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Comparison of Column Chromatographic and Precipitation Methods for the Purification of a Macrocyclic Polyether Extractant

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ABSTRACT

Column chromatography on aminopropyl-derivatized silica and precipitation of a complex with perchloric acid have been evaluated as methods for the purification of di-*tert*-butylcyclohexano-18-crown-6 (DtBuCH18C6), a compound frequently employed for the selective extraction of strontium from acidic nitrate media. Both methods are shown to provide a simple and effective means of eliminating inactive sample components (i.e., impurities or stereoisomers incapable of extracting strontium) from the crown ether and enriching the material in 4(z),4′(z) *cis-syn-cis* DtBuCH18C6, a stereoisomer capable of highly efficient strontium extraction.

Key Words. Column chromatography; Precipitation; Crown ether

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INTRODUCTION

The removal and recovery of radiostrontium from nitric-acid-containing nuclear waste solutions is of considerable importance in the processing of such wastes for final disposal (1–3). Previous work in this laboratory has demonstrated that a solution of dicyclohexano-18-crown-6 (DCH18C6) or its dimethyl- or di-*t*-butyl-derivatives dissolved in any of a number of oxygenated aliphatic solvents can efficiently and selectively extract strontium from aqueous solutions containing a wide range of nitric acid concentrations (4, 5). On the basis of these results, new processes for the treatment of acidic nuclear waste streams employing a solution of di-*t*-butylcyclohexano-18-crown-6 (DtBuCH18C6) in either 1-octanol (SREX, for *str*ontium *ex*traction) or a tri-*n*-butyl phosphate/paraffinic hydrocarbon mixture (SREX-PUREX) have been proposed (6, 7). In addition, a novel extraction chromatographic material, consisting of an octanol solution of DtBuCH18C6 supported on an inert polymeric substrate, has been devised for the analytical-scale isolation of radiostrontium from a variety of biological and environmental samples for subsequent determination (8–10).

The preparation of DtBuCH18C6, like that of many other aliphatic crown ethers, involves the catalytic hydrogenation of an appropriate aromatic precursor (11–13). The efficiency of this hydrogenation step, and thus the yield of the reduced product, vary with the reaction conditions (e.g., temperature, pressure, catalyst) (13). As a result, unless purified, DtBuCH18C6 will contain unreacted starting materials and various side products, none of which is particularly effective as an extractant for strontium. Adding to the complexity of the product mixture is the fact that the catalytic hydrogenation of di-*t*-butylbenzo-18-crown-6 can produce a number of stereoisomers (13, 14) which are expected to differ significantly in complexation and extraction behavior (14–16). Because of these complications, commercial DtBuCH18C6 can vary considerably in composition and, therefore, in the efficiency with which it extracts strontium (13). [In a previous report (6) we noted that the distribution ratios for strontium extraction from nitric acid into 1-octanol by several samples of the crown ether obtained from two commercial suppliers differed by nearly a factor of seven.] Waste processing applications and the preparation of extraction chromatographic resins, however, require extractants that perform in a consistent and predictable manner. There is an obvious need, therefore, for simple methods by which DtBuCH18C6 can be rendered free of any inactive (i.e., incapable of extracting strontium) materials present and by which its most effective stereoisomers can be isolated.

A number of separation and purification methods have been previously described for crown ethers, among them chromatography on alumina (17), fractional distillation (18), and recrystallization of crown ether–acetonitrile com-

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plexes (19). These methods are not, however, universally applicable or especially convenient. More recently, attempts have been made to exploit the complexation properties of crown ethers as the basis for their separation. Okada (20, 21), for example, has examined the separation of various benzo- and dibenzo-crown ethers on protonated amino-bonded silica. Similarly, Ueno et al. (22) have described the separation of several azo-crown ethers on metal-loaded cation exchange resins ("ligand-exchange chromatography"). Combinations of reversed-phase and ligand-exchange chromatography suitable for the separation of mixtures of benzo- and dibenzo-crown ethers have also been described (23). In each of these cases, however, work was confined to analytical-scale separations. Moreover, the application of these methods to aliphatic crown compounds has not been demonstrated.

