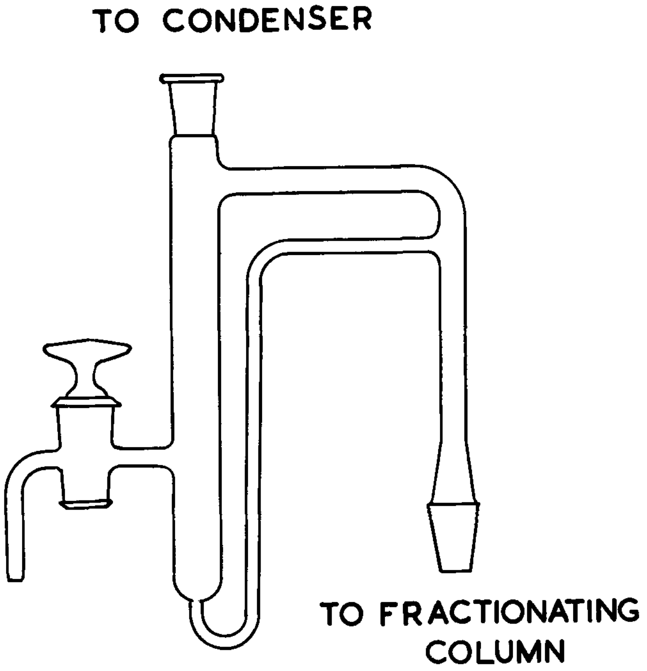
A Method for Synthesis of *a*-Monoricinolein

THE EARLIER METHODS (1,2) for the synthesis of α-monoglycerides employ fatty acids or the corresponding acid chlorides as the starting materials. Ricinoleyl chloride does not exist (3), despite contrary claims (4), and free ricinoleic acid can readily form estolides. Perhaps it is these difficulties which have rendered the synthesis of monoricinolein a difficult task. However, we have found that the interesterification technique of Gadgoli and Kane (5) is eminently suitable for the synthesis of α-monoricinolein in good yield. Our procedure is as follows:

Isopropylidene glycerol (IPG) was synthesized by Hartman's procedure (2), modified as follows:



Glycerol (200 g), acetone (300 ml), chloroform (200 ml), and *p*-toluenesulfonic acid (3 g) were placed in a 2-liter round-bottomed flask fitted with a fractionating column. A modified Dean-Stark tube (Fig. 1), provided with an outlet on its stem to enable removal of water forming the upper layer, was fitted to the top of the column. It is similar in construction to the liquid-liquid extraction apparatus (6) for extraction with solvents heavier than water. Attached to the Dean-Stark tube was a double-walled water-cooled condenser. The mixture was refluxed for 10 hr, after which time the formation of IPG was complete, as indicated by water drops ceasing to fall into the Dean-Stark tube. The catalyst was removed by shaking the mixture with an excess of lead carbonate. The precipitates were filtered off and the excess chloroform and acetone removed on a water bath under suction. The crude IPG was distilled under vacuum and the pure distillate employed for the synthesis of monoricinolein.

Methyl ricinoleate was prepared from castor oil, by alkaline methanolysis followed by fractional distillation under reduced pressure (7).

The ricinoleic acid ester of IPG was synthesized as follows:

Methyl ricinoleate (0.3 mole), IPG (0.6 mole), and sodium methoxide powder (2 g) were put in a three-necked round-bottomed flask fitted with a mercury-sealed stirrer, nitrogen inlet, distillation head, condenser, and receiver. The mixture was heated in an oil bath for 3 hr at 170C, after which time the reaction was complete. Thin-layer chromatography was employed to monitor the course of the reaction (8). The reaction mixture was cooled, mixed with 300 ml ether, and washed four times with 200-ml portions of distilled water. The solution was dried over anhydrous sodium sulfate and the ether evaporated under vacuum.

The scission of the IPG-ester was achieved by dissolving the ester in 400 ml of 2-methoxyethanol and 150 g of boric acid and refluxing over a steam bath for 3 hr. The mixture was mixed with 1.5 liters of diethyl ether, washed four times with 1-liter portions of distilled water, and dried over sodium sulfate. The volume of the solution was reduced to 400 ml under suction, 600 ml of petroleum ether (40–60C) was added, and monoricinolein crystallized from this solution at −10C. The product was recrystallized and dried. The purity was checked on boric acid–coated silica gel plates using a developing solvent system of chloroform and methanol (90:10).

A more than 97% pure α-monoricinolein was obtained in 90% yield.

