ELSEVIER

PII: S0032-3861(96)00791-4

Polymer Vol. 38 No. 10, pp. 2467–2473, 1997

0032-3861/97/$17.00 + 0.00

Castor oil-based polyurethanes: 1. Structural characterization of castor oil—nature of intact glycerides and distribution of hydroxyl groups

Ngoc Buu Trân
Centre de Service d'Analyse et d'Experimentation, 2 Nguyên van Thu, Q. 1, Hô Chi Minh-Ville, Vietnam

and Jean Vialle and Quang Tho Pham*
Service Central d'Analyse et URA 507, BP 22, F-69390 Vernaison, France
(Received 22 May 1996; revised 29 July 1996)

An in-depth study of the structure of castor oil by ^{1}H and ^{13}C n.m.r. has allowed the quantitative determination of conversions of alcohol groups in tridimensional polycondensation of castor oil with diisocyanates. Fatty acid methyl ester gas chromatography (FAME-g.c.) and fast bombardment mass spectrometry (FAB-m.s.) examinations of intact glycerides separated by semi-preparative reverse phase high performance liquid chromatography (RP-h.p.l.c.) show that castor oil's number average hydroxyl functionality ($\overline{F_n}$(OH)) of 2.7 (by chemical analysis) results from the contributions of 70% of triol (triricinoleate of glycerol) and 30% of diols (triacylglycerols having only 2 ricinoleyl groups). No monoalcohol (triacylglycerols having 1 ricinoleyl group) was detected. The calculated weight-average hydroxyl functionality ($\overline{F_w}$ (OH)) and hydroxyl polydispersity index (I(OH)) are 2.8 and 1.03 respectively.

(Keywords: castor oil; ^{1}H and ^{13}C n.m.r.; RP-h.p.l.c.; fractionation; VPO; FAME-g.c.; FAB-m.s.; $\overline{F_n}$(OH); $\overline{F_w}$ (OH))

INTRODUCTION

Castor oil (CO), a vegetable triglyceride possessing hydroxyl groups, extracted from *Ricinus Communis L.* beans[1,2], is frequently utilized as a polyol in the synthesis of cross-linked polyurethanes[3] and/or interpenetrating networks (IPNs)[4,5] in industry because of its excellent electrical, shock-absorbing properties and hydrolytic stability[1].

Gas chromatography (g.c.) analysis of the fatty acids' methyl ester (FAME)[1,2] obtained by methanolysis shows that the fat oil contains 87–90% of ricinoleic acid (*cis*-12-hydroxyoctadec-9-enoic acid), the only common fatty acid bearing an OH group. CO is thus one of the few almost pure natural glycerides. The other minor non-hydroxylated fatty acids include linoleic (9,12-octadecadienoic ≈ 4%), oleic (9-octadecenoic ≈ 3%), stearic (octadecanoic ≈ 1%) and linolenic (9,12,15-octadecatrienoic ≈ 0.3%) acids. By the mere fact of methanolysis, the distributions of these different fatty acids on the glyceryl skeletons remain ignored. In other words, if the CO's number average hydroxyl functionality ($\overline{F_n}$(OH)) is known to be about 2.7[6], the proportions of triricinoleate (triol), diricinoleate(s) (diol(s)) and monoricinoleate(s) (monoalcohol(s)) in CO are unknown. The knowledge of these data is of importance because only triol is responsible for crosslinking in the tridimensional polyaddition of CO with diisocyanates.

The present work deals with the in-depth study of CO by ^{1}H and ^{13}C n.m.r. Semi-preparative liquid chromatography (l.c.) combined with FAME-g.c. allows identification of the natures of the three acyls of each intact triacylglycerol fraction separated, and determination of their molecular weight by mass spectrometry (m.s.). These data are necessary for the calculation of the weight-average hydroxyl functionality ($\overline{F_w}$(OH)) and the hydroxyl polydispersity index (I(OH)), essential parameters in the study of tridimensional polycondensation of CO with diisocyanates.

EXPERIMENTAL

Reagents

Castor oil (CO, Aldrich) was vacuum dried and stored under nitrogen atmosphere. Filtered (Millipore 0.22 μm) solutions of 1% and 2% (w/v) were utilized for analytical separation and fractionation, respectively.

Because of the slight variation of chemical composition depending on its source[1], one batch only of CO has been employed for all the work done here.

