperature under a nitrogen atmosphere for an additional 2 h before the reaction was quenched by carefully adding, under ice cooling, a solution of 130 g of NH_4Cl in 750 mL of water. Extraction with 1000 mL of MTBE, washing of the organic layer with water (2 × 1000 mL), drying over $MgSO_4$, filtration, and solvent removal yielded 91 g of 4-(1-hydroxypropyl)phenol as an orange-colored oil, which was acetylated without further purification.

To the stirred and chilled solution of the crude 4-(1-hydroxypropyl)-phenol in 250 mL of acetic anhydride, 300 mL of anhydrous pyridine followed by 1.0 g of solid dimethylaminopyridine was added dropwise. The clear mixture was agitated at room temperature overnight before excess reagent was removed by repeated evaporation with toluene (rotary evaporator). A solution of the resulting oily residue in 1000 mL of MTBE was then extracted sequentially with 10% aqueous sodium metabisulfite (2 × 500 mL) and water (2 × 500 mL). Drying over $MgSO_4$, filtration, and solvent removal yielded 106.5 g of crude dihydrogalangal acetate as a pale-yellow oil that gradually crystallized upon standing. Recrystallization from hexane eventually provided 91 g of racemic dihydrogalangal acetate of high chemical purity (>99% by GC-FID) with an mp of 41.5−43.5 °C.

Synthesis of (−)-(*S*)-Dihydrogalangal Acetate. The (*S*)-configuration of natural galangal acetate isolated from galangal root has previously been established (*4*), and reduction of the terminal methylene group was not expected to affect its chiral center. A solution of 200 g of galangal root extract (50−60% galangal acetate) in 600 mL of ethanol was hydrogenated at room temperature under pressure (150−200 psi) in the presence of Adam's catalyst (0.4 g) until conversion was complete (8 h). Filtration and solvent removal provided a crude product that was purified by silica gel chromatography (heptane:ethyl acetate in a ratio of 5:1) followed by fractional distillation to yield 102 g of (−)-(*S*)-dihydrogalangal acetate as a colorless liquid (bp 95−105 °C at 0.05 mmHg) of high chemical purity (>99% by GC-FID) and enantiomeric purity 96.9% as determined by chiral high-performance liquid chromatography (HPLC) analysis; $[\alpha]_D^{20} = -89.3°$ ($c = 5.05$, EtOH).

Synthesis of (+)-(*R*)-Dihydrogalangal Acetate. A stirred suspension of 20 g of lipase acrylic resin from *Candida antarctica* in a solution of 20 g of racemic 4-(1-hydroxypropyl)phenol in 500 mL of vinyl acetate was incubated at room temperature for 20 h. Filtration and removal of vinyl acetate under reduced pressure (rotary evaporator) provided 28 g of a crude product mixture, which, upon silica gel chromatography (heptane:ethyl acetate 3:2), yielded 8 g of (*R*)-4-(1-acetoxypropyl)phenol.

A solution of the above intermediate in 30 mL of acetic anhydride and 40 mL of anhydrous pyridine was agitated at room temperature overnight in the presence of a catalytic amount of dimethylaminopyridine (0.1 g). Removal of excess reagent by repeated stripping with toluene (rotary evaporator) gave 10 g of crude product as an orange-colored oil. Silica gel chromatography (heptane:ethyl acetate, 4:1) followed by flash distillation then provided 6 g of (+)-(*R*)-dihydrogalangal acetate as a colorless liquid (bp 98−100 °C at ca. 0.05 mmHg) of high chemical purity (99% by GC-FID) and enantiomeric purity 94.8% as determined by chiral HPLC analysis; $[\alpha]_D^{20} = +81.6°$ ($c = 5.15$, EtOH).

Isolation of Dihydrogalangal Acetate. Natural dihydrogalangal acetate was isolated from a crude natural galangal extract obtained from dried galangal roots. The isolation was performed using an Agilent 1100 preparatory HPLC system equipped with a reversed phase column [Phenomenex Luna C18(2), 21.2 mm i.d., 250 mm length, 5 μm particle size] and a diode array detector. The mobile phase was composed of 60% methanol and 40% water (isocratic) at a flow rate of 20 mL/min. For each injection, 300 μL of 10% galangal acetate in methanol was used. The dihydrogalangal peak was collected in multiple injections. Methanol of the collected effluent was removed by rotary evaporator, and the remaining aqueous phase was extracted with hexane. After the hexane extract was dried under a gentle nitrogen stream, an oily liquid was obtained. Identification of dihydrogalangal acetate was performed by NMR, GC−mass spectrometry (MS), and chiral GC analysis.

