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Note

Gas chromatographic analysis of 1-monoacylglycerols as cyclic carbonate derivatives

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Diacetates or trimethylsilyl (TMS) ethers are commonly used derivatives for the gas-liquid chromatographic (GLC) or gas-liquid chromatographic-mass spectrometric (GLC-MS) analysis of monoacylglycerols¹. Though both exhibit excellent gas chromatographic properties they are less suitable for the mass spectrometric identification of molecular species because the mass spectra show either no molecular ion or one of poor intensity²⁻⁵.

During our investigations of the synthesis of enantiomeric diacyl-*sn*-glycerols, we used for protection of the free hydroxy moieties of monoacylglycerols the β,β,β -trichloroethylcarbonate group, which rearranged spontaneously in the presence of pyridine to the cyclic carbonate. These monoacylglycerolcarbonates also seemed to be appropriate for the analysis of molecular species.

In this investigation the 1-monoacylglycerols were separated by GLC as cyclic carbonate derivatives (Fig. 1), a class of compounds which shows a characteristic mass spectrometric fragmentation pattern. The advantage of monoacylglycerol cyclic carbonates for application in mass spectrometry has been shown earlier⁶. The mass spectra show molecular ions and acyl radical cations of great intensity, and the glycerol cyclic carbonate moiety in the molecule is well established by two prominent radical cations at $m/e = 160$ and $m/e = 173$, respectively, forming the base peak in almost all spectra.

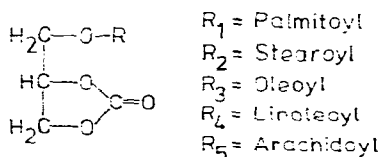


Fig. 1. Structure of *rac*-1-monoacylglycerol-2,3-carbonates.

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MATERIALS

Enantiomeric glycerol cyclic carbonates were synthesized from naturally occurring precursors such as D-mannitol or D- and L-serine. The cyclic carbonate moiety was introduced into the glycerol backbone by the cyclization of 1- β,β,β -trichloroethylcarbonate glycerol in pyridine at 80°. In an alternative procedure the reaction of 1-O-benzylglycerol with potassium hydrogencarbonate/diethyl carbonate to form 1-O-benzylglycerol-2,3-carbonate was used. The glycerol cyclic carbonates were converted into the corresponding 1-monoacylglycerol-2,3-carbonates by different acylation methods. The complete synthesis is described elsewhere⁶. All reagents and solvents were from Merck (Darmstadt, G.F.R.). The unsaturated fatty acids and fatty acid chlorides were from Sigma (St. Louis, Mo., U.S.A.) and NU CHEK PREP (Elysian, Minn., U.S.A.).

METHODS

GLC analysis was performed on a Packard Becker Model 419 gas chromatograph (Delft, The Netherlands) equipped with a flame ionization detector (FID), a recorder (Kipp & Zonen, Delft, The Netherlands), and a 6-ft. glass column (3 mm I.D.) packed with 10% Silar 5 CP on Gas-Chrom Q (80-100 mesh) (Applied Science Labs., State College, Pa., U.S.A.).

The column was preconditioned at the column oven temperature of 290° for 20 h, and at a constant flow-rate of helium (40 ml/min). Temperatures were maintained at 268° for the column, 270° for the injector, and 300° for the detector. The helium carrier gas flow-rate was 26 ml/min. The FID gas flow-rates were: hydrogen 30 ml/min and air 300 ml/min.

RESULTS AND DISCUSSION

The retention times of the 1-monoacylglycerol-2,3-carbonates are listed in Table I, relative to that of 1-palmitoylglycerol-2,3-carbonate.

TABLE I

RELATIVE RETENTION TIMES OF FIVE 1-MONOACYLGLYCEROL-2,3-CARBONATES
GLC conditions: see under Methods.

<i>Compound</i>	<i>Relative retention time</i>
1-Palmitoylglycerol-2,3-carbonate	1.00*
1-Stearoylglycerol-2,3-carbonate	1.58
1-Oleoylglycerol-2,3-carbonate	1.76
1-Linoleoylglycerol-2,3-carbonate	2.02
1-Arachidoylglycerol-2,3-carbonate	2.43

* The true retention time was 32.7 min.

Fig. 2 shows a typical chromatogram of a mixture of 1-monoacylglycerol-2,3-carbonates. All peaks are completely separated within 80 min, and no interfering peaks are found in the range of the peaks of the acylglycerolcarbonates. The 1-mono-

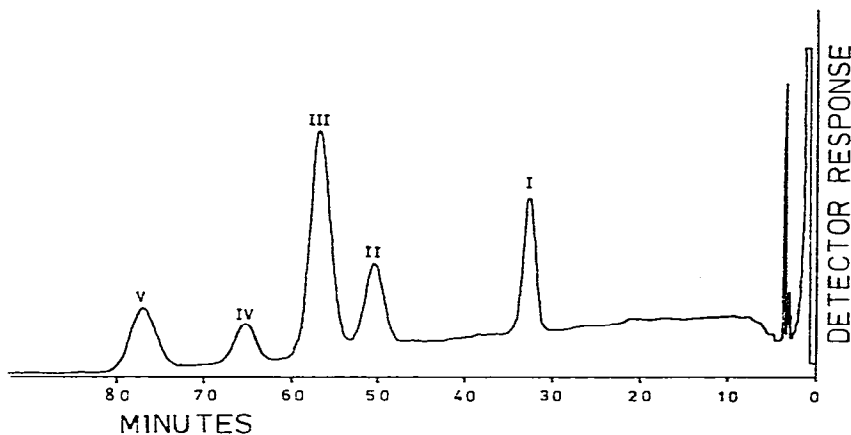


Fig. 2. Gas chromatographic separation of 1-monoacylglycerol-2,3-carbonates on 10% Silar 5 CP on Gas-Chrom Q. Column oven temperature 268°. I: 1-palmitoylglycerol-2,3-carbonate; II: 1-stearoylglycerol-2,3-carbonate; III: 1-oleoylglycerol-2,3-carbonate; IV: 1-linoleoylglycerol-2,3-carbonate; V: 1-arachidoylglycerol-2,3-carbonate.

acylglycerol-2,3-carbonates elute in the same order as found in other fatty acid derivatives, *e.g.* methyl esters⁷.

The other derivatives of monoacylglycerols for GLC or GLC-MS, diacetates and TMS ethers, exhibit shorter retention times than the monoacylglycerol cyclic carbonates, but we think that the latter are more appropriate for GLC-MS analysis because of their outstanding mass-spectrometric properties, which permit a simplified detection of molecular species of monoacylglycerols.

CONCLUSION

The GLC separation of 1-monoacylglycerol-2,3-carbonates has been attempted using 10% Silar 5 CP on Gas-Chrom Q. The peaks of the compounds were separated completely within 80 min.

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