Synthesis and Characterization of Polyethoxylate Surfactants Derived from Phenolic Lipids

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ABSTRACT: Polyethoxylates from cardanol and from cardol, the main component phenolic lipids in technical cashew nut-shell liquid derived from the replenishable source *Anacardium occidentale*, were obtained by reaction with ethylene oxide under base-catalyzed conditions. Oligomeric mixtures resulted. In the cardanol series, the first six members of the mixture were independently synthesized for characterization purposes by a variety of reactions. The members in the oligomeric mixture were separated by HPLC, and the composition was determined by ^{1}H NMR spectroscopy and by chromatography. These studies were preparatory to surfactant and biodegradation studies involving comparison with commercially available polyethoxylates derived from petrochemical nonylphenol.

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KEY WORDS: Anacardic acid, cardanol, cardol, cashew, ethylene oxide, HPLC, NMR of polyethoxylates, nonylphenol polyethoxylate.

The economic importance of nonionic surfactants (1,2) for detergent formulations has increased considerably in the past three decades, and more attention is being paid to their environmental compatibility, necessitating proof of their biodegradability under natural conditions. Although test criteria exist as required by legislation, detailed knowledge of the environmental fate of nonionic surfactants and of their biodegradability in sewage treatment plants is vital. Important nonionic surfactant families are the polyethoxylates based on fatty alcohols or alkylphenols. *t*-Nonylphenol ethoxylates have many industrial, commercial, institutional, and domestic uses since they are very efficient and cost-effective surfactants. The environmental occurrence of alkylphenols and their ethoxylates has been reviewed extensively (3,4), although only raw materials of petrochemical origin were discussed and no reference was made to phenolic materials derived from natural sources. However, a preliminary publication (5) described the use of cashew phenolic lipids for producing ethoxylates as well as their biodegradability. The present paper gives full experimental information relating to the synthesis and characterization of those polyethoxylates. The basis of the project was the supposition that a biosynthesized oleo-based product and its derivatives might be more degradable than a conventional nonylpolyethoxylate.

The phenolic lipids from *Anacardiun occidentale* (the cashew) (6,7) constitute a natural mixture of mainly **1**, anacardic acid (70%), and **2**, cardol (20%), together with **3**, 2-methylcardol (5%), and **4**, cardanol (5%) (Fig. 1). Upon industrial processing by heating (8), anacardic acid is decarboxylated to yield the technical product widely known as cashew nut-shell liquid, CNSL, containing principally cardanol (*ca.* 70%) and cardol/2-methylcardol together with some polymeric material. Each component phenol contain saturated, monoene, diene, and triene constituents, as shown. Cashew phenols are replenishable raw materials from a number of countries, notably India and Brazil, as in ethanol in the latter country and thence a source of ethylene for the potential formation of ethylene oxide by hydrochlorination or catalytic oxidation.

The objective of the present work was to prepare polyethoxylates from each unsaturated component phenol and from the fully saturated analogs, to characterize the constituents of the resulting mixtures, and then to study their biodegradability compared with the petrochemically derived *t*-nonylphenol polyethoxylate. Although the reaction of cardanol with ethylene oxide was noted briefly (9), the members of the mixture were not characterized and their biodegradability was not studied. An ethoxylated product from cardanol has been patented (10) based on the present work.

Cashew phenols have many other industrial uses (8), and their ozonization has been described (11).

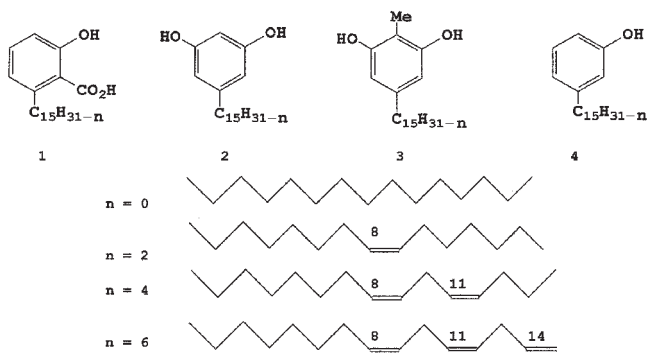

FIG. 1. Formulae of cashew phenols from *Anacardium occidentale*.

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Abbreviations: ASTM, American Society for Testing and Materials; bp, boiling point; BSS, British Standard Specification; CNSL, cashew nut-shell liquid; HPLC, high-performance liquid chromatography; mp, melting point; NMR, nuclear magnetic resonance; ODS, octadecylsilane; THF, tetrahydrofuran; TLC, thin-layer chromatography; UV, ultraviolet.

EXPERIMENTAL PROCEDURES

Materials. Intermediates were obtained from Aldrich Chemical Co (Milwaukee, WI). CNSL was obtained from 3M Research Ltd. (Harlow, Essex, United Kingdom). Raw cashew nuts were supplied by Wigglesworth and Co. Ltd. (London, United Kingdom).