Efforts to resolve individual crown ether stereoisomers have focused primarily on dicyclohexano-18-crown-6 (DCH18C6) (24–27). Izatt et al. (24), for example, have described a method for the separation of the *cis-syn-cis* (A) and *cis-anti-cis* (B) isomers of this compound that exploits the solubility differences between the lead perchlorate and perchloric acid complexes of the two isomers. Similarly, Guyon et al. (25) have achieved separation of these two isomers via selective crystallization of the uranyl nitrate–DCH18C6-B complex. A process for the preparative-scale separation of all five DCH18C6 stereoisomers by perchloric acid precipitation has also been described (26). More recently, high performance liquid chromatography (HPLC) on octadecyl- (ODS) or aminopropyl-derivatized silica (AMPS) has been employed for the analytical-scale separation of DCH18C6 stereoisomers (27).

To date, no determination of the suitability of any of these approaches to the purification of DtBuCH18C6 or to the isolation of individual DtBuCH18C6 stereoisomers has been performed. In this report, column chromatography of the crown ether on aminopropyl silica and selective precipitation of the crown ether by addition of perchloric acid are evaluated as methods for DtBuCH18C6 purification. Both methods are shown to provide a simple and effective means of eliminating inactive sample components. In addition, a combination of precipitation and recrystallization is shown to provide a means of isolating the 4(z),4′(z) *cis-syn-cis* stereoisomer of DtBuCH18C6, the isomer expected (14) to yield the most efficient strontium ion extraction from acidic nitrate media.

EXPERIMENTAL

Reagents

Ultrex nitric and perchloric acids (Mallinckrodt Baker, Inc., Phillipsburg, NJ) and deionized water were used to prepare all acid solutions. Strontium-85

was obtained from Isotope Products Laboratories (Burbank, CA) as a solution in 0.1 M HCl. Prior to use, aliquots of this solution were evaporated to dryness and redissolved in concentrated nitric acid. This evaporation/dissolution procedure was repeated several times and the final residue dissolved in 0.1 M nitric acid. Column chromatographic purification of DtBuCH18C6 was performed using 40 μm Bakerbond Amino flash chromatography packing (aminopropyl-bonded silica gel). For thin-layer chromatography, precoated glass high-performance thin-layer chromatographic (HPTLC) NH_2 plates (EM Separations, Gibbstown, NJ) were employed. DtBuCH18C6 was obtained from EiChroM Industries, Inc. (Darien, IL), Parish Chemical Co. (Orem, UT), and Fluka Chemical Corp. (Milwaukee, WI). Prior to use, all DtBuCH18C6 samples were dissolved in methylene chloride (2 g/40 mL) and washed three times with deionized water ($V = 120$ mL) to remove metal salts (particularly NaCl). The methylene chloride was removed by rotary evaporation to leave the metal-free crown ether. Acetonitrile and methanol (Aldrich Chemical Co., Milwaukee, WI) were HPLC grade. All other reagents (e.g., 1-octanol, *n*-hexane) were ACS reagent grade and used without further treatment.

Procedures

Thin-Layer Chromatography

Solutions of DtBuCH18C6 in acetonitrile were applied to the HPTLC plates (1 cm × 5 cm) using disposable glass microcapillaries. Following air drying, the plates were developed with the solvent(s) of interest by standard techniques and the sample components visualized using iodine vapors or Dragendorff's reagent (28).

Column Chromatography

A 25-g portion of aminopropyl-bonded silica was slurried in methanol and transferred under nitrogen pressure to a 2.4 cm i.d. × 25 cm glass Bio-Rad column equipped with FP plastic compression fittings (Fischer Porter Co., Warminster, PA). When the transfer was complete, glass wool was placed atop the bed to prevent its disruption during sample introduction. The column was washed with 125 mL of absolute methanol (ca. 4 bed volumes) and preconditioned with an equal volume of 10% (v/v) methanol–acetonitrile. A solution of the crown ether in 10% (v/v) methanol–acetonitrile (1 g of DtBuCH18C6 in 10 mL of solvent) was then introduced (2 × 5 mL), and the column rinsed with the same solvent. In initial studies to establish conditions for DtBuCH18C6 purification, the column effluent was collected as a series of small (typically 1–2 mL) aliquots. Each of these was evaporated to dryness, and the residue taken up in 1-octanol. The distribution ratio of ^{85}Sr between

