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Stereoisomeric Flavor Compounds. 18. Enantiodiscrimination of Chiral Flavor Compounds by Diastereomeric Derivatization

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The stereodifferentiation of chiral secondary alcohols, 4(5)-alkyl-substituted $\gamma(\delta)$ -lactones via corresponding 1,4(1,5)-diols, chiral 1,3-diols, and chiral 1,3-monothioglycols was carried out by diastereomeric derivatization with (*S*)-*O*-acyllactyl chlorides as chiral auxiliaries. The acetyl, propionyl, isobutyryl, and hexanoyl moieties, respectively, were used as protecting groups of the alcoholic function of the chiral auxiliary lactyl chloride. These methods allow evaluation of the enantiomeric composition of the above-mentioned naturally occurring flavor components by HRGC in an inexpensive, convenient, and reliable manner.

1. INTRODUCTION

"Chiral recognition" has been found one of the most exciting principles in biological activity. Intensive efforts were started in pharmacology, pharmacy, and medicine, since one has recognized that enantiomeric drugs exhibit pharmacodynamic and pharmacokinetic differences and metabolic interactions (Williams and Lee, 1985; Testa, 1986). In the field of flavor chemistry too, it is well established that chiral discrimination is an important principle of odor perception (Ohloff, 1986).

Therefore, research on structure-activity relationships can be connected with the following targets: biogenesis and evaluation of the optical purity of naturally occurring chiral flavor compounds; analytical differentiation between natural and nature identical chiral flavor components; development of efficient and reliable analytical methods for the determination of enantiomeric (diastereomeric) volatiles by HRGC, HRGC/MS, and HPLC with chiral and achiral phases (Mosandl et al., 1987).

Referring to recently published results (Deger et al., 1986; Mosandl et al., 1987), this paper demonstrates that

optically pure references with definite chirality are indispensable for reliable interpretation of chiral stereodifferentiation in flavor chemistry.

The enantiodifferentiation of chiral secondary alcohols, 4(5)-alkyl-substituted $\gamma(\delta)$ -lactones via corresponding 1,4(1,5)-diols, alkane-1,3-diols, and chiral 1,3-monothioglycols by diastereomeric esters of (*S*)-*O*-acetyl, propionyl-, isobutyryl-, and hexanoyllactic acid esters, was proved to be a convenient method for chirality evaluation by HRGC on the achiral phase DB 210-30W.

2.0. EXPERIMENTAL SECTION

Synthesis and Separation of Compounds. 2.1. *Diastereomeric Carbamates from (R)-1-(1-Naphthyl)ethyl Isocyanate and Octan-2-ol (Nonan-2-ol).* (*R*)-(-) (70%) and (*S*)-(+)-alkan-2-ol (30%) were mixed to yield alkan-2-ol solutions of definitive ee values. These solutions were used for synthesis of diastereomeric esters of (*R*)-2-phenylpropionic acid (HTS) and for synthesis of diastereomeric carbamates from (*R*)-1-(naphthyl)ethyl isocyanate (Deger, 1988). The elucidation of absolute configuration of alkan-2-ols from their corresponding diastereomeric HTS esters is a well-established method (Helmchen and Schmierer, 1976).

Therefore, ^1H NMR spectroscopy of mixtures of diastereomeric HTS alkan-2-yl esters is an unambiguous method for the interpretation of the HRGC behavior of their corresponding diastereomeric carbamates from (*R*)-1-(naphthyl)ethyl isocyanate.

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2.2. Synthesis of the Chiral Auxiliaries (S)-O-Acylactyl Chloride. A 30-mmol portion of (S)-(+)-lactic acid and 60 mmol of acyl chloride were stirred for 2 h at 20 °C. Then the excess of acyl chloride reagent was removed in vacuo, and final traces of the acylation reagent were removed by distillation with benzene. (S)-O-acyllactic acid was transformed to the corresponding acid chloride by stirring with 90 mmol of thionyl chloride (12 h, 20 °C). After excess thionyl chloride was removed, the optically pure (S)-O-acyllactyl chloride was distilled.

acyl gp	bp, °C (P, mbar)
acetyl	50–52 (10–11)
propionyl	73–75 (15)
isobutyryl	50–54 (4)
hexanoyl	76–78 (1)

2.3. Reduction of Chiral Esters with LiAlH_4 (Deger, 1987; Günther, 1987; Gessner, 1987). 2-Alkylalkanoates and 4(5)-alkyl-substituted $\gamma(\delta)$ -lactones, respectively, were reduced by LiAlH_4 in dry diethyl ether solution to yield chiral secondary alcohols. Their enantiomeric compositions are identical with those of the chiral molecules to be analyzed.

2.4. Diastereomeric (S)-O-Acylactic Acid Esters. General Procedure. By means of a gas-tight syringe, the dried reagents, solvents, and chiral alcohols to be analyzed were transferred to a dry and sealed GC reaction tube at 20 °C in the following order: 50 μL of pyridine, 100 μL of diethyl ether, 15 μL of (S)-O-acyllactyl chloride, and 10 μL of chiral alcohol (5 μL of chiral diol) to be analyzed and diluted with 100 μL of diethyl ether. After the mixture was allowed to stand for 10 min at room temperature, stereodifferentiation was carried out by HRGC on DB 210-30W. For identification of the analyzed stereoisomers optically pure references with definite chirality were used (Deger, 1988; Günther, 1988; Gessner, 1988; Singer, 1988).

