# ⁂Fatty Acids: XXIII. A Rapid Method for the Preparation of $C_{18}$ Furanoid Fatty Ester Involving Dry-Column Chromatography

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## ABSTRACT

A rapid method for the synthesis of methyl 9,12-epoxyoctadeca-9,11-dienoate from methyl ricinoleate was developed. Methyl ricinoleate was oxidized to the corresponding keto ester, which was treated with mercury (II) acetate to give the required furanoid ester. Dry column silica gel chromatography was used for the purification process and was found to be reliable and efficient.

## INTRODUCTION

The numerous requests from biochemists and physiologists for small samples of synthetic $C_{18}$ furanoid fatty esters prompted us to suggest an improved and rapid method for the synthesis and purification of methyl 9,12-epoxyoctadeca-9,11-dienoate as described earlier by Lie Ken Jie and Lam (1).

Our immediate objective was to search for a time-saving procedure and this, we felt, could be achieved by a multi-step synthesis with no purification of intermediates. Another objective was to effect purification of the product by the dry-column adsorption chromatographic technique (2-4) at the last stage.

## EXPERIMENTAL PROCEDURES

### Preparation of Methyl 9,12-Epoxyoctadeca-9,11-Dienoate

Pure ricinoleic acid was obtained from castor oil according to the partition procedure described by Gunstone (5). Esterification of ricinoleic acid in the presence of boron trifluoride-methanol complex gave methyl ricinoleate.

Chromic acid (prepared from 5 g $Na_2Cr_2O_7$, 7 g $H_2SO_4$, 16 ml $H_2O$) was added by drops to a well stirred solution of methyl ricinoleate (5 g) in diethyl ether (250 ml). The two-phase mixture was stirred for an additional 4 hr. The ethereal layer was separated and the chromic acid reaction sequence was repeated twice on the isolated ether layer. The ether layer was subsequently isolated, washed with water (50 ml), sodium bicarbonate (2 M, 50 ml) and dried over anhydrous sodium sulfate. The solvent was removed by distillation.

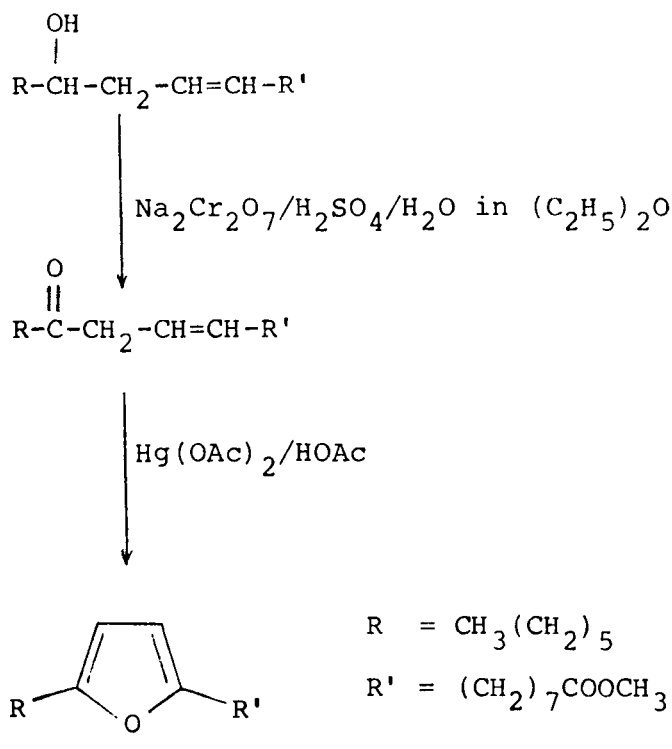
The residue was dissolved in glacial acetic acid (100 ml), mercury (II) acetate (7.6 g) was added and the mixture refluxed for 3 hr. The glacial acetic acid was removed under reduced pressure and the cooled reaction mixture was diluted with water (50 ml) and extracted with petroleum ether (3 x 70 ml). The petroleum extract was washed with water (2 x 100 ml) and dried over sodium sulfate. The solvent was evaporated on a rotary evaporator to yield the crude furanoid ester (4.7 g).

### Purification of Furanoid Ester by Dry-Column Chromatography

The crude furanoid ester (4.7 g) was thoroughly mixed with silica gel (5 g). A polyethylene sheet was rolled into a cylinder (2 cm diameter, 40 cm in length) and one end loosely tied with a string or rubber band. A wad of cotton wool was inserted into the bottom of this column and the remaining part of the plastic column tightly packed with dry silica gel particles (50 g). The packed column of silica gel was then suspended to keep the chromatographic column in a vertical position.

