Synthesis of Dodecanedioic Acid from *Vernonia galamensis* Oil

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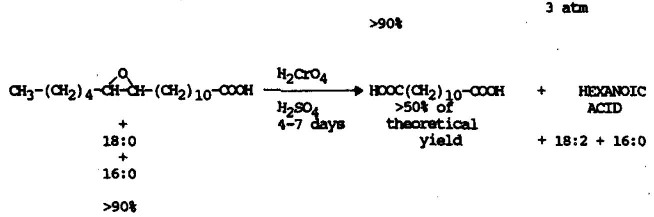
Dodecanedioic acid, currently available from elaborate synthesis utilizing petrochemical feedstock, was synthesized from *Vernonia galamensis* oil via an efficient, relatively simple three-reaction sequence that involved the room temperature oxidation of 12,13-epoxystearic acid. The first and second steps of the reaction scheme were saponification and hydrogenation, both of which were almost quantitative. The third reaction, involving chromic acid oxidation of the resulting epoxy acid, afforded greater than 50% of the theoretical yield of dodecanedioic acid (>95% purity, m.p. 123–125°C; lit. m.p. 128–130°C).

We recently reported the synthesis of suberic acid and azelaic acid from the oil of *Vernonia galamensis* (Powers, F. T., R. L. Shepard and F. O. Ayorinde, unpublished work). This annual herb, native to semi-arid regions of Africa, is cultivated as an industrial crop in Zimbabwe, in addition to undergoing promising agronomic trials in Kenya, Tanzania and Pakistan (1,2). The seed of this plant contains 40% oil, which, when hydrolyzed, yields 79.81% vernolic (*cis*-12,13-epoxy-*cis*-9-octadecenoic) acid, 10.23% linoleic acid, 5.3% oleic acid, 2.22% stearic acid and 2.37% palmitic acid (3,4).

The present communication reports the synthesis and isolation of dodecanedioic acid from this epoxytriglyceride oil. Aliphatic dibasic acids are established industrial raw materials that are used as plasticizers and in the manufacture of engineering fibers, synthetic fabrics and impact resistant elastomers (5,7). Dodecanedioic acid, currently available from elaborate synthesis utilizing petrochemical feedstock (8), was synthesized from *V. galamensis* oil via an efficient, relatively simple three-reaction sequence that included the room temperature oxidation of 12,13-epoxystearic acid (Scheme 1).

EXPERIMENTAL

The vernonia oil was obtained from K. D. Carlson, Agricultural Research Service, U.S. Department of Agriculture, Peoria, Illinois. Reactions and products were monitored with a Perkin-Elmer 983G infrared spectrophotometer and a Finnigan gas chromatograph (GC, model 9611) equipped with a splitless injector and interfaced with a Finnigan MAT 4500 automated mass spectrometer with a Superincos data system. The interface oven and transfer line were maintained at 300°C, ionizer temperature setting at 140°C, electron energy at 70 eV, and injector temperature at 250°C. The mass spectrometer (MS) was operated in the electron impact (EI) mode with emission current 0.27 mA, and electron multiplier 1200 V. High resolution capillary gas chromatography was obtained with the use of Supelco fused silica SPB-1 (30 m, 0.25 mm i.d., 0.25 μm film) temperature programmed from 50 to 300°C, helium as carrier gas with a head pressure of 10 psi. Characterizations of the dibasic acids by GC/MS were performed with methylated samples, prepared by adding ethereal solution of diazomethane to samples containing the dibasic acids (4). The experimental procedures given below only typify the numerous trial experiments that were conducted.



SCHEME 1. Synthetic scheme for dodecanedioic acid from *V. galamensis* oil. The oxidation step used only 5.20 g of the acid mixture. 5.20 g × 0.8 = 4.16 g of 12,13-epoxystearic acid.