each solution and 1 M nitric acid was then determined (as described below). In this way the volume corresponding to complete elution of the inactive (i.e., incapable of extracting strontium) portion of the sample could be established. In subsequent runs this rinse was followed by a column strip with absolute methanol to remove sorbed DtBuCH18C6 more efficiently. Initially, the strip solution was also collected as a series of small aliquots and treated in the same way as the load/rinse fraction to establish the elution behavior of the active (i.e., capable of extracting strontium) portion of the sample. On the basis of these results it was determined that a column load/rinse consisting of ca. 40 mL of 10% (v/v) methanol–acetonitrile followed by a column strip with ca. 100 mL of absolute methanol provides satisfactory removal of inactive materials and adequate (≥85%) sample recovery. This load/rinse/strip sequence was therefore adopted for all subsequent work. Gravity flow rates (ca. 2–3 mL/min) were employed throughout. Upon completion of the chromatographic run, the solvents were removed from the load/rinse and strip fractions by rotary evaporation.

Precipitation of a DtBuCH18C6–Perchloric Acid Complex

A 0.5 M solution of DtBuCH18C6 in hexane was contacted with twice its volume of a 0.25–4 M solution of perchloric acid and vigorously agitated for several minutes. Following overnight refrigeration, during which time a white precipitate formed at the liquid–liquid interface, the hexane and perchloric acid were removed. The precipitate was dissolved in 1–2 mL of methylene chloride, then washed three times with 3 mL of deionized water. Removal of the methylene chloride by evaporation afforded the crown ether.

Distribution Ratios

All strontium distribution ratios were determined radiometrically using ^{85}Sr. Prior to a distribution experiment, the organic solution of the crown ether was preequilibrated by duplicate contacts with twice its volume of the appropriate nitric acid solution. An aliquot of this preequilibrated organic phase and an equal volume of fresh, tracer-spiked acid were then mixed for several minutes and centrifuged until phase separation was complete. Measured aliquots were removed from each phase for analysis. The ^{85}Sr activity in each phase was determined using gamma spectroscopy. Standard radiometric assay and counting procedures were employed throughout. Distribution ratios were typically reproducible to within ±5%. All measurements were performed at 23 ± 2°C.

HPLC-MS Studies

All sample solutions were passed through a 0.45-μm filter to remove particulates prior to injection.

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Apparatus

An HP-1090 liquid chromatograph (Hewlett-Packard, Palo Alto, CA) equipped with a 4.6 mm (i.d.) × 25 cm Dynamax (Rainin Instrument Co., Woburn, MA) aminopropyl silica column (particle size: 8 μm) was used in conjunction with the frit-FAB interface of a Model JMS-HX110A forward-geometry, double-focusing mass spectrometer (JEOL Ltd, Akishima, Japan) equipped with a FAB gun that produces a 6-kV xenon atom bombardment for all HPLC/MS studies. A 0–90% (v/v) methanol–acetonitrile gradient (90 min) was employed for all chromatographic runs. Between runs the column was held at 90% methanol for 10 minutes, then ramped back to 0% methanol. To establish the holdup time for the system (t_0) and permit calculation of adjusted retention times, all samples (as solutions in acetonitrile) were spiked with isopropyl alcohol prior to injection (5 μL).

