Analysis of the Optical and Geometrical Isomer Distributions in Selected Propylene Glycol Acetals

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Abstract

For the first time, relative distributions of optical and geometrical isomers in selected propylene glycol acetals are determined. Resolution of the four acetal isomers possible through the reaction of racemic propylene glycol (PG) with selected aldehydes is demonstrated. The four isomers are ascribed to the presence of *syn* and *anti* geometrical isomers for each optically active PG acetal enantiomer. Thus, the (+) and well as (–) enantiomer are found to have a pair of *syn* and *anti* geometrical isomers. The ratio of the (+) and (–) isomers in the product remains at an approximate 50:50 ratio, as expected. However, somewhat unexpectedly, the *syn/anti* geometrical isomer ratio systematically varies with the nature of the substituent comprising the side chain of the aldehyde. Mechanisms involving electronic and minimal steric effects are advanced as possible reasons for the change in the *syn/anti* PG acetal ratios.

Introduction

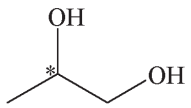
Certain molecules, whose molecular mirror images are not superimposable, are optically active. Although the molecules possess the same empirical formula, they, thus, differ in their steric structure, very similar to the left hand from the right hand. One isomer will rotate the plane of polarized light to the right (+, dextrorotatory), and the other will rotate the light to the left (–, levorotatory). These two mirror-image isomers, which do not differ in any physical property, are termed enantiomers. Should a mixture of equal amounts of the optical isomers exist, any rotation of light would be cancelled out by the opposing enantiomers. Such mixtures are referred to as racemic (1).

The root of optical rotation rests with the presence of an asymmetric, chiral carbon in the molecules of interest. This particular carbon is most often characterized as having four different groups directly attached. Chiral molecules of a large number of different classes of substances have been described in the literature as constituents of natural and synthetic aromatic materials and essential oils (1). Examples of natural and synthetic optically active compounds include alcohols, diols, aldehydes, acetals, ketones, carboxylic acids, and lactones. Of particular importance to this work is the chiral nature of 1,2-propanediol or propylene glycol (PG) (Figure 1).

The number two carbon (marked with an asterisk) is a chiral carbon; thus, racemic PG consists of a mixture of two enantiomers. Therefore, reactions with PG that proceed with retention of configuration about carbon number two will yield a pair of enantiomers. Of noteworthy substance to the work here is the presence of optical isomers in the products formed when reactions between aldehydes and PG occur to form PG acetals (Figures 1 and 2).

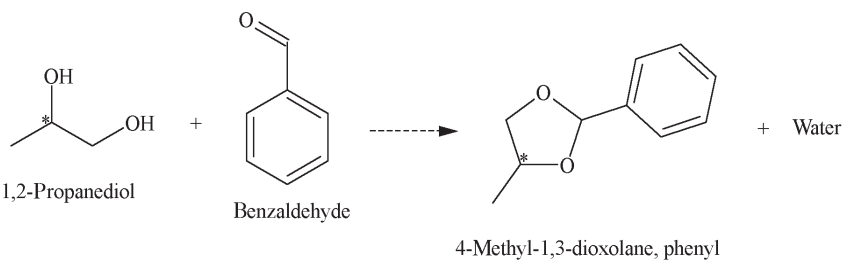
In addition to the formation of enantiomers in the reactions between PG and aldehydes, a second pair of isomers, geometrical, are formed (2) (Figure 3). These geometrical isomers are called *syn* and *anti* according to the positions of the aldehyde group and methyl group relative to the plane of the dioxolane ring.

Thus, when aldehydes react with PG, four, not two, isomers are produced. That is, for the



1,2-Propanediol

Figure 1. The structure of 1,2-propanediol or propylene glycol. The asterisk is the number two carbon.



1,2-Propanediol

Benzaldehyde

4-Methyl-1,3-dioxolane, phenyl

Figure 2. Reaction between optically active PG and benzaldehyde to form 4-methyl-1,3-dioxane phenyl (benzaldehyde PG acetyl).

geometrical isomer termed *syn*, two optical isomers, ±, will be produced. Likewise for the geometrical isomer termed *anti*, two optical isomers, ±, will be produced. These geometrical isomers could possess different physical properties, like slight differences in boiling points, and thus, in some cases, partial resolution of the *syn* and *anti* isomers by capillary gas chromatography (GC) has been attained (2).