Triricinoleate (R_3G) and diricinoleate (R_2G) standards (Sigma), fatty acid methyl esters (FAME) standards

* To whom correspondence should be addressed

mixtures (Alltech) were used as purchased for identification and calibration.

Transesterification

Transesterifications of CO and CO fractions were performed by using solutions of 0.2 M methanolic (*m*-trifluoromethyl phenyl) trimethylammonium hydroxide (1 ml ampoules, Alltech).

^1H and ^{13}C n.m.r. spectroscopy

^1H and ^{13}C n.m.r. spectra were recorded at room temperature using a Bruker AC 200 spectrometer (200 MHz and 50.3 MHz for ^1H and ^{13}C respectively). Typical analysis conditions were as follows.

^1H n.m.r. Concentration of CO = 5% (w/v) in $CDCl_3$; pulse angle = 13°; acquisition time = 3.9 s for 16 k-words; sweep width = 2994 Hz; repetition time = 5.9 s; number of scans = 1000.

^{13}C n.m.r. Concentration of CO = 40% (w/v) in $COCl_3$; diameter of sample tube = 5 mm; pulse angle = 40°; acquisition time 1.4 s for 32 k-words; sweep width = 11627 Hz; repetition time = 21.4 s; number of scans = 10^4. These analysis conditions allow quantitative determination without addition of any relaxation reagent which would affect spectral resolution.

Reverse-phase high performance chromatography (RP-h.p.l.c.) and gas chromatography (g.c.)

A Shimadzu LC-6A chromatograph was used with 20 μl and 100 μl loops for analytical separation and semi-preparative fractionation respectively. A Hewlett-Packard HP 1040 diode array detector (DAD) and a Shimadzu RID 6A refractive index detector (RID) were connected in series after the column for eluate detection monitoring. The output signals were collected and computed by a Shimadzu CR 4A integrator and a Hewlett-Packard HP 98562 computer for RID and DAD respectively. Analytical chromatographic conditions for CO separation were achieved on an Adsorbosphere HS 18–3 μm (4.6 × 150 mm) column (Alltech) and transferred for semi-preparative RP-h.p.l.c. experiments using a column (10 × 250 mm) packed with Spherisorb ODS 25 μm. The mobile phase was acetonitrile–ethanol 85/15 v/v (Prolabo, h.p.l.c. grade). FAME-g.c. analysis was performed on a Perkin-Elmer Sigma 300 chromatograph equipped with a Resteck RTX 30 column (0.25 mm i.d.).

Flash chromatography

Pure triricinoleate (R_3G) and diricinoleate (R_2XG) of glycerol were extracted from CO by using a silica gel 60 (400–600 mesh, E-Merck ref. 9385)-packed column (25 × 500 mm). Solutions of 20% (w/v) of CO in diethyl ether (40) + hexane (60), v/v, were used. The flow rate was 25 ml min^{-1}.

Mass spectrometry (m.s.)

All the spectra were acquired using a VG Analytical ZAB 2-SEQ reverse-geometry mass spectrometer. For molecular weight (MW) determinations of intact CO fractions separated by semi-preparative RP-h.p.l.c., samples were dissolved in *m*-nitrobenzyl alcohol (*m*NBA) matrices with NaI added. Fast atom bombardment (FAB) was carried out using Cs^+ produced at a mean energy of 30 keV.

Vapour pressure osmometry (v.p.o.)

Absolute number-average molecular weights ($\overline{M_n}$) were determined by means of an AIS vapour pressure osmometer with toluene as solvent at 38.6 ± 0.2°C. Isomolecular polypropylene glycol with $M = 2000$ was utilized as calibration standard. Precise and repeated measurements allow an accuracy of 5% for $\overline{M_n}$s < 5000.

$$\overline{M_n}(CO) = 920 \pm 46$$

Determination of hydroxyl number-average functionality ($\overline{F_n}(OH)$)

Hydroxyl groups of CO were esterified with an excess of acetic anhydride in pyridine at 100°C for 3 h. The hydroxyl equivalent (OH mol kg^{-1}) was determined by back titration after hydrolysis of the excess of anhydride by KOH in the presence of phenolphthalein. $\overline{F_n}(OH)$ may be calculated as follows:

$$\overline{F_n}(OH) = OH\,(mol\,kg^{-1}) \times \overline{M_n}\,(kg\,mol^{-1}) \quad (1)$$

With OH = 2.9 ± 0.1 mol kg^{-1} we obtain:

$$\overline{F_n}(OH)(CO) = 2.7 \pm 0.1$$

RESULTS AND DISCUSSION

In contrast with other vegetable triglycerides of fatty acids, with 87–90% ricinoleic acid, castor oil (CO) is one of the few natural fats that may be considered as a pure compound. Meanwhile, with an $\overline{F_n}(OH)$ of 2.7 (chemical analysis), CO certainly has non-hydroxylated acyl groups.