The mass spectrometer was operated at an accelerating voltage of 8 kV and the slits set for a resolution of 3000 (10% valley). During each chromatographic run the magnetic field was scanned over a 0–1500 amu mass range at a rate of 5 s/scan. To facilitate detection of the DtBuCH18C6 isomers in the mass spectrometer and to provide the proper level of matrix for the frit-FAB interface probe, a methanol solution of 4% glycerol containing 1 mM potassium acetate was added postcolumn using a zero-dead-volume tee (Valco Instruments Co., Houston, TX). The postcolumn solution was delivered to the tee from a Waters 600-MS liquid chromatograph (Waters, Inc., Milford, MA) set to a flow rate of 0.75 mL/min. A 4.6 mm (i.d.) × 15 cm C-18 column was placed between the Waters solvent pump and the tee in order to maintain sufficient backpressure to ensure a steady flow of the glycerol/potassium acetate solution (0.75 mL/min) and its proper mixing with the aminopropyl column effluent. The combined effluent (1.5 mL/min flow rate) was then introduced into the pneumatic splitter (adjusted to deliver a 5-μL/min flow of liquid to the tip of the frit FAB probe) of the JMS-HX110A mass spectrometer.

Gamma spectroscopy was performed using a Cobra-II Auto-Gamma counter (Packard Instruments, Inc., Downers Grove, IL).

RESULTS AND DISCUSSION

In an examination of the HPLC separation of DCH18C6 stereoisomers on several modified silica gels, Laskorin et al. (27) concluded that the properties of the stationary phase are less important in determining the elution behavior of the stereoisomers than are the structure of the isomers and the composition of the mobile phase. As might be expected from these observations, our preliminary investigations of the thin-layer chromatographic behavior of DtBuCH18C6 indicated that although better results (as

indicated by both the total number of spots and by the difference between the largest and smalles value of R_f) were obtained with phenyl-, cyano-, or aminopropyl-derivatized silica than with silica or alumina, more significant effects on the chromatograms were observed upon changes in solvent. Examination of the elution behavior of several different samples of DtBuCH18C6 indicated that optimum results are typically obtained with a mobile phase consisting of acetonitrile containing a small quantity ($\leq$10% v/v) of water or methanol.

Laskorin et al. (27) also noted that in the HPLC separation of DCH18C6 stereoisomers on Zorbax-NH_2, the isomers with the largest number of *cis*-substituents are most strongly retained. Accordingly, the order of elution for the five DCH18C6 isomers is *trans-anti-trans* $<$ *trans-syn-trans* $<$ *cis-anti-trans* $<$ *cis-anti-cis* $<$ *cis-syn-cis* (27). This sequence corresponds to the order of the formation constants observed for the interaction of four of these stereoisomers with Na^+, K^+, and Cs^+ (15), indicating that on amino-derivatized silica the isomers will elute in the order of their effectiveness as metal ion extractants. For the purposes of preparative-scale column chromatographic purification/isomeric enrichment of DCH18C6 (and other crown ethers to which this may apply), this is particularly convenient, as it indicates that the less effective crown ether stereoisomers should elute quickly from the column along with unretained impurities, while the isomer(s) capable of efficient metal ion extraction remain sorbed on the column. We therefore chose to focus our efforts on aminopropyl silica as a possible stationary phase for DtBuCH18C6 purification.

Figure 1 depicts the chromatographic behavior of a sample of DtBuCH18C6 on an aminopropyl silica column, employing 10% (v/v) methanol in acetonitrile as the eluent. For this experiment the elution of the sample components was followed by collecting a series of aliquots of column effluent, evaporating off the solvent, dissolving each of the residues remaining in 1-octanol (600 μL), and determining the distribution ratio of Sr-85 between each octanol solution and 1 M nitric acid. The resultant distribution ratios were then normalized by dividing each by the residue mass per milliliter of 1-octanol, thus eliminating differences in D_{Sr} values arising solely from differences in residue mass. The result is a chromatogram (filled circles) that represents the strontium extraction efficiency of the column effluent as a function of elution volume. Also shown in this figure (open circles) is the cumulative mass of material collected during the run. It is apparent from these results that a significant fraction of the original sample (i.e., all of the material recovered in the first ~45 mL of column effluent, or nearly 25% of the total material applied to the column) exhibits no measurable ability to extract strontium ion from nitric acid. In addition, most of the sample (ca. 70%) fails to meet the minimum requirement for strontium

