Vernonia galamensis: A Rich Source of Epoxy Acid

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A percolation extraction of *Vernonia galamensis* seed, affording 38.6% of crude vernonia oil, is described. The dark colored crude oil was degummed with water, treated with activated charcoal and bleached with a neutral agent, to give a light colored oil (Lovibond: 0.9 red, 3.5 yellow). Gas chromatographic/mass spectrometric analysis of the refined oil indicates a relative fatty acid composition of 79–81% vernolic (*cis*-12,13-epoxy-*cis*-9-octadecenoic) acid, 11–12% linoleic acid, 4–6% oleic acid, 2–3% stearic acid, 2–4% palmitic acid, and a trace amount of arachidic acid.

KEY WORDS: Seed oil, vernolic acid, *Vernonia galamensis.*

The past decade has witnessed a growing interest in *Vernonia galamensis.* The seed of this indigenous African plant, being cultivated in Zimbabwe as an industrial crop, contains ca. 40% triglyceride oil, of which ca. 80% of the constituent acids is an epoxy acid commonly known as vernolic (*cis*-12,13-epoxy-*cis*-9-octadecenoic) acid (1-3). Thus *V. galamensis* is a rich source of epoxidized triglyceride oil that has both current and potential applications in coatings and plastic formulations, and as a reagent for laboratory and industrial feedstock (4-6). As part of a study on the metabolism of acids in humans, Rakoff (7) recently indicated the use of vernonia oil in a 2-step synthesis of methyl 12-oxo-*cis*-9-dodecenoate, a synthesis that would usually involve several steps. We recently reported the synthesis of several dibasic acids from vernonia oil (6,8). These dibasic acids have established applications as plasticizers and raw materials for synthetic fibers (9-11). Studies in our laboratory have developed synthetic procedures that involve the use of vernonia oil in training both undergraduate and graduate students. However, one of the most promising major commercial applications is in paint formulation, where there is urgent need to reduce the volatile organic components (VOC). In a recent publication by Perdue (12), Graham, director of the Coatings Research Institute at Eastern Michigan University, estimated the use of vernonia oil as a diluent for alkyd-resin paints at 40 million gallons per year.

This paper describes laboratory scale procedures that will enable interested researchers to obtain refined vernonia oil from *Vernonia galamensis* seed.

EXPERIMENTAL PROCEDURES

The *V. galamensis* seed used in this study was provided by the Department of Research and Specialist Services, Zimbabwe, which included crops from the 1987 planting in Chiredzi, and the 1986 planting in Chipinge. Infrared Spectroscopic (IR) analyses of crude and refined oil were obtained on a Perkin-Elmer 983G spectrophotometer. Samples were run neat using sodium chloride plates. Preparation of samples for gas chromatographic/mass spectrometric (GC/MS) analysis was accomplished as previously described (3). Mass spectrometric data were obtained on a Finnigan MAT 4500 computerized GC/MS spectrometer operating in the electron impact (EI) mode, with emission current of 0.45 mA, electron energy 70 eV and electron multiplier at 1450 V. Ionizer temperature setting was 150°C. High resolution capillary gas chromatography was obtained using a Supelco fused silica SPB-1 column (30 m, 0.32 mm I.D., 0.25 μm film) temperature programmed from 50°C to 300°C at 12°C/min, with helium as carrier gas at a head pressure of 10 psi. Injector temperature was set as 230°C. Colorimetric data was obtained on a Lovibond Colorscan Spectrophotometer (The Tintometer Co., Williamsburg, VA) at 41°C with a cell path of 1 inch.

Deactivation of vernonia lipase. A 4 L Presto pressure cooker was charged with 1.1 kg vernonia seed and a 1.1 L tap water, and heated to 90–100°C for 1 hr. The seed was then air dried for 3 days to give a moisture content of ca. 6%, and ground in an Osterizer blender to afford 1.04 kg (94.5% recovery).

Extraction of oil. Ground seed was loosely packed into a 2 L separatory funnel to allow a percolation rate of ca. 20–50 mL/min. One liter of extract was collected using 2 L hexane. The slightly dark colored extract was stripped of solvent to afford a dark colored oil. The recovered hexane was then used to initiate another extraction cycle. After three cycles, a total of 400 mL crude oil (density 0.891 g, 34.27% recovery) was obtained. The solvent then remained in the seed bed for 24 hr to obtain an additional 50 mL of crude vernonia oil (total volume 450 mL, 38.6%).