Detailed studies of the fatty acids composition of CO were carried out many years ago by g.c. analysis of methanolysed CO[1,2], but only recently has h.p.l.c. separation (without quantitative determination) of CO been performed[7]. To our knowledge, there are no known precise identification and quantitative determination of separated intact CO fractions.

^1H and ^{13}C n.m.r. spectrometry

In-depth knowledge of CO's n.m.r. spectral features is essential for quantitative determination of the conversion of CO hydroxyl groups by isocyanate functions in CO-based polyurethanes (PU) before (with soluble PUs by ^1H n.m.r.) and after (with swollen PU gels by ^{13}C n.m.r.[8,9]) the gel points (GP). There is no suitable chemical method that can be applied for the determination of non-reacted OH and/or NCO groups in polycondentates, particularly those obtained beyond the GPs.

The assignments of all the CO ^1H n.m.r. resonances reported in *Figure 1* are easily verified by ^1H, ^1H decoupling experiments. At first sight, this well-resolved ^1H spectrum appears like that of pure triricinoleate of

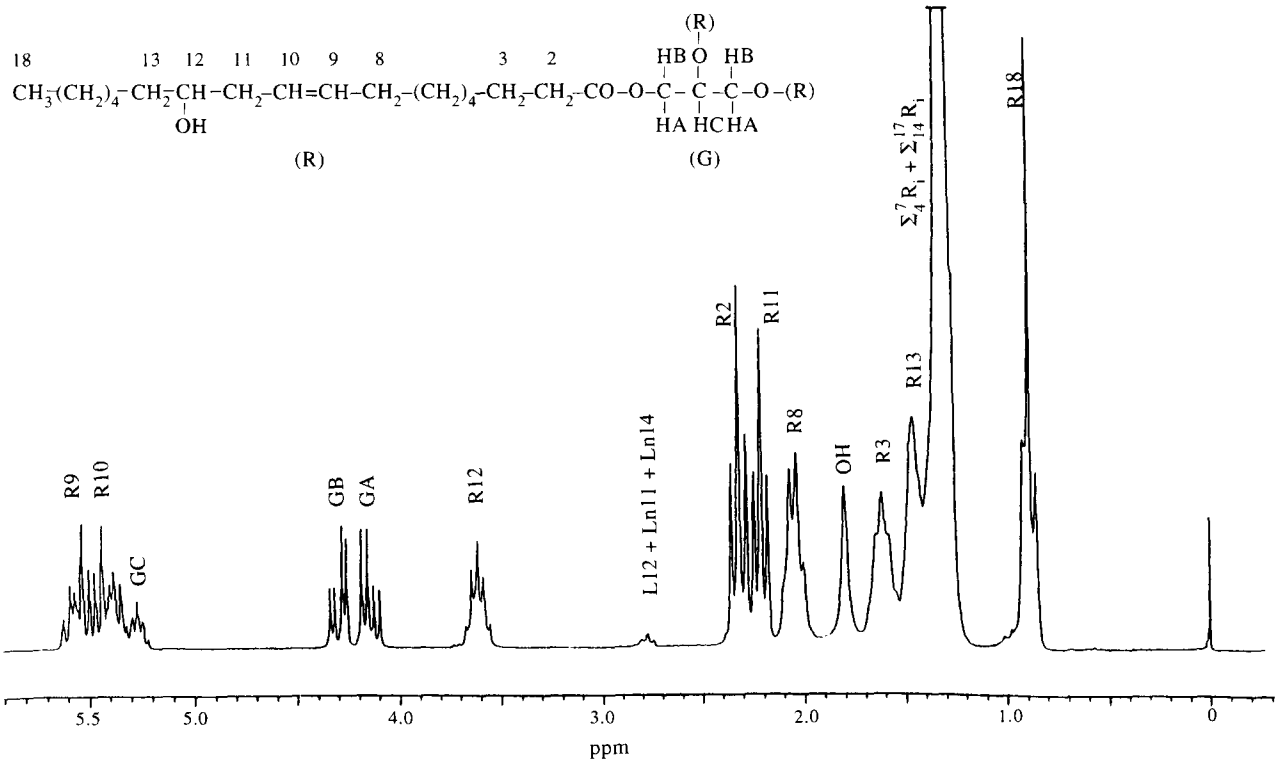


Figure 1 ^1H (200 MHz) spectrum of castor oil in $CDCl_3$ at room temperature: concentration 5% (w/v)

