Synthesis, Structure Elucidation, and Olfactometric Analysis of Lilac Aldehyde and Lilac Alcohol Stereoisomers

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Structure elucidation of the lilac aldehyde and lilac alcohol stereoisomers was ascertained by ^{1}H nuclear magnetic resonance (NMR) spectroscopy, including intramolecular nuclear Overhauser effects of the separated diastereoisomers and anisotropic effects of the diastereomeric 2-phenylpropionyl ester, and ^{1}H, ^{1}H COSY NMR spectroscopy of synthesized (5′R)-configured stereoisomers, synthesized from (R)-linalool. Direct stereodifferentiation of the eight stereoisomers of lilac aldehyde and lilac alcohol, respectively, has been achieved, using enantioselective capillary GC. The elution order of the isomers was deduced from the chromatographic behavior of the (5′R)-configured diastereoisomers. Additionally, the odor thresholds of lilac aldehyde and lilac alcohol stereoisomers are reported.

KEYWORDS: Lilac aldehyde stereoisomers; lilac alcohol stereoisomers; enantioselective multidimensional gas chromatography; olfactometry

INTRODUCTION

Lilac aldehydes and lilac alcohols have been described as characteristic monoterpenes in *Syringa vulgaris* L. flowers, with a desirable influence on lilac flavor quality (*1–5*). In previous papers, the enantioselective separation and biogenesis of lilac aldehyde and lilac alcohol stereoisomers in *S. vulgaris* flowers have been reported (*6*). Four diastereoisomers of 2-[(5′-methyl-5′-vinyl)tetrahydrofuran-2′-yl]propanal and -propanol were assigned as the naturally occurring structures of lilac aldehyde and lilac alcohol in *S. vulgaris*, but little recent research has been carried out on the clarification of the absolute configurations of the eight possible stereoisomers. This investigation describes the determination of the elution order and clarification of the absolute configurations of all eight isomers of lilac aldehyde and lilac alcohol, respectively, by synthesis and chromatographic separation. Synthesis was started from (R)-linalool, and the corresponding mixture of the four 5′(R)-configured diastereoisomers of lilac alcohol was separated using preparative cyclic HPLC (**Figure 1**). Structure elucidation of the separated *cis*- and *trans*-lilac alcohols and their absolute configurations at C-2′ were investigated on the basis of ^{1}H nuclear magnetic resonance (NMR) spectroscopy (*7, 8*), including intramolecular nuclear Overhauser effects (NOE) of the separated diastereoisomers. Determination of the absolute configuration at C-2 was deduced from ^{1}H NMR spectral data of the corresponding diastereomeric 2(R)-phenylpropionyl esters. This method is well established in the case of compounds with alcoholic or primary amine functionalities at the chiral center and based on the chemical shift difference for protons with equivalent constitutions, due to anisotropic effects caused by the phenyl ring of the acid moiety (*9–16*). In the case of primary alcoholic functions adjacent to a stereogenic center, Latypov et al. (*17*) introduced (R/S)-9-anthrylmethoxyacetic acid (9-AMA) as auxiliary reagent with good diagnostic results for nearly all cases. They demonstrated that the $MeO-C_{\alpha}-CO-O-C_{1'}-C_{2'}-H$ bonds are in the same plane and that the substituents at the asymmetric center show a shift to higher field depending on the absolute configuration at $C_{2'}$. However, in this investigation, the assignment of the absolute configuration of lilac alcohol has been determined from ^{1}H NMR spectroscopic analysis of the corresponding (R)-2-phenylpropionic acid ester.

MATERIALS AND METHODS

Gas Chromatography—Mass Spectrometry (GC-MS). GC-MS analysis of the synthesized monoterpenes was carried out with a GC 8065, coupled to an MD800 mass spectrometer (Fisons Instruments, Egelsbach, Germany), equipped with a 30 m × 0.25 mm i.d., 0.23 μm SE 52 coated fused silica capillary column.

Conditions were as follows: carrier gas, helium, 65 kPa; split, 20 mL/min; injector temperature, 230 °C; oven temperature, 40 °C (5 min isothermal) raised at 5 °C/min to 250 °C (30 min isothermal); ion source temperature, 200 °C; interface temperature, 250 °C; mass range, 40–250 amu; EI, 70 eV.

