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Determination of optical purity of substituted β-lactones

Sylvie Brochu[1], Rodica Plesu[1], Robert E. Prud'homme[1,*], Nicolas Spassky[2], and Alain Le Borgne[2]

[1]Centre de Recherche en Sciences et Ingénierie des Macromolécules, Department of Chemistry, Laval University, Québec, Canada G1K 7P4

[2]Université Pierre et Marie Curie, Laboratoire de Chimie Macromoléculaire, F-75952 Paris Cedex, France

ABSTRACT

An octakis (3-O-butyryl-2,6-di-O-pentyl)-γ-cyclodextrin capillary gas chromatographic column was used to determine the optical purity of seven different β-lactones, having substituents in α- or β-position, and DL-lactide. The resolving power varied from one lactone to another. The optical purity values determined by GC were in agreement with those obtained from NMR spectroscopy or optical rotation.

INTRODUCTION

Linear polyesters derived from β-propiolactones, with substituents in α- or β-positions, have been synthesized in recent years with a variety of initiators (1-11). Furthermore, optically active polymers can be prepared by using appropriate catalysts (2-6) or from the corresponding optically active β-lactone (7-11). These polymers can be compared to the family of polyalkanoates, or poly(β-alkyl-β-propiolactones), which can be synthesized from bacteria (12,13).

The presence of optical activity or chirality is important because it confers to the polymer unique properties, such as a melting temperature when the atactic polymer is amorphous (7-11), or an increased melting temperature when the atactic polymer is already semi-crystalline (14). Furthermore, chiral polymers of opposite configurations lead to the formation of stereocomplexes which exhibit an increased thermal stability (15-17).

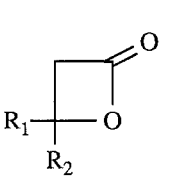
It is therefore important to be able to determine precisely the optical purity of the monomers and the polymers involved. For the monomers, this has been done by forming diastereoisomers from one of the precursors of the lactone (14), which exhibits obviously the disadvantage that racemization may occur at a later stage of the synthesis. Recently, a more direct method involves the formation of a diastereoisomeric complex with the lactone, using trifluoro-2,2,2,-(anthryl-9)-1-ethanol as suggested by Pirkle et al. (18,19), followed by NMR spectroscopy. This method has been used successfully in several instances in our previous studies (8,11,20) but it does not work in all cases (9). Similarly, an europium chiral complexing agent has been proposed (21) and has given interesting results with β-lactones, after the NMR analysis (7-9). However, again, some of the spectra are difficult to interpret, especially when the substituents are bulky (9,22).

*Corresponding author

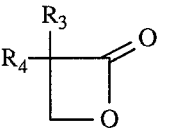
In that context, a chromatographic technique would be ideal due to its simplicity of interpretation and since, in addition, it can lead to preparative separation of racemates. König et al. (23) have tested one of our lactones, namely β-trichloromethyl-β-propiolactone, and shown that an octakis(3-O-butyryl-2,6-di-O-pentyl)-γ-cyclodextrin column can achieve this goal. It is the purpose of this study to compare the resolving ability of this column with various β-lactones bearing subtituents in α- or β- positions.

EXPERIMENTAL

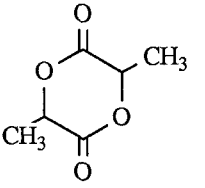
Eight different lactones were analysed: six β-propiolactones with substituents in β-position (I), one with substituents in α-position (II), and DL-lactide (III):



I



II



III

R_1 = H	and	R_2 = CH_3 :	β-CH_3-PL
R_1 = H	and	R_2 = CCl_3 :	β-CCl_3-PL
R_1 = H	and	R_2 = CH_3CCl_2 :	β-CH_3CCl_2-PL
R_1 = H	and	R_2 = $C_2H_5CCl_2$:	β-$C_2H_5CCl_2$-PL
R_1 = H	and	R_2 = $C_3H_7CCl_2$:	β-$C_3H_7CCl_2$-PL
R_1 = CH_3	and	R_2 = CCl_3 :	β-CH_3, CCl_3-PL
R_3 = CH_3	and	R_4 = C_3H_7 :	α-CH_3, C_3H_7-PL

Some were provided by Aldrich Chemical Co. and others synthesized in our laboratory (9,22).

Each compound was dissolved in chloroform at a concentration of 0.01 g/ml. 1 μL of these solutions was injected in the capillary gas chromatograph at a temperature and a helium pressure which depend upon the structure of the lactone. Half of them were run at a temperature of 130°C and a pressure of 25 psi, whereas the others were run under the following conditions: 130°C and 15 psi for β-CH_3-PL, 145°C and 20 psi for β-$C_3H_7CCl_2$-PL, and 120°C and 20 psi for β-CH_3,CCl_3-PL. For the DL-lactide, a scan at a heating rate of 20°/min, between 110 and 160°C, was required, at a constant pressure of 25 psi. A Hewlett Packard, model 5890 Series II, chromatograph was used in conjunction with a Hewlett Packard 3396A integrator and a 22 m Pyrex glass column coated with octakis(3-O-butyryl-2,6-di-O-pentyl)-γ-cyclodextrin.

Mixtures of intermediate optical purity were prepared by weighting the proper quantity of each isomer, and dissolving in chloroform.