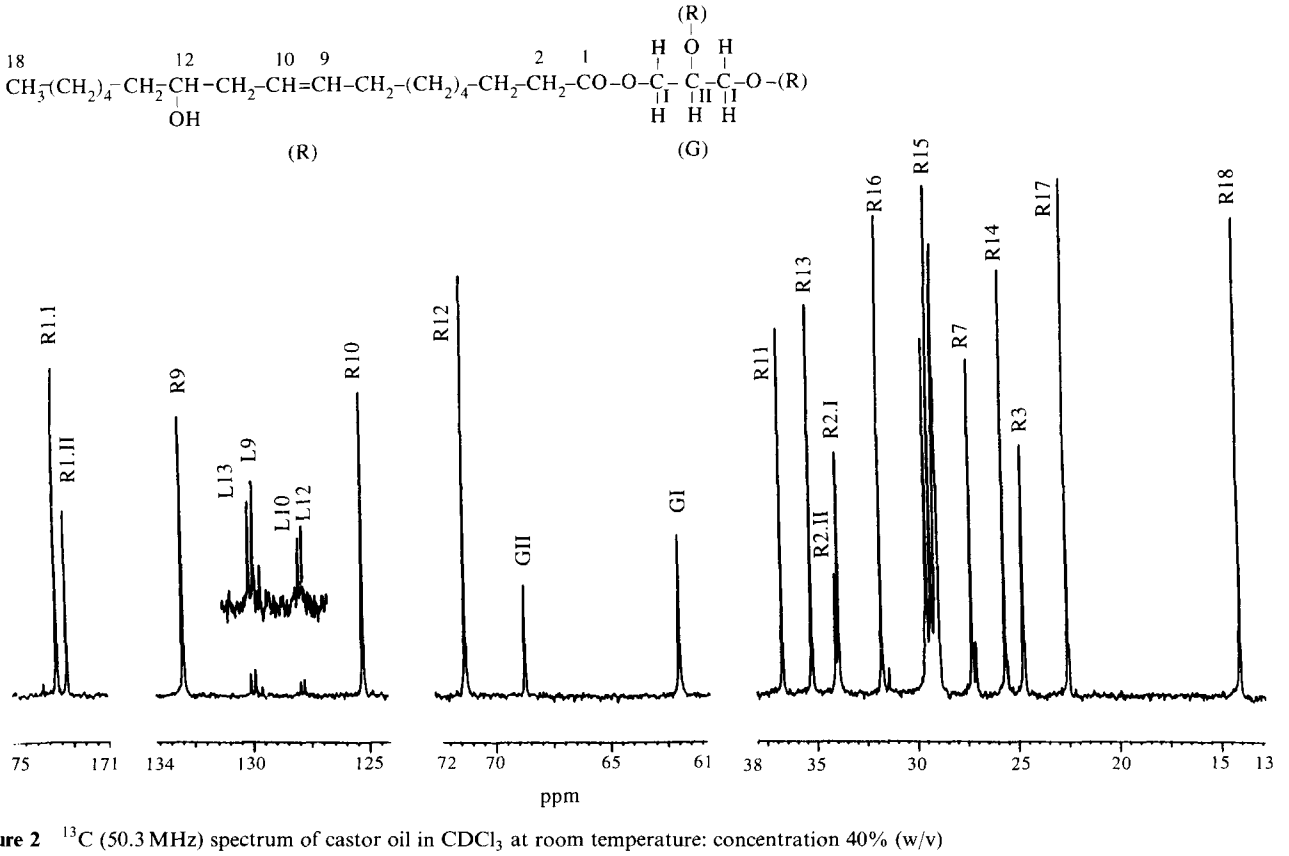
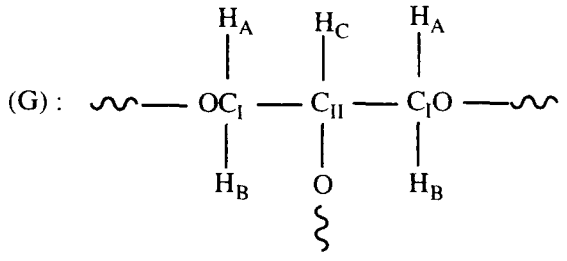