2.5. Gas-Liquid Chromatography. A DANI 6500 gas chromatograph with a flame ionization detector, equipped with a fused silica column (30 m \times 0.32 mm (i.d.)) coated with DB 210-30 W, was used.

2.6. Resolution (R_s) and Separation Factors (α Values) of (S)-O-Acylactic Acid Derivatives. (S)-O-Acetylactic acid esters of alkan-2-ols are given in Mosandl et al. (1987).

Figure 2. (S)-O-Hexanoyllactic acid esters: butan-2-ol ($R_s = 2.4$, $\alpha = 1.018$), pentan-2-ol ($R_s = 3.3$, $\alpha = 1.023$), hexan-2-ol ($R_s = 4.3$, $\alpha = 1.026$), heptan-2-ol ($R_s = 4.5$, $\alpha = 1.026$), octan-2-ol ($R_s = 4.1$, $\alpha = 1.025$), nonan-2-ol ($R_s = 4.1$, $\alpha = 1.023$). (S)-O-Propionoyllactic acid esters: butan-2-ol ($R_s = 3.3$, $\alpha = 1.041$), pentan-2-ol ($R_s = 4.3$, $\alpha = 1.045$), hexan-2-ol ($R_s = 5.3$, $\alpha = 1.048$), heptan-2-ol ($R_s = 5.3$, $\alpha = 1.044$), octan-2-ol ($R_s = 5.1$, $\alpha = 1.040$), nonan-2-ol ($R_s = 4.8$, $\alpha = 1.035$).

Figure 3a. (S)-O-Acetylactic acid diesters: butane-1,3-diol ($R_s = 1.40$, $\alpha = 1.045$), hexane-1,3-diol ($R_s = 0.50$, $\alpha = 1.031$). (S)-O-Hexanoyllactic acid diesters: butane-1,3-diol ($R_s = 2.38$, $\alpha = 1.021$), hexane-1,3-diol ($R_s = 1.63$, $\alpha = 1.012$).

Figure 3b. (S)-O-Acetylactic acid diesters: 4-mercaptobutan-2-ol ($R_s = 2.0$, $\alpha = 1.021$), 6-mercaptohexan-4-ol ($R_s = 1.40$, $\alpha = 1.014$). (S)-O-Hexanoyllactic acid diesters: 4-mercaptobutan-2-ol ($R_s = 2.36$, $\alpha = 1.014$), 6-mercaptohexan-4-ol ($R_s = 1.59$, $\alpha = 1.010$).

Figure 4. (S)-O-Acetylactic acid diesters of chiral diols: hexane-1,5-diol ($R_s = 6.1$, $\alpha = 1.039$), heptane-1,5-diol ($R_s = 3.34$, $\alpha = 1.026$), octane-1,5-diol ($R_s = 2.53$, $\alpha = 1.019$), nonane-1,5-diol ($R_s = 1.86$, $\alpha = 1.013$), decane-1,5-diol ($R_s = 1.35$, $\alpha = 1.010$), undecane-1,5-diol ($R_s = 1.0$, $\alpha = 1.007$), dodecane-1,5-diol ($R_s = 0.85$, $\alpha = 1.006$). (S)-O-propionoyllactic acid diesters of chiral diols: Hexane-1,5-

diol ($R_s = 6.1$, $\alpha = 1.037$), heptane-1,5-diol ($R_s = 3.5$, $\alpha = 1.026$), octane-1,5-diol ($R_s = 2.6$, $\alpha = 1.018$), nonane-1,5-diol ($R_s = 1.9$, $\alpha = 1.012$), decane-1,5-diol ($R_s = 1.7$, $\alpha = 1.010$), undecane-1,5-diol ($R_s = 1.35$, $\alpha = 1.008$), dodecane-1,5-diol ($R_s = 1.0$, $\alpha = 1.006$).

Figure 5. (S)-O-Hexanoyllactic acid diesters of chiral diols: Hexane-1,5-diol ($R_s = 6.2$, $\alpha = 1.049$), heptane-1,5-diol ($R_s = 3.57$, $\alpha = 1.038$), octane-1,5-diol ($R_s = 2.65$, $\alpha = 1.027$), nonane-1,5-diol ($R_s = 1.94$, $\alpha = 1.019$), decane-1,5-diol ($R_s = 1.73$, $\alpha = 1.016$), undecane-1,5-diol ($R_s = 1.38$, $\alpha = 1.013$), dodecane-1,5-diol ($R_s = 1.20$, $\alpha = 1.011$). (S)-O-Isobutyryllactic acid diesters of chiral diols: Hexane-1,5-diol ($R_s = 6.0$, $\alpha = 1.036$), heptane-1,5-diol ($R_s = 4.0$, $\alpha = 1.027$), octane-1,5-diol ($R_s = 2.7$, $\alpha = 1.019$), nonane-1,5-diol ($R_s = 2.0$, $\alpha = 1.014$), decane-1,5-diol ($R_s = 1.75$, $\alpha = 1.011$), undecane-1,5-diol ($R_s = 1.40$, $\alpha = 1.008$), dodecane-1,5-diol ($R_s = 1.20$, $\alpha = 1.007$).

