

Note

Chromatographic methods for the determination of monomer, dimer and trimer fractions in dimer fatty acids^a

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Chromatographic techniques, namely column¹, thin-layer (TLC)^{2,3}, gel permeation (GPC)^{4–6}, high-performance gel permeation (HPGPC)⁷, gas-liquid (GLC)^{3,8–12} and high-performance liquid chromatography (HPLC)¹², and TLC and HPLC coupled with flame ionization detection (FID)^{12,13}, have been reported for the determination of dimer acids^{1,4–6,12,13} and their methyl esters^{2,3,7,8–12}. This paper describes improved GLC, HPGPC and TLC-FID methods for the determination of monomer, dimer and trimer contents in methyl esters of dimer acids.

EXPERIMENTAL

Materials

Commercial dimer acids were purchased from Emery Industries (Cincinnati, OH, U.S.A.). Dimer acids were also prepared in our laboratory's pilot plant by a process developed by us consisting in splitting castor oil in an autoclave¹⁴, heating the split products and fractionation by molecular distillation into pure monomer, dimer (2.5% monomer, 94% dimer and 3.5% trimer as determined by GLC) and trimer (residue consisting of 27% dimer and 73% trimer plus higher polymers, as determined by GLC). The fractions and the residue were converted into their corresponding methyl esters using sulphuric acid as catalyst.

Methods

The GLC analysis was carried out using a Hewlett-Packard HP 5840 A instrument with dual flame ionization detectors and a stainless-steel column (61 cm × 4 mm I.D.) packed with 5% SE-30 on Chromosorb W and programmed from 170 to 330°C at 13°C/min. For HPGPC analysis a Waters Assoc. ALC/GPC 244 liquid chromatograph unit having a refractive index detector and μ Styragel (styrene-divinylbenzene copolymer) columns (30 cm × 7.8 mm I.D.) of porosity 1000, 500, 500 and 100 Å connected in series was used. Tetrahydrofuran (freshly distilled over lithium aluminium hydride) was used as the eluent at a flow-rate of 1.5 ml/min. In the

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TLC-FID method an Iatroscan Mark II TH-10 unit was used. *n*-Hexane-cyclohexane-diethyl ether (55:15:5, v/v/v) was used to develop the Chromarods.

RESULTS AND DISCUSSION

The methods were standardized using prepared mixtures of monomers (5–57%), dimers (28–79%) and trimers (9–28%).

The attempts of previous workers^{11,12} to elute and determine monomer, dimer and trimer fractions in methyl esters of crude dimer acids by GLC using the dimer as a relative standard were unsuccessful because of the fluctuating response for the trimer fraction. This was ascribed to the retention of some of the less volatile polymers of the trimer fraction on the column¹². Conditions were therefore chosen to elute only the monomer and dimer fractions (Fig. 1A). A known amount of methyl heptadecanoate (ACME Synthetic Chemicals, Bombay, India) was added as an internal standard to prepared mixtures of monomer and dimer fractions and the mean relative response factors of the monomer and dimer fractions with respect to the internal standard were calculated and found to be 0.79 ± 0.01 (S.D.) and 0.58 ± 0.01 , respectively. Using these relative response factors, the amounts of monomer and