Chromatography. Thin-layer chromatography (TLC) was carried out on 0.25 mm silica gel GF254 and column chromatography on Kieselgel 60 [70–230 mesh, British Standard Specification (BSS)] or, where improved resolution was required, on Kieselgel 60 (230–400 mesh, BSS).

Preparative high-performance liquid chromatography (HPLC) was carried out on a Gilson modular auto-prep system with 21.4 mm (i.d.) column prepacked with functionalized silica gel (5 µm particle size).

Analytical HPLC was carried out with a PerkinElmer LC-55 variable wavelength ultraviolet (UV) spectrophotometer, two Altex metering pumps (Model 110A), a Rikadenki recorder, and a Columbia Scientific Instruments Supergrator 3A computing integrator, and, more recently, a Jones Chromatography JC6000 computing integrating system. The reversed-phase partition experiments were conducted with 5 µm Magnusphere and Spherisorb (Waters, Elstree, United Kingdom) bonded with octadecylsilane (ODS) in 250 × 4.6 mm stainless steel columns for phenols and a Dynamax (Houston, TX) 5 µm aminopropyl column for polyethoxylates.

Analysis of phenols. A gradient elution system was used with solvent A (acetonitrile/water/acetic acid, 66:22:2) and solvent B [tetrahydrofuran (THF), 100%] according to the following two programs: for **1**, and a flow rate of 2.7 mL/min, time (min) and composition (%) were: 0, 100% A; 25, 70% A, 30% B; 38, 0% A, 100% B; 52, 100% A; and for **2**, with a flow rate of 2 mL/min: 0, 100% A; 20, 100% B; 25, 100% A. Solutes were 5% in diethyl ether, with injections of 5–10 µL and UV detection at 275 nm.

Analysis of polyethoxylates. A gradient elution system was based on solvent A (20% THF in *n*-hexane and solvent B (10% water in isopropanol) at a flow rate of 1 mL/min, time (min) and compositions (%): 0, 98% A, 2% B; 60, 50% A, 50% B; 65, 98% A, 2% B; 70, 98% A, 2% B. Solutes (200 µg) were dissolved in solvent A (20 µL), and UV detection was at 275 nm. It was essential to clean columns with THF, water, methanol, acetonitrile, dichloromethane, and isooctane followed by the reverse of this sequence.

Commercially available HPLC-grade solvents were filtered and degassed before use.

Spectroscopy. Proton nuclear magnetic resonance (NMR) spectroscopy was obtained with a Varian CF-T 20 (80 MHz Fourier transform) or JEOL JNM FX-200 (200 MHz), depending on the expected complexity of the spectra and the peak resolution required. Spectra were recorded in $CDCl_3$, $(CD_3)_2CO$, or $(CD_3)_2SO$ with tetramethylsilane as internal standard. For the NMR analysis of samples from polyethoxylation reactions, 1% solutions in $CDCl_3$ were used.

Mass spectra were obtained on an EMI EM902 double-focusing spectrometer.

Microanalyses were performed by Butterworths (Teddington, Surrey, United Kingdom) Micronalytical Laboratories and by MEDAC Ltd. (Uxbridge, Middlesex, United Kingdom).

*Separation of cardanol, **4**, from technical CNSL. (i) Mannich reaction (12) for removal of cardol.* A mixture of technical CNSL (60.92 g), 40% aqueous formaldehyde solution (20 mL, 26 mmol), and diethylene triamine (2.5 g, 25 mmol) in methanol (250 mL) was allowed to stand at ambient temperature for 30 min, after which time two layers had separated, an upper reddish solution and a lower dark solid. Water (40 mL) was added to the decanted upper phase, and the mixture was extracted with light petroleum (3 × 50 mL). Evaporation of the combined extracts gave a red residue that, as measured by TLC and HPLC, contained cardanol, some cardol, a small amount of 2-methylcardol, and polymeric material. Distillation *in vacuo* gave three fractions: (i) 3.42 g, boiling point (bp) 160°C, (ii) 11.27 g, bp 160–180°C, and (iii) 13.24 g, bp 180–220°C. The total yield was 27.93 g (46%). Fractions (ii) and (iii), as analyzed by HPLC, contained saturated cardanol, cardanol monoene, diene, and triene. Generally, this method resulted in a residual cardol level of about 2%.

(ii) Base addition method (13). Typically, technical CNSL (151 g, 0.5 mol; ave. molecular weight 302) containing cardanol (86.9%), cardol (10.3%), and 2-methylcardol (2.3%) was treated with diethylene triamine (0.5 mol) and the mixture allowed to stand for 24 h at ambient temperature. Distillation *in vacuo* afforded a 62.3% recovery of cardanol containing cardanol (97.7%) and cardol (2.0%).