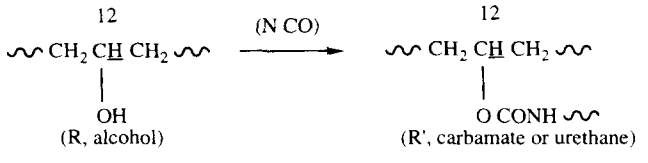
Figure 2 ^{13}C (50.3 MHz) spectrum of castor oil in $CDCl_3$ at room temperature: concentration 40% (w/v)

glycerol (R_3G). The five protons of the glycerol (G) segment resonate at 5.26 (1 GC), 4.30 (2 GB) and 4.15 (2 GA) ppm (*Figure 1*),



with $^2J(GA, GB)_{gem} = 12.8$ Hz, $^3J(GA, GC)_{cis} = 5.9$ Hz and $^3J(GB, GC)_{trans} = 4.3$ Hz.

After the condensation reaction between the secondary OH with NCO, the ricinoleyl's methine proton R12 (alcohol) at 3.6 ppm, becoming R'12 (carbamate),



will be shifted down-field in the (4.5–5) ppm region in which there are no other resonances (*Figure 1*). Thus, direct quantitative determinations of the conversions are feasible by ^1H n.m.r., at least for soluble PUs obtained before gelation.

It is instructive to calculate the molar ratio R/G by comparing the relative intensity of R12 (1 proton) to that of G's four protons (2GA + 2GB) (4.05–4.45 ppm) of the glycerol (G) segment. In the present case, we have (*Figure 1*):

$$\frac{R}{G} = \frac{(R12) \div 1}{[2(GA) + 2(GB)] \div 4} = 2.7 \qquad (2)$$

(instead of 3 for pure R_3G)

where (R12), (GA), (GB) are the relative intensities of the corresponding protons.

Because, among the CO acyl groups, only R has a hydroxyl function, the R/G molar ratio represents the average number of OHs per mole of glyceride or $\overline{F_n}(OH)_{RMN}$, in good agreement with that given by chemical analysis, $\overline{F_n}(OH)_{CA} = 2.7 \pm 0.1$. So only 90% ($10^2 \times 2.7/3$) of the acyls are ricinoleyls. Finally, the small triplet at 2.77 ppm, characteristic of methylene groups located between two double bonds, is due to both linoleyl L11 (L ≈ 4%) and linolenyl (Ln 11 + Ln 14) (Ln ≈ 0.3%) protons (*Scheme 1*). But in this case no reliable quantitative determination is possible by ^1H n.m.r.

The quantitative ^{13}C n.m.r. spectrum of CO is illustrated in *Figure 2*. The carbon peaks of R and G segments, the most intense, were identified by using (i) their relative intensities and (ii) the classical calculations of chemical shifts, taking into account the cumulative effects of double bonds, hydroxyl and carboxyl substituents[10]. Here, the presence of linoleyl and linoleyl branches is revealed by olefinic carbon resonances in the 127–131 ppm region.

For the glycerol (G) segment there is a difference between the two primary δs: δ(2R2.I) = 33.8 ppm; δ(1R2.II) = 34 ppm. Here again, by comparing the relative intensities of R12 (72.4 ppm), GI and GII, we obtain:

$$(GI)/(GII) = 2$$

and

$$(R12)/[(GI) + (GII)] \div 3 = 2.6 = \overline{F_n}(OH) \qquad (3)$$

where (GI), (GII), (R12) are the corresponding relative intensities.

Thus, within experimental errors, the value of $\overline{F_n}(OH)$ determined by quantitative ^{13}C n.m.r. is in good agreement with those given by ^1H n.m.r. and chemical analysis. Unfortunately, n.m.r. data cannot give precise information concerning the nature of the minor acyls of non-fractionated CO.