RESULTS AND DISCUSSION

Figure 1 shows some representative examples of chromatograms obtained with various β-lactones. It is seen that two well isolated peaks are obtained, except with β-$C_3H_7CCl_2$-PL where there is an overlap between the two peaks.

The separation ability of the column can be quantified by calculating its resolving power, R, which is defined by:

$$R = 2(t_B - t_A)/(w_A + w_B) \qquad (1)$$

where t_i and w_i are the retention time and the base-width of the peak of species i, respectively (24). The analysis of the chromatograms leads to R values between 0.6 and 5.8 for the β-lactones (Table I) and a value of 14.4 for DL-lactide. These values indicate a complete separation, with R values equal or larger than 1.5 (24), in all cases but two. Table I gives a comparison of the isomer composition measured from the chromatograms with those calculated. Some compounds were

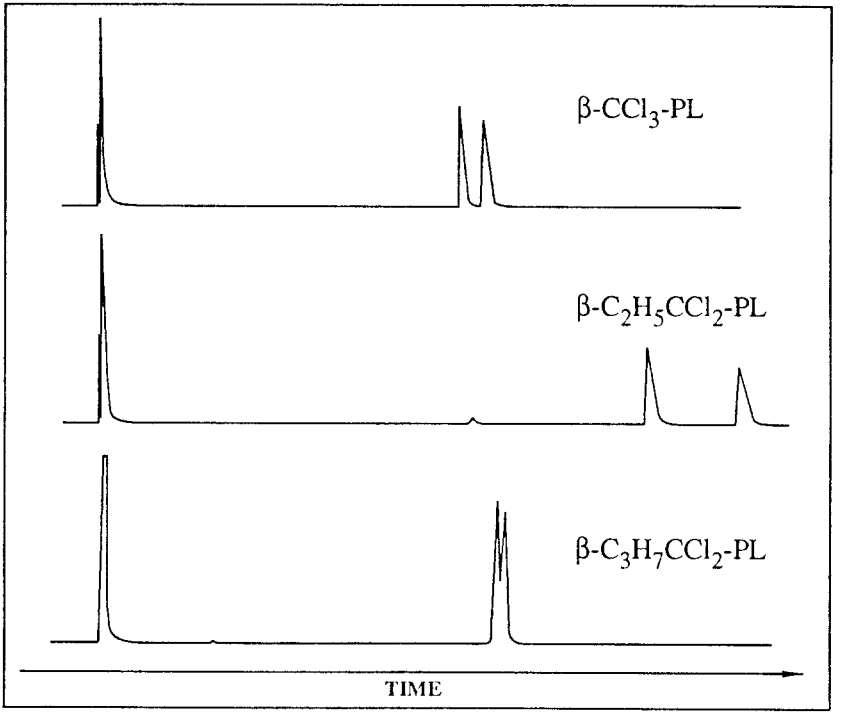


Figure 1: Gas chromatography separation of enantiomers of some β-lactones

Table 1: Isomer composition expected (see the text) and obtained from gas chromatography (% S_{gc}); the resolving power R for each lactone is also reported

Lactone	% S expected	% S_{gc}	R[#]
β-CH_3-PL	50.0[†]	50.2	1.5
β-CCl_3-PL	50.0[†]	49.9	2.3
	39.4	39.7	
	24.6	22.6	
	13.7	13.4	
	5.4	5.3	
	0.0[♦]	0.0	
β-CH_3CCl_2-PL	50.0[†]	48.9	4.6
	0.0[♦]	0.	
β-$C_2H_5CCl_2$-PL	75.1[♦] (89.1)	88.4	5.8
	51.4 (53.9)	53.9	
	37.3 (32.9)	32.3	
	15.6[♦] (2.1)	2.0	
β-$C_3H_7CCl_2$-PL	52.2	57.	0.6
β-CH_3,CCl_3-PL	100.0[♦]	100.	0.6
	50.0	59.	
	0.0[♦]	0.0	
α-CH_3,C_3H_7-PL	84.0[♦]	87.6	2.3
	50.0[†]	50.0	
Lactide	50.0[†]	50.5	14.4

[†] Racemic compound.

[♦] Determination by optical rotation using the $[\alpha_o]$ value proposed in Refs. 8,9 and 22.

[#] Conditions of separation specified in the text.

obtained in the racemic form; the optical purity of the enantiomeric compounds was determined by optical rotation; the mixtures of intermediate optical purities were prepared by mixing the proper amount of each isomer. Table I indicates that, within the experimental uncertainty, there is a good agreement in most cases with 2% between the measured and the expected results. The only significant difference concerns the two compounds with a resolving power of 0.6, and the β-$C_2H_5CCl_2$-PL series. In the latter case, the disagreement may be due to an erroneous $[\alpha_o]$ value. If $[\alpha_o]$ is taken equal to 19.4°, instead of 22.5° as given in Ref. 9, then the composition indicated in parenthesis in Table 1 is obtained, in good agreement with the chromatography results.

CONCLUSIONS

The above results indicate that the cyclodextrin column leads to an easy determination of optical purity of a variety of lactones, without the difficulties of interpretation which occur in the NMR analysis (8-10, 22). It also gives a resolution which seems, as far as the limited number of compounds available permits to tell, to be better than that which is obtained with the columns which are derived from cellulose (25). Using preparative columns, it would be possible to resolve racemic β-lactones in large quantities, therefore eliminating the tedious and delicate preparation of optically active monomers or the low yields often encountered with the catalysts presently available.

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