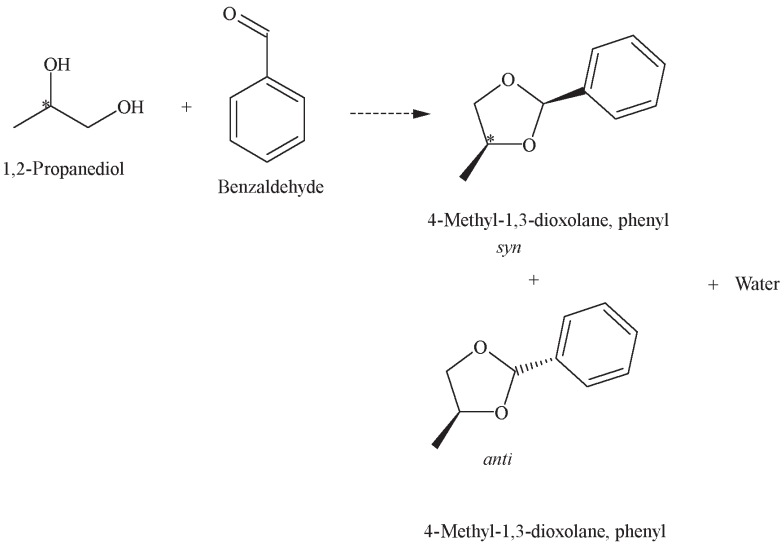


Figure 3. Reaction between optically active PG and benzaldehyde to form optically active geometrical isomers of 4-methyl-1,3-dioxane, phenyl.

Table I. Odor Characteristics of Selected Enantiomers

Compound	Odor description
(–) 2-Methylbutanoic acid	Cheese, sweat
(+) 2-Methylbutanoic acid	Sweet, fruity
(–) Ethyl-2-methylbutanonate	Medicinal, phenolic
(+) Ethyl-2-methylbutanonate	Sweet, apple
(–) Limonene	Fresh, orange-like
(+) Limonene	Mint, turpentine-like
(+) γ-Decalactone	Sweet, milk-note
(–) γ-Decalactone	Fruity, peach-like

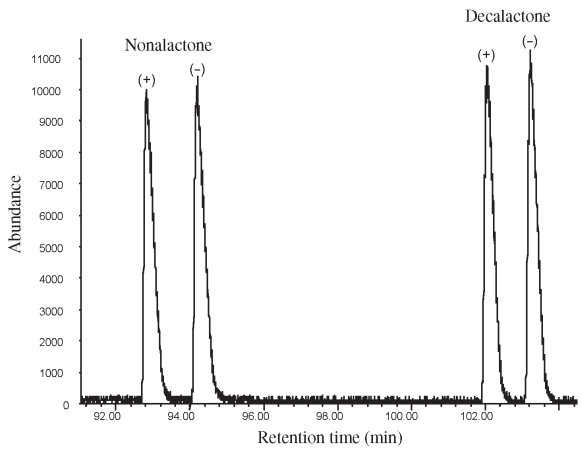


Figure 4. Total ion chromatograph depicting the separation of the optical isomers of selected γ-lactones.

Aldehydes, as a class of compounds, provide powerful flavors to foods and beverages. Of note, for example, is vanillin, an aromatic aldehyde responsible for vanilla flavor. Likewise, benzaldehyde is associated with cherry flavor, and *cis*-3-hexenal is linked to fresh green leafy odor. PG is a popular solvent used in the preparation of processed artificial flavors, such as artificial chocolate. Thus, the potential for acetal formation exists in mixtures of PG and flavorful aldehydes. Temperature, time, pH, and moisture are known to influence the rate of reaction between aldehydes and PG. In addition, the substituent located on the aromatic ring of selected flavors has been shown to have a significant impact on the rate of acetal formation (3). This work shows that PG acetals can form easily at room temperature.

The conversion of an aldehyde to an acetal most often changes the vapor pressure, solubility, and aroma characteristics of the aldehyde (4). Thus, the flavor characteristics of the precursor aldehyde would be anticipated to change from both a qualitative and a quantitative perspective. For example, isovaleraldehyde possesses an unpleasant stench. However, conversion to the comparable PG acetal renders a pleasant aroma (2). In a similar fashion, conversion of benzaldehyde to its comparable PG acetal changes the powerful cherry note of benzaldehyde into an almost flavorless compound (5). However, in some cases, the notes observed could have been attributable to relatively low concentrations of precursor aldehydes present in the PG acetal product. One manner to eliminate this possibility rests with the separation of the acetals from their precursor reagents by GC followed by olfactory assessments of the pure acetals.

