Fatty Acid Composition of Castor Oil by Gas-Liquid Chromatography

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Abstract

Acetylation of fatty acid methyl esters from castor oil makes possible accurate determination of all components in a single run by gas-liquid chromatography with butanediol succinate as the stationary phase.

Introduction

COMPOSITION OF CASTOR OIL has attracted attention mainly because of the presence of hydroxy fatty acids. Binder et al. (1) used liquid-liquid partition chromatography for the separation of hydroxy and nonhydroxy fatty acids of castor oil. While they depended on this for the quantitative estimation of the hydroxy acids, they analyzed the nonhydroxy acids for their individual components by gas-liquid chromatography (GLC) after conversion into methyl esters. Achaya et al. (2) noted that when methyl esters of castor oil were applied on polyester columns, methyl ricinoleate emerged at a carbon number of 22.5 and methyl dihydroxy-stearate did not emerge at all. On a silicone column both esters were observed to emerge but needed a correction factor for quantitative analysis as with test mixtures of methyl ricinoleate and methyl stearate the amount of the former by GLC was lower than the actual. They therefore used a silicone column with appropriate corrections for the composition of hydroxy acids and a polyester column for the composition of nonhydroxy acids. Morris et al. (3) and Tulloch et al. (5) have observed that alteration of hydroxy acids can occur during GLC. Morrissette and Link (4) analyzed mixtures containing 12-hydroxy and dihydroxy stearate on polyamide columns and showed that good separation and symmetrical peaks could be obtained by temperature programming to high levels (325C) but did not attempt quantitative analysis due to suspected side reactions. Some investigators (6–9) have reported that acetylation improves greatly the performance of hydroxyl containing materials in GLC. Acetylation has not been used so far for the quantitative analysis of castor oil esters possibly because the effect of this on the response of thermal conductivity detectors used by most of the investigators referred to above, is not known. The response of the flame-ionization detector (10,11) has been shown to be dependent on the combustible carbon atoms of the compounds and area percentage (12–15) obtained are close to actual weight percentage of the components. We have analyzed methyl esters of castor oil as such and after acetylation on a polyester column under temperature programming using a flame-ionization detector; this note reports our results.

Results and Discussion

Fig. 1 compares the chromatograms of methyl esters of groundnut oil (S.V. 194.1, I.V. 90.9); castor oil (S.V. 183.4, I.V. 85.8, OH.V. 160.2) and acetylated methyl esters of castor oil. It is seen that palmitate, etc., nonhydroxy components emerge at about the same levels as with groundnut esters. Methyl ricinoleate emerges just beyond lignocerate (C_{24}) with marked tailing (greatly exaggerated by lowered attenuation) and methyl dihydroxystearate does not emerge even at 34 min. Acetylation has reduced the retention time of ricinoleate, produced a symmetrical peak and caused the emergence of dihydroxystearate. It is thus obvious that the reduction in polarity due to the esterification of the hydroxyl groups has greatly offset the influence of increase in molecular weight due to the acetyl groups. Acetyl ricinoleate emerges just before lignocerate (C_{24}) and diacetoxyl stearate emerges at about the place for hexacosanate (C_{26}). However, acetylation has interfered with linoleate as seen by a smaller peak (relative to oleate) with the acetylated esters as compared to the nonacetylated ones. In an earlier study (17) it was noted that such nonhydroxy acids containing materials as methyl esters of groundnut oil have a hydroxyl value of about 5. In the present study acetylation was done by boiling with excess acetic anhydride as recommended by AOCS (16) methods Cd-4-40 and it is likely that