Figure 6. (S)-O-Acetylactic acid diesters: Pentane-1,4-diol ($R_s = 3.0$, $\alpha = 1.031$), hexane-1,4-diol ($R_s = 2.0$, $\alpha = 1.018$), heptane-1,4-diol ($R_s = 1.3$, $\alpha = 1.012$), octane-1,4-diol (partially resolved), nonane-1,4-diol, decane-1,4-diol, undecane-1,4-diol, dodecane-1,4-diol (no resolution). (S)-O-Propionoyllactic acid diesters: Pentane-1,4-diol ($R_s = 4.0$, $\alpha = 1.033$), hexane-1,4-diol ($R_s = 2.1$, $\alpha = 1.020$), heptane-1,4-diol ($R_s = 1.5$, $\alpha = 1.013$), octane-1,4-diol ($R_s = 1.0$, $\alpha = 1.008$), nonane-1,4-diol (partially resolved), decane-1,4-diol, undecane-1,4-diol, dodecane-1,4-diol (no resolution). (S)-O-Hexanoyllactic acid diesters: pentane-1,4-diol ($R_s = 5.0$, $\alpha = 1.024$), hexane-1,4-diol ($R_s = 2.5$, $\alpha = 1.017$), heptane-1,4-diol ($R_s = 1.8$, $\alpha = 1.011$), octane-1,4-diol ($R_s = 1.5$, $\alpha = 1.008$), nonane-1,4-diol ($R_s = 1.0$, $\alpha = 1.006$), dodecane-1,4-diol, undecane-1,4-diol, dodecane-1,4-diol (partially resolved).

RESULTS AND DISCUSSION

Enantiodifferentiation of secondary asymmetric alcohols via chiral carbamates on a chiral phase has already been described (König, 1984). For stereoanalysis of chiral alkan-2-ols their reaction with chiral isocyanates to yield diastereomeric urethanes was supposed to be a further suitable method for estimation of their optical purity (Deger, 1988).

With (R)-(+)-1-phenylethyl isocyanate as a chiral auxiliary reagent and racemic alkan-2-ols, the resulting carbamates are resolved on the achiral phase DB 210-30 W. The order of elution was determined with synthesized optically pure references for each pair of diastereoisomers (Deger et al., 1986; Deger, 1988). Within this series of homologues, the order of elution is *R,S* (first) and *R,R* (second). However, this reagent is not always available in optically pure form. Therefore, the accuracy of estimation of a high enantiomeric excess (ee) is seriously limited.

In the case of (R)-(-)-1-(1-naphthyl)ethyl isocyanate as a chiral auxiliary reagent, the resolution of the corresponding diastereomeric carbamates is still better, but in the case of octan-2-ol, the order of elution is inverted. To prove this irregular behavior of the octan-2-yl carbamates, a definite solution of octan-2-ol (nonan-2-ol) enantiomers [70% (R)-(-) and 30% (S)-(+)] were at first investigated by ^1H NMR spectroscopy of their corresponding diastereomeric esters of α -phenylpropionic acid (HTS) and by HRGC of their diastereomers with (R)-(-)-1-(1-naphthyl)ethyl isocyanate. NMR spectroscopic behavior of the investigated octan-2-yl (nonan-2-yl) esters of (R)-HTS proved unambiguously the *R,R* configuration for the main diastereomer and the *R,S* configuration for the minor product: In both cases the methyl doublet of the alcoholic moiety of the *minor product* is upfield shifted (δ 0.96), and the equivalent signals of the main products are deshielded