The molecular ion (M^+) and the fragmentation ions were given as *m/z* with relative peak intensities to the base peak (percent).

Enantioselective Gas Chromatography—Olfactometry (Enantio-GC-O). Olfactometric analysis of the lilac aldehyde and lilac alcohol stereoisomers was carried out with an HRGC Mega 2 (Carlo Erba Instruments), equipped with a 30 m × 0.23 mm i.d. fused silica capillary coated with a 0.23 μm film of heptakis(2,3-di-O-methyl-6-O-*tert*-butyldimethylsilyl)-β-cyclodextrin (DIME-β-CD) in SE 52.

Conditions were as follows: carrier gas, hydrogen, 105 kPa; on-column injector temperature, 250 °C; retention gap, 3 m × 0.32 mm

Lilac Aldehyde/Alcohol Stereoisomers

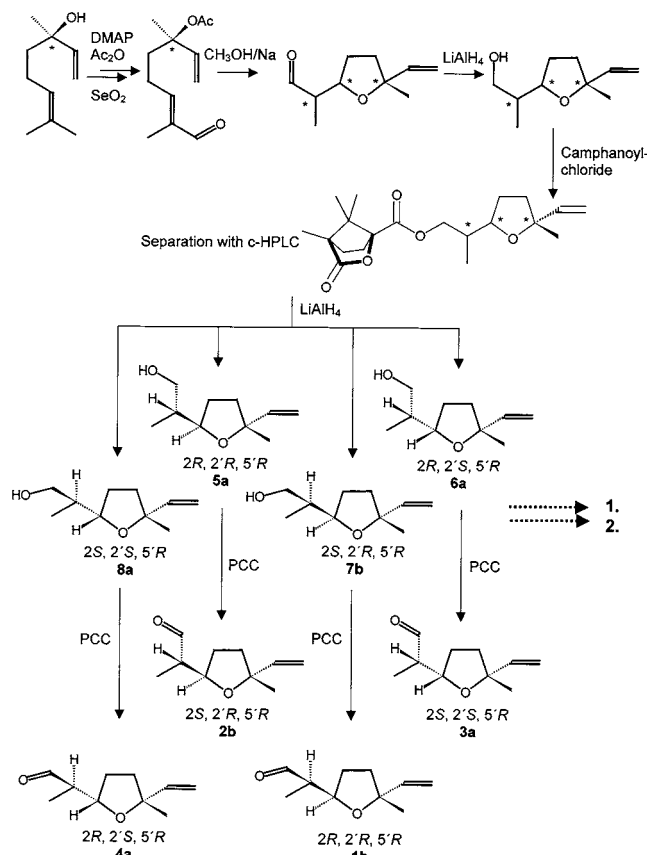*J. Agric. Food Chem.,* Vol. 51, No. 9, 2003 **2723**

Figure 1. Synthesis pathway and chromatographic separation of the 5′(*R*)-configured lilac aldehyde and lilac alcohol stereoisomers: (1) NOE experiments; (2) esterification with 2(*R*)-phenylpropionic acid chloride and ¹H NMR measurement.

i.d. deactivated fused silica capillary; oven temperature, 40 °C (5 min isothermal) raised at 1.5 °C/min to 210 °C (10 min isothermal); Y-piece, coupled with two 50 cm × 0.32 mm i.d. deactivated fused silica capillaries to (A) sniffing port, 220 °C, and (B) FID, 250 °C.

Enantio-multidimensional (MD) GC-MS. The enantio-MDGC-MS analyses were performed with a SiChromat 2-8 (Siemens, Mannheim, Germany), equipped with two independent column oven programs and a live-T-switching device. The main column was coupled to the transfer line of an MAT ITD800 (Finnigan, Bremen, Germany), using an open split interface. GC conditions were as follows: precolumn, 30 m × 0.23 mm i.d., 0.23 μm SE 52 fused silica capillary; carrier gas, helium at 155 kPa; split, 20 mL/min; injector temperature, 220 °C; detector, FID, 250 °C; oven temperature, 60 °C (10 min isothermal) raised at 3 °C/min to 250 °C (20 min isothermal); cut times, 31.5−33.0 min for lilac aldehyde and 34.5−37.5 min for lilac alcohol; main column, 30 m × 0.23 mm i.d. fused silica capillary coated with a 0.23 μm film of heptakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)-β-cyclodextrin (DIME-β-CD) in SE 52; carrier gas, helium at 102 kPa; oven temperature, 60 °C (30 min isothermal) raised at 1 °C/min to 200 °C; detector, ITD 800; transfer line, 250 °C; open split interface, 250 °C; helium sweeping flow, 1 mL/min; ion trap manifold, 230 °C; EI, 70 eV.