(iii) Phase separation method (14). Technical CNSL (53.1 g) in butane-1,4-diol (50 mL) was extracted with light petroleum (500 mL) in a continuous extraction apparatus (lighter-than-water type); concentration of the petroleum layer yielded cardanol (44.7 g, 84.2%). Dilution of the brown lower phase with water and extraction with light petroleum led to the recovery of cardol (8.4 g) containing some 2-methylcardol. The method generally reduced the level of cardol to 0.5–0.9%. If technical CNSL was recovered from pentane-1,5-diol, residual cardol was 0.1%.

Separation of cardol by column chromatography (15). Technical CNSL (52.17 g) was added to a wide-bore glass column (6.5 cm i.d. × 50 cm) containing silica gel H (250 g, type 60, article 7736; Merck, Alton, Hampshire, United Kingdom). Stepwise elution with petroleum/diethyl ether mixtures gave cardanol (41.64 g, 80%), cardol (6.14 g, 12%), and 2-methylcardol (1.10 g, 2%). Four similar separations were carried out with the same column.

*Separation of anacardic acid, **1**, from CNSL. Precipitation of metallic salts (16).* Whole cashew nuts (500 g) suspended in liquid nitrogen were cracked by light hammering to obtain the shells (348.7 g) free from kernels. The shells were coarsely ground in a blender, and CNSL was extracted with carbon tetrachloride (1000 mL) for 6 h. Further crushing of the shells and extraction for 12 h with carbon tetrachloride (1500 mL), followed by filtration and evaporation of the combined extracts, gave CNSL (145.7 g, 29.1%). Lead hydroxide was added to this material in methylated spirit (300 mL). [Lead hydroxide was prepared from lead nitrate (70.6 g, 212

mmol) in water (400 mL) and sodium hydroxide (17.0 g, 424 mmol) in water (250 mL), followed by filtration and copious washing.] The suspension was stirred at ambient temperature for 16 h, and the precipitated lead anacardate was filtered and washed with methylated spirit (100 mL). Anacardic acid, liberated by treatment of the precipitate with 3 M hydrochloric acid (200 mL), was extracted with diethyl ether (3 × 100 mL), dried (sodium sulfate), and evaporated *in vacuo* to give the final product (84.1 g, 58%).

Phase separation of CNSL (14). CNSL (2.03 g) in light petroleum (20 mL, 60–80°C) was shaken with butane-1,4-diol (2 mL), and the separated upper phase evaporated *in vacuo* to give anacardic acid (1.07 g), free from cardol by TLC. Second and third extractions each with 10 mL of solvent afforded 0.24 and 0.22 g, respectively, giving a total recovery of 1.53 g (75.3%). Dilution of the residual aqueous phase with water and extraction with light petroleum gave cardol containing a small amount of 2-methylcardol. Extraction also was carried out continuously in a glass extractor with a slightly improved yield but at a cost of increased experimental time.

Spectroscopic properties of component phenolic lipids. Cardanol (**4**) typically (8) contained 49.2% triene, 18.1% diene, 28.4% monoene, and 4.3% saturated. λ_{max} (nm, ε): 201, 16,582; 273, 1356 cm^{-1} mol^{-1} L^{-1}. δ_H ($CDCl_3$): 0.80–0.90 (CH_3, *t*), 0.88–1.59 (n-CH_2, *m*, 27H), 1.85–2.25 (CH_2CH=, *m*, 4H), 2.56 (CH_2Ar, *t*, 2H, *J* = 7.4 Hz), 2.9 [$CH_2(CH=)_2$, *m*], 5.05–5.42 (CH=, CH_2=CH–, *m*, 4H), 6.63–6.80 (HAr, *m*, 3H), 6.95–7.05 (HAr, *m*, 1H). *m/z* reqd. [for saturated, monoene, diene, and triene constituents, respectively]: 304.514, 302.499, 300.483, 298.468; found 304.1, 302.2, 300.1, 298.1.

Cardol (**2**) typically (8) contained 74.7% triene, 19.2% diene, and 6.1% monoene. λ_{max} (nm, ε): 207, 3306; 273, 209; 278, 169 cm^{-1} mol^{-1} L^{-1}. δ_H ($CDCl_3$): 0.80–0.90 (CH_3,*t*), 0.89–1.59 (n-CH_2, *m*, 27H), 1.85–2.25 (CH_2C=, *m*, 4H), 2.54 (CH_2Ar, *t*, 2H, *J* = 7.4 Hz), 2.9 [$CH_2(CH=)_2$, *m*], 5.05–5.45 (CH=, CH_2=C, *m*, 4H), 6.20–6.34 (HAr, *m*, 3H). *m/z* reqd. 320.508, 318.492, 315.476, 314.461; found 320.2, 318.2, 316.2, 314.2.

2-Methylcardol (**3**) constituents are similar to cardol. λ_{max} (nm, ε): 207, 4399; 273, 324; 278, 169 cm^{-1} mol^{-1} L^{-1}. δ_H ($CDCl_3$): 0.89–1.59 (n-CH_2, *m*, 27H), 1.85–2.25 (CH_2C=, *m*, 4H), 2.54 (CH_2Ar, *t*, 2H, *J* = 7.4 Hz), 2.6–2.9 [$CH_2(CH=)_2$, *m*], 2.98 (MeAr, *s*, 3H), 6.35 (HAr, *s*, 3H). *m/z* reqd. 334.535, 332.519, 330.503, 328.487; found 334.4, 332.4, 330.4, 328.4.