Chiral Separation/Analysis of Galangal Acetate and Dihydrogalangal Acetate. Solutions of 1% synthetic racemic mixtures were prepared in hexane for chiral separation. A Perkin-Elmer Series 200 HPLC system equipped with a diode array detector was used. The enantiomer separation was achieved using a chiral HPLC column [Whelk-O 1(*S*,*S*), 4.6 mm i.d., 250 mm length, 5 μm particle size, Regis Technologies, Morton Grove, IL] and an isocratic mobile phase, composed of 95% hexane and 5% methanol, at a flow rate of 1.5 mL/min. The enantiomer peaks were collected in multiple injections. The fractions were concentrated by rotary evaporator to a volume of approximately 20 mL, dried over $MgSO_4$, filtered, and further dried under a nitrogen stream. All fractions were obtained as an oily liquid. The identification and purity of the isolated compounds were determined by chiral HPLC and GC analysis.

Analytical Methods. *Standard Addition Extraction.* Pure galangal acetate was dissolved in the solvent mixture (hexane:acetone in a ratio of 10:1) to make 2, 5, and 10% stock solutions. Pure dihydrogalangal acetate was dissolved in the solvent mixture at concentrations of 0.02, 0.05, and 0.1%. Fresh galangal root obtained from a local market was cut into small pieces (ca. 5 mm). The mixture of hexane and acetone in a ratio of 10:1 was used as the extraction solvent. A sample (2 g of ground dry galangal root or 15 g of fresh galangal root) was extracted with 100 mL of solvent (hexane:acetone in a ratio of 10:1). The standard addition experiments were composed of four extractions, spiked with 2 mL of one of the galangal acetate and dihydrogalangal acetate stock solutions or a blank solvent mixture, respectively. The mixture was blended for 5 min using an Omni mixer homogenizer with a grinding blade. The solids were filtered and extracted again with 100 mL of the extraction solvent twice. The extract solution was combined and concentrated to 20 mL by rotary evaporation and a gentle nitrogen stream. The extraction recovery for both galangal acetate and dihydrogalangal acetate was greater than 95%, estimated by the analysis of the residue solids.

GC-MS Analysis. Galangal root extracts (1−3 μL) were injected into a GC-MS system with an Agilent 6890 GC equipped with 5973 mass selective detector and a DB-5 ms capillary column (30 m length, 0.25 mm i.d., and 0.25 μm film, Agilent, Wilmington, DE). Helium was used as a carrier gas with a flow rate of 30 cm/s. A split mode (50:1) was used for the sample introduction. The GC oven temperature was held at 120 °C for 1 min and then programmed to 180 at 3 °C/min and held for 4 min at 180 °C. The mass selective detector was operated in positive electron ionization (EI) mode with a mass scan range from *m*/*z* 30 to 350 at 70 eV. Identification of the target analytes by GC-MS was performed by comparing the full-scan mass spectra and relative retention indices with the data of authentic reference samples.

GC-FID Analysis of Enantiomers. Analysis of enantiomers of galangal acetate and dihydrogalangal acetate was achieved using a chiral column Cyclosil-B (30 m length, 0.32 mm i.d., and 0.25 μm film, Agilent). A sample of 0.5 μL (0.05−0.1%) in ethyl acetate was analyzed in an Agilent 6890N GC equipped with a split injector (split ratio 50:1) and a FID detector. The GC oven temperature was held at 120 °C for 2 min and then programmed to 170 at 2 °C/min.