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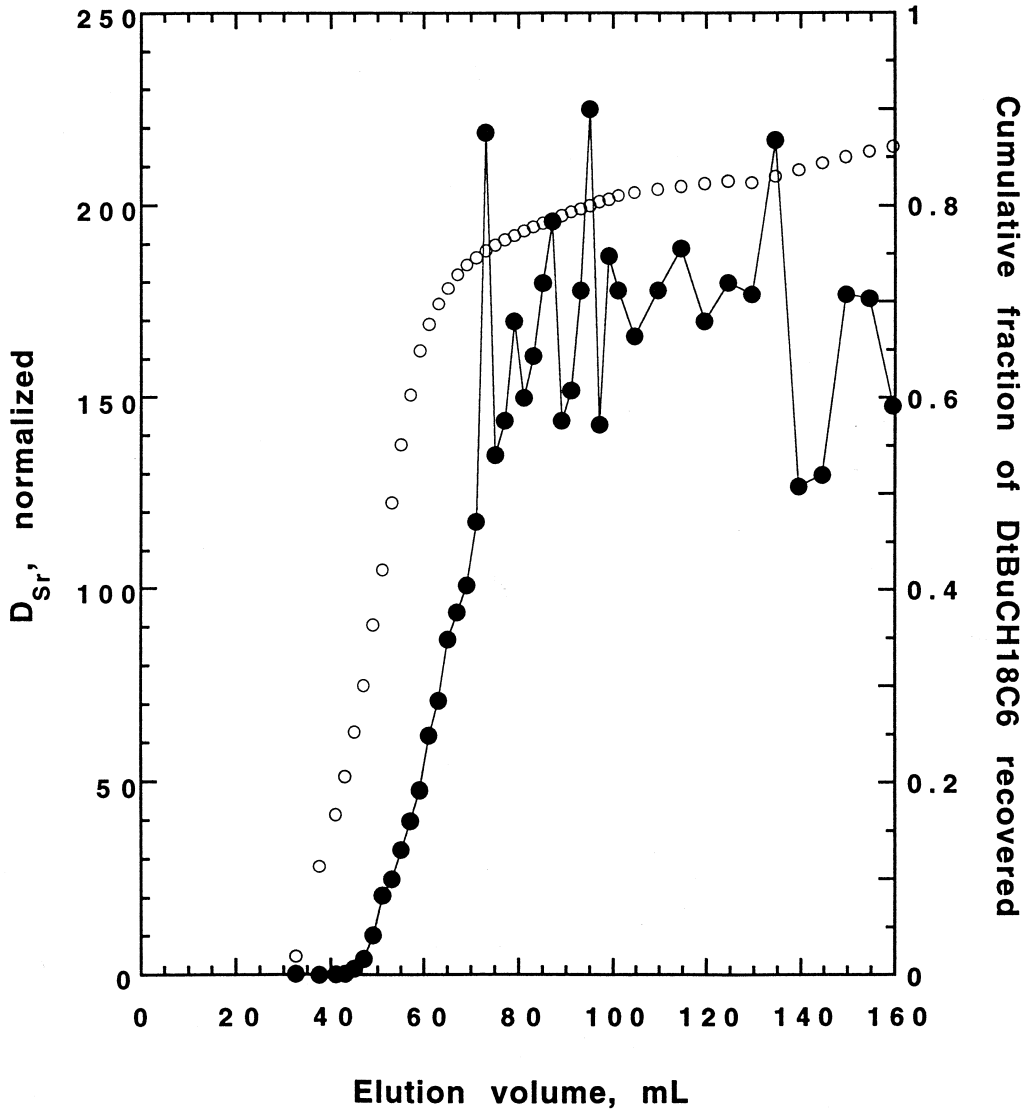

FIG. 1 Elution behavior of DtBuCH18C6 (Parish Chemical Co., Lot 3IIJ) on aminopropyl-bonded silica [mobile phase = 10% (v/v) methanol in acetonitrile].

extraction efficiency for the SREX reagent ($D_{Sr,\ normalized}$ = 62 mL/g). The overall sample meets this requirement only because a small portion of it exhibits a high D_{Sr} value. Given that the highest values of D_{Sr} are not observed at the highest elution volumes, it also appears from the results that the DtBuCH18C6 isomers may not elute in order of increasing strontium extraction efficiency. Nonetheless, column chromatography on aminopropyl silica does appear to provide a means of resolving DtBuCH18C6 into active and inactive fractions.