*Preparation of side-chain saturated component phenols. (i) 3-Pentadecylphenol (**4**, n = 0).* Cardanol (10.32 g) in ethanol (100 mL) containing 5% Pd-C (1.5 g) was hydrogenated at constant atmospheric pressure for 8 h until hydrogen (1680 mL) had been absorbed. The mixture released under nitrogen was filtered and the filtrate evaporated *in vacuo* to give 3-pentadecylphenol (10.28 g, 99%). λ_{max} (nm, ε): 207, 1603; 212, 1705; 268, 456; 278, 420 cm^{-1} mol^{-1} L^{-1}. δ_H ($CDCl_3$): 0.89–1.33 (n-CH_2, *m*, 29H), 2.53 (CH_2Ar, *t*, 2H, *J* = 7.4 Hz), 6.63–6.81 (HAr, *m*, 3H), 7.09–7.18 (HAr, *m*, 1H). *m/z* reqd. 304.514; found 304.2.

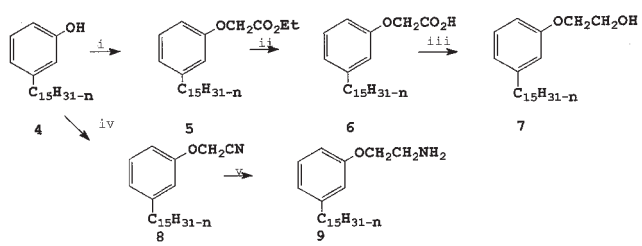
*(ii) 1,3-Dihydroxy-5-pentadecylbenzene (**2**, n = 0).* Cardol (1.03 g) in ethanol containing 5% Pd-C (0.21 g) was hydrogenated until hydrogen uptake ceased after 4 h. Recovery as described for 3-pentadecylphenol yielded saturated cardol (0.98 g, 96%). λ_{max} (nm, ε): 207, 5473; 273, 530; 279, 525 cm^{-1} mol^{-1} L^{-1}. δ_H ($CDCl_3$): 0.88–1.59 (n-CH_2, *m*, 29H), 2.55 (CH_2Ar, *t*, 2H, *J* = 7.4 Hz), 6.30–6.35 (HAr, *s*, 2H), 6.43 (HAr, *s*, 1H). *m/z* reqd. 320.508; found, 320.4.

*(iii) 1-Hydroxy-6-pentadecylbenzoic acid, (**1**, n = 0).* Anacardic acid (10.13 g) was hydrogenated in ethanol (100 mL) in a similar way with catalyst (1.43 g) and hydrogen (1642 mL) to give **1** (10.99 g, 98%). λ_{max} (nm, ε): 207, 7681; 240, 1681; 304, 1045 cm^{-1} mol^{-1} L^{-1}. δ_H ($CDCl_3$): 0.84–1.60 (CH_2, *m*, 29H), 2.94 (CH_2Ar, *t*, 2H, *J* = 7.41 Hz), 6.79 (HAr, *d*, 1H, *J* = 7.32 Hz), 6.89 (HAr, *d*, 1H, *J* = 7.33 Hz), 7.36 (HAr, *t*, 1H, *J* = 8.06 Hz), 10.99 (HO, CO_2H, *bs*, 2H, D_2O exch.). *m/z* reqd. 348.525; found 348.4.

*(iv) Ethyl anacardate (from **1**).* Anacardic acid (4.23 g) was refluxed in ethanol (100 mL) containing concentrated sulfuric acid (2 mL) for 24 h. The mixture was evaporated *in vacuo* to a small volume, diethyl ether (20 mL) was added, and the ethereal solution was washed with 5% sodium bicarbonate solution, dried with sodium sulfate, and evaporated to give ethyl anacardate (3.97 g, 87%). δ_H ($CDCl_3$): 0.89–1.58 (n-CH_2, *m*, 29H), 1.41 (Me, *t*, 3H, *J* = 7.1 Hz), 2.89 (CH_2Ar, *t*, 2H, *J* = 7.4 Hz), 4.45 (OCH_2, *q*, 2H, *J* = 7.1 Hz), 6.71 (HAr, *m*, 1H), 7.17–7.24 (HAr, *m*, 2H). *m/z* reqd. 374.417; found: 376.1.

*Synthesis of the first ethoxylate from 3-pentadecylphenol (**4**, n = 0). Scheme 1: Synthesis of intermediates.* Reagents: (i) Na, PhH, $BrCH_2CO_2Et$; (ii) KOH, H_3O^+; (iii) $LiAlH_4$, THF; (iv) K_2CO_3, PhH, $BrCH_2CN$; (v) $LiAlH_4$, THF. Compounds **8** and **9** were potential intermediates for the synthesis of **7** by reduction and diazotization, respectively.