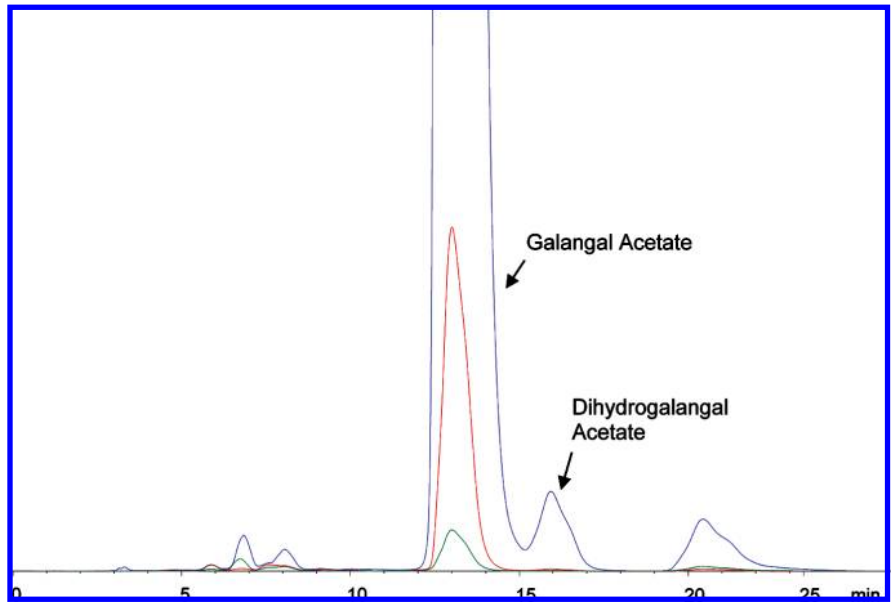

Figure 2. HPLC chromatogram of galangal root extract. Column, Phenomenex Luna C18(2), 21.2 mm × 250 mm, 5 μm; mobile phase, 60% methanol, 40% water, isocratic; flow rate, 20 mL/min; and detection, λ = 280 (green), 254 (red), and 210 nm (blue).

NMR Spectroscopy. NMR experiments [^{1}H, ^{13}C, distortionless enhancement by polarization transfer (DEPT), correlation spectroscopy (COSY), heteronuclear multiple quantum coherence (HMQC), heteronuclear multiple bond correlation (HMBC)] were performed for structure elucidation using a Bruker DRX 500 spectrometer equipped with a 5 mm inverse probe and a 5 mm BBO probe.

Optical Rotation Measurements. Optical rotation measurements were conducted on a Rudolph Research Analytical Autopol IV system. Samples were prepared in ethanol solutions, and specific rotation values were recorded using a sample cell of 50 mm length and 1.0 mL volume.

Sensory Methodology. The objective of this experiment was to determine whether 15 ppm galangal acetate in 40 proof cordial base and 15 ppm dihydrogalangal acetate in 40 proof cordial base are different from one another in strength of alcohol intensity. Twenty milliliters of each solution was presented in random order to 30 panelists from the discriminator database. Panelists were asked to select the solution that was perceived as having a stronger alcohol intensity. The data were subject to a binomial test to determine significance. The same methodology was used to evaluate the optical isomers of galangal acetate and dihydrogalangal acetate.

Analytical Data. *Melting Point and Boiling Point.* Dihydrogalangal acetate isolated from galangal root is present in the form of oily liquid. Synthetic (−)-(*S*)-dihydrogalangal acetate has a bp 95−105 °C at 0.05 mmHg, and synthetic (+)-(*R*)-dihydrogalangal acetate has a bp 98−100 °C at ca. 0.05 mmHg. The racemic mixture of dihydrogalangal acetate can be crystallized in hexane, mp 41.5−43.5 °C.

Optical Rotation. Galangal acetate from galangal roots, $[\alpha]_D^{20}$ −55.337 (*c* = 0.550, EtOH); purified (*S*)-galangal acetate, $[\alpha]_D^{20}$ −58.760 (*c* = 0.535, EtOH); purified (*R*)-galangal acetate $[\alpha]_D^{20}$ +59.699 (*c* = 0.540, EtOH); purified (*S*)-dihydrogalangal acetate, $[\alpha]_D^{20}$ −93.822 (*c* = 0.51, EtOH); and purified (*R*)-dihydrogalangal acetate, $[\alpha]_D^{20}$ +92.340 (*c* = 0.49, EtOH).

Spectroscopic Data. 1′-Acetoxydihydrochavicol acetate (dihydrogalangal acetate): ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.33 (2H, d, *J* = 8.6 Hz, $H_{3,5}$), 7.05 (2H, d, *J* = 8.6 Hz, $H_{2,6}$), 5.66 (1H, t, *J* = 6.9 Hz, $H_{1'}$), 2.28 (3H, s, H_8), 2.06 (3H, s, $H_{5'}$), 1.91 (1H, m, $H_{2'a}$), 1.79 (1H, m, $H_{2'b}$), 0.88 (3H, t, *J* = 7.4 Hz, $H_{3'}$). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ ppm): 170.35 (C, $C_{4'}$), 169.40 (C, C_7), 150.17 (C, C_1), 138.11 (C, C_4), 127.76 (2CH, $C_{3,5}$), 121.47 (2CH, $C_{2,6}$), 76.71 (CH, $C_{1'}$), 29.26 (CH_2,$C_{2'}$), 21.25 (CH_3, $C_{5'}$), 21.15 (CH_3, C_8), 9.93 (CH_3, $C_{3'}$). IR (neat): 2972 m, 2939 m, 2880 w, 1734 s, 1609 w, 1510 s, 1458 w, 1434 w, 1371 s, 1239 s, 1196 s, 1167 s, 1086 m, 1043 m, 1017 s, 966 m, 912 s, 852 m, 339 w, 557 w, 544 w cm^{-1}. UV absorption maxima (in hexane): 217 nm (intensive), 261 nm (weak). MS (EI), *m*/*z* 39 (11), 43 (100), 65 (9), 77 (16), 95 (10), 107 (16), 123 (71), 133 (16), 134 (18), 135 (11), 165 (25), 194 (17), 236 (2).