¹H NMR. A 300 MHz ARX 300 (Bruker) was employed for recording the ¹H NMR spectra. CDCl₃ was used as solvent. In NOE experiments, each peak was integrated alternately with non-irradiated power and optimum irradiated power.

Preparative Cyclic HPLC. Conditions: Sep Tech TM pump, flow = 70 mL/min; optional cyclic flow (System: Cyclomat, Merck), eluent diethyl ether/petroleum ether (1:1, v/v); injector, Rheodyne 7125, 1000 μL loop; detector, Knauer variable-wavelength monitor with Sonntek Vari-prep cell VP1100; wavelength, 218 nm; column, 250 mm × 50 mm i.d., 12 μm mesh LiChrospher Si 60 (self-prepared).

Synthesis of 5′(*R*)-Lilac Alcohols. *Synthesis of 5′(R)-2-[(5′-Methyl-5′-vinyl)tetrahydrofuran-2′-yl]propanol (5a, 6a, 7b, 8a).* 5′(*R*)-Lilac

alcohol synthesis was performed analogously to the method reported in ref 6 starting with (*R*)-linalool. MS: *m/z* 170 (1, M⁺), 155 (41), 111 (28), 93 (100), 77 (25), 55 (57).

Synthesis of (5′*R*,1″*S*,4″*R*)-Camphanoic Acid Lilac Ester. *Synthesis of (1″S,4″R)-Camphanoic Acid 5′(R)-2-[(5′-Methyl-5′-vinyl)-tetrahydrofuran-2′-yl]propyl Ester.* (−)-(1S,4R)-Camphanoic acid chloride (1.1687 g, 5.8 mmol) was dissolved in 50 mL of dry CCl₄ under an N₂ atmosphere. After 0.659 g of DMAP had been added, 0.71 g (4.1 mmol) of lilac alcohol dissolved in 10 mL of dry CCl₄ was added dropwise. The solution was stirred at 40 °C for 15 h and then stopped by adding diethyl ether and H₂O. The solution was extracted with diethyl ether, and the organic layer was washed with H₂O, 0.5 N NaOH, and H₂O and then dried over sodium sulfate. After removal of the solvent. 3.6 mmol (1.25 g) of (5′*R*,1″*S*,4″*R*)-camphanoic acid lilac ester was obtained: MS, *m/z* 350 (1, M⁺), 240 (7), 181 (14), 153 (25), 137 (22), 111 (100), 93 (77), 83 (49), 67 (46), 55 (78).

Isolation of Pure 5′(*R*)-Configured Lilac Alcohol Diastereoisomers (5a, 6a, 7b, and 8a). The mixture of four camphanoic acid ester diastereomers was separated by preparative cyclic HPLC as described above, and the isolated 5′(*R*)-configured diastereomeric esters were transferred to their corresponding alcohols by reductive ester cleavage with LiAlH₄ as described in ref *18*; 18.4 mg of **5a**, 18.1 mg of **6a**, 24.4 mg of **7b**, and 21.9 mg of **8a** were obtained. MS, *m/z* 170 (1, M⁺), 155 (43), 111 (26), 93 (100), 77 (36), 55 (62). ¹H NMR of the diastereomers **5a** and **6a**: δ 5.92 and 5.87 (dd, 1H, 6′-H, *J* = 10.7 Hz), 5.17 and 5.12 (dd, 1H, 7′-H_A, *J* = 1.9 Hz), 5.01 and 4.97 (dd, 1H, 7′-H_B, *J* = 1.9 Hz), 3.86−3.71 (m, 1H, 2′-H), 3.67−3.53 (m, 1H, 2-H), 1.86−1.57 (m, 4H, 3′-H, 4′-H), 1.32 (s, 3H, 5′-CH₃), 0.81 and 0.78 (d, 3H, 2-CH₃, *J* = 7.0 Hz). ¹H NMR of the diastereomers **7b** and **8a**: δ 5.90 and 5.84 (dd, 1H, 6′-H, *J* = 10.7 Hz), 5.18 and 5.14 (dd, 1H, 7′-H_A, *J* = 1.9 Hz), 5.02 and 4.98 (dd, 1H, 7′-H_B, *J* = 1.9 Hz), 4.29−4.13 (m, 1H, 2′-H), 3.69−3.46 (m, 1H, 2-H), 1.92−1.76 (m, 4H, 3′-H, 4′-H), 1.31 (s, 3H, 5′-CH₃), 0.97 and 0.93 (d, 3H, 2-CH₃, *J* = 7.0 Hz). NOE difference spectroscopy of the *cis*-lilac alcohol diastereoisomers **6a** and **8a**: 5′-CH₃ → 2′-H-strong positive effect; 5′-CH₃ → 7′-H_A-strong positive effect; 5′-CH₃ → 6′-H-strong positive effect; 5′-CH₃ → 3′-H, 4′-H-strong positive effect; 2′-CH₃ → 2-H-weak negative effect. NOE difference spectroscopy of the *trans*-lilac alcohol diastereomers **5a** and **7b**: 5′-CH₃ → 2′-H-no effect; 5′-CH₃ → 7′-H_A-strong positive effect; 5′-CH₃ → 6′-H-strong positive effect; 5′-CH₃ → 3′-H, 4′-H-strong positive effect; 3′-H → 2-H-negative effect.

