Synthesis of Azelaic Acid and Suberic Acid From *Vernonia galamensis* Oil

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We have demonstrated the potential of *Vernonia galamensis* seed oil as a source of dibasic acids. Reaction of nitric acid with *V. galamensis* oil afforded a homologous series of dibasic acids that include butanedioic acid, pentanedioic acid, hexanedioic acid (adipic), heptanedioic acid (pimelic), octanedioic acid (suberic), nonanedioic acid (azelaic), decanedioic acid (sebacic), and undecanedioic acid. Using a combination of chloroform extraction and subsequent water crystallizations, we have isolated suberic acid (~95% purity by GC) and azelaic acid (~95% purity by GC). The isolated yield of suberic acid is 15% and of azelaic acid is 11%. Reported reaction of nitric acid with ricinoleic acid (from castor oil) gave 8.8% suberic acid and 7.2% of a mixture of suberic and azelaic acids.

Vernonia galamensis is an herbaceous annual currently being developed as a commercial crop in Zimbabwe, Kenya and Pakistan (1,2). The seed contains 40% oil, of which the vernolic (*cis*-12,13-epoxyoctadec-*cis*-9-enoic) acid content is 72-80%; palmitic acid, 2.7-3.3%; stearic acid, 2.7-3.9%; oleic acid, 3.6-5.6%, and linoleic acid, 12.6-14.0% (3,4). The high level of vernolic acid in the seed oil makes *V. galamensis* a promising source of epoxytriglycerides and epoxy acids, important raw materials used in plastic formulations, chemical coatings, adhesives, plasticizers and stabilizers (5,6), thus giving the species and other epoxy producing plants such economic importance that the U.S. Department of Agriculture (USDA) has shown interest in their agronomic potential for U.S. agriculture (1,7).

As part of our focus on the potential of seed oils for industrial raw materials, we are currently studying the possibilities of using *V. galamensis* seed oil as a source of dibasic acids, many of which are already well established industrial raw materials, notably hexanedioic acid (adipic), nonanedioic acid (azelaic), decanedioic acid (sebacic), and dodecanedioic acid. These dibasic acids and their derivatives are used in the manufacture of polyurethanes, polyamides (nylons), alkyd resins, plasticizers, elastomers (synthetic rubber), lubricants and hydraulic fluids (8). Azelaic acid is obtainable from triglyceride oils and fatty acids containing unsaturation between C_9-C_{10}; on the other hand, castor oil is the only triglyceride oil that has been used as a commercial source of suberic acid.

V. galamensis oil recently has been shown by Carlson and co-workers (3) to have great promise as a stabilizer and plasticizer for polyvinylchloride (PVC), and as a chemical coatings material. Sperling and his group (9) recently studied the potential of the oil as a monomer in the synthesis of interpenetrating polymer networks (IPN), used as toughened elastomers. Thus far, many of the utilization studies have focused on the direct application of the oil. However, there has been no reported transformation of the oil into key industrial raw materials such as the dibasic acids and their derivatives. Noteworthy is the fact that castor oil (Fig. 1), a commercial source of many dibasic acids, is structurally related to trivernolin (the major component of vernonia oil).

Alkaline potassium permanganate reacts with ricinoleic acid to give a 23% yield of azelaic acid (10). Basic hydrolysis of castor oil followed by oxidation with nitric acid was reported to give about 20% of a mixture of azelaic and suberic acids, which was recrystallized with benzene/ethanol to afford 8.8% nearly pure suberic acid and 7.2% of a mixture of azelaic and suberic acids (11). Consequently, *V. galamensis* oil, due to unsaturation and unusual reactivity of its epoxy functionality, should be a potential source of many of these dibasic acids. The present preliminary paper reports the synthesis of azelaic and suberic acids by direct action of nitric acid on the seed oil from *Vernonia galamensis*.

