Stabilization of Aldehydes as Propylene Glycol Acetals

Alka Sharma,† S. Nagarajan, and K. N. Gurudutt*

Plantation Products, Spices and Flavour Technology Department,
Central Food Technological Research Institute, Mysore 570 013, India

Propylene glycol (PG) acetals (substituted 1,3-dioxalans) of a few representative aldehydes are prepared according to standardized methods in yields of 80−90%. A comparative study of the regeneration of citral from the corresponding dimethyl and PG acetals under mild acidic conditions showed that, although the former readily decomposed to an extent of 85%, the latter formed a near 1:1 equilibrium mixture with the generated aldehyde.

Keywords: *Propylene glycol acetals; 1,3-dioxalans; aldehydes; stabilization; regeneration*

INTRODUCTION

Aldehydes form an important class of aroma chemicals (Arctander, 1969; Burdock, 1995; Heath, 1986). They may be simple aliphatic (C_1−C_{12}), unsaturated, benzylic, phenolic, or terpenic type. They are highly susceptible to oxidation and readily undergo condensation with other carbonyl compounds and alcohols to give aldols and acetals, respectively. Simple aldehydes trimerize on standing at room temperature. Essential oils, which are rich in aldehydic components [e.g. lemon (Heath, 1986) and coriander leaf (Potter et al., 1990) oils] deteriorate quickly due to the action of heat, light, and air. Therefore, the stabilization of aldehydic flavorants is necessary. Derivatization of aldehydes as acetals not only renders stability to them but also gives nuance, at least in some cases, to their flavor/odor quality. In fact, simple monosaccharides generally exist as hemiacetals (reducing sugars) and acetals (nonreducing sugars).

Condensation of an aldehyde with an alcohol takes place in the presence of an acid catalyst, and removal of water formed in the process by azeotropic distillation shifts the equilibrium in the forward direction to yield an acetal (Loewenthal, 1973). Regeneration or deprotection of aldehyde occurs when this process is reversed. When the alcohol is a glycol or glycerol, 1,3-dioxalans (five-membered) and 1,3-dioxans (six-membered ring) are formed, respectively. Dioxalans are also formed when the carbonyl compounds condense with an oxiran (epoxide) in the presence of a variety of catalysts (Meskens, 1981; Yadav, 1994).

Formation of dioxalans has been observed in commercial beef flavorings, cherry flavor, grapes and wines, cranberries, bilberries, and tomato (McLeod et al., 1980). This is attributed to the interaction of propylene glycol (PG), a commonly used solvent for flavors, with the carbonyl compounds present in tne material (Heydanek et al., 1976). Thus, PG acetals are generally regarded as potential aldehydic flavorants. However, the ease of release of carbonyls from PG acetals vis-à-vis acyclic acetals (derived from monohydric alcohols) has not been systematically studied. Such a study, using citral dimethyl and PG acetals as the model compounds, is the basis ofthis paper. Incidentally, laboratory methods for the preparation of PG acetals of aldehydes were also standardized.

* Author to whom correspondence should be addressed.
† Present address: Defence Institute of Physiology and Applied Sciences, Delhi Cantt., Delhi 110 010, India.

MATERIALS AND METHODS

Acetaldehyde was freshly generated from paraldehyde (vide infra). The rest of the aldehydes and citral dimethyl acetal were from commercial sources and distilled before use. Other chemicals and solvents were of analytical grade. Gas chromatographic (GC) analyses were carried out on a 5730 Hewlett-Packard GC with HP 3380 reporting integrator. An SS column (6 ft × $^1/_8$ in. o.d.) having Carbowax 20 M (10%) on Chromosorb W was used under the following conditions: carrier gas, N_2 30 mL/min; injection port temperature, 200 °C; detector (H_2 FID) temperature, 250 °C; temperature program, 100 °C, raised at 8 °C/min to 200 °C.

^{1}H NMR spectra of acetals were recorded on a Varian EM 390 (90 MHz) instrument in CCl_4 with tetramethylsilane as the internal standard.