Chiral discrimination has been long recognized as a most important principle in biological activity and odor perception (6,7). For example, the (–) and (+) isomers of carvone have the odor of caraway and spearmint, respectively (8). Studies on the odor characteristics of enantiomers have been extended to a large collection of compounds (2,6,9–21). These types of compounds include, for example, lactones, acids, esters, ketones, terpenes, and aldehydes (Table I) (14).

The ability to adequately assess the olfactory characteristics of any material rests with the evaluation of the pure material in the absence of any potential interferences. This is of particular significance in the case of aldehydes and their acetals because most aldehydes have powerful sensory attributes at relatively low concentrations (15). Thus, the separation and analysis of the enantiomers has become increasingly important to flavor development. At present, the mechanisms of GC enantiomer separations have not been well defined (16,17). Unusual chromatographic behaviors, such as column overload at very

low analyte levels (25 ng) and reversal of the elution order of enantiomers, have been observed. Thus, it is difficult to assess the usefulness of any given chiral stationary phase for the separation of enantiomers. Nonetheless, the addition of derivatized cyclodextrin macromolecules to common stationary phases has led to capillary columns with the ability to separate enantiomers.

This report will describe the evaluations of the capability of selected chiral stationary phases to provide adequate separation of the chiral and geometrical isomers of selected PG acetals. Percent distributions of these isomers will be discussed and possible reasons for the distributions will be postulated.

Experimental

Instrumental settings chiral GC–mass selective detection

The analyses were performed using the following equipment and reagents: methylene chloride (Burdick and Jackson, Muskegon, MI) solutions of the PG acetals were manually injected into an Agilent 6890 GC equipped with an Agilent 5973 mass selective detector (MSD) (Little Falls, DL). The GC was fitted with a selected specific Rt-β-DEX fused-silica column (30-m × 0.32-mm i.d., 0.25-µm film thickness) (Restek Corp., Bellefonte, PA). A number of Rt-β-DEX fused-silica columns were evaluated for their capacity to separate the PG acetal isomers. The helium carrier gas linear velocity was set at 40 cm/s at 60°C, and 1-µL injections were made in the split (100/1) mode. The GC oven was held at an initial temperature of 60°C for 0 min, and then programmed to 230°C at either 1°C/min, 2°C/min, or 4°C/min. The multiple temperature ramp rates were investigated in attempts to obtain adequate resolution of the isomers. The GC injection port was held at 250°C, and the MSD interface was set at 230°C. The MSD was operated in the electron impact mode at 70 eV. Identifications were facilitated using Wiley and NIST library search routines, as well as interpretative mass spectrometry techniques and skills.

Sample preparation

The PG acetals were prepared in the following manner: 100 µL of the selected aldehyde was added to 400 µL of PG in a 1-mL reaction vial (Pierce Chemical Co., Rockford, IL). The vial was sealed with a Teflon-lined septum cap and heated for 48 h at 80°C in a heating block. After the heat treatment was complete, the heat-treated vials were removed from the heating block and allowed to come to room temperature. When the vials reached room temperature, the contents were transferred to a 20-mL glass vial and 10 mL of deionized water was added followed by 5 mL of methylene chloride. The vial was capped and shaken vigorously for a few minutes. The layers were allowed to separate, and the bottom methylene chloride layer was gently transferred using a Pasteur pipet (Fisher Scientific, Pittsburgh, PA) to a 4-mL glass vial, being careful not to transfer any of the water layer. In a few cases, the samples were placed in a centrifuge at 2000 rpm for 20 min to facilitate phase separations. The 4-mL vial was the capped using a Teflon-lined septum cap. The extracts were stored at room temperature. The water layer was discarded. A portion of the methylene chloride layer was diluted 1:10 with fresh methylene chloride. Approximately 2 mL of this diluted sample was then placed in a 1.8-mL GC vial for analysis.