Synthesis of the Isolated 5′(*R*)-Lilac Aldehyde Diastereoisomers. *Synthesis of 5′(R)-2-[(5′-Methyl-5′-vinyl)tetrahydrofuran-2′-yl]propanal (1b, 2b, 3a, and 4a).* The four isolated 5′(*R*)-configured lilac alcohol stereoisomers were oxidized separately with pyridinium chlorochromate, analogous to the method described in ref *19*; 8.1 mg of **1b**, 13.7 mg of **2b**, 11.8 mg of **3a**, and 12.4 mg of **4a** were obtained. MS, *m/z* 168 (1, M⁺), 153 (32), 111 (26), 93 (58), 67 (100), 55 (52). ¹H NMR δ 9.77 (s, 1H, 1-H), 5.88 and 5.82 (dd, 1H, 6′-H, *J* = 10 Hz), 5.21 and 5.15 (dd, 1H, 7′-H_A, *J* = 1.9 Hz), 4.99 and 4.97 (dd, 1H, 7′-H_B, *J* = 1.9 Hz), 4.29−4.22 (m, 1H, 2-H), 4.20−4.08 (m, 1H, 2′-H), 1.96−1.52 (m, 4H, 3′-H, 4′-H), 1.31 (s, 3H, 5′-CH₃).

Synthesis of (5′*R*,2″*R*)-2″-Phenylpropionic Acid Lilac Ester. *2″(R)-Phenylpropionyl-2(R/S)-[((R)-5′-Methyl-5′-vinyl)tetrahydrofuran-2′-yl]propyl Ester (5*a and 8*a).* Synthesis was performed separately with **8a** and **5a** as starting material analogous to the method described in ref *20*; 4 mg (0.01 mmol) of **5*a** and 5 mg (0.02 mmol) of **8*a** were obtained. MS, *m/z* 219 (6), 169 (2), 152 (31), 137 (32), 111 (99), 105 (100), 93 (97), 81 (45), 67 (57), 55 (85). ¹H NMR **5*a** δ 5.89 and 5.83 (dd, 1H, 6′-H, *J* = 10.7 Hz), 5.28 and 5.12 (dd, 1H, 7′-H_A, *J* = 1.9 Hz), 4.98 and 4.92 (dd, 1H, 7′-H_B, *J* = 1.9 Hz), 4.31−4.22 (m, 1H, 2′-H), 4.11 and 3.98 (dd, 2H, 1-H, *J* = 0.5 Hz), 3.73 (q, 1H, 2″-H, *J* = 7.2 Hz), 3.52−3.43 (m, 1H, 2-H), 1.92−1.61 (m, 4H, 3′-H, 4′-H), 1.50 (d, 3H, 2″-CH₃, *J* = 7.2 Hz), 1.35 (s, 3H, 5′-CH₃), 0.75 and 0.72 (d, 3H, 2-CH₃, *J* = 7.0 Hz). ¹H NMR **8a*** δ 5.89 and 5.82 (dd, 1H, 6′-H, *J* = 10.7 Hz), 5.17 and 5.10 (dd, 1H, 7′-H_A, *J* = 1.9 Hz), 4.97 and 4.92 (dd, 1H, 7′-H_B, *J* = 1.9 Hz), 4.08 and 3.99 (dd, 2H, 1-H, *J* = 0.5 Hz), 3.79−3.65 (q, 1H, 2″-H, *J* = 7.2 Hz; and m, 1H, 2′-H), 3.52−3.41 (m, 1H, 2-H), 1.89−1.61 (m, 4H, 3′-H, 4′-H), 1.50 (d, 3H, 2″-CH₃, *J* = 7.2 Hz), 1.29 (s, 3H, 5′-CH₃), 0.96 and 0.93 (d, 3H, 2-CH₃, *J* = 7.0 Hz).