Preparation of Citral and Other PG Acetals (Method I). To a mixture of toluene (300 mL), PG (50 mL) and orthophosphoric acid (85%, 1.5 mL) in a 1 L round-bottomed flask was added citral (21.08 g, 0.15 mol) slowly under stirring. Then, with the flask hooked to a Dean−Stark apparatus, the mixture was set to reflux under stirring for 12 h, and water collected in the side arm was periodically drained off. When no more water collected, the heating was stopped and the mixture allowed to stand overnight. The upper toluene layer was decanted into a separatory funnel and washed with 5% aqueous $NaHCO_3$ (50 mL × 2) and then with water (50 mL × 3). The organic layer was dried over anhydrous Na_2SO_4 (10 g, 2 h) and concentrated in a flash evaporator to yield a pale yellow oil. The crude product was fractionated under reduced pressure (0.5−0.8 Torr) to afford pure citral PG acetal (29.4 g). Its purity was determined by GC. Acetals from nonanal, hexenal, and cinnamic aldehyde were prepared in a similar manner. Their yields and boiling points are given in Table 1, and their structural identities confirmed by their ^{1}H NMR spectra.

PG Acetals of Acetaldehyde (Method II). Paraldehyde (100 g) was taken in a 250 mL round-bottom flask and set up for distillation on a water bath using a Vigreux column, an ether condenser with chilled water circulation, and a receiver

S0021-8561(97)00582-7 CCC: $15.00
Published on Web 01/14/1998

Table 1. Preparation of PG Acetals of Aldehydes[a]

Sl no.	aldehyde	amount of aldehyde, g (mol)	amount of PG, g	yield g	yield %	bp, °C (0.5 mmHg)
1	acetaldehyde	22.00 (0.50)	50	43.35	85	82
2	*cis*-3-hexenal	9.80 (0.10)	40	12.48	80	98
3	nonanal	7.36 (0.05)	20	9.79	90	92
4	citral	7.60 (0.05)	16	8.20	78	82
5	cinnamic aldehyde	6.60 (0.05)	20	7.79	82	102
6	cinnamic aldehyde	6.60 (0.05)	20[b]	7.20	69	118 (mp)

[a] For acetaldehyde, method II, and for the rest, method I were employed. [b] Glycerol was used in place of PG.

flask cooled in an ice−water bath. Dilute (1:1) H_2SO_4 (2 mL) was added to the flask and the mixture gradually heated to 50 °C when pure acetaldehyde distilled at 21−22 °C (88 g).

PG (50 mL) was taken in a 250 mL glass-stoppered conical falsk and cooled to 0 °C in an ice bath. Powdered anhydrous $CaCl_2$ (3.5 g) was added to it in small portions while the flask was shaken. Acetaldehyde (28 mL) was then added slowly along the sides of the flask with gentle swirling. After the addition, the flask was stoppered and the mixture vigorously shaken for 10−15 min. The mixture was then filtered through a fluted filter paper and the solid washed with toluene (60 mL). The combined filtrates were washed with 5% aqueous $NaHSO_3$ (20 mL × 2), followed by water (20 mL × 3), and dried over anhydrous Na_2SO_4. The residue, obtained on evaporation of the solvent, was distilled under reduced pressure to afford pure acetaldehyde PG acetal (43 g).

Regeneration of Citral from the Corresponding Dimethyl and PG Acetals (CDMA and CPGA). *Method A.* HCl (1 N; 2 mL) and acetone (8 mL) were mixed in a 25 mL conical flask, and the mixture was thermostated at 25 °C. To this was added a solution of acetal (1 g) in acetone (4 mL) in one lot. An aliquot (1.5 mL) was drawn immediately into a semimicro test tube containing $NaHCO_3$ (100 mg) and shaken vigorously. The supernatant (1 μL) was injected on the GC column and the peak area at zero time recorded. Subsequently, aliquots were withdrawn every 15 min for 1 h and then every 30 min for the next 2 h and analyzed as before. Peak area percents of both acetals and citral were plotted against time (Figure 2).