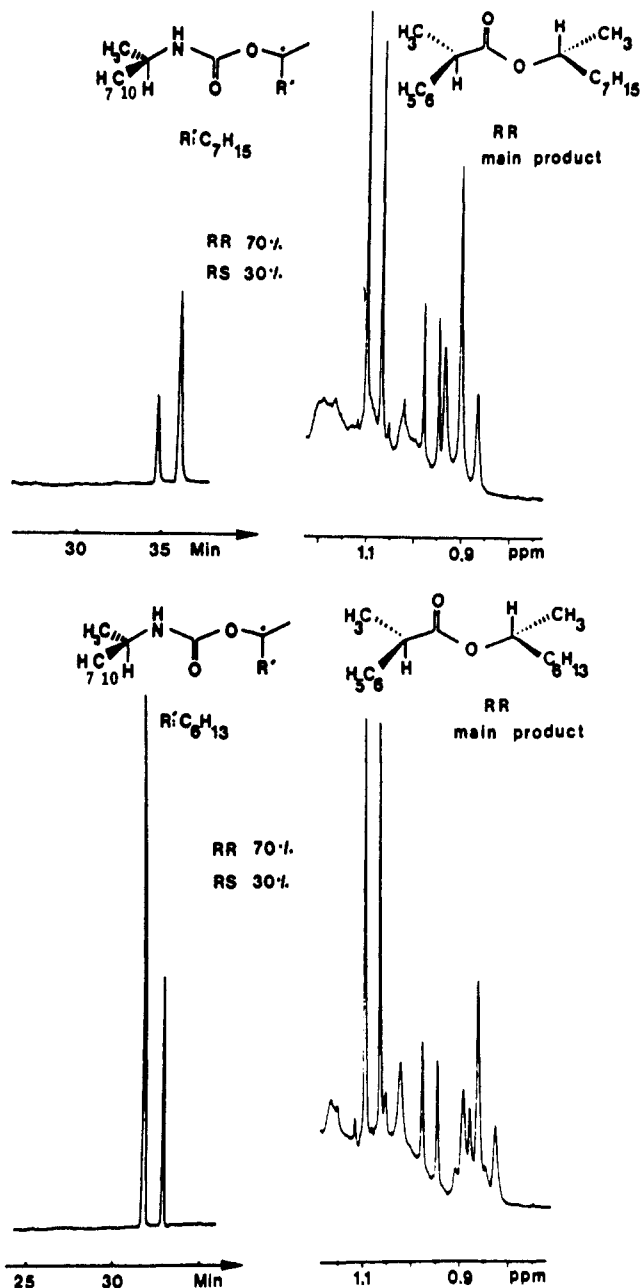


Figure 1. Enantiodifferentiation of nonan-2-ol (octan-2-ol) via diastereomeric esters with (*R*)-hydratropic acid (HTS) and diastereomeric carbamates with (*R*)-1-(1-naphthyl)ethyl isocyanate, respectively (*R,R:S* = 70:30). Conditions: diastereomeric (*R*)-HTS esters ^1H NMR (200 MHz, $\text{C}_6\text{D}_6/\text{TMS}$). HRGC: diastereomeric carbamates on DB 210-30 W fused silica column (30 m); carrier gas, He, 0.8 bar; 150 $^\circ\text{C}$ at 2 $^\circ\text{C}/\text{min}$, 245 $^\circ\text{C}$ maximum. Resolution and separation factors: nonan-2-ol ($R_s = 3.2$, $\alpha = 1.037$), octan-2-ol ($R_s = 3.2$, $\alpha = 1.033$).

(δ 1.07) (Figure 1). By comparison of the corresponding (*R*)-(-)-(1-naphthyl)ethyl carbamates is demonstrated that in case of octan-2-ol the order of elution is inverted: *R,R* first and *R,S* second. This is a significant exception within this series of homologues (Mosandl et al., 1987).

On the other hand, this paper demonstrates that (*S*)-*O*-acyllactyl chlorides are inexpensive, reliable alternatives for chirality evaluation of asymmetric secondary alcohols (Figures 2 and 3). This method is of some interest for the stereochemical analysis of chiral alkane-1,3-diols and monothio-1,3-glycols (Figure 3), which are important with respect to their role as key intermediates for synthesis of optically pure 1,3-dioxanes and 1,3-oxathianes (Singer, 1988). In principle, this method allows stereodifferentia-

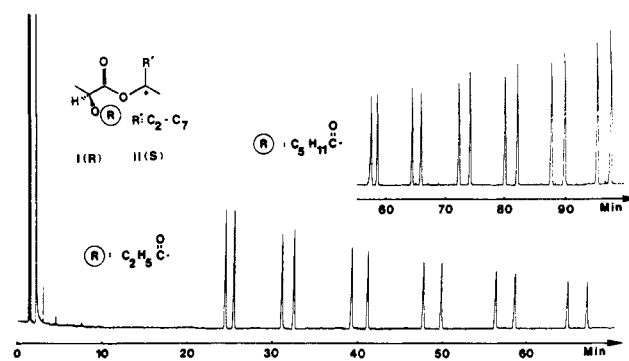


Figure 2. Separation of chiral secondary alcohols as their esters of (*S*)-*O*-acyllactic acid on a DB 210-30 W fused silica column (30 m). Conditions: carrier gas, He, 0.8 bar; 70 $^\circ\text{C}$, 10 min isothermal, 1 $^\circ\text{C}/\text{min}$. Resolution and separation factors: see the Experimental Section.

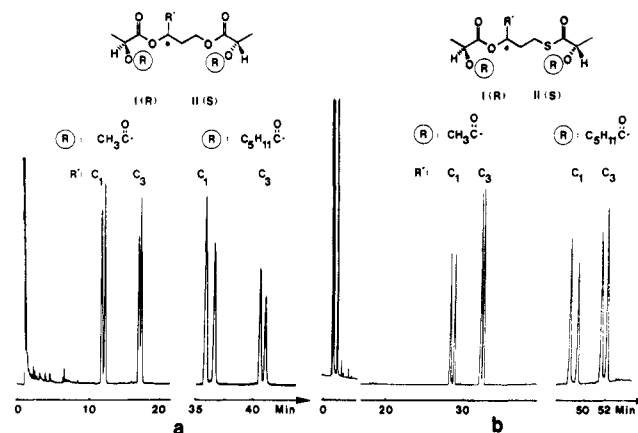


Figure 3. Analytical differentiation of chiral alkane-1,3-diols and monothio-1,3-glycols via diastereomeric esters with (*S*)-*O*-acyllactic acid on fused silica columns. (a) SE 54 column; carrier gas, N_2 , 0.8 bar; 140 $^\circ\text{C}$, 2 min isothermal, 2 $^\circ\text{C}/\text{min}$. (b) DB 210-30W column; carrier gas, He, 0.8 bar; 140 $^\circ\text{C}$, 2 min isothermal, 2 $^\circ\text{C}/\text{min}$, 245 $^\circ\text{C}$ maximum. Resolution and separation factors: see the Experimental Section.

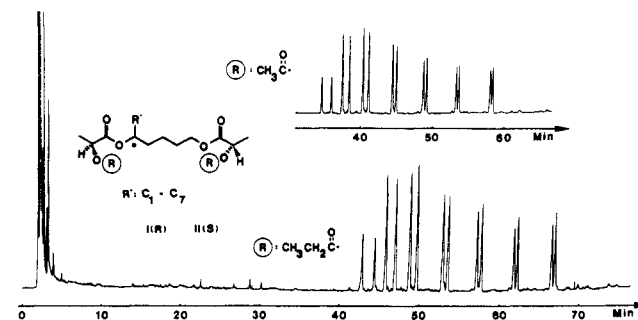


Figure 4. Stereodifferentiation of 5-alkyl-substituted δ -lactones via corresponding chiral 1,5-diols as their diesters of (*S*)-*O*-acyllactic acid on a DB 210-30 W fused silica column (30 m). Conditions: carrier gas, He, 0.8 bar; 140 $^\circ\text{C}$, 2 min isothermal, 2 $^\circ\text{C}/\text{min}$ \rightarrow 180 $^\circ\text{C}$; 180 $^\circ\text{C}$, 1 $^\circ\text{C}/\text{min}$ \rightarrow 245 $^\circ\text{C}$. Resolution and separation factors: see the Experimental Section.

tion for all classes of chiral substances that can be reduced by LiAlH_4 to products with chiral secondary alcoholic functions.