In cases where optically active PG was employed, the pro-

Table II. Performance Characteristics, Number of Peaks, for Chiral Capillary Columns Regarding the Separation of Selected PG Acetals

Acetal	β-DEXsm	β-DEXsp	β-DEXsa	β-DEXse	β-DEXcst
Benzaldehyde	4R*	4U	4R	3R	4R
p-Tolualdehyde	4R	2R	4R	3R	4R
p-Anisaldehyde	3U†	4U	4R	3R	2U
Cinnamaldehyde	4R	4U	4R	4R	2U
m-Anisaldehyde	3U	3U	4R	4R	2U
Salicyaldehyde	3R	3R	4U	4U	0‡
Octanal	4R	3R	4R	3R	4R

* R = resolved.
† U = unresolved.
‡ 0 = no resolution.

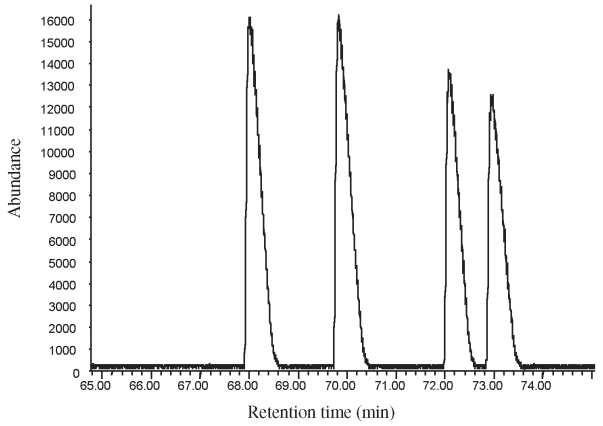


Figure 5. Total ion chromatograph depicting the separation of benzaldehyde PG acetal isomers. Column used: β-DEXcst.

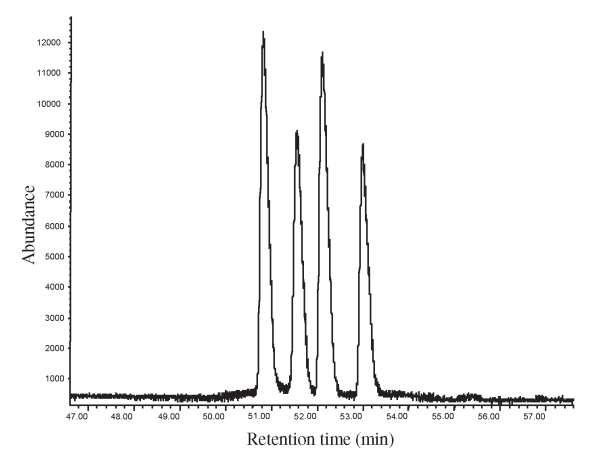


Figure 6. Total ion chromatograph depicting the separation of benzaldehyde PG acetal isomers. Column used: β-DEXsm.

cedure outlined previously was followed, substituting the desired PG isomer. All of the reagents were obtained from Aldrich Chemical Company (Milwaukee, WI) and used as received.

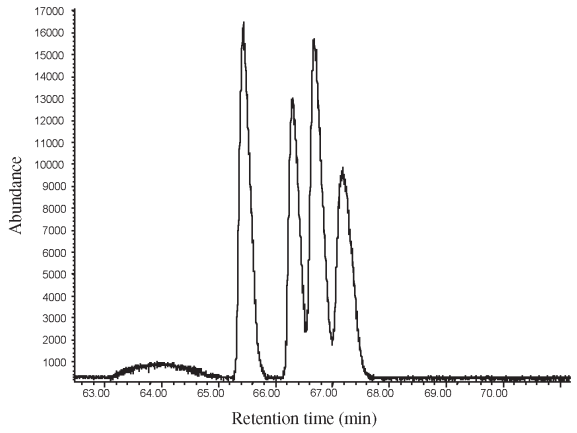


Figure 7. Total ion chromatograph depicting the separation of *p*-tolualdehyde PG acetal isomers. Column used: β-DEXsm.

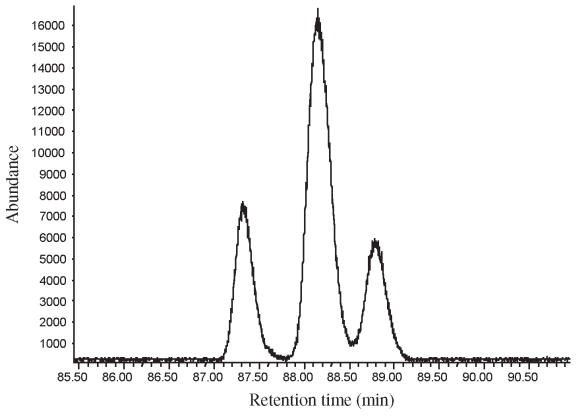


Figure 8. Total ion chromatograph depicting the separation of *p*-anisaldehyde PG acetal isomers. Column used: β-DEXsm.