Method B. To 20 mL of 10% orthophosphoric acid solution were added acetal (1 g) and Tween 50 (0.5 mL), and the mixture was gently refluxed under stirring on a sand bath. Aliquots (1.5 mL) were drawn at regular time intervals (cf. method 1) and extracted with an equal volume of CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4 and 1 μL of the solution injected into the GC.

RESULTS AND DISCUSSION

Two laboratory methods were standardized for the preparation of PG acetals—one for very volatile, low molecular weight aldehydes (method I) and another for higher homologues and aromatic aldehydes (method II). Both methods gave excellent yields (Table 1) of acetals. They had the added merit of involving GRAS status chemicals and solvents. ^{1}H NMR spectra of PG acetals showed characteristic spectral patterns due to 4-methyl-1,3-dioxalan (Willy et al., 1970), confirming their identities. A typical spectrum of nonal PG acetal with assignment of signals is given in Figure 1.

Acetals, both cyclic and acyclic, revert to carbonyl compounds upon treatment with acids. The rate of hydrolysis in the case of 1,3-dioxalans is influenced to a large extent by the substituent in position 2, in other words, by the nature of parent carbonyl compound. Exchange with acetone in the presence of a mineral acid is considered to be the best general method of cleavage (Loewenthal, 1973). A mixture of ethanol, aqueous HCl, and trifluoroacetic acid has been employed for the hydrolysis of butylidine α-chloralose (Yuceer, 1977).

Citral dimethyl and PG acetals (CDMA and CPGA) were selected as model substrates, and catalytic amounts of 1:1 aqueous HCl in acetone medium at 65 °C were employed for their decomposition. The amounts of citral released by the reaction as well as the acetal remaining were simultaneously determined by GC at regular time intervals over a period of 3 h. The results are graphically presented in Figure 2. While CDMA decomposed to an extent of 85% in 15 min, CPGA reacted only to a maximum extent of 50% in 45 min. The composition of the reaction mixture altered only marginally thereafter. Apparantly, the acyclic CDMA readily and almost completely decomposed, whereas the cyclic CPGA formed only a 1:1 equilibrium mixture with the citral generated. The latter acetal also failed to undergo complete cleavage even under drastic conditions of refluxing with 10% phosphoric acid, which indicated the remarkable stabil-

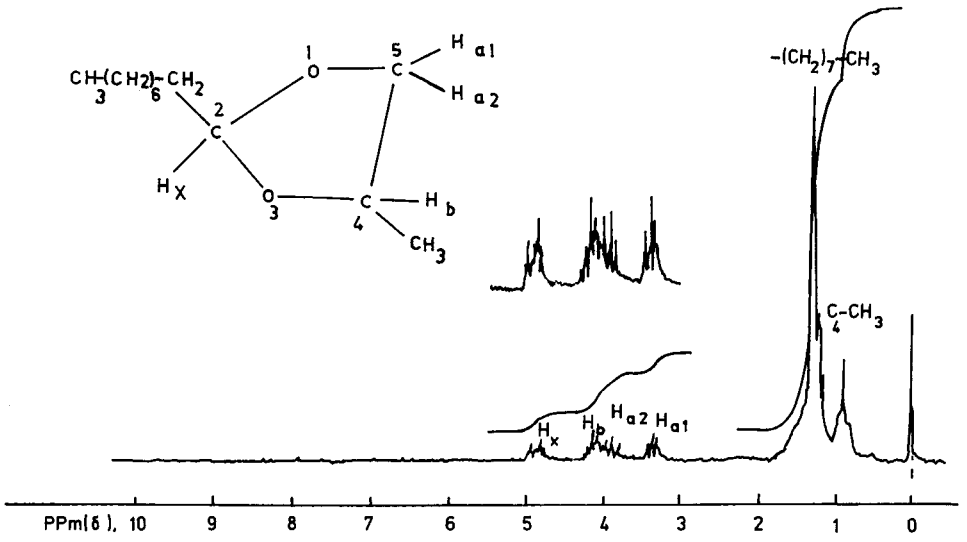

Figure 1. ^{1}H NMR spectrum of nonyl acetal.