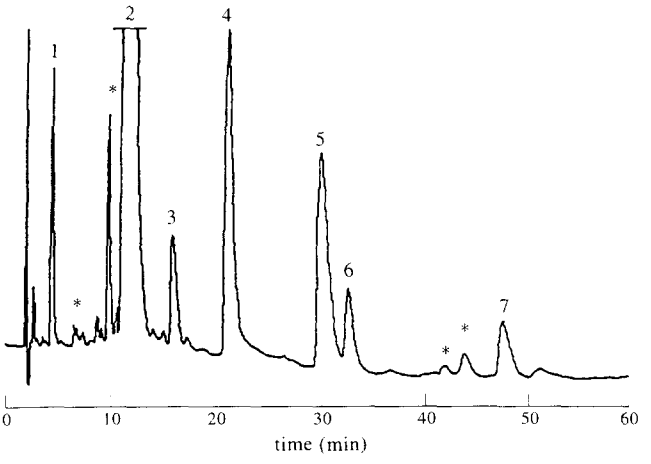
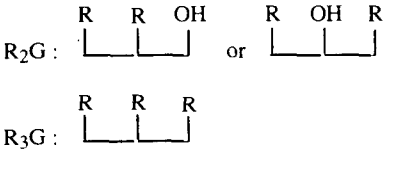


Figure 3 RP-h.p.l.c. chromatogram of castor oil. Column: Adsorbosphere C18-3 μm, 150 × 4.6 mm. Mobile phase: acetonitrile–ethanol (85/15 v/v). Flow rate: 1 ml min^{-1}. RID detection: 1,2,...: identified triglycerides (see text); *: non-identified compounds

Liquid and gas chromatographies

As for all natural fats, the complexity of the composition of CO requires several complementary analytical techniques for the structural analysis of its components. The CO global fatty acid composition obtained by FAME-g.c. with quantitative calibration using commercial standard mixtures, reported in *Table 1*, is not noticeably different from the data found in published works[1,2,11]. Because of the number of acyl species, their possible combinations in different triglycerides may be many. The object of the FAME-g.c. examination of the separated fractions is to reconstitute the intact glycerides whose natures will be checked by FAB-m.s.

The relatively good resolution of the RP-h.p.l.c. CO chromatogram (*Figure 3*) allows its fractionation into seven main fractions. Before transesterification, fractions 1 (*Figure 3*, peak 1—traces ≈ 1%) and 2 (*Figure 3*—majority peak) were identified, by using commercial standards, as diricinoleins (R_2G) and triricinolein (R_3G) respectively,



Linoleic acid (L: 9,12-octadecadienoic acid ≈ 4%, MW = 280.5):

$^{18}CH_3(CH_2)_3CH_2\ ^{13}CH =^{12} CHCH_2\ ^{10}CH =^{9} CHCH_2(CH_2)_5CH_2\ ^{1}CO\,OH$

Linolenic acid (Ln: 9,12,15-octadecatrienoic acid ≈ 0.3%, MW = 278.5):

$^{18}CH_3CH_2CH =^{15} CHCH_2CH =^{12} CHCH_2CH =^{9} CHCH_2(CH_2)_5CH_2\ ^{1}CO\,OH$

Oleic acid (0: 9-octadecenoic acid ≈ 3%, MW = 282.5):

$^{18}CH_3(CH_2)_6CH_2\ ^{10}CH =^{9} CHCH_2(CH_2)_5CH_2\ ^{1}CO\,OH$

Palmitic acid (P: hexadecanoic acid ≈ 1%, MW = 256.5):

$CH_3(CH_2)_{13}CH_2CO\,OH$

Ricinoleic acid (R: cis-12 hydroxyoctadeca 9-enoic acid = 87–90%, MW = 298.5):

$$^{18}CH_3(CH_2)_4CH_2\ ^{12}CHCH_2CH =^{9} CHCH_2(CH_2)_5CH_2\ ^{1}CO\,OH$$
$$\qquad\qquad\quad |$$
$$\qquad\qquad\quad OH$$

Stearic acid (S: octadecanoic acid ≈ 1%, MW = 284.5):

$CH_3(CH_2)_{16}COOH$

Glycerol (G: 1,2,3-propanetriol, MW = 92.1):

$HOC^{I}H_2 -^{II} CH\,OH -^{I} CH_2\,OH$

Scheme 1 Developed formulae and percentages of fatty acids in castor oil[1,2,11]. MW = molecular weight

with $F(OH)(R_2G) = F(OH)(R_3G) = 3$ (where $F(OH)$ = hydroxyl functionality).