RESULTS AND DISCUSSION

Isolation and Structure Elucidation. During the investigation of the pungent principles of galangal, we observed that there was a trace peak after galangal acetate in the GC chromatograms of galangal extracts. No match was found for the mass spectrum of the GC peak from our in-house and commercial mass spectra libraries. For structure identification, this unknown compound was isolated from galangal extracts by semiprep HPLC (**Figure 2**).

The high-resolution chemical ionization mass spectrum of the isolated compound showed an ammonium adduct of the molecule ion at *m*/*z* 254.1379, corresponding to the element composition of $C_{13}H_{16}O_4 \cdot NH_4^+$ (exact mass, 254.1392). As compared with the formula of galangal acetate, $C_{13}H_{14}O_4$, the double bond equivalent of the unknown was reduced from 7 to 6.

NMR experiments (^{1}H, ^{13}C, DEPT, COSY, HMQC, and HMBC) were conducted for chemical structure elucidation. It is obvious by the comparison of the ^{13}C spectra that the unknown has some similar patterns as galangal acetate: two carbonyl groups with chemical shifts at around 170 ppm and a benzene ring with para-substitution. The large difference is that the two aliphatic double bond carbons in galangal acetate are shifted from 117 (=CH_2) and 136 ppm (−CH=) to 9.93 (−CH_3) and 29.26 ppm (−CH_2−), which strongly indicates that the unknown compound is a derivative of galangal acetate with the aliphatic double bond saturated. Further analysis of the couplings and connectivity of carbon and proton atoms in the NMR correlation spectra confirmed that the unknown has the structure of dihydrogalangal acetate (1′-acetoxydihydrochavicol acetate).

Dihydrogalangal acetate was synthesized, and the mass spectrum and GC retention indices were measured. The synthetic dihydrogalangal acetate has the same GC retention index (1651 on a DB-5 column) and mass spectrum as that of the unknown peak. A standard solution of synthetic dihydrogalangal acetate was spiked into the galangal extract and then analyzed by GC, resulting in a higher intensity at the same retention time of the unknown trace peak.

The contents of dihydrogalangal acetate in fresh and dried galangal roots were determined by standard addition extraction

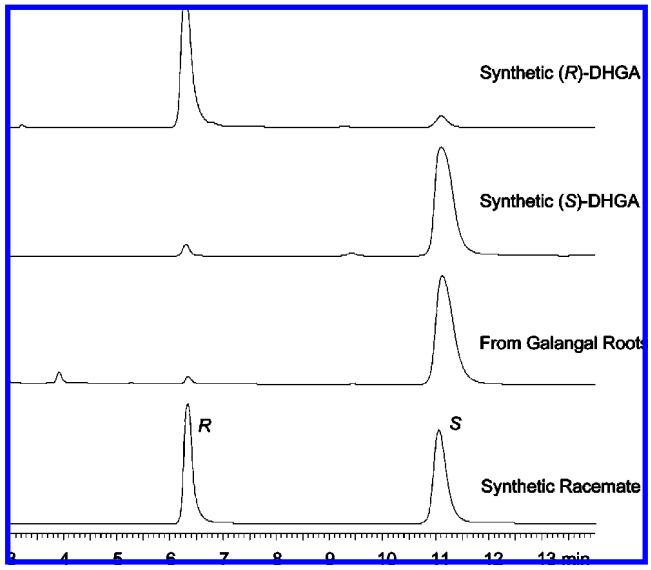

Figure 3. Chiral HPLC chromatograms of dihydrogalangal acetate. Column, Whelk-O 1(*S*,*S*), 4.6 mm × 250 mm, 5 μm; mobile phase, 95% hexane, 5% methanol, isocratic; flow rate, 1.5 mL/min; and detection, λ = 210 nm.

method, although the results vary depending on the quality of galangal products. The fresh galangal roots contain approximately 0.0005% dihydrogalangal acetate, and the dried roots contain about 0.004%.