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Table 1 summarizes the effect of this column chromatographic treatment on the extraction behavior of several commercial DtBuCH18C6 samples. In these trials the crown ether was loaded onto the column in 10% (v/v) methanol–acetonitrile. The column was then rinsed with methanol–acetonitrile (2 bed volumes or ca. 45 mL) and, finally, stripped with absolute methanol until elution was complete. Evaporation of this methanol strip fraction left the purified crown ether. [Note that although material balance calculations typically indicate essentially quantitative recovery of the sample, a not insignificant portion (5–15%) of certain samples remains sorbed on the aminopropyl silica, despite extensive column washing. The identity of this material has not yet been ascertained.] The distribution ratio of strontium was then determined between a 1-octanol solution of the purified DtBuCH18C6 and 1 M nitric acid, and compared with that observed for the same crown ether prior to column treatment. As shown in Table 1, prior to treatment, none of the samples met the minimum requirement for strontium extraction efficiency for the SREX reagent, which corresponds to a $D_{Sr} \geq 3.0$ under the experimental conditions. Following column treatment, however, all but one of the samples yielded a D_{Sr} of 3 or more. In one instance, in fact, treatment more than doubled (to 6.17) the distribution ratio observed for the crown ether. A check of the residue from the load and rinse fraction for four of the samples shows that,

TABLE 1
Effect of Aminopropyl-Bonded Silica Column Treatment on the Strontium Extraction Efficiency of Di-[*tert*-butyl-cyclohexano]-18-crown-6

	Strontium distribution ratio[b]		
		Treated sample	
Sample[a]	Untreated sample	Strip fraction	Load/rinse fraction
E-1	1.50	4.10	ND[c]
F-3	1.21	2.84	0.11
P-3IIJ	2.50	3.58	0.21
P-3IIJ-2	2.50	3.36	0.57
P-4VEA	2.58	6.17	1.25

[a] E, F, and P-series samples were provided by EiChroM Industries, Fluka Chemical Corp., and Parish Chemical Co. respectively.

[b] Values shown refer to the distribution ratio of strontium-85 between a 0.1 M solution of the sample of interest (assuming a molecular weight of 484.7 g/mol) in 1-octanol and a 1 M nitric acid solution.

[c] Not determined.

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as expected, each extracts strontium poorly. Column chromatography on aminopropyl silica thus provides a means of upgrading otherwise unusable samples of DtBuCH18C6.

Column treatment appears less effective as a means of isolating individual DtBuCH18C6 stereoisomers. As can be seen from Fig. 1, although a number of peaks are present in the chromatogram, no two are fully resolved under the experimental conditions. Yakshin et al. (26) noted that individual stereoisomers of DCH18C6 can be precipitated from the complex mixtures that result from the hydrogenation of dibenzo-18-crown-6 simply by contact of a solution of the mixture in carbon tetrachloride with an appropriate perchloric acid solution. We have therefore investigated a similar approach as a means of isolating DtBuCH18C6 stereoisomers. In preliminary experiments designed to test the feasibility of this approach, it quickly became apparent that the large number of possible isomers of DtBuCH18C6, arising from differences in the connectivity of the *t*-butyl group (4,4′ vs 4,5′), the stereochemistry of the cyclohexano-group (*cis* vs *trans*), and the stereochemistry of the *t*-butyl groups (e vs z), renders the precipitation of a single stereoisomer difficult. Nonetheless, as shown in Table 2, by appropriate choice of conditions, precipitation of a DtBuCH18C6–perchloric acid complex can be used to effect a significant improvement in the strontium extraction efficiency of the crown ether. For example, if 0.25 M $HClO_4$ is used as the aqueous phase, the crown recovered yields a D_{Sr} of 6.01 (using a 0.1 M solution in 1-octanol vs 1 M nitric acid), a significant increase over the value originally observed ($D_{Sr} = 3.47$). If the acid concentration is raised to 0.5 M, the recovery of the crown ether doubles to ca. 40%, but the distribution ratio of the material falls to 4.13. Further increases