If non-identified fractions (*Figure 3*—*), the sum of which amounts to 2% approximately (from chromatographic surface evaluation), are left out of account, in spite of visible interferences between some peaks (*Figure 3*—peak 2 and its adjoining peaks (*), peaks 5 and 6), FAME-g.c. analysis—after transesterification of the seven intact glycerides—gives the data reported in *Table 1*. In fractions 1 (R_2G) and 2 (R_3G), R is effectively found as their unique acyl. But in fractions 3–7, R represents only two of the three acyls. The general formula of these triacylglycerols is R_2XG (with X = Ln, L, O, P, S—*Scheme 1*). Finally, no triglyceride with general formula RXYG (with Y = Ln, L, O, P, S) is detected. Consequently, the $F(OH)$ of 3 is mainly due to R_3G (fraction 2), R_2G (fraction 1) being negligible and the $F(OH)$s of all the fractions 3–7 equal 2. There is no monoalcohol ($F(OH) = 1$).

Pure R_3G may be extracted from CO by flash chromatography. ^1H n.m.r. examination of R_3G shows only the disappearance of the small triplet at 2.77 ppm (*Figure 1*).

FAB-m.s.

As already observed with FAB-m.s. studies of other triglycerides[12], for all the CO fractions examined here,

Table 1 Concentrations of fatty acids in the fractions separated by semi-preparative RP-h.p.l.c. determined by fatty acid methyl ester (FAME)-g.c. (see *Scheme 1* and *Figure 3*). Non-identified fractions (*Figure 3*—peaks X) are not presented

	Fatty acid methyl ester (mol%)							
Fraction	Ricinoleyl (R)	Linolenyl (Ln)	Linoleyl (L)	Oleyl (O)	Palmityl (P)	Stearyl (S)	Glyceride proposed formula	
1	99	--	--	--	--	--	RRG	triols
2	98	--	--	--	--	--	RRRG	
3	66	34	--	--	--	--	RRLnG	
4	67	--	33	--	--	--	RRLG	
5	67	--	--	33	--	--	RROG	diols
6	66	--	--	--	34	--	RRPG	
7	67	--	--	--	--	33	RRSG	
Castor oil[a]	87%	1%	5%	4%	1%	2%		

[a] Non-fractionated castor oil. Composition determined by FAME-g.c.

Table 2 Identification of intact glycerides of the fractions separated by semi-preparative RP-h.p.l.c. by positive ion FAB-m.s.

Fraction (*Figure 3*)	MIKE *m/z* (%)[a]	Proposed identity of fragment[b]	Proposed identity of parent intact glyceride (MW)[c]
1	654 (1)	$[M + H]^+$	RRG
	618 (1)	$[(M + H) - 2H_2O]^+$	(653.1)
	600 (2)	$[(M + H) - 3H_2O]^+$	
2	956 (35)	$[M + Na]^+$	RRRG
	934 (17)	$[M + H]^+$	(933.5)
	880 (57)	$[(M + H) - 3H_2O]^+$	
	599 (100)	$[M - RO - H_2O]^+$	
3	936 (1)	$[M + Na]^+$	RRLnG
	914 (3)	$[M + H]^+$	(913.5)
	878 (10)	$[(M + H) - 2H_2O]^+$	
	600 (11)	$[M - LnO - 2H_2O]^+$	
	598 (12)	$[M - RO - H_2O]^+$	
4	938 (16)	$[M + Na]^+$	RRLG
	916 (5)	$[M + H]^+$	(915.5)
	880 (37)	$[(M + H) - 2H_2O]^+$	
	600 (100)	$[M - RO - H_2O]^+$ or $[M - LO - 2H_2O]^+$	
5	940 (17)	$[M + Na]^+$	RROG
	918 (8)	$[M + H]^+$	(917.5)
	882 (40)	$[(M + H) - 2H_2O]^+$	
	602 (100)	$[M - RO - H_2O]^-$	
	600 (71)	$[M - OO - 2H_2O]^-$	
6	892 (9)	$[M + H]^+$	RRPG
	856 (40)	$[(M + H) - 2H_2O]^+$	(891.5)
	600 (67)	$[M - PO - 2H_2O]^+$	
	576 (100)	$[M - RO - H_2O]^+$	
7	942 (19)	$[M + Na]^+$	RRSG
	920 (2)	$[M + H]^+$	(919.5)
	884 (26)	$[(M + H) - 2H_2O]^+$	
	604 (100)	$[M - RO - H_2O]^+$	
	600 (47)	$[M - SO - 2H_2O]^+$	

[a] Mass-analysed ion kinetic energy (intensity percentage)
[b] RO, LnO, LO... = ricinoleate, linolenate, linoleate... (see *Scheme 1* and text)
[c] MW = molecular weight

the protonated molecular ions $[M + H]^+$ are present only in small or negligible proportions (*Table 2*). The simultaneous losses of H_2O and one carboxylate anion (CA) (CA = ricinoleate (RO^-) or linolenate (LnO^-), linoleate (LO^-),...) give various $[M - CA - 1 \text{ or } 2\ H_2O]^+$ in abundance. Except for fraction 1, in all cases the sodium adduct ions $[M + Na]^+$ define the glycerides' molecular weights (MW).