*(i) 2-(3-Pentadecylphenoxy)ethyl acetate (**5**, n = 0).* 3-Pentadecylphenol (10.05 g, 33.0 mmol) in benzene (100 mL) containing sodium metal (0.761 g, 33.7 mmol) was refluxed for 3 h. Ethyl bromoacetate (7.521 g, 45.1 mmol) was then added, and the mixture was stirred and refluxed for 18 h, after which sodium bromide was filtered off and the benzene was removed *in vacuo*. TLC indicated some residual starting material and the less polar product. These were separated by flash chromatography (2% ethyl acetate, 98% chloroform) to give 2-(3-pentadecylphenoxy)ethyl acetate (7.86 g, 61%), which was recrystallized to afford white needles, melting point (mp) 37–38°C; ($C_{25}H_{42}O_3$ requires C, 76.97%; H, 10.84%; found: C, 76.95%; H, 10.59%). λ_{max} (nm, ε): 207, 3407; 273, 490 cm^{-1} mol^{-1} L^{-1}. δ_{max} ($CDCl_3$): 0.89–1.33 (n-CH_2, Me, *m*, 31H), 2.57 (Me, *t*, 3H, *J* = 7.4 Hz), 2.53 (CH_2Ar,



SCHEME 1. Synthesis of intermediates.

t, 2H, *J* = 7.4 Hz), 4.22–4.33 (OCH_2, *q*, 2H, *J* = 7.7 Hz), 4.61 (OCH_2CO, *s*, 2H), 6.69–6.83 (HAr, *m*, 3H), 7.15–7.25 (HAr, *m*, 1H).

*(ii) 2-(3-Pentadecylphenoxy)acetic acid (**6**, n = 0).* Pentadecylphenoxyethyl acetate (1.11 g, 2.87 mmol) in dioxane (10 mL) containing potassium hydroxide (1.25 g, 21.0 mmol) was refluxed for 18 h. Upon cooling, the mixture resulted in a solidified organic layer. This was acidified with 3 M HCl (5 mL) and extracted with diethyl ether (3 × 20 mL). The combined extracts were dried and filtered, and the filtrate was evaporated to dryness *in vacuo* (TLC indicated that no starting material remained) to give the product (0.97 g, 93%), which crystallized from light petroleum as white needles, mp 102–104°C ($C_{23}H_{38}O_3$ requires C, 76.24%; H, 10.49%; found: C, 76.47%; H, 10.39%). λ_{max} (nm, ε): 207, 5436; 273, 1922 cm^{-1} mol^{-1} L^{-1}. δ_H ($CDCl_3$): 0.89–1.33 (n-CH_2, Me, *m*, 31H), 2.53 (CH_2Ar, t, 2H, *J*, 7.4 Hz), 4.83 (OCH_2CO, s, 2H), 6.69–6.83 (HAr, *m*, 3H), 12.31 (HO_2C, *s*, 1H, D_2O exch.).

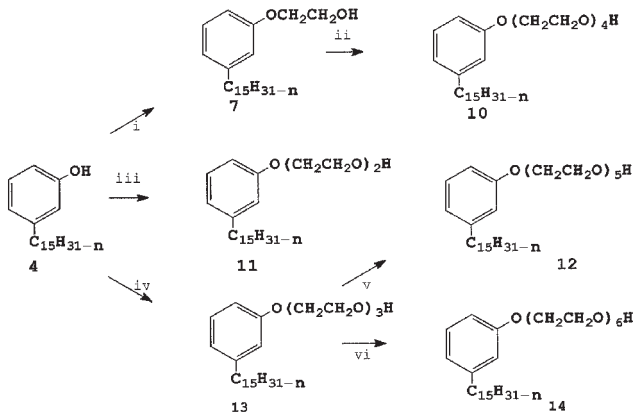
*(iii) 2-(3-Pentadecylphenoxy)ethanol (**7**, n = 0).* To 2-(3-pentadecylphenoxy)acetic acid (4.05 g, 11.2 mmol) in THF (12 mL), lithium aluminum hydride (2.09 g, 55.0 mmol) was added under nitrogen, and the mixture was stirred at ambient temperature for 18 h. Ethyl acetate (1 mL), 3 M NaOH (1 mL), and water (2 mL) were then added, and the mixture was extracted with diethyl ether (3 × 10 mL). The combined extracts were dried, filtered, and evaporated *in vacuo* to give the product as an oil (3.27 g, 78%), which was purified by flash chromatography ($C_{23}H_{40}O_2$ requires C, 78.41%; H, 11.57%; found: C, 78.20%; H, 11.76%).