Degumming and decolorization. The 450 mL crude oil was mixed with 20 mL of tap water, heated at 60–70°C for 1 hr, and centrifuged at 5,000 rpm for 1 hr. The top, oily portion was then carefully removed and 300 mL of the crude oil was mixed with 10.7 g (4%) activated carbon (Norit A, <100 mesh, Aldrich Chemical Co., Inc., Milwaukee, WI) for 1 hr under vacuum at ca. 70°C. The dark mixture was vacuum filtered through 3 layers of filter paper (Whatman #1) that were saturated with refined vernonia oil. The filtration usually lasted 30–40 min and afforded ca. 276 mL (92% recovery) oil. The clear but reddish oil (Lovibond: 1.6 red, 24.0 yellow; AOCS: 1.7 red, 24.0 yellow) was stored at room temperature.

Bleaching. Oil (300 mL) was mixed with 10.7 g (4%) TONSIL L-80 (L.A. Salomon Inc., Montville, NJ) for 1 hr at ca. 70°C. The resulting grayish brown mixture was vacuum filtered through three layers of filter paper (Whatman #1) that were soaked with refined vernonia oil. The filtration took 15–20 min and afforded 283 mL (94% recovery) of golden light orange oil (Lovibond: 0.9 red, 3.5 yellow; AOCS: 0.9 red, 3.5 yellow).

RESULTS AND DISCUSSION

Filtration of the charcoal-treated vernonia oil required careful attention in order to prevent some charcoal passing through the filter bed; hence it was initiated with a small amount of refined oil prior to adding the charcoal-treated oil to the filter bed. In some trials, we used a bed of celite in addition to the filter paper, however oil

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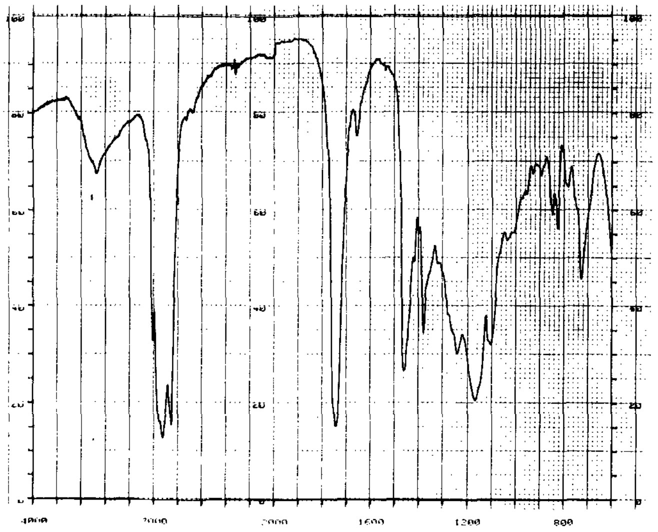

FIG. 1. Infrared spectrum of degummed, charcoal-treated and bleached vernonia oil. Characteristic epoxy absorptions at 846 cm^{-1} and 824 cm^{-1}.

recovery was only about 85%, consistent with the result previously obtained by Carlson and co-workers (2). Thus, in order to minimize loss of oil, we adopted the procedure described above. For the bleaching experiments, we were limited to choosing a neutral bleach because of the presence of epoxy groups in vernonia oil. Indeed, the use of an acidic bleach, TONSIL ACTISIL FF (L.A. Salomon), resulted in the loss of the epoxy group as evident from the infrared spectrum. Various neutral bleaches were tried, however, TONSIL L-80 appeared to be the most effective. The rate of vacuum filtration was significantly increased when the buchner funnel was preheated prior to filtration. Infrared spectroscopic and gas chromatographic analysis of the refined oil indicate no detectable free fatty acids (Fig. 1); however, it appears as though there is some hydroxyl absorption probably due to residual water and/or oxidative product. GC/MS analysis of the oil subsequent to methylation and transesterification gave the following relative fatty acid composition: vernolic acid 79–81%, linoleic acid 11–12%, oleic acid 4–6%, stearic acid 2–3%, palmitic acid 2–4%, and a trace amount of arachidic acid. Analysis of a saponified oil gave a similar fatty acid profile with insignificant amounts of unsaponifiable material.

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