Derivatives of Eleostearic Acid

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ABSTRACT

Eleven new derivatives of the carboxyl function of eleostearic acid have been prepared and characterized by elemental analysis, physical constants, and spectrophotometric data. It is shown that α-eleostearyl alcohol can be distilled without rearranging to the β-isomer if high vacuum and low temperature are employed.

INTRODUCTION

Tung oil has been employed in a wide variety of products which include varnishes, alkyd resins, inks, corrosion inhibitors for oil wells, insecticides, plasticized nitrile rubber, and others (1). Moreover, tung oil and its derivatives have been reported as remedies for insanity, burns, bruises, swelling, and hypertension (2), although many of these uses have not been well substantiated.

Despite these claims relative to tung oil and products derived therefrom, only a limited number of derivatives of eleostearic acid, the major fatty acid constituent of tung oil, have been prepared. Thus, it was the objective of this research group to synthesize and characterize derivatives of various types from eleostearic acid which could be employed in products or applications where the usefulness of tung oil has been claimed. A number of such derivatives have been reported in a previous communication (3).

EXPERIMENTAL PROCEDURES

α-Eleostearic Acid (I)

The procedure of Thames et al. (3) was used for the preparation of this material.

β-Eleostearic Acid (II)

β-tung oil was prepared by blending potassium iodide (1 g of a saturated water solution) into α-tung oil (200 g) and allowing exposure to sunlight for 24 hr. The β-eleostearic acid was then prepared in a manner analogous to the procedure for the preparation of I. The product (136 g, 85% yield) was produced as white flakes melting at 70-71 C.

α-Eleostearyl Alcohol (III)

I (16 g, 0.0575 mol) in anhydrous ether was added dropwise to an ethereal solution of $LiAlH_4$ (3 g, 0.079 mol) in a three-neck flask equipped with a $CaCl_2$ drying tube, tru-bore stirrer, and dropping funnel. Upon completion of the addition, the dropping funnel was replaced with a reflux condenser and the reaction mixture refluxed overnight. The excess $LiAlH_4$ was decomposed by the addition of a water saturated ether solution, and the $Al(OH)_3$ was removed by filtration. The filtrate was washed with a $NaHCO_3$ solution and subsequently dried over $MgSO_4$. The solvent was removed in vacuo and the product recovered by distillation at 128-129 C/0.005 mm Hg. Analysis: Percent calculated for $C_{18}H_{32}O$: C, 81.82; H, 12.12. Found: C, 81.89; H, 12.14.

β-Eleostearyl Alcohol (IV)

The procedure employed in the preparation of III was followed. Thus, β-eleostearyl alcohol melting at 56-58 C was obtained in 60% yield from II after recrystallization from heptane.

α-Eleostearyl Trimethylsilyl Ether (V)

III (13.2 g, 0.05 mol) and hexamethyldisilazane (4.04 g, 0.025 mol) were charged to a three-neck flask equipped with a thermometer, nitrogen inlet, and tru-bore stirrer. Five drops (0.3 ml) of trimethylchlorosilane were added as catalyst and the mixture heated at 105-110 C until no more ammonia was expelled by a dry nitrogen purge (ca. 24 hr). The residue was distilled in vacuo to give V boiling at 128-130 C/0.015 mm Hg, η_d^{24}:1.4875. Analysis: Percent calculated for $C_{21}H_{40}SiO$: C, 74.92; H, 11.91; Si, 8.34. Found: C, 74.84; H, 11.95; Si, 8.16.

β-Eleostearyl Trimethylsilyl Ether (VI)

IV (10.1 g, 0.038 mole), hexamethyldisilazane (3.2 g, 0.02 mol), and 5 drops (0.3 ml) of trimethylchlorosilane were heated at 115-119 C for 24 hr. The product was dissolved in petroleum ether, cooled, filtered to remove unreacted IV, placed in vacuo to remove the solvent, and subsequently distilled to provide VI boiling at 129 C/0.0025 mm Hg, η_d^{24}:1.4884. Analysis: Percent calculated for $C_{21}H_{40}SiO$: C, 74.92; H, 11.91; Si, 8.34. Found: C, 74.79; H, 11.92; Si, 8.12.