The crude furanoid ester adsorbed on silica gel particles was then transferred to the top of the dry chromatographic column. A wad of cotton wool was placed on top of the loaded column. A mixture of diethyl ether/petroleum ether (70 ml, 1:9, v/v) was dispensed to the top of the column at such a rate as to maintain a 2-cm solvent head above the wad of cotton wool. When the solvent front reached the lower wad of cotton wool, the supply of solvent was discontinued.

The chromatographic column was taken down from its support, laid on the bench and the portion of the column located between 9-13 cm (measured from the top end of the silica column) was sectioned off. The adsorbent was extracted with diethyl ether (4 x 50 ml). The compound isolated was wholly methyl 9,12-epoxyoctadeca-9,11-dienoate (2.7 g, 57% based on the amount of methyl ricinoleate). The spectral data of this product were identical to those recorded previously (1,6).




**SCHEME I. Synthesis of methyl 9,12-epoxyoctadeca-9,11-dienoate from methyl ricinoleate.**

## DISCUSSION

The route selected for the preparation of methyl 9,12-epoxyoctadeca-9,11-dienoate is presented in Scheme I.

Pure ricinoleic acid was readily prepared from castor oil according to Gunstone's partition procedure (5). The methyl ester derivative was oxidized according to the two-phase method recommended by Brown et al. (7). The resulting product was subsequently refluxed with mercury (II) acetate in glacial acetic acid, and the crude product was loaded on top of a *dry* silica gel column and developed with a mixture of diethyl ether/petroleum ether (1:9, v/v). This chromatographic technique was rapid, efficient and economical. A portion of the developed column of silicic acid was sectioned off and the support extracted with diethyl ether to furnish (~57%, based on methyl ricinoleate) pure $C_{18}$ furanoid ester. The entire operation required less than 8 hr of actual (manual) laboratory time. The time for refluxing of reaction mixtures and evaporation of solvents was not included in this count.

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# ⁂Heterogeneity within Commercial Contract Analysis Samples of Shea-Nut Kernels

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## ABSTRACT

Shea-nuts are a commercial oilseed crop with relatively large mean kernel weight. Results are presented to demonstrate that the individual kernels making up single contractual samples are heterogeneous in their individual analyses for oil, free fatty acids in oil and moisture contents. These results are discussed and an effective technique giving reproducible results is described.

## INTRODUCTION

Shea-nut kernels are the oil-bearing seeds of the deciduous Shea-nut or Shea butter tree, *Butyrospermum paradoxum* (Gaertn. f.) Hepper subsp. *parkii* (G. Don) Hepper. The major source of this crop is the Savannahs of West Africa (estimated annual production 0.5 million tons), where the trees occur naturally but may be protected and cultivated (1). The oil extracted from imported kernels (45-60%) is important in the U.K. as a cocoa butter substitute in chocolate manufacture. The extreme heterogeneity in the oil and free fatty acid contents of individual kernels within analysis samples representing single parcels from single sources has been noted in this laboratory (2). The long periods to first fruition (12-15 years) and maturation (30 years), as well as passive cultivation of this crop are prohibitive regarding selective breeding, but this study is relevant to the commercial analysis of this crop, because the kernel weight for the Shea-nut (up to 8 g) is relatively much greater than for most other commercially available oilseeds.

## METHODS

Samples of West African Shea-nuts were made available subsequent to contractual analyses having been completed in this laboratory. Reduction of contract samples, removal of impurities, and determination of oil, free fatty acids in oil, and moisture and volatile matter were based on ISO methods (3-7). Mineral matter was determined by ashing at 550 C (8).

Analysis samples of Shea-nuts of at least 1 kg, taken from contract samples after determination of admixture, and Shea-nut shell were each milled in specially modified mechanical mills, without expression of oil, to a meal not exceeding 4-mm particle size. Individual Shea-nut kernels, or parts of kernels, selected at random from samples, were grated using a Moulinex metal hand grater, and analyzed in accordance with the applicable methods. Milled or grated materials were subjected to analysis immediately after preparation. Oil determinations were made by continuous extraction with light petroleum (bp 40-60 C). The regime for extraction of portions of milled whole sample, done in quadruplicate, was: extracted 2 hr, hand-ground after drying, extracted 1 hr, micropulverized in prolabo mill after drying, extracted 2 hr, and solvent removed. Individual kernels or parts of kernels were extracted for 2 hr, exhaustively hand-ground, and extracted for a further 2 hr before removal of the solvent. All grinding operations were aided by the additon of portions of 40-60 mesh, neutral pH silver sand.

The preparation of methyl esters and gas liquid chromatographic (GLC) analysis for determination of fatty acid composition followed IUPAC recommendations (9), and results were calculated by hand-integration of peaks identified by comparison with known standards.

## RESULTS AND DISCUSSION

Contract samples of Shea-nut kernels have been analyzed in this laboratory since about 1930. It has been common practice for two independent laboratories to receive con-