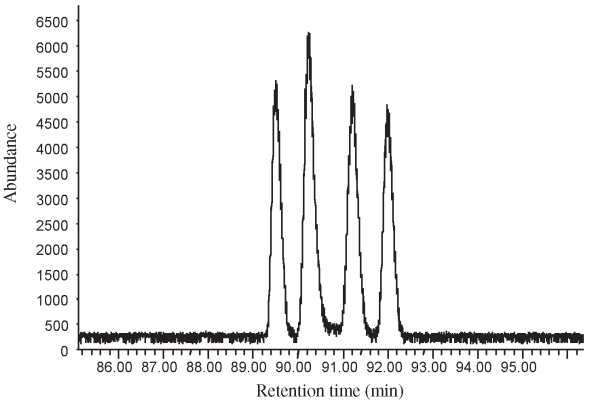


Figure 9. Total ion chromatograph depicting the separation of *cin*namaldehyde PG acetal isomers. Column used: β-DEXsm.

Results and Discussion

Prior to beginning work with the PG acetals, separations were performed on a series of linear lactones to test the chromatographic rigor of the system. Figure 4 reveals that acceptable enantiomer resolution was obtained with nona and deca lactones using a Rt-β-DEScst capillary column. This separation was found to be very similar to that published by Restek (22).

As mentioned in the introduction section, four isomers were to be expected as products from the reaction between 1,2-propanediol (PG) and selected aldehydes, a (+) enantiomer with *syn* and *anti* geometrical isomers and a (–) enantiomer with *syn* and *anti* geometrical isomers. For the adequate separation of the four isomers to be effective employing a chiral column, most likely both the chiral nature of the column and the normal liquid phase separation mechanisms must be operative. Five chiral columns (all 30-m × 0.32-mm i.d., 0.25-µm film thickness) were evaluated for their capability to separate the four isomers, *vide supra* (described previously), expected to be formed as a result of the reaction between racemic 1,2-PG and selected aldehydes: β-DEXsm,β-DEXsp, β-DEXsa, β-DEXse, and β-DEXcst (Table II).

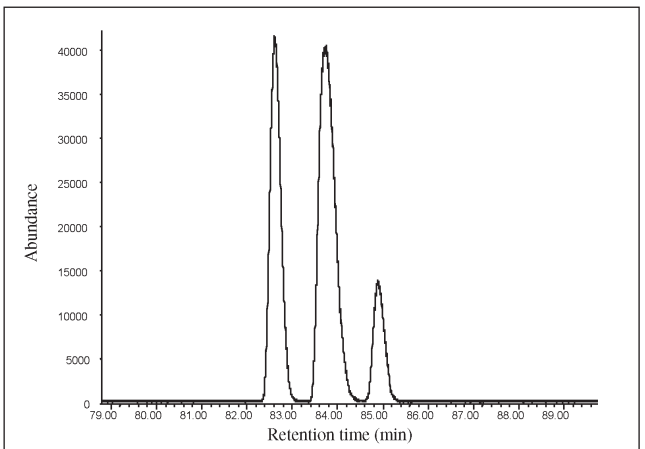


Figure 10. Total ion chromatograph depicting the separation *m*-anisaldehyde PG acetal isomers. Column used: β-DEXsm.

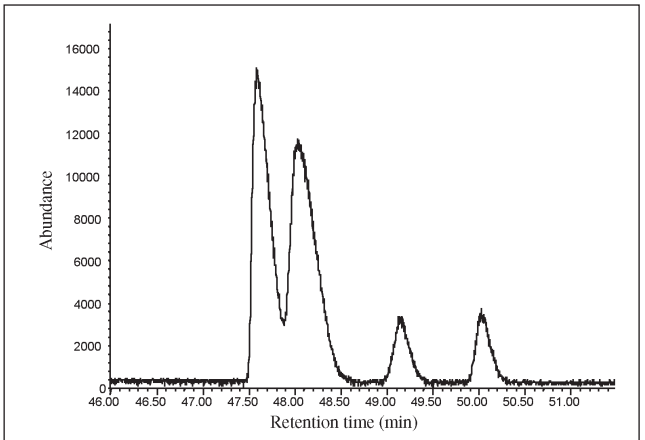


Figure 11. Total ion chromatograph depicting the separation of oxtanal PG acetal isomers. Column used: β-DEXsm.