Ethylene Di-α-Eleostearamide (VII)

I (27.8 g, 0.1 mol) was charged to a 250 ml three-neck flask equipped with a tru-bore stirrer, thermometer, nitrogen inlet, and dropping funnel. Mild heating was begun concomitant with the dropwise addition of ethylene diamine (3 g, 0.05 mol). Upon completion of the addition, the flask was equipped with a reflux condenser and the reaction mixture heated at 105 C for 4 hr. The product (85% yield) was recrystallized from a mixture of ethanol and ethyl acetate to yield a white solid melting at 128-129 C. The infrared (IR) spectrum was consistent with the proposed structure. Analysis: Percent calculated for $C_{38}H_{64}N_2O_2$: N, 4.83. Found: N, 4.57.

1,3-Propylene Di-α-Eleostearamide (VIII)

I (52.7 g, 0.189 mol) and 1,3-diaminopropane (6.97 g, 0.094 mol) were charged to a 250 ml three-neck flask equipped as in the preparation of VII and heated for 8 hr at 120-125 C. The pure white crystalline solid obtained in 95% yield by recrystallization from ethanol melted at 103-108 C. The IR spectrum was consistent with the propsoed structure. Analysis: Percent calculated for $C_{39}H_{66}N_2O_2$: C, 78.79; H, 11.11; N, 4.71. Found: C, 78.63; H, 10.98; N, 4.66.

1,3-Propylene Di-β-Eleostearamide (IX)

II (12.5 g, 0.045 mol) and 1,3-diaminopropane (2.04 g, 0.028 mol) was heated at 130 C for 4 hr. The product, which melted at 112-114 C, was obtained in 97% yield after recrystallization from 95% ethanol. The IR spectrum was consistent with the proposed structure. Analysis: Percent calculated for $C_{39}H_{66}N_2O_2$; N, 4.71. Found: N, 4.68.

1,4-Butylene Di-α-Eleostearamide (X)

White crystals melting at 131-132 C were collected after heating I (8.03 g, 0.029 mol) with 1,4-diaminobutane (1.6 g, 0.018 mol) at 120-125 C for 3 hr. The structure of the product, which was obtained in 93% yield, was confirmed by IR spectroscopy.

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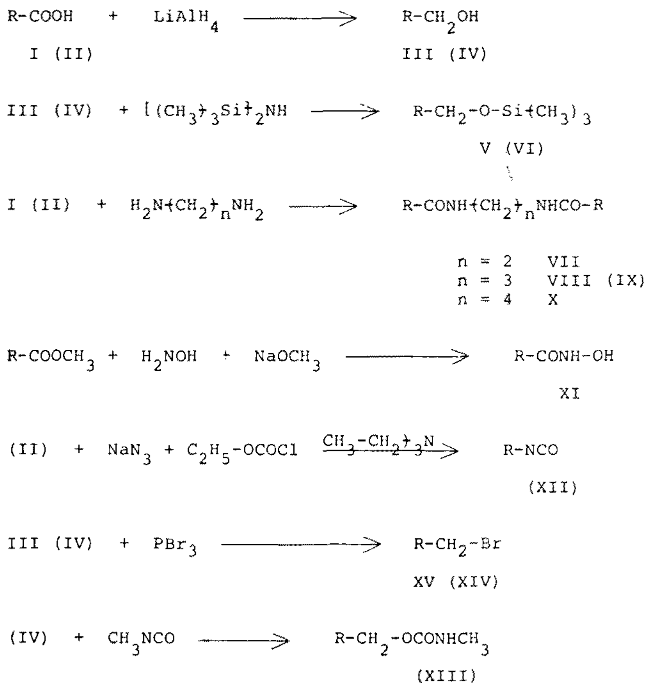