On treatment with LiAlH_4 , 2-alkylalkanoates and 4-(5)-alkyl-substituted γ -(δ)-lactones are reduced to alkan-2-ols with 1,4(1,5)-alkanediols (Figure 4-6).

Their stereodifferentiation by (*S*)-*O*-acyllactyl chlorides exactly reflects the chirality of the chiral compound analyzed, because LiAlH_4 reduction takes place without any racemization (Heusinger and Mosandl, 1984; Mosandl and

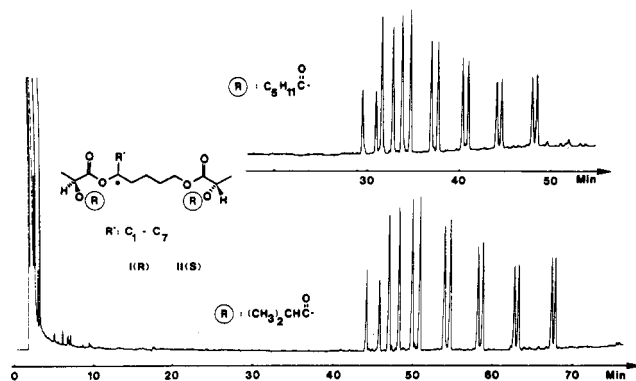


Figure 5. Stereodifferentiation of 5-alkyl-substituted δ -lactones via corresponding chiral 1,5-diols as their diesters of (*S*)-*O*-acetylactic acid on a DB 210-30 W fused silica column (30 m). (*S*)-*O*-Hexanoyl derivatives: 200 °C, 2 min isothermal, 1 °C/min \rightarrow 245 °C. (*S*)-*O*-Isobutyryl derivatives: 140 °C 2 min isothermal, 2 °C/min \rightarrow 180 °C; 180 °C, 1 °C/min \rightarrow 245 °C. Resolution and separation factors: see the Experimental Section.

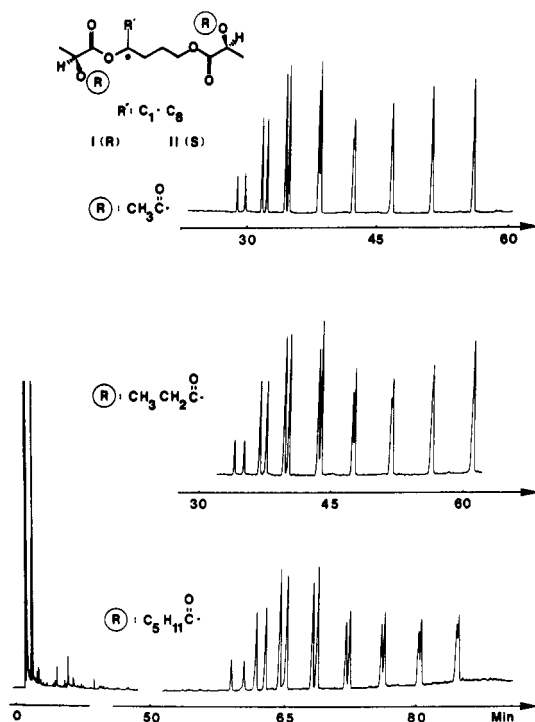


Figure 6. Stereodifferentiation of 4-alkyl-substituted γ -lactones via the corresponding chiral 1,4-diols as their diesters of (*S*)-*O*-acetylactic acid on a DB 21-30W fused silica column (30 m). Conditions: carrier gas, He, 0.8 bar; 140 °C, 2 min isothermal, 2 °C/min \rightarrow 180 °C; 180 °C, 1 °C/min \rightarrow 245 °C. Resolution and separation factors: see the Experimental Section.

Heusinger, 1985). These analytical possibilities for enantiomeric discrimination are of interest with respect to flavor analysis. The esters of the C_2 , C_4 , C_6 , and C_8 alkanic acids with the secondary chiral alcohols butan-, pentan-, hexan-, heptan-, octan-, and nonan-2-ol are widespread aroma components of fruits and essential oils. $\gamma(\delta)$ -Lactones are of special interest in flavor chemistry, because they possess potent, pleasing, and varied sensory properties (Maga, 1976). First attempts at stereodifferentiation of γ -lactones were carried out via diastereomeric Mosher esters (Tressl and Engel, 1984). Now alkan-2-ols, 1,4-alkanediols, and 1,5-alkanediols are separated as their mono- and diesters (*S*)-*O*-acetylactic acids. In all cases the order of elution was proved to be *S,R* first and *S,S* second by means of synthesized optically pure references.

