# Chirality Evaluation of 1,4-Decanolide in Peach

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Chirality of 1,4-decanolide in peach was evaluated via chiral 4-hydroxy isopropyl ester as its (*S*)-*O*-acetyllactic acid ester. Sample preparation was performed using solvent extraction (pentane–dichloromethane, 2:1), silylation of the concentrated extract, and LC preseparation on silica gel into two fractions. Fraction I (pentane–diethyl ether, 9:1) containing silylated compounds was discarded; fraction II (diethyl ether) was treated with methanolic KOH and 2-bromopropane. After derivatization with (*S*)-*O*-acetyllactic acid chloride, capillary gas chromatography (HRGC) revealed the occurrence of 11% *S* and 89% *R* enantiomers. Results of HRGC analysis were verified by comparison of HRGC retention and mass spectral data with those of authentic reference compounds.

Many volatile compounds identified in biological systems are chiral molecules. Contrary to the studies performed in pheromone chemistry (Hummel and Miller, 1984), in flavor research this aspect has not been thoroughly considered. Recently, however, increasing attention has been devoted to chirality evaluation of flavor compounds. Meanwhile, the chiral structures of several enantiomeric natural volatiles have been elucidated (Tressl and Engel, 1984; Singer et al., 1986; Tressl and Albrecht, 1986; Günther and Mosandl, 1986, 1987; Engel, 1988; Krammer et al., 1988; Mosandl et al., 1988).

In the recent work of Mosandl et al. (1987) a number of 1,4- and 1,5-alkanolides were available in optically pure form, and chromatographic separation of enantiomers was achieved via corresponding chiral 4-hydroxy isopropyl esters as their (*S*)-*O*-acetyllactic acid esters. In our present study, this technique was applied for chirality evaluation of 1,4-decanolide in peach, an essential constituent of its fruit flavor (Spencer et al., 1978).

## EXPERIMENTAL SECTION

**Fruit.** Fresh ripe peaches (cultivar not determined; origin Greece) were purchased from the local market.

**Sample Preparation.** After they were cut and the kernels separated, 6.5 kg of peaches was homogenized with a Braun blender and the pulp diluted with distilled water (1:1, v/v). After addition of 1,4-pentanolide (1.0 mg/kg) as internal standard, the diluted pulp was continuously extracted over 48 h with pentane–dichloromethane (2:1, v/v). The extract was dried over $Na_2SO_4$ (sicc.) and carefully concentrated (45 °C) to approximately 0.5 mL on a Vigreux column.

**Silylation.** For the silylation, 100 $\mu$L of the concentrated extract, 50 $\mu$L of dried pyridine, and 600 $\mu$L of silyl 21 reagent (Macherey & Nagel, Düren) were added into a screw-capped vial. After 30 min at 80 °C the supernatant was separated and subjected to LC fractionation on silica gel.

**Liquid Chromatography on Silica Gel.** LC separation was carried out with silica gel 60 (Merck, activity grade II) and a 30 × 2 cm (i.d.) water-cooled glass column. Elution was performed with 300 mL of pentane–diethyl ether (9:1) and 300 mL of diethyl ether, yielding fractions I and II, respectively. Fraction I was discarded; fraction II was dried over $Na_2SO_4$ (sicc.) and carefully concentrated (45 °C) to 0.1 mL on a Vigreux column.

**Derivatization to 4-Hydroxy Isopropyl Esters.** To 50 $\mu$L of the concentrated fraction II was added 1 mL methanolic KOH (2.2 mM) and the mixture stirred at ambient temperature for 20 h. After removal of the solvent by distillation in vacuo, the residue was treated three times with dried diethyl ether and concentrated under vacuum to dryness. After addition of 200 $\mu$L of dried dimethylformamide, 75 $\mu$L of 2-bromopropane was added. After the mixture was stirred at room temperature for 6 days in the dark, 2 mL of diethyl ether was added and the mixture extracted with 5 mL of NaCl-saturated water. The collected organic phases were dried over $Na_2SO_4$ (sicc.) and concentrated to approximately 50 $\mu$L.

**Derivatization with (*S*)-Acetyllactic Acid Chloride ((*S*)-*O*-AcLC).** In a screw-capped vial were added 20 $\mu$L of pyridine, 20 $\mu$L of dried diethyl ether, 15 $\mu$L of (*S*)-*O*-AcLC (Mosandl et al., 1987), and 30 $\mu$L of derivatized fruit extract.