Examples of the types of separations obtained employing these columns can be found in Figures 5–11. Numerous types of separations were observed, ranging from complete resolution of the four isomers to partial resolutions revealing only three peaks. Thus, the reaction between aldehydes and racemic PG does produce four isomers, *vide supra*. The β-DEXsa column proved to provide the best resolution for the majority of the PG acetals. In a limited number of cases, the β-DEXcst column was effective for the remaining PG acetals.

However, because of the unpredictable nature of the resolution order of optical isomers, assignment of eluting components to specific optical isomers was not possible using the racemic PG. On the other hand, use of optically active PG as a reagent for the formation of optically active PG acetals would present the potential for assigning optical isomers to specific peaks. Thus, a series of reactions were performed wherein the *R* and *S* isomers of PG were reacted with selected aldehydes. Figures 12 and 13 illustrate examples of the separations obtained when the enantiomers of PG were employed as reagents. Obviously then, the two responses obtained from the *R* as well as *S* optically active PG enantiomer must be the geometrical isomers with the geometrical configurations *syn* and *anti*. From a stereochemical perspective, the *anti* isomer would most likely be expected to be the preferred product because the methyl group from the PG and the substituent attached to the carbonyl group would be well separated in space, one from another. In the *syn* configuration, a significant potential for spacial overlap of the methyl group from PG and the substituent attached to the carbonyl carbon was found to be possible.

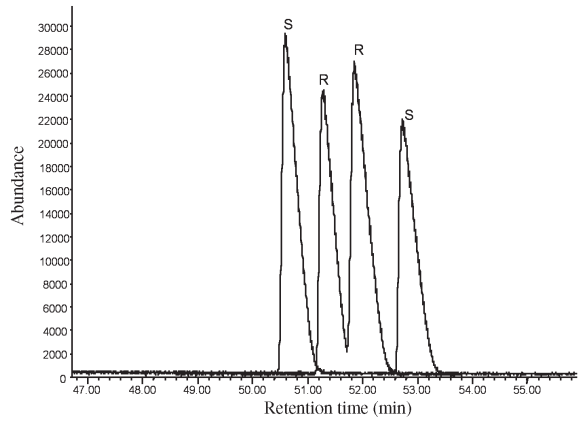


Figure 12. Total ion chromatograph depicting the separation of optical isomers of benzaldehyde PG acetal. Column used: β-DEXsm.

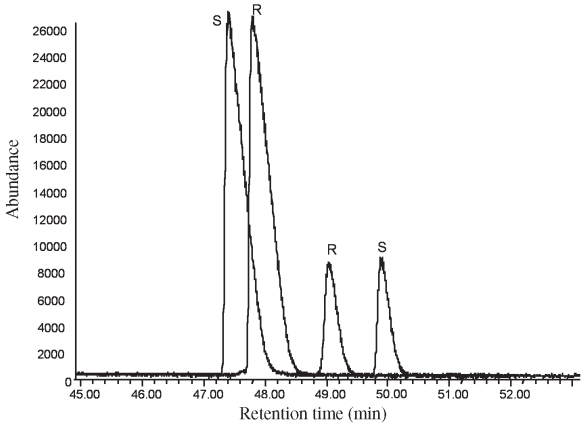


Figure 13. Total ion chromatograph depicting the separation optical isomers of octanal PG acetal. Column used: β-DEXsm.