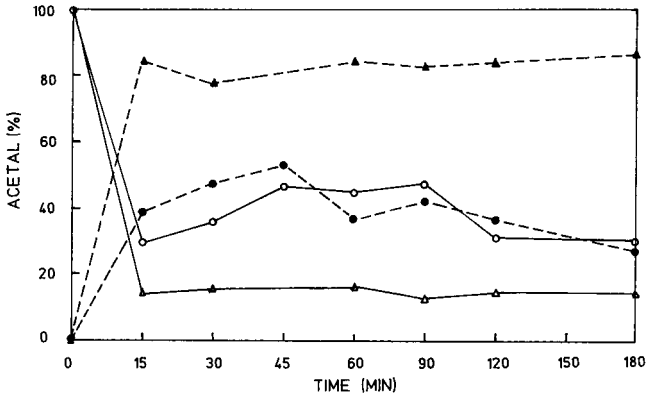

Figure 2. Generation of citral from CDMA* and CPGA: (△) CDMA; (▲) citral from CDMA; (○) CPGA; (●) citral from CPGA.

ity of the five-membered 1,3-dioxalan ring with substituents at positions 2 and 4.

CONCLUSION

Although aldehydes can be protected as their PG acetals, the latter are not quite suitable as potential aldehydic flavorants, because the aldehydes could be recovered only partially from them under normal hydrolytic conditions. Nevertheless, PG acetals of some aldehydes may find application, in their own right, as flavorants (Hartmann et al., 1984).

ACKNOWLEDGMENT

A.S. is thankful to Dr. M. L. Shankaranarayana, former head, PPSFT department of CFTRI, for encouragement and support to submit this work as a dissertation, in partial fulfilment of the M.Sc. (Food Technology) degree of the University of Mysore.

LITERATURE CITED

Arctander, S. *Perfume and Flavor Chemicals*; Montclair, NJ, 1969; Vol. I and II.

Burdock, G. A. *Fenaroli's Handbook of Flavor Ingredients*, 3rd ed.; CRC Press: Boca Raton, FL, 1995; Vol. I and II.

Hartmann, G. J.; Scheide, J. D.; Ho, C. T. Formation of volatile compounds from the reaction of leucine and D-glucose in propylene glycol. *Perfum. Flavor.* **1984**, *8*, 81−86.

Heath, E. *Source Book of Flavors*, 2nd ed.; AVI Publishing: Westport, CT, 1986.

Heydanek, G.; Min, D. B. S. Carbonyl-propylene glycol interactions in flavour systems. *J. Food Sci.* **1976**, *41*, 145−147.

Loewenthal, H. J. E. Protection of aldehydes and ketones. In *Protective Groups in Organic Chemistry*; McOmie, J. F. W., Ed.; Plenum Press; London, 1973; Chapter 9.

McLeod, G.; Ardebili, M. S.; McLeod, A. J. Substituted 4-methyl-1,3-dioxalans. *J. Agric. Food Chem.* **1980**, *28*, 441−446 and references cited therein.

Meskens, F. A. J. Methods for the preparation of acetals from alcohols or oxiranes and carbonyl compounds. *Synthesis* **1981**, 501−522.

Potter, T. L.; Fagerson, I. S. Comparison of coriander leaf volatiles. *J. Agric. Food Chem.* **1990**, *38*, 2054−2056.

Willy, W. E.; Binch, G.; Eliel, E. L. Conformational analysis XXIII. 1,3-dioxalans. *J. Am. Chem. Soc.* **1970**, *92*, 5394−5402.

Yadav, V. G. Perfumery Nitriles and Acetals, Part III. Synthesis and Characteristics of Acetals. *Pafai J.* **1994**, *16* (3), 15−23.

Yuceer, L. Formation of butylidine acetals of α-chloralose. *Carbohydr. Res.* **1977**, *56*, 87−91.

Received for review July 9, 1997. Revised manuscript received October 24, 1997. Accepted November 5, 1997.

JF970582C