2724 *J. Agric. Food Chem.,* Vol. 51, No. 9, 2003
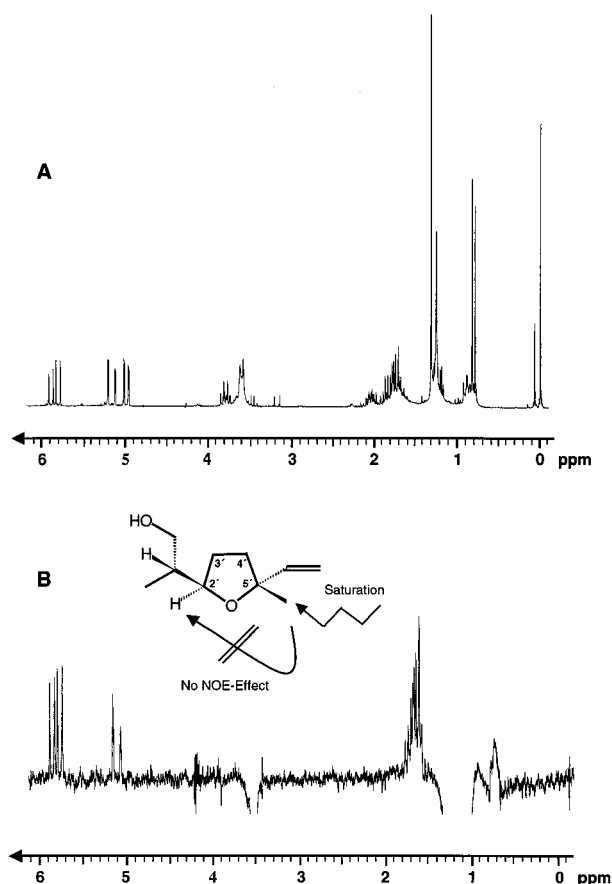
Kreck and Mosandl

Figure 2. ¹H NMR spectra (300 MHz; δ, TMS internal standard) of (A) *trans*-lilac alcohol diastereomer **5a** and (B) NOE experiment of **5a**. There was no change in 2′-H intensity during 5′-CH₃ decoupling.

RESULTS AND DISCUSSION

Starting from (R)-linalool all four 5′(R)-configured diastereoisomers of lilac aldehyde were generated as outlined in **Figure 1**. After reduction to lilac alcohol and esterification with (−)-(1S,4R)-camphanoyl chloride, the diastereomeric esters were separated by preparative liquid chromatography and converted to the corresponding 5′(R)-configured lilac alcohol diastereoisomers by reductive cleavage with LiAlH₄, with an enantiomeric purity of >95%. ¹H NMR and NOE measurements were recorded to clarify the absolute configuration of the asymmetric center at C-2′.

¹H NMR spectra and the difference spectrum of the NOE experiment are shown in **Figures 2** and **3**. The intramolecular NOEs have been studied by irradiation at the frequency of the C5′-CH₃ signal (1.32 ppm) and simultaneous integration of the 2′-H intensities; the resulting difference spectra are shown in **Figures 2B** and **3B**. Significant increase in the 2′-H intensities was observed in the case of the **6a** and **8a** diastereoisomers, whereas no change of the 2′-H intensities was detectable for the diastereoisomers **5a** and **7b**. The increase of the 2′-H signal is probably due to a *cis*-configuration of the furanoid system. It is therefore obvious that the absolute configuration of **5a** and **7b** at the C-2′ and C-5′ positions must be 2′(R),5′(R) and for the diastereoisomers **6a** and **8a** 2′(S),5′(R). By oxidation with pyridinium chlorochromate to the corresponding lilac aldehydes, the configuration of **1b** and **2b** was proved to be 2′(R),5′(R), and **3a** and **4a** must be 2′(S),5′(R)-configured compounds.