Thus, through the use of the *R* and *S* enantiomers of PG, as well as racemic PG, coupled with optimized chromatography, retention times and isomer distributions for the optical isomers of selected PG acetals were obtained (Table III). Several observations were made from the data in Table III: (*i*) the relative contribution of each PG enantiomer to the *syn* and *anti* geometrical isomers remained constant, as expected, because there was no difference in reactivity of the *R* and *S* enantiomers of PG toward the aldehydic carbonyl group. For example, in the benzaldehyde case, the *R* and *S* distributions of *syn* and *anti* geometrical isomers were approximately 56% and 44%. (*ii*) This *syn* and *anti* geometrical isomer distribution was consistent with reported distributions (2). (*iii*) The aromatic PG aldehydes, in general, had similar *anti*/*syn* geometrical isomer distributions, an approximate 55:45 ratio. For example, in the majority of cases, the largest *R* enantiomer accounted for approximately 57% of the distribution, and the smaller *R* isomer accounted for approximately 43% of the distribution. (*iv*) Obviously, *p*-bromobenzaldehyde and *m*-anisaldehyde PG acetals were dissimilar from the others, *vide infra* (described later). (*v*) A slight shift toward equal distribution of all isomers was found for cinnamaldehyde PG acetal. (*vi*) The *syn* and *anti* geometrical isomer distributions for the aliphatic PG acetals were similar at approximately 27% and 83%, respectively, and were substantially different from the *syn* and *anti* geometrical isomer distributions for the aromatic PG acetals. (*vii*) This *syn* and *anti* geometrical isomer distribution was inconsistent with reported distributions (2), and, thus, represented a new finding. (*viii*) The *syn* and *anti* geometrical isomer distributions for *trans*-2-methyl-2-butenal, approximately 40% and 60%, respectively, were dissimilar to the *syn* and *anti* geometrical isomer distributions for the other aliphatic PG acetals, *vide infra*.

Absolute *syn* and *anti* assignments to a specific component is not possible with GC–MSD data, however, stereochemical considerations would probably favor the *anti* geometrical isomer, *vide supra*. However, one plausible reason for the observed shift in *syn* and *anti* geometrical isomer distributions for the aliphatic aldehydes could rest with possible steric interferences because of the presence of the relatively long aliphatic chain or significant chain branching adjacent to the carbonyl carbon. Molecular models of the aliphatic acetals strongly suggest, in the *syn* geometrical configuration, significant possibility for spatial overlap between the methyl group of the propylene glycol moiety with the aliphatic chain of the precursor aldehyde. Such steric constraints would most likely shift the *syn* and *anti* distributions toward the *anti* geometrical configuration. Such a distribution was a common factor shared by the aliphatic PG acetals. Furthermore, molecular models indicate no possibility for special overlap for the aromatic aldehydes. Thus, if there was some type of stereochemical influence

on the distribution of *syn* and *anti* isomers, then the PG acetals from 2-ethylbutyraldehyde should display this phenomenon. The presence of the ethyl group in the two position of butyraldehyde would seem, from molecular models, to offer some potential for significant steric crowding in the vicinity of the acetal oxygens. However, the distribution of the *syn* and *anti* isomers for 2-ethylbutyraldehyde, approximately 17% and 83%, respectively, was very similar to the distribution found for linear aldehydes and, thus, does not provide support any meaningful stereochemical influence.

Table III. Retention Times and Percent Distributions for Optical Isomers of Selected PG Acetals, β-DEXsm or β-DEXsa

	R Isomers	*S* Isomers	*R* Isomer	*R* Isomer	*S* Isomer	*S* Isomer
Aldehyde	t_R (min)	Time (min)	Area (%)	Area (%)	Area (%)	Area (%)
Benzaldehyde	51.28 51.85	50.59 52.72	43.29	56.71	55.55	44.45
p-Fluorobenzaldehyde	51.23 52.80	50.61 52.22	56.49	43.51	56.14	43.86
p-Chlorobenzaldehyde	61.48 62.78	61.01 62.25	55.20	44.80	55.39	44.61
p-Bromobenzaldehyde	66.17 67.23	65.81 66.80	72.75	27.25	70.32	29.68
p-Tolualdehyde	66.15 66.60	65.34 67.11	41.12	58.88	55.05	44.95
o-Anisaldehyde	64.39 64.56	63.75 64.07	39.20	60.80	39.60	60.40
p-Anisaldehyde	58.25 59.72	57.76 60.09	53.38	46.62	54.97	45.03
m-Anisaldehyde	57.19 58.94	56.68 58.63	72.94	27.06	73.06	26.94
Salicylaldehyde	57.96 58.12	57.42 57.74	58.69	41.39	56.18	43.82
Cinnamaldehyde	90.22 91.20	89.58 92.00	52.36	47.64	52.59	47.41
Vanillin	74.04 74.49	73.83 74.30	55.74	44.26	55.56	44.44
Ethylvanillin	75.37 75.76	75.18 75.59	55.25	44.75	55.81	44.19
Propanal	15.84 17.87	15.51 16.89	82.74	17.26	82.64	17.36
Butanal	22.32 24.66	21.94 23.88	82.74	17.26	83.24	16.76
3-Methylbutanal	24.41 25.68	23.98 25.21	83.76	16.24	83.76	16.24
Pentanal	28.42 30.80	28.23 30.14	84.14	15.86	84.06	15.94
2-Ethylbutyraldehyde	25.69 26.99	25.33 26.65	82.42	17.58	82.53	17.47
trans-2-Methyl-2-butenal	33.69 35.44	32.27 34.11	59.44	40.56	59.49	40.51
Hexanal	23.31 24.14	23.25 24.87	82.79	17.21	82.96	17.04
Octanal	47.81 49.04	47.40 49.91	83.30	16.70	84.08	15.92
Decanal	72.77 73.96	72.43 74.61	83.60	16.40	83.70	16.30