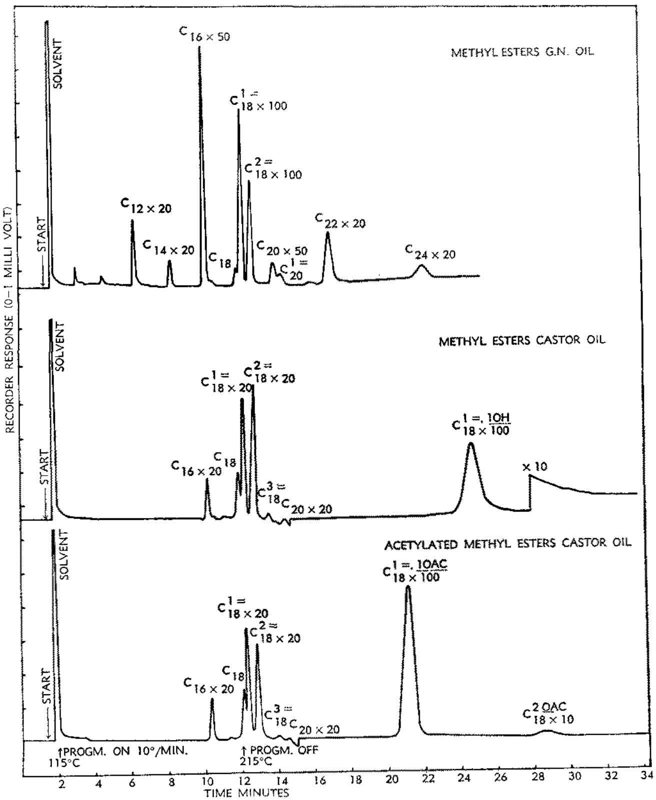

Fig. 1

FIG. 1. Gas chromatograms of methyl esters of groundnut oil, castor oil and acetylated methyl esters of castor oil. Instrument: Perkin-Elmer Model 800 gas chromatograph with flame ionization detector. Column: 2-meter stainless steel ⅛ in. O.D. packed with 8% butanediol succinate on 80–100 mesh HMDS chromosorb W. Carrier gas: nitrogen (temperature programmed from 115–215C at 10C/min. Column flow: at 115C, 62 ml/min, 215C, 41 ml/min peak indentifications and attenuations as noted on the chromatograms.

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TABLE I

Comparison of Fatty Acid Composition Data

Methyl ester, %	Present study		Previous studies[a]	
	Methyl esters	Acetylated methyl esters	Binder et al. (1)	Achaya et al. (2)
Palmitate	1.6	1.4	1.1	0.9
Stearate	1.8	1.7	1.0	1.2
Arachidate	0.5	0.3	0.5	0.2
Palmitoleate	....	....	....	0.2
Oleate	5.7	4.8	3.2	3.3
Linoleate	6.7	4.2	4.6	3.7
Linolenate	0.3	0.2	0.6	0.2
Ricinoleate	83.4	87.0	88.1	89.0
Dihydroxystearate	....	0.4	0.9	1.3

[a] Average of two Indian samples.

linoleate having a reactive methylene group participates in the reaction but this merits a separate study.

In Table I are compared the compositions as obtained in the present study with those of earlier workers. In calculating the composition of acetylated esters the area under the peak of acetyl ricinoleate was multiplied by the factor 0.8817 which is the ratio of methyl ricinoleate to acetyl methyl ricinoleate and that under diacetoxyl stearate by the corresponding factor (0.7972). After applying these corrections the area percentages for the whole chromatograms were calculated. The composition data on the straight methyl esters of castor oil is greatly in error both because of the inaccurate estimation of area due to the skewness of the methyl ricinoleate peak and also to the possibility that all of it has not been eluted. The compositions as obtained with acetylated methyl esters are in fair agreement with those of Binder et al. (1). Thus this study has revealed that acetylation enables all the component acids of castor oil to be estimated in a single run on a polyester column. However acetylation must be done under milder conditions so that it does not affect the linoleic acid. The groundnut oil esters used as reference had the following composition: caprylate, 0.2%; caprate, 0.1%; laurate, 1.4%; myristate, 1.0%; palmitate, 13.0%; palmitoleate, 0.1%; stearate, 3.5%; oleate, 46.8%; linoleate, 27.3%; arachidate, 1.8%; eicosenate, 1.0%; behenate, 2.8%; lignocerate, 1.0%.

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