Within the series of diesters of (*S*)-*O*-acetylactic acid derived from 4-alkyl-substituted γ -lactones only the higher homologues are not resolved (Figure 6). But by changing the acyl residue as a protecting group of the alcoholic function within the chiral auxiliary, the resolution is optimized. The best results are obtained with (*S*)-*O*-hexanoyllactyl chloride: quantitative stereodifferentiation in the case of the 1,4-alkanediols C_5 – C_8 . For the γ -lactones C_9 – C_{12} , which are partially resolved by the method via (*S*)-*O*-hexanoyllactyl diesters of the corresponding 1,4-diols, the derivatization to diastereomeric (*S*)-*O*-acetylactic esters of 4-hydroxyalkanoic acid isopropyl esters may be considered as an interesting alternative (Mosandl et al., 1987; Günther, 1988). These results demonstrate that (*S*)-*O*-acetylactic chlorides are efficient and reliable chiral auxiliaries for stereodifferentiation in chiral flavor analysis.

Remarks. Recently it was demonstrated that chromatographically pure diastereomeric (1*S*,4*R*)-camphanoic acid alkan-2-yl esters yield optically pure (*S*)-(+)- and (*R*)-(–)-alkan-2-ols, respectively, by reductive cleavage with $LiAlH_4$ (Mosandl and Deger, 1987). By means of these optically pure references, only one diastereomeric ester is detected, if optically pure chiral auxiliaries are used.

If commercially available (*S*)-(+)-lactic acid is used for esterification with optically pure alkan-2-ols, two diastereomeric esters are detected. Their diastereomeric distribution (*de* > 99.5%) exactly reflects the optical purity of the chiral auxiliary, as was proved in the following manner: If the main product of these diastereomers is isolated and reduced by $LiAlH_4$ and the isolated alkan-2-ol reesterified with (*S*)-*O*-acetylactic chloride, the recovery of stereoisomeric esters exactly yields the same diastereomeric distribution (*de* > 99.5%). This proves unambiguously that the described derivatization procedure with (*S*)-*O*-acyl chlorides proceeds quantitatively and without any racemization.

Therefore, these methods are suitable for a reliable stereodifferentiation of chiral alkanols.

Before estimation of high *ee* values of chiral alcohols, we recommend testing the optical purity of the available chiral auxiliary with an optically pure reference alkanol.

ACKNOWLEDGMENT

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Registry No. (*S*)-Lactic acid, 79-33-4; (*S*)-*O*-acetylactyl chloride, 36394-75-9; (*S*)-*O*-propionylactyl chloride, 116406-31-6; (*S*)-*O*-isobutyryllactyl chloride, 116406-32-7; (*S*)-*O*-hexanoyllactyl chloride, 116406-33-8; (*R*)-2-butanol (*S*)-*O*-hexanoyllactate, 116499-90-2; (*S*)-2-butanol (*S*)-*O*-hexanoyllactate, 116499-93-5; (*R*)-2-pentanol (*S*)-*O*-hexanoyllactate, 116406-34-9; (*S*)-2-pentanol (*S*)-*O*-hexanoyllactate, 116406-42-9; (*R*)-2-hexanol (*S*)-*O*-hexanoyllactate, 116406-35-0; (*S*)-2-hexanol (*S*)-*O*-hexanoyllactate, 116406-43-0; (*R*)-2-heptanol (*S*)-*O*-hexanoyllactate, 116406-36-1; (*S*)-2-heptanol (*S*)-*O*-hexanoyllactate, 116406-44-1; (*R*)-2-octanol (*S*)-*O*-hexanoyllactate, 116406-37-2; (*S*)-2-octanol (*S*)-*O*-hexanoyllactate, 116406-45-2; (*R*)-2-nonanol (*S*)-*O*-hexanoyllactate, 116406-38-3; (*S*)-2-nonanol (*S*)-*O*-hexanoyllactate, 116406-46-3; (*R*)-2-butanol (*S*)-*O*-propionylactate, 116499-91-3; (*S*)-2-butanol (*S*)-*O*-propionylactate, 116499-94-6; (*R*)-2-pentanol (*S*)-*O*-propionylactate, 116406-39-4; (*S*)-2-pentanol (*S*)-*O*-propionylactate, 116406-47-4; (*R*)-2-hexanol (*S*)-*O*-propionylactate, 116499-92-4; (*S*)-2-hexanol (*S*)-*O*-propionylactate, 116499-95-7; (*R*)-2-heptanol (*S*)-*O*-propionylactate, 116406-40-7; (*S*)-2-heptanol (*S*)-*O*-propionylactate, 116406-48-5; (*R*)-2-octanol (*S*)-*O*-propionylactate, 116406-41-8; (*S*)-2-octanol (*S*)-*O*-propionylactate, 116406-49-6; (*R*)-2-nonanol (*S*)-*O*-propionylactate, 116499-96-8; (*S*)-2-nonanol (*S*)-*O*-propionylactate, 116499-97-9; (*S*)-1,3-butanediol bis((*S*)-*O*-acetylactate), 116406-50-9; (*R*)-1,3-butanediol bis((*S*)-*O*-acetylactate), 116499-98-0; (*S*)-1,3-hexanediol bis((*S*)-*O*-acetylactate), 116406-51-0; (*R*)-1,3-hexanediol bis-