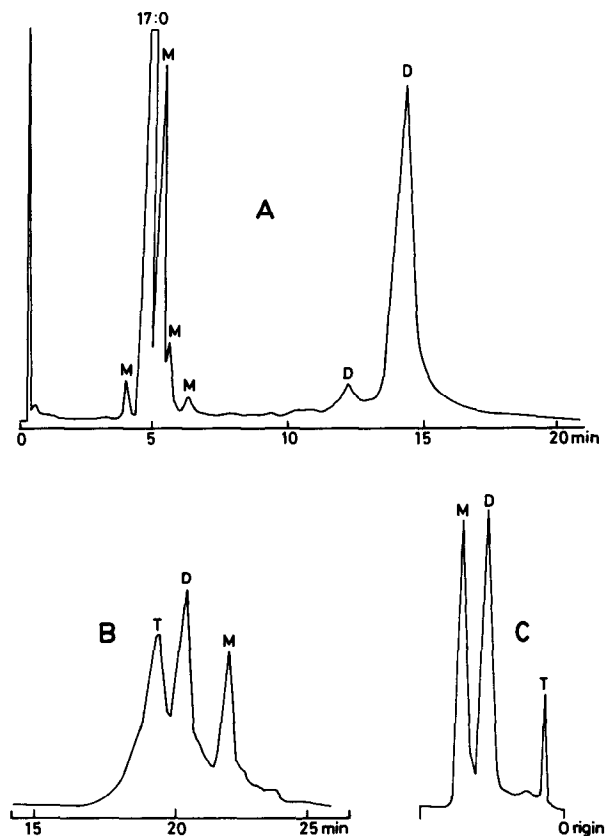


Fig. 1. Separation of dimer acid methyl esters by (A) GLC, (B) HPGPC and (C) TLC-FID. M = Monomer; D = dimer; T = trimer.

TABLE I

COMPARISON OF THE GLC, HPGPC AND TLC-FID ANALYSES OF DIMER ACID METHYL ESTERS

M = Monomer, D = dimer and T = trimer, all in % (w/w); Tr = trace.

Product ^a	GLC			HPGPC			TLC-FID			Stated values ¹⁵		
	M	D	T	M	D	T	M	D	T	M	D	T
Empol 1018	Tr	81.2	18.8	Tr	80.1	19.9	Tr	80.5	19.5	Tr	83.0	17.0
Empol 1024	Tr	74.0	26.0	Tr	76.5	23.5	Tr	73.1	26.9	Tr	75.0	25.0
Empol 1040	Tr	22.4	77.6	Tr	20.1	79.9	Tr	23.0	77.0	Tr	20.0	80.0

^a Emery Industries.

dimer fractions in prepared mixtures were calculated and the amount of trimer was found by difference. However, after analysis of 25–30 samples on the same column, baseline drift was found for the dimer peak, which affected the relative response factor of the dimer fractions.

The reported GPC methods^{4–6} are time consuming. Haken and Obita⁷ have described the determination of dimer acids in resinous polyamides by HPGPC, but detailed quantification was not discussed. The order of elution of monomers, dimers and trimers in the present HPGPC method is shown in Fig. 1B. The relative response factors of the monomer and trimer fractions with respect to the dimer were calculated¹¹ and found to be 0.58 ± 0.02 and 1.01 ± 0.03 , respectively. These factors were used in the analysis of prepared mixtures.

In the reported TLC-FID method¹², dimer acids were analysed as such. To avoid tailing in TLC, methyl esters are generally preferred to acids. Of the various solvent systems tried for the separation of methyl esters of the monomer, dimer and trimer fractions by the present TLC-FID method using Chromarod S II, a mixture of *n*-hexane, cyclohexane and diethyl ether (55:15:5, v/v/v) gave best separations for efficient quantification. A typical chromatogram is shown in Fig. 1C. The monomer, dimer and trimer fractions showed equal responses and hence no correction factor was applied.

TABLE II

COMPARISON OF THE GLC, HPGPC AND TLC-FID ANALYSES OF FIVE CASTOR OIL-DE-RIVED DIMER ACID PREPARATIONS AS THEIR METHYL ESTERS

M = Monomer, D = dimer and T = trimer, all in % (w/w).

GLC			HPGPC			TLC-FID		
M	D	T	M	D	T	M	D	T
26.8	50.5	22.7	28.7	48.2	23.1	27.3	49.8	22.9
28.5	49.1	22.4	27.0	50.9	22.1	27.9	52.9	19.2
25.4	54.9	19.7	23.9	54.1	22.0	25.1	53.8	21.1
27.5	49.0	23.5	29.8	49.2	21.0	27.1	50.5	22.4
29.5	51.8	18.7	30.4	50.5	19.1	30.0	49.6	20.4

The maximum deviation from the actual percentage of any component in the prepared mixtures by any of the three methods was found to be 1.9% (data not shown). All three methods gave monomer, dimer and trimer contents in methyl esters of various commercial dimer acid samples obtained from Emery Industries in agreement with the stated values¹⁵ (Table I), confirming the accuracy of the methods. All three methods gave almost the same compositions for the different batches of dimer acids prepared in the laboratory's pilot plant (Table II), confirming the reproducibility of the methods.

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