In a similar method, cardanol (**4**) was reacted with ethyl bromoacetate to give 2-cardanoxyethyl acetate (**5**), which was reduced with lithium aluminum hydride to give the product, 2-cardanoxyethanol (**7**). λ_{max} (nm, ε): 207, 2467; 275, 479 cm^{-1} mol^{-1} L^{-1}. δ_H ($CDCl_3$): 0.88–1.59 (n-CH_2, Me, *m*, 21H), 2.23 (CH_2CH=, *m*, 4H), 2.57 (CH_2Ar, *t*, 2H, *J* = 7.4 Hz), 3.93–4.60 (CH_2O, *m*, 4H), 5.35–5.42 (CH=, *m*, 4H), 6.71–6.80 (HAr, *m*, 3H), 7.14–7.22 (HAr, *m*, 1H); M^+ [$C_{23}H_{40-n}O_2$ (where n = 0, 2, 4, 6)]. *m/z* reqd. 348.5609, 346.553, 344.537, 342.522; found 348.0, 346.0, 344.0, 342.0.

The remaining saturated oligomers (**10–14**, *n* = 0) and unsaturated members (**10–14**) were synthesized as shown in Scheme 2. The direct route shown to **7** proved less satisfactory than that given in Scheme 1.

Scheme 2: Synthesis of six reference polyethoxylates. Reagents: (i) K (metal), $Cl(CH_2)_2OH$; (ii) K (metal), $Cl(CH_2)_2O(CH_2)_2O$–$(CH_2)_2OH$; (iii) K (metal), $Cl(CH_2)_2O(CH_2)_2OH$; (iv) K (metal), $Cl(CH_2)_2O$–$(CH_2)_2O(CH_2)_2OH$; (v) K (metal), Cl–$(CH_2)_2O(CH_2)_2OH$; (vi) K (metal), $Cl(CH_2)_2O(CH_2)_2O$–$(CH_2)_2OH$.

*Polyethoxylation of phenolic lipids. Scheme 3: (i) 3-Pentadecylphenol polyethoxylate (**15**, n = 0).* 3-Pentadecylphenol (20.6 g, 69.7 mmol) and sodium hydroxide (0.0224 g, 0.55 mmol) were stirred and heated at 180°C for 30 min under nitrogen, followed by introduction of ethylene oxide. Samples were withdrawn every 30 min until polyethoxylation was considered to have reached a sufficient stage. All samples were analyzed by NMR and by HPLC.



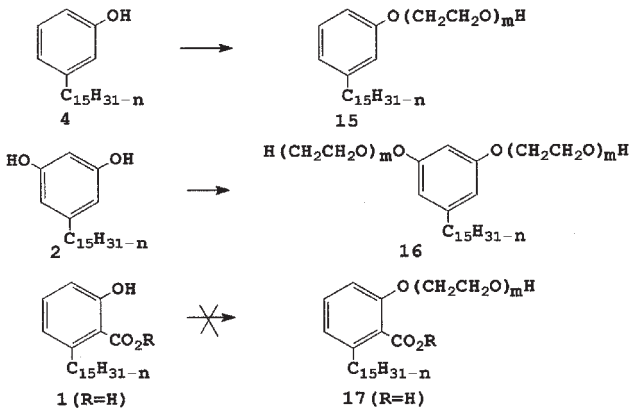
SCHEME 2. Synthesis of six reference polyethoxylates.

*(ii) Cardanol polyethoxylate (**15**).* Cardanol, **4** (21.1 g, 70.3 mmol), and sodium hydroxide (0.023 g, 0.57 mmol) were mixed with stirring under nitrogen at 180°C for 30 min, after which the nitrogen flow was replaced by passage of ethylene oxide. The reaction mixture was sampled for analysis by NMR and HPLC, and after ethoxylation for 10 h the reaction was considered to be complete.

*(iii) Cardol polyethoxylate (**16**).* Cardol, **2** (10.27 g, 32.5 mmol), and sodium hydroxide (0.26 g, 6.5 mmol) were stirred together and heated at 160°C for 30 min under nitrogen. The passage of nitrogen was replaced by ethylene oxide over a period of 10 h with sampling of the reaction mixture at 30-min intervals.

*(iv) 1,3-Polyethoxy-5-pentadecylbenzene (**16**, n = 0).* A solution of cardol polyethoxylate (5.63 g, 5.36 mmol, with an average of 13.8 mol ethylene oxide) in ethanol (100 mL) containing 5% Pd-C (1.43 g) was hydrogenated at ambient temperature and pressure until hydrogen (723 mL) had been absorbed. The mixture was filtered under nitrogen and the filtrate evaporated to dryness *in vacuo* to give (5.24 g, 93%).

*Attempted polyethoxylation of ethyl anacardate (**17**).* Ethyl anacardate (20.61 g) and sodium hydroxide (0.025 g, 0.6 mmol) were stirred together and heated at 180°C under nitrogen for



SCHEME 3. Synthesis of polyethoxylates from cardanol and cardol, where m = number of ethoxylate groups.

30 min. The nitrogen was then replaced by a stream of ethylene oxide, and the reaction was continued for 2 h with sampling and analysis by NMR and HPLC every 30 min. However, it was concluded from the loss of ester chemical shifts in the NMR scans that hydrolysis and subsequent decarboxylation had taken place, leaving insufficient base for catalysis of the ethoxylation reaction, although the polyethoxylation has been claimed (17).