The absolute configuration of the lilac alcohol stereoisomers at C-2 was achieved under the condition described by Schetlick (*18*). Therefore, the diastereoisomers **5a** and **8a** were esterified
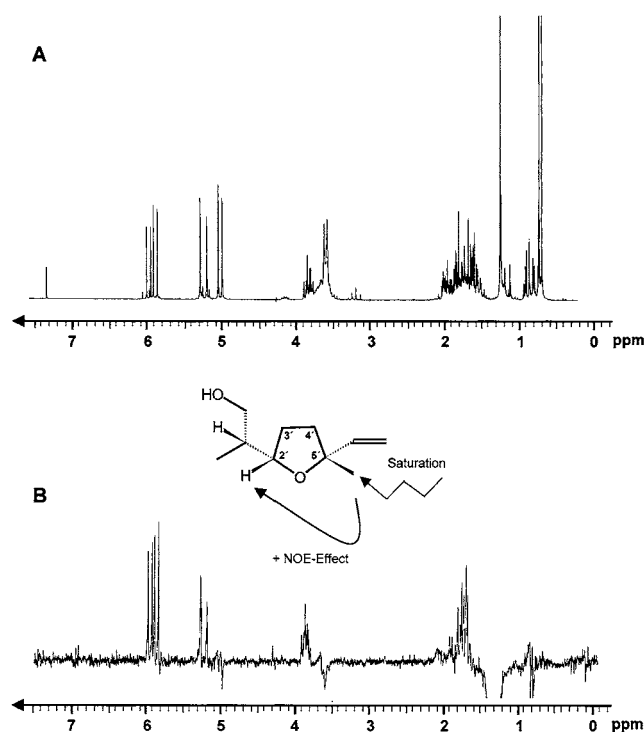

Figure 3. ¹H NMR spectra (300 MHz; δ, TMS internal standard) of (A) *cis*-lilac alcohol diastereomer **6a** and (B) NOE experiment of **6a**. 2′-H intensity was enhanced during 5′-CH₃ decoupling.

with 2(R)-2-phenylpropionic acid chloride, and the diastereomeric esters were analyzed by ¹H NMR experiments.