EXPERIMENTAL

The vernonia oil was obtained from K.D. Carlson, USDA Agricultural Research Service, 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 1300 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°C to 300°C, helium as carrier gas with a head pressure of 10 psi. Characterization of the dibasic acids by GC/MS was performed with methylated samples, prepared by adding ethereal solution of diazomethane to samples containing the dibasic acids (4). The synthetic experimental procedure given below only typifies the numerous trial experiments that were conducted.

Synthesis and purification of suberic and azelaic acids. The reaction was carried out in a fume hood due to the evolution of toxic nitrogen dioxide gas. A 500-ml three-necked flask equipped with a reflux condenser and magnetic stirrer was charged with 10.18 g of Vernonia oil, ca. 67 ml of 70% nitric acid, with continuous stirring. The mixture was heated to maintain a temperature between 90°C and 100°C for 18 hr, after which 110 ml water was added, then heated to give ca. 130 ml and filtered hot to remove any insoluble materials and oily residue. The warm filtrate (45°C) was extracted with 300 ml chloroform. The aqueous layer was evaporated to 22 ml, cooled with ice/water, filtered to give

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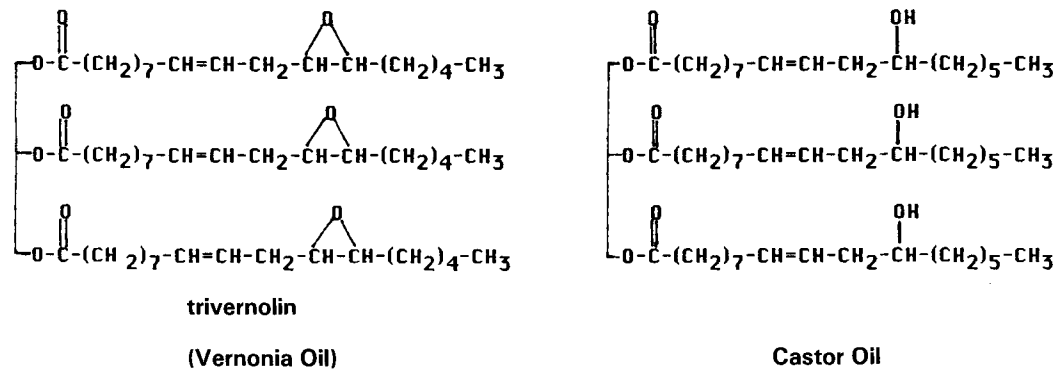

FIG. 1. Predominant triglycerides from Vernonia and castor oils.