((S)-O-acetylactate), 116499-99-1; (S)-1,3-butanediol bis((S)-O-hexanoyllactate), 116406-52-1; (R)-1,3-butanediol bis((S)-O-hexanoyllactate), 116500-00-6; (S)-2,3-hexanediol bis((S)-O-hexanoyllactate), 116406-53-2; (R)-1,3-hexanediol bis((S)-O-hexanoyllactate), 116500-01-7; (S)-4-mercapto-2-butanol bis((S)-O-acetylactate), 116406-54-3; (R)-4-mercapto-2-butanol bis((S)-O-acetylactate), 116500-02-8; (S)-6-mercapto-4-hexanol bis((S)-O-acetylactate), 116406-55-4; (R)-6-mercapto-4-hexanol bis((S)-O-acetylactate), 116500-03-9; (S)-4-mercapto-2-butanol bis((S)-O-hexanoyllactate), 116406-56-5; (R)-4-mercapto-2-butanol bis((S)-O-hexanoyllactate), 116500-04-0; (S)-6-mercapto-4-hexanol bis((S)-O-hexanoyllactate), 116406-57-6; (R)-6-mercapto-4-hexanol bis((S)-O-hexanoyllactate), 116500-05-1; (S)-1,5-hexanediol bis((S)-O-acetylactate), 116406-58-7; (R)-1,5-hexanediol bis((S)-O-acetylactate), 116500-06-2; (S)-1,5-heptanediol bis((S)-O-acetylactate), 116406-59-8; (R)-1,5-heptanediol bis((S)-O-acetylactate), 116500-07-3; (S)-1,5-octanediol bis((S)-O-acetylactate), 116406-60-1; (R)-1,5-octanediol bis((S)-O-acetylactate), 116500-08-4; (S)-1,5-nonanediol bis((S)-O-acetylactate), 116406-61-2; (R)-1,5-nonanediol bis((S)-O-acetylactate), 116500-09-5; (S)-1,5-decanediol bis((S)-O-acetylactate), 116406-62-3; (R)-1,5-decanediol bis((S)-O-acetylactate), 116500-10-8; (S)-1,5-undecanediol bis((S)-O-acetylactate), 116406-63-4; (R)-1,5-undecanediol bis((S)-O-acetylactate), 116500-11-9; (S)-1,5-dodecanediol bis((S)-O-acetylactate), 116406-64-5; (R)-1,5-dodecanediol bis((S)-O-acetylactate), 116500-12-0; (S)-1,5-hexanediol bis((S)-O-propionyllactate), 116406-65-6; (R)-1,5-hexanediol bis((S)-O-propionyllactate), 116500-13-1; (S)-1,5-heptanediol bis((S)-O-propionyllactate), 116406-66-7; (R)-1,5-heptanediol bis((S)-O-propionyllactate), 116500-14-2; (S)-1,5-octanediol bis((S)-O-propionyllactate), 116406-67-8; (R)-1,5-octanediol bis((S)-O-propionyllactate), 116500-15-3; (S)-1,5-nonanediol bis((S)-O-propionyllactate), 116406-68-9; (R)-1,5-nonanediol bis((S)-O-propionyllactate), 116500-16-4; (S)-1,5-decanediol bis((S)-O-propionyllactate), 116406-69-0; (R)-1,5-decanediol bis((S)-O-propionyllactate), 116500-17-5; (S)-1,5-undecanediol bis((S)-O-propionyllactate), 116406-70-3; (R)-1,5-undecanediol bis((S)-O-propionyllactate), 116500-18-6; (S)-1,5-dodecanediol bis((S)-O-propionyllactate), 116406-71-4; (R)-1,5-dodecanediol bis((S)-O-propionyllactate), 116500-19-7; (S)-1,5-hexanediol bis((S)-O-hexanoyllactate), 116406-72-5; (R)-1,5-hexanediol bis((S)-O-hexanoyllactate), 116500-20-0; (S)-1,5-heptanediol bis((S)-O-hexanoyllactate), 116406-73-6; (R)-1,5-heptanediol bis((S)-O-hexanoyllactate), 116500-21-1; (S)-1,5-octanediol bis((S)-O-hexanoyllactate), 116406-74-7; (R)-1,5-octanediol bis((S)-O-hexanoyllactate), 116500-22-2; (S)-1,5-nonanediol bis((S)-O-hexanoyllactate), 116406-75-8; (R)-1,5-nonanediol bis((S)-O-hexanoyllactate), 116500-23-3; (S)-1,5-decanediol bis((S)-O-hexanoyllactate), 116406-76-9; (R)-1,5-decanediol bis((S)-O-hexanoyllactate), 116500-24-4; (S)-1,5-undecanediol bis((S)-O-hexanoyllactate), 116406-77-0; (R)-1,5-undecanediol bis((S)-O-hexanoyllactate), 116500-25-5; (S)-1,5-dodecanediol bis((S)-O-hexanoyllactate), 116406-78-1; (R)-1,5-dodecanediol bis((S)-O-hexanoyllactate), 116500-26-6; (S)-1,5-hexanediol bis((S)-O-isobutyryllactate), 116406-79-2; (R)-1,5-hexanediol bis((S)-O-isobutyryllactate), 116500-27-7; (S)-1,5-heptanediol bis((S)-O-isobutyryllactate), 116406-80-5; (R)-1,5-heptanediol bis((S)-O-isobutyryllactate), 116500-28-8; (S)-1,5-octanediol bis((S)-O-isobutyryllactate), 116406-81-6; (R)-1,5-octanediol bis((S)-O-isobutyryllactate), 116500-29-9; (S)-1,5-nonanediol bis((S)-O-isobutyryllactate), 116406-82-7; (R)-1,5-nonanediol bis((S)-O-isobutyryllactate), 116500-30-2; (S)-1,5-decanediol bis((S)-O-isobutyryllactate), 116406-83-8; (R)-1,5-decanediol bis((S)-O-isobutyryllactate), 116500-31-3; (S)-1,5-undecanediol bis((S)-O-isobutyryllactate), 116406-84-9; (R)-1,5-undecanediol bis((S)-O-isobutyryllactate), 116500-32-4; (S)-1,5-dodecanediol bis((S)-O-isobutyryllactate), 116406-85-0; (R)-1,5-dodecanediol bis((S)-O-isobutyryllactate), 116500-33-5; (S)-1,4-pentanediol bis((S)-O-acetylactate), 116406-86-1; (R)-1,4-pentanediol bis((S)-O-acetylactate), 116500-34-6; (S)-1,4-hexanediol bis((S)-O-acetylactate), 116406-87-2; (R)-1,4-hexanediol bis((S)-O-acetylactate), 116500-35-7; (S)-1,4-heptanediol bis((S)-O-acetylactate), 116406-88-3; (R)-1,4-heptanediol bis((S)-O-acetylactate), 116500-36-8; (S)-1,4-octanediol bis((S)-O-acetylactate), 116406-89-4; (R)-1,4-octanediol bis((S)-O-acetylactate), 116500-37-9; (S)-1,4-nonanediol bis((S)-O-acetylactate), 116406-90-7; (R)-