TABLE 2
Effect of Perchloric Acid Treatment on the Strontium Extraction Efficiency of Di-[*tert*-butyl-cyclohexano]-18-crown-6

[$HClO_4$ (M)	Recovery (%)	Strontium distribution ratio[a]
0.25	19.5	6.01
0.52	40.8	4.13
1.05	87.1	3.96
2.03	80.0	2.96
3.05	82.4	2.50
4.06	85.4	2.72

[a] Values shown refer to the distribution ratio of strontium-85 between a 0.1 M solution of the sample of interest (assuming a molecular weight of 484.7 g/mol) in 1-octanol and a 0.986 M nitric acid solution.

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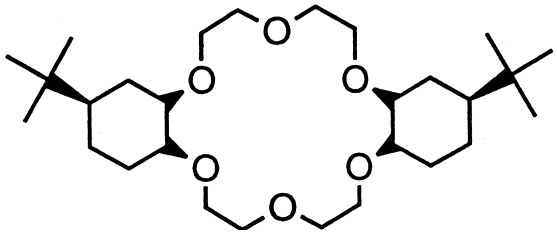

FIG. 2 Structure of the 4(z),4′(z) *cis-syn-cis* isomer of DtBuCH18C6.

in acid concentration eventually yield crown ether exhibiting unacceptably low D_{Sr} values. (At sufficiently high acidities, in fact, the crown ether obtained is actually poorer than the original material, an apparent result of the preferential precipitation of the isomers least capable of extracting strontium.) Thus, treatment of a hexane solution of DtBuCH18C6 with a dilute (~0.25 M) solution of perchloric acid provides a second means of upgrading commercial samples of DtBuCH18C6.

In an effort to determine if a particular DtBuCH18C6 stereoisomer is associated with the increase in D_{Sr} values observed upon aminopropyl silica column treatment or perchloric acid precipitation, the DtBuCH18C6-$HClO_4$ solids obtained by contact of a hexane solution of the crown ether with 0.25 M perchloric acid, which had provided a D_{Sr} of 6.01, were dissolved in methanol, and the solution volume slowly reduced by evaporation. After several days a small quantity of white needles appeared on the walls of the vessel. X-ray crystallographic analysis (29) established that the needles were 4(z),4′(z) *cis-syn-cis* DtBuCH18C6 (Fig. 2), the stereoisomer expected [on the basis of molecular mechanics calculations (14, 16)] to yield the highest distribution ratios for strontium of all DtBuCH18C6 isomers, and shown to yield a D_{Sr} of 7.5 under the experimental conditions. HPLC-MS analysis of this material (Fig. 3C) yielded a chromatogram with a single prominent peak (ca. 95% of total peak area at an m/e of 523) at a retention time ($t_{r,\ uncorrected}$) of 41 minutes. Comparison to the chromatograms of the load/rinse (Fig. 3A; $D_{Sr} = 0.40$) and strip (Fig. 3B; $D_{Sr} = 4.0$) fractions obtained in the aminopropyl silica column treatment of a sample of DtBuCH18C6 (P-3IIJ-3) indicates that an increase in the D_{Sr} value is accompanied by an increase in the relative size of this peak, and a diminution or disappearance of peaks for other sample components, indicating that the improvement in strontium extraction efficiency for DtBuCH18C6 produced by column treatment or $HClO_4$ precipitation is partly the result of the enrichment of the material in the highly efficient 4(z),4′(z) *cis-syn-cis* isomer.