Chiral Separation and Determination. To compare the sensory properties of the enantioisomers of galangal acetate and dihydrogalangal acetate, the racemic mixtures underwent chiral separation. The purified enantiomers have above 99% purity by chiral GC analysis.

To determine the enantiomer configuration of the naturally occurring dihydrogalangal acetate, the purified isolate, synthetic racemic, and synthetic (−)-(*S*)-dihydrogalangal acetate and (+)-(*R*)-dihydrogalangal acetate have been analyzed by chiral GC and chiral HPLC (**Figure 3**). The results showed that the natural dihydrogalangal acetate has mainly the (*S*)-configuration (98%). The (*R*)-configuration of dihydrogalangal acetate was also found in galangal extracts in a minor amount (2%) by chiral HPLC anlaysis, confirmed by retention time and UV spectrum. Optical rotation values of the purified chiral isomers were determined. Dihydrogalangal acetate isolated from galangal extract has a negative rotation value.

It is known that the (*S*)-configuration of galangal acetate is the major optical isomer presented in galangal roots (*4*−*6*). The (*R*)-galangal acetate is also present in galangal extract. The ratio of (*S*)- and (*R*)-isomers is about 95:5 by chiral GC analysis. The two enantiomers of synthetic racemic galangal acetate and those of synthetic dihydrogalangal acetate were separated by a chiral HPLC column for sensory evaluation (**Figures 3** and **4**).

Stability as Flavor Ingredient. Under hydrolytic conditions, galangal acetate is not stable. After 1 h of reflux in aqueous solution, it is completely converted to 1′-hydroxychavicol acetate, *p*-acetoxycinnamic alcohol, and *p*-coumaryl diacetate (*1*). Hydrogenation of the double bond of galangal acetate makes dihydrogalangal acetate more stable. Under the same conditions described above, a practical 100% recovery of dihydrogalangal acetate was achieved after the reflux, determined by solvent extraction and GC-MS analysis. Stability in aqueous solution and even at elevated temperature provides many advantages as a flavor ingredient in food and beverage applications.

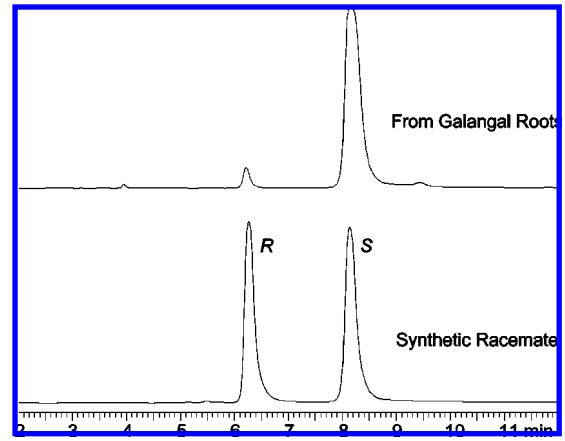

Figure 4. Chiral HPLC chromatograms of galangal acetate. Column, Whelk-O 1(*S*,*S*), 4.6 mm × 250 mm, 5 μm; mobile phase, 95% hexane, 5% methanol, isocratic; flow rate, 1.5 mL/min; and detection, λ = 210 nm.

Sensory Evaluation. It was reported that the optical isomer of galangal acetate with (*R*)-configuration has no odor by GC sniffing (*7*). The odor characters of the purified optical isomers (>99%) were evaluated by flavorists at Givaudan. (*R*)-Dihydrogalangal acetate is odorless, and the corresponding (*S*)-isomer has very weak pungent and woody notes. (*R*)-Galangal acetate has a faint woody and sweet odor, while (*S*)-galangal acetate has a stronger pungent and woody aroma.

The taste attributes of galangal acetate and dihydrogalangal acetate are probably of higher commercial interest as flavor ingredients. One of the potential applications of these compounds is to enhance alcohol sensation in beverages. Odorless or low aroma intensity is advantageous for such applications. Sensory experiments were performed to compare the enhancement potency of galangal acetate vs dihydrogalangal acetate. A nonsignificant difference of evaluations (14 of 30) selected galangal acetate as having a stronger alcoholic enhancement than dihydrogalangal acetate. Therefore, galangal acetate and dihydrogalangal acetate possess practically the same alcoholic enhancement effect. The same sensory procedure was conducted for the two optical isomers of dihydrogalangal acetate. A nonsignificant majority of evaluations (23 of 40) selected (*R*)-dihydrogalangal acetate as having a stronger alcohol intensity than that of (*S*)-dihydrogalangal acetate. The dihydrogalangal acetate isomers were also not significantly different in alcohol enhancement.

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