**Capillary Gas Chromatography (HRGC).** A Carlo-Erba Fractovap 4160 gas chromatograph with FID equipped with a J&W DB-5 capillary column (30 m, 0.25 mm (i.d.); df = 0.25 $\mu$m) was used. Split injection (1:50) was employed. The following temperature program was used: 140–160 °C at 5 °C/min; 160–190 °C at 2 °C/min; 20 min isothermal at 190 °C. The flow rates for the carrier gas were 2.5 mL/min He, for the makeup gas 30 mL/min $N_2$, and for the detector gases 30 mL/min $H_2$ and 300 mL/min air, respectively. Injector and detector temperatures were 220 and 250 °C, respectively.

Results of HRGC analysis were verified by comparison of linear HRGC retention ($R_i$) and mass spectral data with those of authentic reference compounds. The diastereoisomeric esters derived from 1,4-decanolide showed the following data. $R_i$: 1550 (*S*), 1565 (*R*). $m/z$ (%): 43 (100), 115 (48), 171 (30), 87 (27), 41 (27), 153 (20), 42 (18), 55 (16) (identical for *S* and *R*). Quantitative determinations were carried out on a Hewlett-Packard 3388 A data system.

**Capillary Gas Chromatography–Mass Spectrometry (HRGC–MS).** A Varian aerograph 1400 gas chromatograph directly coupled to a Finnigan MAT 44 mass spectrometer with SS 200 data system was used. The apparatus was equipped with a J&W DB-5 capillary column (30 m, 0.25 mm (i.d.); df = 0.25 $\mu$m). On-column injection with a water-cooled injection system was employed. The conditions were as follows: temperature program, 60–300 °C at 5 °C/min; carrier gas, 2.5 mL/min He; temperature of ion source and all connection parts, 200 °C; electron energy, 70 eV; cathodic current, 0.8 mA.

## RESULTS AND DISCUSSION

In previous work carried out on the composition of peach volatiles, 1,4-decanolide has been found among the most abundant components. A number of other 1,4-alkanolides have also been detected, but in very small quantities (Spencer et al., 1978). In our present study, these results were confirmed. HRGC and HRGC–MS analyses revealed, with the exception of 1,4-undecanolide, the occurrence of

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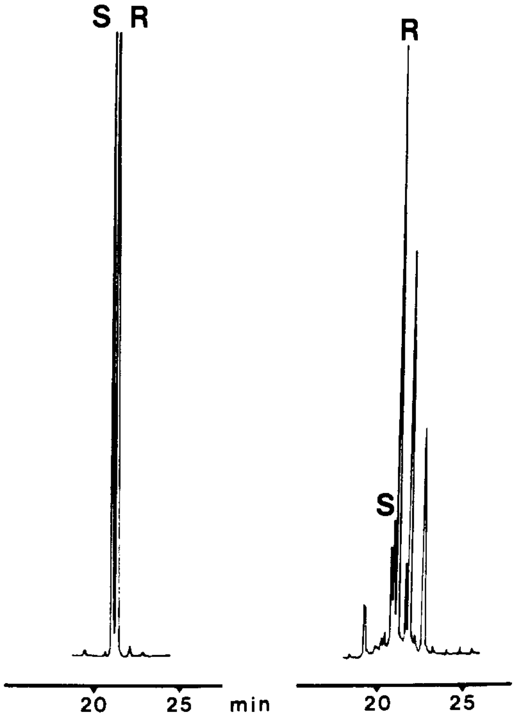

**Figure 1.** HRGC analysis (J&W DB-5, 30 m × 0.25 mm (i.d.); df = 0.25 μm) of derivatized reference compounds (left) and natural constituents from peach (right).

1,4-alkanolides from $C_6$ to $C_{12}$ in peach. Among them, 1,4-decanolide, well-known as a "creamy, fruity, and peachy" flavor component (Maga, 1976) and commonly used as an ingredient in artificial peach formulations (Broderick, 1975), quantitatively predominated. For its chirality evaluation, laborious cleanup of the extract obtained by solvent extraction from peach fruit pulp was necessary. Liquid chromatographic fractionation after silylation of the extract was chosen to facilitate the HRGC separation of 1,4-decanolide as its diastereoisomeric (*S*)-*O*-acetyllactic acid derivatives of 4-hydroxyalkanoic acid isopropyl esters (Mosandl et al., 1987).

As outlined in Figure 1, HRGC analysis of peach fruit volatiles carried out after preseparation of silylated compounds and above-mentioned derivatization revealed the occurrence of 11% *S* and 89% *R* enantiomer. The structural elucidation of the results obtained by HRGC was verified by HRGC–MS analysis. This finding corresponds to data recently published on the enantiomeric composition of nectarines. In this fruit, 1,4- and 1,5-decanolide have been found to exhibit mainly the *R* configuration, but evident proportions of the opposite enantiomer have been also present (13% *S*, 87% *R*) (Engel, 1988).

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