Synthesis of 12,13-epoxystearic acid. A 500-ml distilling flask equipped with a reflux condenser and magnetic stirrer was charged with 20.70 g vernonia oil, 120 ml water and 80.11 g potassium hydroxide. The mixture was heated for one hr at ca. 90°C with continuous stirring, after which it was cooled to room temperature. A 500-ml portion of cold water was added after which the mixture was transferred into a beaker, cooled with ice water, and acidified with concentrated hydrochloric acid. After carefully decanting the aqueous layer, the crude product was rinsed with 50 ml ice-cold water, vacuum filtered and rinsed with an additional 50 ml ice-cold water to afford a light orange crude solid. The resulting crude was transferred into a Paar hydrogenation bottle, charged with 50 ml methanol and 0.15 g platinum oxide (Adam's catalyst, Aldrich Chemical Co., Milwaukee, Wisconsin). The hydrogenation bottle was fitted to a Paar high pressure system, evacuated by means of a water aspirator, and connected to a tank of hydrogen so that a pressure of 3 atm could be maintained for 90 min while it was shaken. After the hydrogenation, 40 ml methanol was added to the gray reaction mixture, which was heated to gentle boiling to dissolve the product. The hot mixture was quickly filtered to remove the suspension of black platinum, after which the filtrate was evaporated to afford 18.06 g of a white powder. GC/MS analysis indicated ca. 80% 12,13-epoxystearic acid, 17% stearic acid and 3% palmitic acid. A portion of this mixture of acids was used in the next step without further purification.

Synthesis and isolation of dodecanedioic acid. A 300-ml chromic acid solution was prepared by adding 250 ml water to 47.62 g K_2Cr_2O7 contained in a one-l Erlenmeyer flask, followed by addition of 38 ml conc. H_2SO_4. The warm mixture was stirred to give an orange-red solution. A 250 ml portion of the chromic acid solution was added to 5.20 g of the acid mixture (epoxystearic acid, stearic acid, palmitic acid) contained in a 500-ml Erlenmeyer flask, equipped with a magnetic stirrer. The resulting mixture was stirred continuously for seven days,

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200 ml water was added, and the mixture was suction filtered to afford a crude grayish solid. The crude material was transferred into a beaker, charged with 350 ml water, 83 ml 40% KOH, then cooled with ice-water for one hr, and suction filtered to give a greenish soapy filtrate and a greenish solid which was transferred into a breaker containing 200 ml water and acidified with conc. HCl to give a white solid (stearic, palmitic) after filtration.

The filtrate obtained above was acidified with conc. HCl, cooled to room temperature, and filtered to give 2.70 g of a cream-white solid (m.p. 110–115°C, 85% dodecanedioic acid). The cream-white solid was recrystallized with water (one l) to afford 1.69 g of a white flaky solid (m.p. 122–125°C, 95% dodecanedioic acid, ca. 5% epoxystearic acid + stearic acid). The dodecanedioic acid was characterized by GC/MS. The mass spectral data, consistent with reported spectra (9), showed the following significant ions (m/z): 259, $MH^{+\cdot}$ (1), 227, $M - OCH_3$ (45), 194, $M - 2\ CH_3OH$ (8), 185 (46), 166 (12), 153 (52), 135 (25), 112 (38), 98 (100), 84 (55), 74 (73), 69 (47), 55 (51), 43 (32).

RESULTS AND DISCUSSION

The synthetic sequence (Scheme 1), though relatively simple, is highly efficient. The saponification and hydrogenation steps are virtually quantitative. For the hydrogenation, reaction time in excess of 90 min resulted in formation of hydroxy acid due to the opening of the epoxy ring. In some trial experiments, when acetic acid was used as the hydrogenation solvent, reaction time was less than 30 min. This might be due to the greater solubility of both the vernolic acid and epoxystearic acid in the reaction mixture. However, using acetic acid as a solvent resulted in significant formation of hydroxy acid, hence the choice of methanol as the optimum solvent. Methanol was much easier to manipulate during work-up. Vacheron and coworkers (9) have synthesized 12,13-epoxystearic acid from linoleic acid, and they reported a partial mass spectrum for the epoxy acid in order to locate the position of the epoxy ring. Ions reported to be characteristic of the 12,13-epoxy functionality were m/z 241, 197 and 113. These ions are consistent with the mass spectrum (Fig. 1) of the 12,13-epoxystearic acid reported in this paper. This is also a further confirmation of the original structure proof of vernolic acid from *Vernonia anthelmintica* reported by Gunstone (10).