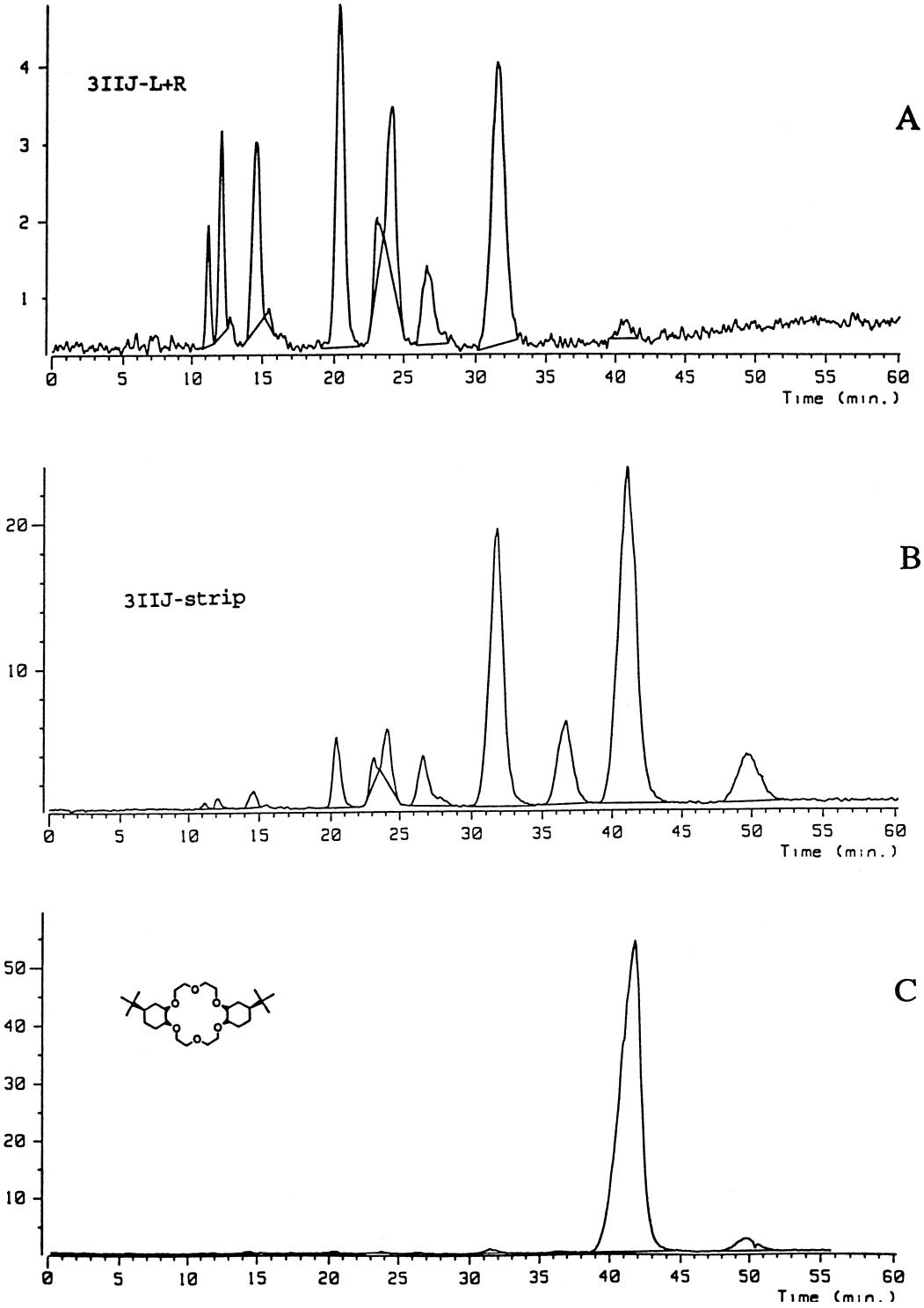

FIG. 3 HPLC-MS elution profiles for aminopropyl-bonded silica column-treated DtBuCH18C6 (panels A and B) and the 4(z),4′(z) *cis-syn-cis* isomer (panel C). (Note that these are mass chromatograms corresponding to an m/e of 523, the mass of the potassium complex of DtBuCH18C6, extracted from the total ion current.)

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CONCLUSIONS

The results of this study demonstrate that either column chromatography on aminopropyl silica or precipitation of a crown ether–perchloric acid complex provides a simple and effective method for the purification of DtBuCH18C6.

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