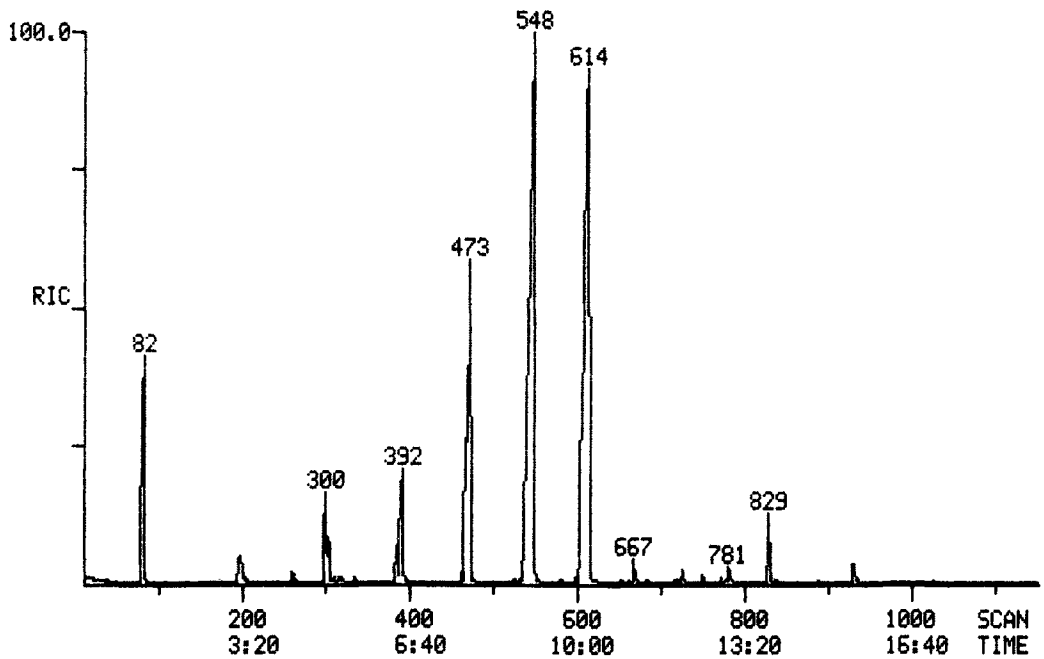

FIG. 2. Reconstituted Ion Chromatogram (RIC) of methylated reaction mixture after 18 hr refluxing of *Vernonia galamensis* oil with 70% nitric acid. Scan 82, hexanoic aid; 198, butanedioic acid; 300, pentanedioic acid; 392, hexanedioic acid (adipic); 473, heptanedioic acid (pimelic); 548, octanedioic acid (suberic); 614, nonanedioic acid (azelaic); 667, decanedioic acid (sebacic); 725, undecanedioic acid; 781, dodecanedioic acid; 829, palmitic acid; 929, stearic acid.

0.45 g suberic acid (m.p. 136–140°C), the aqueous filtrate was allowed to evaporate slowly, then filtered to afford 0.37 g suberic acid (contains about 5% adipic acid by GC), and filtrate that contains mostly pimelic and adipic acids, with minor amounts of azelaic and suberic acids. The chloroform extract, dried with anhydrous Na_2SO_4, was reduced to ca. 15 ml, cooled to room temperature and filtered to give 0.41 g suberic acid (contains about 10% azelaic acid by GC), the resulting filtrate was evaporated to afford 3.22 g of light yellow crude solid. To the crude solid was added 100 ml water, heated to boiling, then evaporated to ca. 80 ml, cooled and maintained at room temperature for 10 hr, filtered to afford 1.09 g azelaic acid (m.p. 104–106°C, contains about 5% suberic acid by GC), the filtrate was evaporated to ca. 30 ml, cooled to room temperature and filtered to give 0.28 g suberic acid. GC/MS analysis of the resulting filtrate showed mostly pimelic acid with minor amounts of hexanoic acid, suberic and azelaic acids. The isolated yields of 1.51 g suberic acid and 1.09 g azelaic acid represent a total isolated yield of 25.5% from Vernonia oil.

RESULTS AND DISCUSSION

Figure 2 is the chromatographic profile showing a methylated product mixture after 18 hr refluxing. Apparently, there is extensive rearrangement and degradation of the unsaturated fatty acid carbon chain. Thus, the major challenge in this reaction is the isolation of the desired reaction products. Palmitic acid (scan 829) and stearic acid (scan 929) were removed by filtration