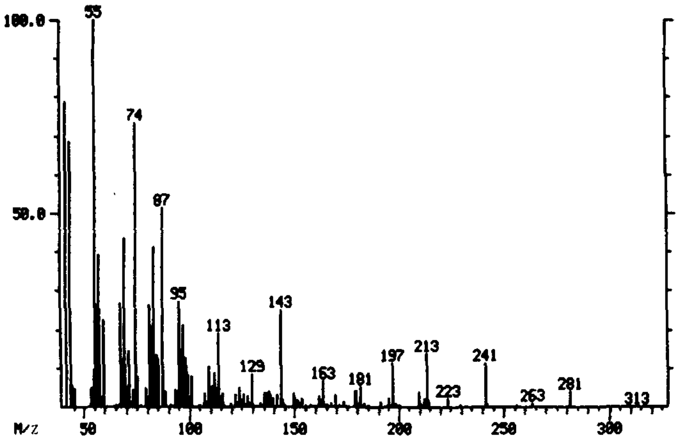

FIG. 1. Electron-impact mass spectrum of methyl 12,13-epoxystearate: m/z 313 ($MH^{+\cdot}$); m/z 281 ($M - OCH_3$); m/z 241 corresponds to $\underset{\overset{\displaystyle O}{+}}{CH{-}CH}{-}(CH_2)_{10}{-}CO_2CH_3$; m/z 113 corresponds to

$$CH_3(CH_2)_4{-}\underset{\overset{\displaystyle O}{+}}{CH{-}CH.}$$

The chromic acid oxidation of the 12,13-epoxystearic acid to give hexanoic and dodecanedioic acids, performed at room temperature, was also very effective; any significant loss of material was due largely to the isolation. There was no attempt to isolate the hexanoic acid, which easily could be accomplished by steam distillation. Purification of the dodecanedioic acid proved to be a challenge. Recrystallization using a variety of solvents (e.g., CH_2Cl_2, $CHCl_3$, petroleum ether, methanol, etc.) was ineffective. However, we found that the potassium salt of dodecanedioic acid was more water soluble than the potassium salts of stearic and palmitic acids, hence the use of excess aqueous potassium hydroxide on the crude product, followed by cooling and suction filtration to afford a filtrate which upon acidification yielded 2.70 g of crude dodecanedioic acid. Considering that only 67% of 12,13-epoxystearic acid can theoretically afford dodecanedioic acid (Scheme 1), the theoretical yield of dodecanedioic acid should be 2.79 g (12.13 mmol). Thus, we have 2.295 g (9.98 mmol = 85% of 2.70 g) of dodecanedioic acid, which translates to a percent yield of 82.3%. Further recrystallization in water afforded 1.61 g (6.98 mmol). Hence, the percent yield of purified dodecanedioic acid is 57.5%.

Many attempts aimed at performing the oxidation at higher temperatures resulted in a low yield of the dibasic acid (40% of theoretical yield).

The reactions discussed in this paper are well known and can easily be adapted for industrial preparation of 12,13-epoxystearic acid and dodecanedioic acid. In addition to the desired dibasic acid, hexanoic acid and stearic acid constitute valuable by-products. Noteworthy is the possibility of using the epoxystearic acid to generate other industrially important intermediates. Presently we are pursuing some of these possibilities. Finally, in this paper we have demonstrated the potential use of *Vernonia galamensis* oil for the synthesis of dodecanedioic acid, which could reduce dependence on petrochemical feedstock as a source of this important C12 dibasic acid.

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