Photolytic Synthesis of Methyl Sterculate Containing Mixture From Methyl Stearolate and Diazomethane[1]

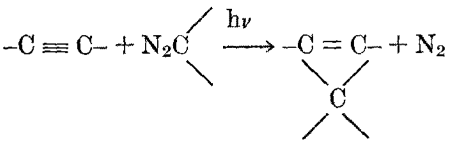
MARTIN M. SCHLOSSER, ANGELO J. LONGO, JAMES W. BERRY and ARCHIE J. DEUTSCHMAN, JR., Department of Agricultural Biochemistry, University of Arizona, Tucson, Arizona 85721

Abstract

A method for synthesis of a mixture containing methyl sterculate is described. The presence of the cyclopropene compound was verified by Halphen Test, infrared absorption and the effect on fatty acid distribution in egg yolks produced by hens consuming the synthetic product.

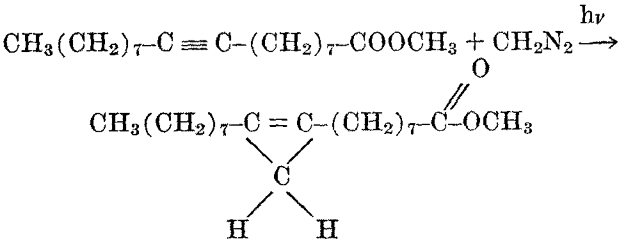
Introduction

Sterculic acid esters have important biological activity (1), which has stimulated efforts to synthesize cyclopropenoid compounds. Deutschman, et al. (2) had reported the preparation of sterculene (1,2-dioctylcyclopropene) from stearolic acid by a copper-metal initiated carbene addition reaction. Lind and Deutschman (3) prepared cyclopropenoid structures by a photolytic decomposition of diazo compounds. The carbene formed by photolytic decomposition of diazomethane adds across an acetylene group to form a cyclopropenoid ring. The general reaction sequence is shown below.



Doering and Mole (4) prepared 1,2-dimethylcyclopropene and methyl 1,2-dimethylcyclopropene-3-carboxylate from 2-butyne and diazomethane and methyl diazoacetate, respectively. Lind and Deutschman (3) by a similar procedure prepared 1,2-di-*n*-propylcyclopropene and ethyl 1,2-di-*n*-propylcyclopropene-3-carboxylate from 4-octyne and diazomethane and ethyl diazoacetate, respectively.

Cyclopropenoid fatty acid esters occur naturally in cottonseed oil and in oil extracts from other plant sources (5,6). Sterculic acid esters found in cottonseed oil feeds have been shown to cause deleterious effects on poultry (1). Our interest in synthesizing methyl sterculate was to prepare a compound containing ^{14}C in the cyclopropene ring. Methyl sterculate was prepared by reacting methyl stearolate and diazomethane in a Pyrex test tube using a high-pressure mercury discharge lamp. Diazomethane was photolytically decomposed to carbene which undergoes a *cis* 1,1-cyclo addition to the carbon-carbon triple bond to form the cyclopropenoid fatty acid ester.



The reaction products were a mixture of methyl stearolate homologues containing one more methyl group in addition to methyl sterculate. No attempt was made to identify the various side products which would have the methyl group randomly inserted around the stearolate molecule. Lind and Deutschman (3) suggest that the relative reactivity of carbene with the carbon-carbon triple bond is about eight times that of the insertion reaction for the compound they studied.

Attempts to synthesize methyl sterculate using *n*-pentane and Freon 11 (trichlorofluoromethane) as solvents resulted in low yields (0.1–0.5% respectively). The synthesis of this compound without solvent produced yields of approximately 10–12%. The concentration of the prepared methyl sterculate was determined by the colorimetric Halphen Test, which is a highly selective and sensitive test for the cyclopropenoid structure (7). Infrared analysis confirmed the presence of the cyclopropene ring. When exposure to ultraviolet radiation was continued for a prolonged period of time, destruction of the cyclopropenoid ring structure occurred, indicated by a decrease of Halphen activity. Storage of the methyl sterculate solution at −30 C resulted in little decline of Halphen activity.

Experimental Procedures and Discussion

Preparation of Methyl Stearolate

Stearolic acid was prepared from methyl oleate by the method of Adkins and Burks (8). The crude product was recrystallized from ethanol-water to yield white crystals; mp 45.5–46.0 C (lit. mp 48 C) (9). Methyl stearolate was prepared by combining stearolic acid (20.0 g) and methanol-7% BF$_3$ (150 ml) and heating under reflux for 15 min. The solution was allowed to stand 3 hr. Water (450 ml) was added to the solution and methyl stearolate was extracted three times with petroleum ether (30–60 C) and the combined extracts were washed once with water. The petroleum ether solvent was evaporated under reduced pressure. The product was vacuum distilled to yield 17.1 g of a colorless liquid: bp 140–143 C (0.08 mm); n_D^{20} 1.4558. Vapor phase chromatography indicated that the liquid was a single, pure compound. The infrared spectrum of the compound was identical with that of an authentic sample of methyl stearolate.

Preparation of Diazomethane

The diazomethane precursor used was N-nitrosomethylurea prepared by the method of Arndt (10). The details for preparing diazomethane from N-nitrosomethylurea have been reported by Lind and Deutschman (3). According to their procedure, the diazomethane was collected in decalin.

Preparation of Methyl Sterculate

Methyl sterculate was prepared by passing diazomethane through methyl stearolate under continuous irradiation with a high-pressure mercury immersion lamp (G.E. bulb H85 As/UV4; mounting designed and built in our laboratory). The irradiation system

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consisted of the mercury lamp surrounded by a Pyrex tube which served as a cooling jacket. A 20 ml Pyrex test tube attached to the lamp cooling jacket served as the reaction vessel. During irradiation the complete assembly was immersed in a dewar flask containing ice and the lamp was cooled by circulating ice water.

The diazomethane was displaced from the decalin solvent and carried to the reaction vessel using a stream of dry nitrogen gas. The amount of diazomethane consumed during the reaction was determined by treating aliquots of the decalin solution before and after the reaction with excess benzoic acid and titrating with sodium hydroxide. The diazomethane was introduced over a 12 hr period. A total of 0.12 mole of diazomethane was displaced from the decalin solution. The amount of diazomethane not decomposed in the reaction vessel was collected in a benzoic acid trap attached to the outlet of the reaction vessel. Only small amounts of diazomethane were found in the trap.

The concentrations of methyl sterculate produced in the photolyzed solution were determined by means of the Halphen Test according to the procedure of Deutschman (7). Photolysis analysis of three samples ranged from 9.9–11.2%. A Coleman spectrophotometer was used for measuring the optical density at 505 mμ.

Infrared (neat) analysis (Perkin-Elmer spectrophotometer, Model 337) showed absorptions at 1825 cm^{-1} (cyclopropenyl ($C = C$ stretch) and 1007 cm^{-1} bands (3).

The presence of the cyclopropenoid structure has been shown to change the fatty acid distribution in egg yolks (11), and the presence of this cyclopropenoid structure in the photolyzed solution was verified by poultry feeding experiments (12). Poultry tests confirmed this effect in egg yolks, verifying the presence of the cyclopropene in the photolysis mixture.

ACKNOWLEDGMENT

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