The results are shown in **Figure 4**. An evident anisotropic effect caused by the phenyl group of the auxiliary reagent is registered for the 2′-H signal in the case of **8*a** and for the 2-CH₃ signal of the **5*a** isomer with a shift to higher field. Hence, it follows that the 2-CH₃ group in **5*a** must be in the same environment as the phenyl group, whereas the 2′-H signal must be in the same region in the case of compound **8*a**. The chemical shifts of the 2″-H and 2-H were identical in **5*a** and **8*a**, so that a preferred conformation with H₂″−C₂″−C₁″O−O−C₁−C₂−H₂ in one plane can be concluded, which is in accordance with the investigations described previously (*18*). The resulting absolute configuration for the lilac alcohol isomer **5a** can be defined as (2R,2′R,5′R) and that for **8a** as (2S,2′S,5′R). When the results of the NOE experiments are considered, it is obvious that the absolute configuration of the diastereoisomer **7b** differs only at C-2 in comparison to **5a** and that of the diastereomer **6a** at C-2 from **8a**, respectively. Therefore, the absolute configuration can be established for **6a** (2R,2′S,5′R) and **7b** (2S,2′R,5′R). Hence, the absolute configurations of all eight stereoisomeric lilac alcohols are as follows: **5a** (2R,2′R,5′R); **5b** (2S,2′S,5′S); **6a** (2R,2′S,5′R); **6b** (2S,2′R,5′S); **7a** (2R,2′S,5′S); **7b** (2S,2′R,5′R); **8a** (2S,2′S,5′R); **8b** (2R,2′R,5′S). After selective oxidation of the lilac alcohols with pyridinium chlorochromate and with consideration for the changing priority (CIP nomenclature) of the substituents at C2, the absolute configurations of the corresponding eight lilac aldehyde stereoisomers are **1a** (2S,2′S,5′S), **1b** (2R,2′R,5′R), **2a** (2R,2′S,5′S), **2b** (2S,2′R,5′R), **3a** (2S,2′S,5′R), **3b** (2R,2′R,5′S), **4a** (2R,2′S,5′R), and **4b** (2S,2′R,5′S). The elution order of the lilac aldehyde and lilac alcohol stereoisomers is shown in **Figure 5**, whereas the structures of the naturally occurring lilac aldehydes and lilac alcohols in lilac flowers are shown in **Figure 6**. The absolute configuration of the naturally occurring stereoisomers corre-
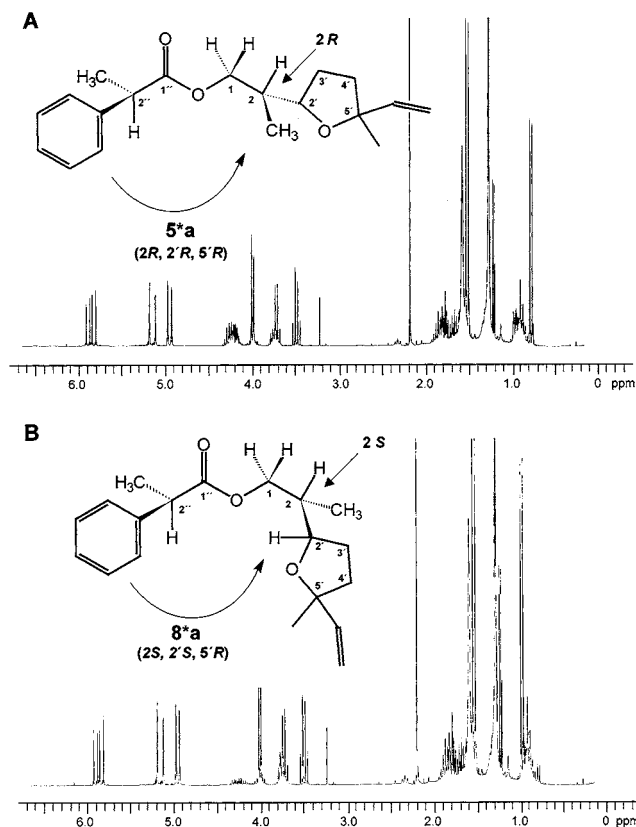
Lilac Aldehyde/Alcohol Stereoisomers

J. Agric. Food Chem., Vol. 51, No. 9, 2003 **2725**

Figure 4. ^{1}H NMR spectra (300 MHz; δ, TMS internal standard) of (A) the 2(*R*)-phenylpropionic acid ester of lilac alcohol **5*a** with chemical shift of the 2-CH$_3$ group to higher field and (B) the 2(*R*)-phenylpropionic acid ester of lilac alcohol **8*a** with chemical shift of the 2′-H signal to higher field.
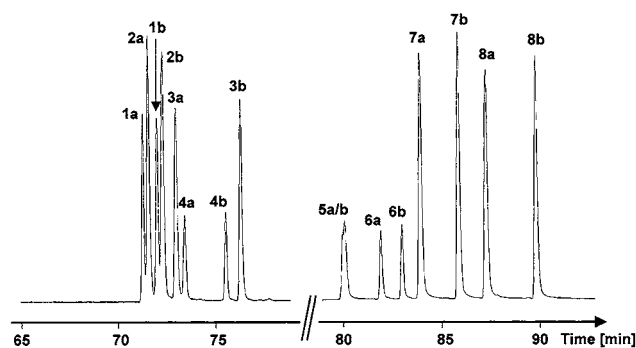

Figure 5. Chromatographic behavior of all eight lilac aldehyde and eight lilac alcohol stereomers using heptakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)-β-cyclodextrin (DIME-β-CD) (30%) in SE 52 (70%) as the chiral stationary phase: **1–4**, lilac aldehyde diastereomers; **5–8**, lilac alcohol diastereomers; **a/b**, enantiomers [**1a** (2*S*,2′*S*,5′*S*), **1b** (2*R*,2′*R*,5′*R*), **2a** (2*R*,2′*S*,5′*S*), **2b** (2*S*,2′*R*,5′*R*), **3a** (2*S*,2′*S*,5′*R*), **3b** (2*R*,2′*R*,5′*S*), **4a** (2*R*,2′*S*,5′*R*), **4b** (2*S*,2′*R*,5′*S*); **5a** (2*R*,2′*R*,5′*R*), **5b** (2*S*,2′*S*,5′*S*), **6a** (2*R*,2′*S*,5′*R*), **6b** (2*S*,2′*R*,5′*S*), **7a** (2*R*,2′*S*,5′*S*), **7b** (2*S*,2′*R*,5′*R*), **8a** (2*S*,2′*S*,5′*R*), **8b** (2*R*,2′*R*,5′*S*)]. Order of elution assigned by references of definite chirality.