*(vi) Isomerization of cardanol (**4**).* Cardanol (5.3 g) was stirred and heated in diethylene glycol (2 mL) containing triethanolamine (1.31 g, 8.79 mmol) and potassium hydroxide (2.51 g, 44.8 mmol) at 180–190°C under nitrogen. The mixture was cooled, acidified with 3 M sulfuric acid, and extracted with diethyl ether (2 × 20 mL). The combined ether extracts were washed with sodium bicarbonate solution (2 × 20 mL), dried, and evaporated to dryness *in vacuo* to give the product (4.92 g, 89%).

RESULTS AND DISCUSSION

Separation of component phenols of technical CNSL and of natural CNSL. In the separation of cardanol from technical CNSL, vacuum distillation alone (9), although straightforward, is unsatisfactory since cardol always accompanies the cardanol product. Molecular distillation of technical CNSL in a 10-stage still at a lower temperature (18) overcomes this problem and gives a 58% yield of cardanol free from cardol. Although cardol itself is also recoverable in low yield, the method is only applicable to small batches of CNSL. In the separation of cardanol from technical CNSL by the base addition method (13), the preferential salt formation of cardol rather than of cardanol enables the removal of a substantial percentage of cardol in the vacuum distillation. In the Mannich reaction (12), cardol forms a polymer and is more completely removed in the final vacuum distillation. The minor component, 2-methylcardol, is present in small quantities in the final cardanol product since it does not undergo the Mannich reaction. In all distillation procedures, some loss of the triene constituent occurs; thus, the phase separation method (14) at ambient temperature has an advantage because it enables the recovery of both cardol and cardanol from technical CNSL without vacuum distillation.

Furthermore, the phase separation method is applicable to natural CNSL (14) and represents the best approach for the recovery of both anacardic acid and cardol with avoidance of the lead salt precipitation, filtration, and acidification steps. Although column chromatography (15) readily separates cardanol and cardol, the procedure is protracted and solvent consumption is high.

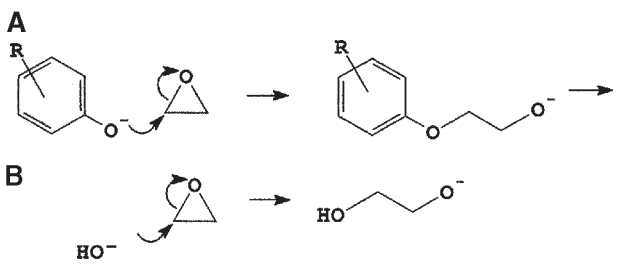


FIG. 2. (A) Formation of first ethoxylate anion (R = $C_{15}H_{31-n}$); (B) formation of minor by-product anion.

Analysis of polyethoxylates. (i) NMR spectroscopy. In the ^{1}H NMR spectrum of cardanol polyethoxylate, compared with that of cardanol, a new pronounced chemical shift appears at δ 3.57 ppm, due to the methylenic protons of the polyethoxy group, as well as a shift due to the terminal hydroxyl group, which is detectable by D_2O exchange. The spectrum also revealed partial loss of the terminal vinyl group and some isomerization of the nonconjugated diene system, which was confirmed by NMR from heating cardanol under basic conditions.

Polyethoxylation of the phenols was accompanied by formation of very small amounts of polyethylene glycol, as reflected by the absorption by methyleneoxy groups at δ 3.63 within the first half hour of reaction time but then with progressive diminution to give predominantly absorption for cardanol polyethoxylate at δ 3.57. From the ratio of the integrated area due to the four aromatic protons at δ 6.4–7.2 to that for the protons of the polyethoxy group (less one for the hydroxyl group), the average number of ethoxy groups relevant to each sample was readily calculated. The mechanisms of the main reaction and of the minor side reaction are depicted in Figure 2.

HPLC analysis. Reversed-phase conditions with gradient elution were found to be the most selective. Thus, a Zorbax ODS column and an eluting solvent of acetonitrile/water, although satisfactory for phenolpolyethoxylates (19), was less satisfactory than a Bondpack semipolar NH_2 type (20) for *t*-octylphenol polyethoxylates with gradient elution and the use of aqueous methanolic solvents. In our experience, the straight methylenic chains in cardanol, cardol, and 3-pentadecylphenolpolyethoxylates rather than the multibranched chains present in commercial *t*-octyl and *t*-nonylpolyethoxylates led to similar resolution and selectivity. Gradient elution based on solvent A (20% THF in hexane) and solvent B (10% water in isopropanol), a

TABLE 1
Retention Times, Peak Areas, and Ethoxylate Numbers for Components of Cardanol Polyethoxylate Obtained by HPLC Analysis[a]

Component	Retention time (min)	Peak area (%)	Ethoxylate number
B	15.24	1.24	2
C	17.47	2.63	3
D	20.01	4.59	4
E	22.36	7.76	5
F	24.64	10.23	6
G	26.99	11.56	7
H	29.14	12.79	8
I	31.32	11.97	9
J	33.45	10.65	10
K	35.45	8.29	11
L	37.73	5.41	12
M	40.16	3.83	13
N	42.45	2.18	14
O	44.59	1.35	15
P	46.30	0.81	16

[a]HPLC, high-performance liquid chromatography.