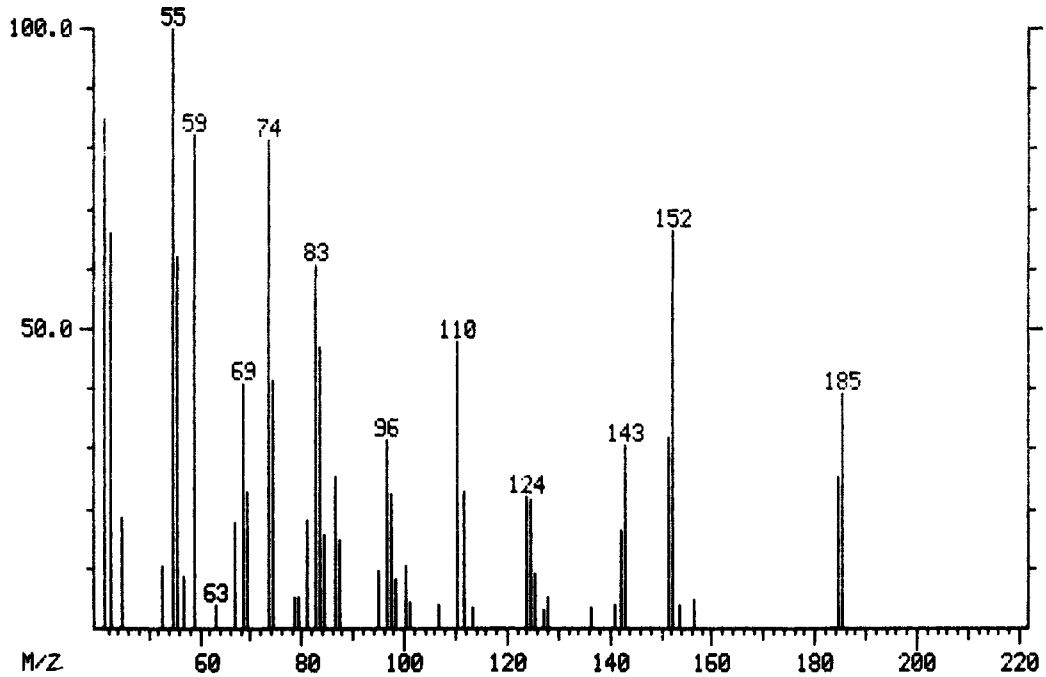

FIG. 3. Mass spectrum of azelaic acid methyl ester, m/z 185 ($M-OCH_3$), m/z, 152 ($M-2CH_3OH$), m/z 143 ($M-CH_2CO_2CH_3$), m/z 124 ($M-2CH_3OH-CO$).

as indicated earlier. Hexanoic acid (scan 82), butanedioic acid (scan 198), pentanedioic acid (scan 300), adipic acid (scan 392) and pimelic acid (scan 473) remained in the final filtrates after the crystallization of suberic acid (scan 548) and azelaic acid (scan 614) from water and chloroform, respectively. Hexanoic acid, though not isolated in this reaction, could constitute an important by-product for industrial use. The 18 hr refluxing time appears to be the optimum reaction time if suberic and azelaic acids are the target compounds; longer reaction times resulted in the formation of lower molecular weight dibasic acids at the expense of azelaic acid. If both pimelic and adipic acids are desired from Vernonia oil, the longer reaction time (30 hr) may be a synthetic advantage. The choice of chloroform and water rather than the reported use of benzene/ethanol to separate suberic and azelaic acids (11) was made because of the apparent cost effectiveness and the fact that ethanol is under government regulation. Furthermore, benzene is more difficult to work with (bad odor, higher boiling) than chloroform.

Identification of the dibasic acids by mass spectrometry was routine, because they all give characteristic fragmentation patterns (12). The mass spectral analysis of methyl azelate (Fig. 3) does not give a molecular ion (M); however, there are many prominent diagnostic ions, m/z 185 ($M-OCH_3$), m/z 152 ($M-2CH_3OH$), m/z 143 ($M-CH_2CO_2CH_3$), m/z 124 ($M-2CH_3OH-CO$). Similar corresponding ions were observed for all the dibasic acids except butanedioic acid and pentanedioic acid. Minor amounts of decanoic acid (scan 385), sebacic acid (scan 667), undecanedioic acid (scan 725) and dodecanedioic acid (scan 781) were detected in each of the trial reactions.

In this paper, we have demonstrated the potential use of *Vernonia galamensis* seed oil as a source of dibasic acids using a very simple and potentially cost effective procedure, in which a 15% isolated yield of suberic acid is obtained compared to the reported 8.8% from castor oil. It should be noted that the *V. galamensis* oil used in this study is derived from unimproved germplasm (R.E. Perdue Jr., personal communication). Thus, any genetic improvement that seeks to increase the oil content and/or epoxytriglyceride would greatly improve its potential as a source of dibasic acids.

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