1,4-nonanediol bis((S)-O-acetylactate), 116500-38-0; (S)-1,4-decanediol bis((S)-O-acetylactate), 116406-91-8; (R)-1,4-decanediol bis((S)-O-acetylactate), 116500-39-1; (S)-1,4-undecanediol bis((S)-O-acetylactate), 116406-92-9; (R)-1,4-undecanediol bis((S)-O-acetylactate), 116500-40-4; (S)-1,4-dodecanediol bis((S)-O-acetylactate), 116406-93-0; (R)-1,4-dodecanediol bis((S)-O-acetylactate), 116500-41-5; (S)-1,4-pentanediol bis((S)-O-propionyllactate), 116406-94-1; (R)-1,4-pentanediol bis((S)-O-propionyllactate), 116500-42-6; (S)-1,4-hexanediol bis((S)-O-propionyllactate), 116406-95-2; (R)-1,4-hexanediol bis((S)-O-propionyllactate), 116500-43-7; (S)-1,4-heptanediol bis((S)-O-propionyllactate), 116406-96-3; (R)-1,4-heptanediol bis((S)-O-propionyllactate), 116500-44-8; (S)-1,4-octanediol bis((S)-O-propionyllactate), 116406-97-4; (R)-1,4-octanediol bis((S)-O-propionyllactate), 116500-45-9; (S)-1,4-nonanediol bis((S)-O-propionyllactate), 116406-98-5; (R)-1,4-nonanediol bis((S)-O-propionyllactate), 116500-46-0; (S)-1,4-decanediol bis((S)-O-propionyllactate), 116406-99-6; (R)-1,4-decanediol bis((S)-O-propionyllactate), 116500-47-1; (S)-1,4-undecanediol bis((S)-O-propionyllactate), 116407-00-2; (R)-1,4-undecanediol bis((S)-O-propionyllactate), 116500-48-2; (S)-1,4-dodecanediol bis((S)-O-propionyllactate), 116407-13-7; (R)-1,4-dodecanediol bis((S)-O-propionyllactate), 116500-57-3; (S)-1,4-pentanediol bis((S)-O-hexanoyllactate), 116407-01-3; (R)-1,4-pentanediol bis((S)-O-hexanoyllactate), 116500-49-3; (S)-1,4-hexanediol bis((S)-O-hexanoyllactate), 116407-02-4; (R)-1,4-hexanediol bis((S)-O-hexanoyllactate), 116500-50-6; (S)-1,4-heptanediol bis((S)-O-hexanoyllactate), 116407-03-5; (R)-1,4-heptanediol bis((S)-O-hexanoyllactate), 116500-51-7; (S)-1,4-octanediol bis((S)-O-hexanoyllactate), 116407-04-6; (R)-1,4-octanediol bis((S)-O-hexanoyllactate), 116500-52-8; (S)-1,4-nonanediol bis((S)-O-hexanoyllactate), 116407-05-7; (R)-1,4-nonanediol bis((S)-O-hexanoyllactate), 116500-53-9; (S)-1,4-decanediol bis((S)-O-hexanoyllactate), 116407-06-8; (R)-1,4-decanediol bis((S)-O-hexanoyllactate), 116500-54-0; (S)-1,4-undecanediol bis((S)-O-hexanoyllactate), 116407-07-9; (R)-1,4-undecanediol bis((S)-O-hexanoyllactate), 116500-55-1; (S)-1,4-dodecanediol bis((S)-O-hexanoyllactate), 116407-08-0; (R)-1,4-dodecanediol bis((S)-O-hexanoyllactate), 116500-56-2; (R)-2-octanol (R)-1-(1-naphthyl)ethylcarbamate, 62197-98-2; (S)-2-octanol (R)-1-(1-naphthyl)ethylcarbamate, 107724-46-9; (R)-2-nonanol (R)-1-(1-naphthyl)ethylcarbamate, 116407-11-5; (S)-2-nonanol (R)-1-(1-naphthyl)ethylcarbamate, 116407-12-6; (R)-2-octanol (R)- α -phenylpropionate, 116407-09-1; (S)-2-octanol (R)- α -phenylpropionate, 116436-90-9; (R)-2-nonanol (R)- α -phenylpropionate, 116436-91-0.

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