TABLE 2
Reaction Time for Cardanol Polyethoxylate and Ethoxylate (EO) Numbers (EN) by HPLC (weight and molar-average) and by NMR Spectroscopy[a]

Reaction time (min)	Weight-average EN	Molar-average EN	Average EO units (NMR)
30	0.93	0.62	0.6
60	1.47	1.14	1.0
90	2.14	1.86	1.8
120	6.14	5.71	5.5
150	8.38	7.52	7.2
180	11.62	10.98	10.7
210	14.21	13.44	13.5
240	17.59	16.98	16.9
270	19.67	18.55	18.3
300	22.61	21.33	21.1
330	27.72	27.24	25.9
360	30.11	28.47	28.2
390	35.16	33.02	32.6
420	39.27	37.17	37.2
450	44.56	42.37	42.2
480	50.17	48.51	48.0

[a]NMR, nuclear magnetic resonance; for other abbreviation see Table 1.

Table 4
Polyethoxylation of 3-Pentadecylphenol with EN Determined by HPLC and NMR Spectroscopy[a]

Reaction time (min	Weight-average EN	Molar-average EN	Average EO units (NMR)
30	0.82	0.71	0.7
60	1.47	1.28	1.2
90	2.16	1.82	1.7
120	1.33	1.96	2.0
150	2.51	2.03	2.2
180	3.39	2.74	2.4
210	4.67	4.39	4.0
240	7.18	6.21	6.5
270	11.59	10.12	10.0
300	15.99	14.81	15.2
330	20.03	18.66	18.5
360	25.83	24.29	24.1
390	28.91	27.13	26.9
420	36.62	34.61	32.8
450	40.71	38.68	39.5
480	49.56	47.22	47.1

[a]For abbreviations see Tables 1 and 2.

flow rate of 1 mL/min, a loading of 200 µg solute in 20 µL diethyl ether, and UV detection proved effective. Table 1 represents a typical HPLC run for cardanol polyethoxylate; there were 16 peaks, of which 15 are included in the table. The table also shows the relation between peak area (%), retention time (min), and ethoxylate number. Each ethoxylate peak of the 16 components, from the very minor first ethoxylate, A (retention 13.6 min), to the 16th, P (retention 46.3 min), contains the combined saturated, monoene, diene, and triene constituents for that component.

The first six peaks, A to F, in the chromatogram were first identified by spiking with the six synthetic cardanol polyethoxylates, **7**, **10–14**. Second, by incorporating known weights of each in a known weight of the polyethoxylate mixture, the peak areas could then be used to calculate weight-average and molar-average ethoxylate numbers, respectively. The derived figures were compared with ethoxylate numbers determined from NMR spectroscopy (from the ratio of methylenic to aromatic protons), as shown in Table 2, for the reaction of cardanol with ethylene oxide for 8 h.

TABLE 3
Reaction Time for Cardol Polyethoxylate with EN from HPLC and from NMR Spectroscopy[a]

Reaction time (min)	Weight-average EN	Molar-average EN	Average EO units (NMR)
30	0.42	0.27	0.2
60	1.03	0.66	0.6
90	1.44	0.91	0.9
120	2.61	2.38	2.3
150	3.71	3.21	3.1
180	5.28	4.87	4.9
210	7.41	6.89	6.7
240	10.96	10.31	9.3
270	12.68	11.92	11.4
300	16.23	15.22	14.8
330	18.94	17.81	17.3
360	20.47	19.28	19.9
390	25.56	24.21	22.6
420	26.57	25.17	25.1
450	31.04	29.64	29.3
480	38.11	36.49	34.7

[a]For abbreviations see Tables 1 and 2.

Similar NMR and HPLC analytical procedures were used for the polyethoxylates obtained from the reaction of cardol and from 3-pentadecylphenol, as depicted in Tables 3 and 4, respectively, for 16 reaction samples in each case. In the case of cardol, the lower reaction temperature resulted in a lower extent of polyethoxylation. The first six peaks in the HPLC of 3-pentadecylphenyl-polyethoxylate were identified, as with cardanol polyethoxylate, by spiking with the synthetic compounds **7, 10–14** ($n = 0$), respectively.

Cardanol polyethoxylate, cardol polyethoxylate, and nonylphenol polyethoxylate, with an average of 13, 10, and 8 ethyleneoxy groups, respectively, were studied for surfactancy and biodegradability properties and for comparison with *t*-nonyl polyethoxylate. It is planned that a report of these data will be submitted for publication.

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