$$\underset{\text{I (II)}}{\text{R-COOH}} + \text{LiAlH}_4 \longrightarrow \underset{\text{III (IV)}}{\text{R-CH}_2\text{OH}}$$

$$\text{III (IV)} + [(\text{CH}_3)_3\text{Si}]_2\text{NH} \longrightarrow \underset{\text{V (VI)}}{\text{R-CH}_2\text{-O-Si(CH}_3)_3}$$

$$\text{I (II)} + \text{H}_2\text{N(CH}_2)_n\text{NH}_2 \longrightarrow \text{R-CONH(CH}_2)_n\text{NHCO-R} \qquad \begin{array}{ll} n = 2 & \text{VII} \\ n = 3 & \text{VIII (IX)} \\ n = 4 & \text{X} \end{array}$$

$$\text{R-COOCH}_3 + \text{H}_2\text{NOH} + \text{NaOCH}_3 \longrightarrow \underset{\text{XI}}{\text{R-CONH-OH}}$$

$$\text{(II)} + \text{NaN}_3 + \text{C}_2\text{H}_5\text{-OCOCl} \xrightarrow{\text{CH}_3\text{-CH}_2)_3\text{N}} \underset{\text{(XII)}}{\text{R-NCO}}$$

$$\text{III (IV)} + \text{PBr}_3 \longrightarrow \underset{\text{XV (XIV)}}{\text{R-CH}_2\text{-Br}}$$

$$\text{(IV)} + \text{CH}_3\text{NCO} \longrightarrow \underset{\text{(XIII)}}{\text{R-CH}_2\text{-OCONHCH}_3}$$

FIG. 1. Derivatives of eleostearic acid. These equations are intended to demonstrate the synthetic routes employed to prepare the various derivatives and thus show only the product of interest. R = the alpha isomer when compound numbers are not in parentheses and the beta isomer when compound numbers are in parentheses.

TABLE I

Characterization Data on III, IV, V, and VI

Monomer	Refractive Index, 24 C	Melting point (C)	Boiling point (C)
III	–	25	128-129/0.005 mm Hg[a]
IV	–	56-58	–
V	1.4875	–	128-130/0.015 mm Hg[a]
VI	1.4884	–	129/0.025 mm Hg[a]

[a] Two vacuum pumps were employed in tandem to achieve these low pressures.

α-Eleostearyl Hydroxamic Acid (XI)

This product was prepared via the general procedure of Urbanski (4). Methyl α-eleostearate (20 g, 0.0685 mol), obtained by distillation of commercially available methyl esters of tung oil, was added to an alcoholic solution of hydroxyl amine produced from hydroxylamine hydrochloride (4.8 g, 0.069 mol) and sodium methoxide (7.56 g, 0.14 mol). The mixture was heated for 0.5 hr. at the reflux temperature of ethanol, cooled to 0 C where crystallization of the sodium salt of the hydroxamic acid took place, and filtered. The white sodium eleostearyl hydroxamate was dissolved in water and the solution acidified. A white solid (XI) precipitated and was recrystallized from ethanol, giving a melting point of 97-98 C. The IR spectrum was consistent with the proposed structure. Analysis: Percent calculated for $C_{18}H_{31}NO_2$: N, 4.78. Found: N, 4.56.

9,11,13,trans,trans,trans-Heptadecatrienyl Isocyanate (XII)