sponds with the investigations in lilac reported by Wakayama et al. (*3*).

Additionally, the relationship between structure and odor of all eight stereoisomers of lilac aldehyde and lilac alcohol, respectively, was determined. For this purpose all stereoisomers were separated by on-column enantioselective gas chromatography, connected with a sniffing port for direct olfactometric
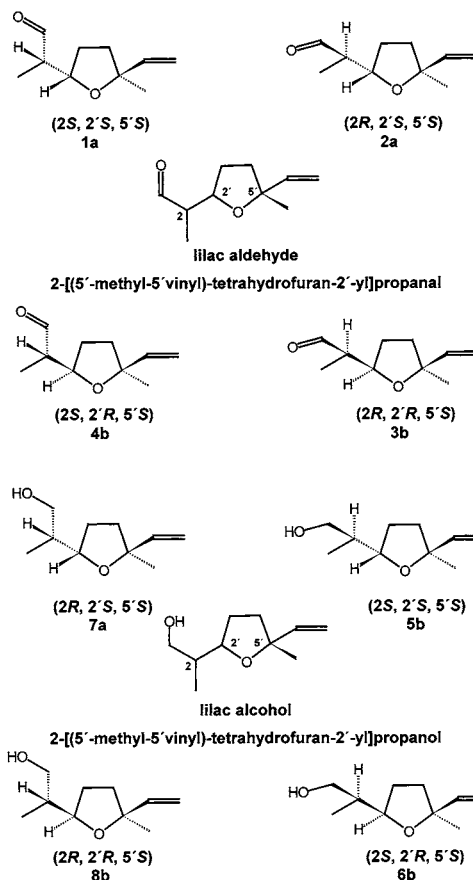

Figure 6. Absolute configurations of all four genuine lilac aldehyde stereomers **1a**, **2a**, **4b**, and **3b** and lilac alcohol stereomers **5b**, **6b**, **7a**, and **8b**, respectively.

Table 1. Odor Threshold Value of the Lilac Alcohol and Lilac Aldehyde Stereoisomers[a]

substance	odor threshold (ng)	odor impression
1a	0.2	fresh, flowery
2a	0.3	pleasant, flowery, fresh
1b	22	flowery
2b	20	flowery
3a	4	flowery, fresh
4a	18	flowery, fresh
4b	0.3	sweet, flowery
3b	0.4	sweet, flowery
5a	>100	odorless
5b	2	flowery
6a	22	sweet
6b	2	sweet, flowery
7a	4	green, grassy, fresh
7b	80	sweet
8a	74	herbaceous, slightly flowery
8b	4	flowery, sweet, body

[a] **1a**, **2a**, **3b**, and **4b** are genuine lilac aldehydes; **5b**, **6b**, **7a**, and **8b** are genuine lilac alcohols; **1–4** are lilac aldehydes; **5–8** are lilac alcohols; and **a/b** are enantiomers.

detection (enantio-GC/O, see Materials and Methods). The results are shown in **Table 1**. Although the enantiomers **5a/b** remain unresolved, the sensorial analysis of **5a** can be performed by direct injection of the synthesized enantiomer **5a**, which has a very high odor threshold. Hence, it follows that for the insufficiently separated mixture **5a/b** assignment of the resulting low flowery odor threshold can be attributed to enantiomer **5b**. It is remarkable that the odor threshold of all four naturally occurring lilac aldehyde diastereomers **1a**, **2a**, **4b**, and **3b** and

2726 *J. Agric. Food Chem.,* Vol. 51, No. 9, 2003

Kreck and Mosandl

lilac alcohol diastereoisomers **5b**, **6b**, **7a**, and **8b** in lilac flowers, respectively, show significantly lower thresholds than those of the enantiomers that do not occur.

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