Chemical and elemental analyses of the product were as follows:

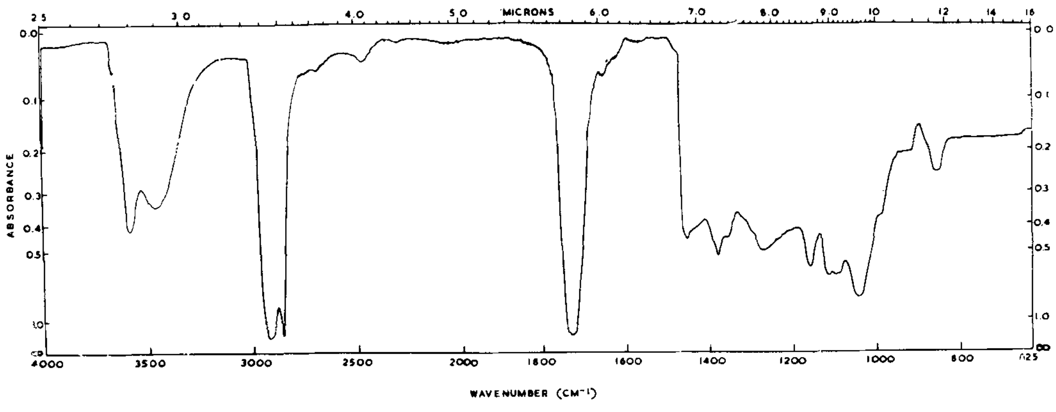


FIG. 2. Infrared spectrum of a 2% solution of α-monoricinolein in chloroform, taken on a Perkin-Elmer grating infrared spectrophotometer, Model 257, using a 1-mm sodium chloride cell.

TABLE I

Analytical Data

Characteristics	Calculated	Determined
Iodine value	68.2	69.2
Hydroxyl value	450.00	452.00
Saponification value	150.00	151.00
C	67.7%	66.7%
H	10.8%	10.7%
Monoricinolein[a]		98%
Melting point		39.1C

[a] AOCS Cd-11-57.

Figure two is an infrared spectrum of a 2% solution of the sample in chloroform, taken on a Perkin-Elmer grating infrared spectrophotometer, Model 257, using a 1-mm sodium chloride cell.

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Gas Flowmeter From a Leak Detector and Potentiometer

Carrier-gas flow from a flame ionization detector (FID) is often troublesome to measure because the burner housings must be opened or partially dismantled. A Gow-Mac Leak Detector (GM-LD), formerly Gas Hound, can be operated as a specialized flowmeter that particularly applies to this measurement problem.

A 50K ten-turn potentiometer with locking duodial when wired in the meter line of the GM-LD allows its sensitivity to be attenuated so that, on the "low" range, large amounts of helium carrier-gas may be monitored against a background of air from the FID. Usually the measurement is made with no hydrogen flowing through the burners. However if the flames are adjusted to combust the hydrogen stoichiometrically, helium measurements may be made while the burners are operating. Results are best without hydrogen since no water vapor will be introduced into the GM-LD.

A typical GM-LD/flowmeter calibration procedure is as follows:

1) Hydrogen and helium to detector temporarily shut off.

2) Airstream through burner housings adjusted to 200 cc/min with the aid of a soap-film flowmeter.

3) Helium carrier turned on and adjusted to 70 cc/min (soap-film meter).

4) GM-LD used to monitor FID effluent from any convenient opening in the burner housing while 50K potentiometer is adjusted so that 70 cc/min helium in 200 cc/min air causes full-scale meter deflection. The potentiometer adjustment is locked and recorded so that it may be returned to this value without recalibration. Measurements should be made at the same opening in the FID housing so that readings are not influenced by variations in probe location.

5) Helium flow reduced, measured with the soap-film meter, and recorded;

6) GM-LD meter deflection at this lower helium flow recorded; and

7) Repeat steps 5 and 6.

Typical calibration data are:

Actual He Flow (measured with soap-film meter) cc/min	GM-LD Meter Deflection (divisions right)
8	12
16	19
24	24
31	28
38	32
46	35
53	38
59	42
66	44
72	47

This table or a plot from its data allows a quick and fairly accurate measurement of column flow without dismantling the FID assembly. The adjustable 50K resistance, when turned to its lowest value, restores the GM-LD to its former sensitivity.

Addition of this single potentiometer is a simple modification that has made the GM-LD in this laboratory a more useful instrument.

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