II (23.9 g, 0.086 mol) was suspended in a water-acetone mixture and cooled to 0 C. Triethylamine (10.2 g, 0.1 mol) in acetone (175 ml) was added, and ethylchloroformate (12.5 g, 0.115 mol) in acetone (45 ml) was subsequently charged to the reaction flask in a dropwise fashion. After stirring for 90 min at 0 C, an aqueous solution (30 ml) of NaN_3 (8.6 g, 0.13 mol) was added dropwise. The mixture was stirred for 3 additional hours and subsequently poured into an excess of ice water. The oil which separated was extracted with ether. The solvent was removed in vacuo, and the residue dissolved in 50 ml of anhydrous toluene. The toluene solution was heated on a steam bath until all nitrogen had been liberated as evidenced by the creation of bubbles. The toluene was removed in vacuo and the residue distilled to afford the pure colorless liquid product (XII) (10.7 g, 45% yield) boiling at 125 C/0.003 mm Hg, η_d: 1.5166. The IR spectrum of the material possessed the isocyanate band at 4.4μ and is in agreement with the proposed structure. Analysis: Percent calculated for $C_{18}H_{29}NO$: C, 78.54; H, 10.55; N, 5.09. Found: C, 78.41; H, 10.61; N, 5.15.

β-Eleostearyl Methyl Urethane (XIII)

IV (20 g, 0.076 mol), in tetrahydrofuran (75 ml), was treated with methyl isocyanate (10.7g, 0.199 mol) After refluxing the mixture overnight, the solvent was removed in vacuo and the resultant crystalline material recrystallized from an acetone-pentane mixture. The product, XIII (21.2 g), whose IR spectrum was consistent with its structure, was obtained in 87% yield. Analysis: Percent calculated for $C_{20}H_{35}NO_2$: C, 74.96; H, 10.90; N, 4.36. Found: C, 74.74; H, 10.83; N, 4.20.

β-Eleostearyl Bromide (XIV)

PBr_3 (27.1 g, 0.10 mol) was added dropwise to a cold (-8 C) solution of IV (26.4 g, 0.10 mol) in 250 ml of ether. While stirring overnight, the temperature of the solution was slowly allowed to rise to ambient. A 5% solution of NH_4OH 250 ml) was then added to the reaction mixture. The ether layer separated, was removed from the aqueous layer, and subsequently dried over magnesium sulfate. After removal of the ether in vacuo, the product was fractionally distilled at 152-155 C/0.025 mm Hg to give XIV (10 g, 30% yield). Analysis: Percent calculated for $C_{18}H_{31}Br$: C, 66.05; H, 9.48. Found: C, 65.92; H, 9.44.

α-Eleostearyl Bromide (XV)

α-Eleostearyl bromide was prepared by the addition of a pyridine (15 ml) solution of III (18.48 g, 0.067 mol) to a cold solution of PBr_3 (18.16 g, 0.067 mol), pyridine (13.2 ml), and benzene (25 ml). After stirring overnight and bringing to room temperature, the reaction mixture was washed with a 5% NaOH solution (300 ml). The benzene layer was dried over $MgSO_4$, filtered, and removed from the product in vacuo, leaving XV as a viscous liquid which could only be identified by its IR spectrum. The IR spectrum possessed no O-H stretching band at 3μ, but did possess a C-BR stretching band at 13.85μ, and absorption at 10.1 and 10.4μ characteristic of the cis,trans,trans conjugated triene of I and its carboxyl derivatives. The IR spectrum of XIV differed from XV only by the absence of the 10.4μ absorption.

RESULTS AND DISCUSSION

The carboxyl function of eleostearic acid has been employed to generate eleven new derivatives while maintaining the 9, 11, 13 conjugated triene system characteristic of α- and β-eleostearic acid and their derivatives. The synthetic routes employed in the preparation of these products are described in Figure 1.