Thus, having discounted to a large degree any stereochemical influence on the distribution of *syn* and *anti* isomers, the focus shifted to the examination of possible electronic effects. PG acetal product distributions (Table III) were examined for the possibilities of electronic influences. For example, two compounds, *p*-tolualdehyde and *p*-anisaldehyde, contain electronic donating groups *para* to the carboxyl group, and three compounds, *p*-fluorobenzaldehyde, *p*-chlorobenzaldehyde, and *p*-bromobenzaldehyde, contain electronic withdrawing groups *para* to the carboxyl group. Though no influence on *syn* and *anti* isomer distribution was noted in the fluoro and chloro groups, a notable shift in *syn* and *anti* isomer distribution was observed for the *p*-bromobenzaldehyde. In fact, the distribution of *syn* and *anti* isomers in *p*-bromobenzaldehyde, approximately 27% and 73%, respectively, were found to be more like the distribution found with the linear aliphatic aldehydes. In a similar fashion, *m*-anisaldehyde, containing a meta methoxy group, an electron withdrawing, possessed a similar distribution of *syn* and *anti* isomers (~27% and ~73%). In addition, the *syn* and *anti* isomer distribution of *trans*-2-methyl-2-butenal was found to be similar to that of the majority of aromatic PG acetals. For the *trans*-2-methyl-2-butenal case, the double bond is located adjacent to the carboxyl group just as it would be with the aromatic aldehydes.

An examination of any electronic impact on the *syn* and *anti* isomer distribution of the PG acetals necessitates a detailed assessment of the nature of any transition state(s) that may exist just prior to final PG acetal formation. The literature is rather clear that the transition state prior to acetal formation involves carbonium ion formation at the carboxyl carbon followed by attachment of the remaining hydroxyl carbon to complete ring closure (23). Thus, any substituent that has the potential to alter the electron distribution of the carbonium ion would most likely either stabilize or destabilize the carbonium ion and, consequently, possibly alter the subsequent *syn* and *anti* isomer distribution. Thus, relative to benzaldehyde, the electron withdrawing groups, *p*-bromo and *m*-methoxy, would destabilize the transition state, resulting in a shift in the *syn* and *anti* isomer distribution of the respective PG acetals. In the same fashion, the alkene group in *trans*-

2-methyl-2-butenal serves as an electron-releasing substituent, thereby stabilizing the transition state and resulting in a more even *syn* and *anti* isomer distribution of the PG acetal. Furthermore, from this perspective, the vast majority of the aromatic aldehydes could then be viewed as providing stabilization to the carbonium ion through electron density within the aromatic ring. Such stabilization would lead to a more even *syn* and *anti* isomer distribution of the aromatic PG acetals. This type of carbanion stabilization would not be possible with the aliphatic aldehydes, and as such, their *syn* and *anti* PG acetal isomer distributions differed from the distributions observed from the aromatic aldehydes.

Conclusion

For the first time, resolution of the four isomers possible through the reaction of racemic propylene glycol with selected aldehydes was demonstrated. The four isomers were ascribed to the presence of *syn* and *anti* geometrical isomers for each enantiomer. Thus, the (+) as well as (–) enantiomers were found to have a pair of *syn* and *anti* geometrical isomers. Though the ratio of the (+) and (–) isomers in the product remains, as expected, at an approximate 50:50 ratio, somewhat unexpectedly, the *syn*/*anti* ratio systematically varied with the nature of the substituent comprising the balance of the aldehyde. Mechanisms involving electronic influences on the transition state were advanced as possible reasons for the change in the *syn*/*anti* PG acetal ratios.

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