The natures of the intact glycerides of fractions 1–7 identified here are in agreement with those found by FAME-g.c. as reported in *Table 1*.

Distribution of diols and triol(s)

It is instructive to remember that no monohydroxylated triacylglycerol (RXYG) is present and that the $\overline{F_n}(OH) = 2.7 \pm 0.05$ of CO determined by chemical analysis is due only to the contributions of diols (R_2XG) and triol (R_3G, R_2G being neglected). Thus the fractions of diols and triol may be calculated by using the classical relation defining $\overline{F_n}(OH)$:

$$\overline{F_n}(OH) = \frac{\sum n_i F_i}{\sum n_i} \qquad (4)$$

where n_i is the weight fraction of triglycerides with hydroxyl functionality F_i. $\Sigma n_i = 1$.

Here

$$\overline{F_n}(OH) = \frac{(n_2 \times 2) + (n_3 \times 3)}{n_2 + n_3} \text{ with } n_2 + n_3 = 1$$

where n_2, n_3 are the fractions of diols and triol respectively. We obtain:

$$n_2 = 0.3 \pm 0.05 \text{ and } n_3 = 0.7 \pm 0.05$$

Consequently, the hydroxyl weight-average functionality ($\overline{F_w}(OH)$) and the hydroxyl polydispersity index ($I(OH)$) are easily deduced:

$$\overline{F_w}(OH) = \frac{\sum n_i F_i^2}{\sum n_i F_i} \approx 2.8$$

$$I(OH) = \overline{F_w}(OH)/\overline{F_n}(OH) = 1.02 - 1.04$$

Despite the presence of 30% of diols, $I(OH)$ does not markedly differ from unity.

These facts are of importance in the study of the tridimensional polycondensation of CO with diisocyanates that will be the subject matter of our next paper. The

presence of diols and the absence of monoalcohol will positively affect the values of the critical conversions vs NCO/OH ratios.

REFERENCES.

1. Naughton, F. C., Duneczky, F., Swenson, C. R., Kroplinski, T. and Cooperman, M. A., in *Kirk–Othmer Encyclopedia of Chemical Technology*, Vol. 5, John Wiley and Sons, New York, 1979, p. 1.
2. Johnson, R. W. and Fritz, E., *Fatty Acids in Industry—Process, Properties, Derivatives, Applications*, Marcel Dekker, New York and Basel, 1989, p. 13.
3. Saxena, P. K., Srinivasan, S. R., Hrouz, J. and Ilavsky, M., *J. Appl. Polym. Sci.* 1992, **44**, 1343.
4. Suthar, Bh, Dave, M. and Jadav, K., *J. Appl. Polym. Sci.* 1993, **50**, 2143.
5. Homan, J. G., Yu, X. H., Connor, T. J. and Cooper, S. L., *J. Appl. Polym. Sci.* 1991, **43**, 2249.
6. Naughton, F. C., *J. Am. Chem. Soc.* 1974, **51**, 65.
7. Heron, S. and Tchapla, A., *Analusis* 1994, **22**, 114.
8. Petiaud, R., Waton, H., Coyard, H. and Pham, Q. T., *Polymer* 1992, **33**, 5056.
9. Allard-Breton, B., Audenaert, M. and Pham, Q. T., *Macromol. Chem. Phys.* 1996, **197**, 1651.
10. Presch, Clerc, Seibl and Simon, *Tables of Spectral Data for Structure Determination of Organic Compounds*, 2nd edition. Springer Verlag, Berlin, 1989..
11. Holmberg, K., *High Solid Alkyd Resins*, Marcel Dekker, New York, 1987, p. 100.
12. Evans, C., Traldi, P., Bambagiotti-Alberti, M., Giannellini, V., Coran, S. A. and Vincieri, F. F., *Biol. Mass Spectrom.* 1991, **20**, 351.