α-Eleostearyl alcohol (III) was prepared by the reaction of α-eleostearic acid (I) with lithium aluminum hydride by the method of Lighthelm (5). The product, which melts very close to room temperature (25 C), was distilled at 128-129 C/0.005 mm Hg. β-Eleostearyl alcohol (IV) was prepared in a similar fashion from β-eleostearic acid (II) and was found to melt at 56-58 C. Although III was reported to isomerize to IV when vacuum distillation was attempted at 150-154 C/0.2 mm Hg (5), it was obtained without isomerization under the conditions employed by the present investigators. To insure that III did not isomerize to IV, the trimethylsilyl ethers of III and IV, i.e., V and VI, were prepared and characterized. The data in Table I demonstrate the melting and/or boiling points of III, IV, V, and VI and the refractive indices of V and VI. The IR and UV spectral data on III, IV, V, and VI are shown in Tables II and III, respectively. The data in Table I indicate that III and IV have different physical properties and that V and VI have very similar but different physical characteristics. A comparison of IR data shows the absence of the 10.4μ absorption which is characteristic of cis,trans conjugated olefinic unsaturation in IV and VI, while III and V possess this absorption band. Moreover, the data in Table III show the absorption maxima of IV and VI being more intense (larger molar absorptivity) than those of III and V, which is in agreement with previous experience (6). These data show that III has been prepared and purified via vacuum distillation without isomerization to IV. Moreover, the UV spectral data for IV compare very favorably with that of Lighthelm (5).

Initial efforts to demonstrate the myriad of products which can be prepared from eleostearic acid involved the preparation of four diamides from aliphatic diamines. Thus, I was reacted with ethylene diamine, 1,3-diaminopropane, and 1,4-diaminobutane to yield VII, VIII, and X in high yields under relatively milk conditions. II was also reacted with 1,3-diamino propane to give IX in good yield. VII, VIII, IX, and X are white crystalline solids with melting points above 100 C.

In work recently conducted by Turner (7), it has been shown that hydroxamic acids may have some potential as plant growth regulators. Since the tung tree often blooms too early in the spring, it seemed reasonable that the hydroxamic acid of eleostearic acid could have some activity in delaying its bloom. To this end, the hydroxamic acid (XI) of I was synthesized. IR and elemental analysis data were employed to confirm the preparation of the product.

In an effort to prepare additional novel derivatives of eleostearic acid which could be employed in polyurethane coatings that dry by autoxidation, the isocyanate of II was synthesized. This product, XII, was formed by the action of ethyl chloroformate and sodium azide on II to yield the isocyanate in 45% yield. This material may be reacted with prepolymers containing excess hydroxyl functions to limit the mol wt during polymer preparation and to engender air drying character to the coating. The methyl urethane derivative (XIII) of IV has been prepared to demonstrated the utilization of eleostearyl alcohol with isocyanate terminated polyurethane prepolymers. This reaction could also be employed to limit the mol wt of the prepolymer and/or to improve the air-drying properties of the polymer.

TABLE II

Infrared Spectra of Compounds III, VI, V, and VI

Monomer	Infrared Spectral Data (μ)
III	3.0 (O-H Stretch) 3.3-3.5 (C-H Stretch) 7.25 (C-H bend) 10.1 (trans, trans conjugated olefinic unsaturation) 10.4 (cis, trans conjugated olefinic unsaturation)
IV	3.0 (O-H Stretch) 3.3-3.5 (C-H Stretch) 7.25 (C-H bend) 10.1 (trans, trans conjugated olefinic unsaturation)
V	8.0 (Si-C Stretch) 11.4-11.9 ($(CH_3)_3$Si-O band) 10.1 (trans, trans conjugated olefinic unsaturation) 10.4 (cis, trans conjugated olefinic unsaturation)
VI	8.0 (Si-C Stretch) 11.4-11.9 ($(CH_3)_3$ Si-O band) 10.1 (trans, trans conjugated olefinic unsaturation)

TABLE III

Ultraviolet Spectral Data on Compounds III, IV, V, and VI

Monomer	Ultraviolet spectral data (mμ)	Molar absorptivity x 10^{-4}
III	262[a]	–
	272 (maximum)	5.16
	282	–
IV	258[a]	–
	268 (maximum)	6.40
	279	–
V	262[b]	–
	272 (maximum)	5.14
	282	–
VI	258[b]	–
	268 (maximum)	6.08
	279	–

[a] Spectrum obtained in ethanol.

[b] Spectrum obtained in cyclohexane.

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