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Technical Note

The synthesis of oxime reagents from natural and semi-synthetic phenolic lipid and alkanoic acid resources for the solvent recovery of copper(II)†

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Abstract: In a study of the relationship between structure and efficiency towards recovery of copper(II) by chelation/solvent extraction, a series of homologous aldoximes has been synthesised from natural phenolic lipidic, and fatty lipidic renewable sources, for comparison with commercial reagents prepared from petrochemical sources. From cardanol, in technical cashew nut-shell liquid, isoanacardic aldoxime, [2-hydroxy-4-pentadec(en)yl]aldoxime, and from the natural phenolic lipid, anacardic acid, the isomer, 2-hydoxy-6-pentadec(en)ylaldoxime, have been synthesised. A C_{11} analogue of anacardic aldoxime from *Anacardium giganteum* has been prepared. The isomeric *n*-octyl aldoximes have been synthesised, the *o*- and *p*-isomers from the readily available fatty acid *n*-octanoic acid and the *m*-isomer from cardanol. Related *m*-aldoximes have been prepared from the ketonic intermediates methyl isoamyl and methyl amyl ketones. The solvent extraction properties for copper(II) of the synthesised aldoximes have been compared with those of a current commercial reagent, 2-hydroxy-5-*t*-nonylbenzaldoxime (Acorga 5100, Cytec), and two former extractants, 2-hydroxy-5-*t*-nonylacetophenone ketoxime (SME 529, Shell) and 2-hydroxy-5-*t*-nonylbenzophenone ketoxime (LIX 65N, Henkel). All the aldoximes possessed useful properties in extraction efficiency, notably the isoanacardic and the C_8 aldoximes with the C_8 *o*-isomer, 2-hydroxy-3-*n*-octylbenzaldoxime, exhibited optimal extraction, stripping and phase separation characteristics.

Keywords: solvent extraction; copper; 2-hydroxy-*x*-alkylbenzaldoximes; octanoic acid phenolic lipids; cardanol; anacardic acid and aldoxime; isoanacardic acid and aldoxime; bioresources; octylsalicylaldehydes

INTRODUCTION

Oxime reagents have achieved importance[1] in hydrometallurgical practice for the leach/solvent extraction and electrowinning of copper(II) from minerals occurring in a variety of feed-stocks, leading to the worldwide production of 7700 tonnes of copper per day. Commercial reagents are the current aldoxime, 2-hydroxy-5-*t*-nonylbenzaldoxime (Acorga 5100, originally from Zeneca now Cytec), the formerly used 2-hydroxy-5-*t*-nonylacetophenoneketoxime, SME 529, Shell) and 2-hydroxy-5-*t*-nonyllbenzophenoneketoxime, LIX65N, Henkel, now Cognis), although a great range of alternative LIX hydroxyoxime reagents is now available. Commercial reagents are still based on petrochemical intermediates, 4-*t*-nonylphenols obtained by the alkylation of phenol with C_9 alkenes. In the last decade, aspects of the use of Acorga 5100 have continued to be studied,[2,3] and alternative reagents[4] and technology[5–7] have been investigated worldwide.

The objective of the present work, partially patented and completed some years ago,[8,9] was to synthesise aldoximes and ketoximes from renewable resources. The natural and semi-synthetic phenolic lipids[10] having C_{15}, C_{11} and C_8 side-chains were examined initially and the C_{11} and C_{15}, natural and semi-synthetic, sources are depicted in Fig 1. They comprise cardanol **(1)** from commercial technical cashew nut-shell liquid (CNSL), isoanacardic acid **(2)**, from the carboxylation of cardanol, anacardic acid from natural CNSL (*Anacardium occidentale)* **(3)** and the C_{11} source, anagigantic acid (*Anacardium giganteum)* **(4)**. The readily

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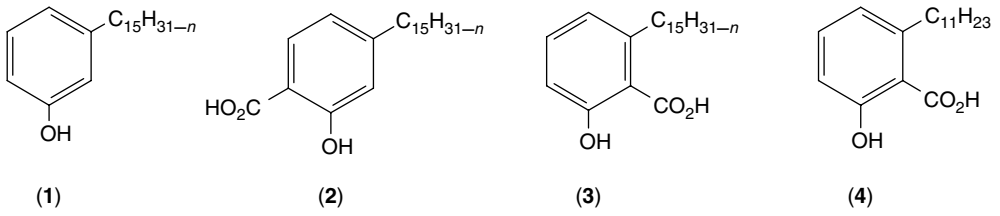
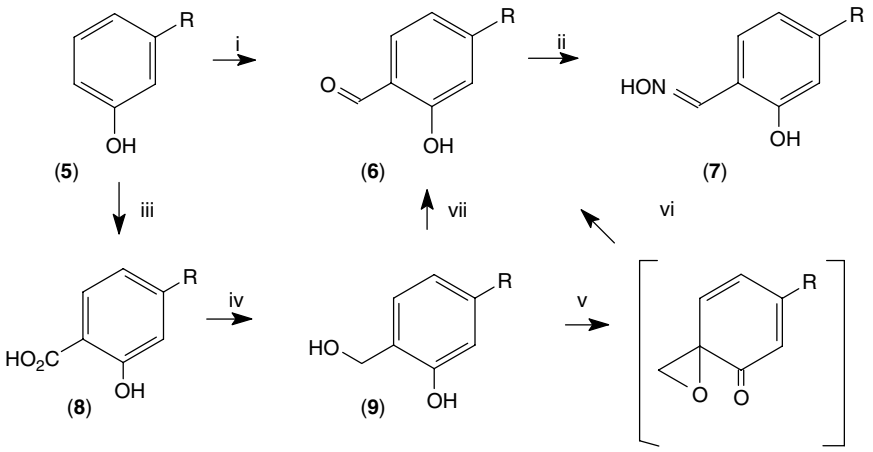
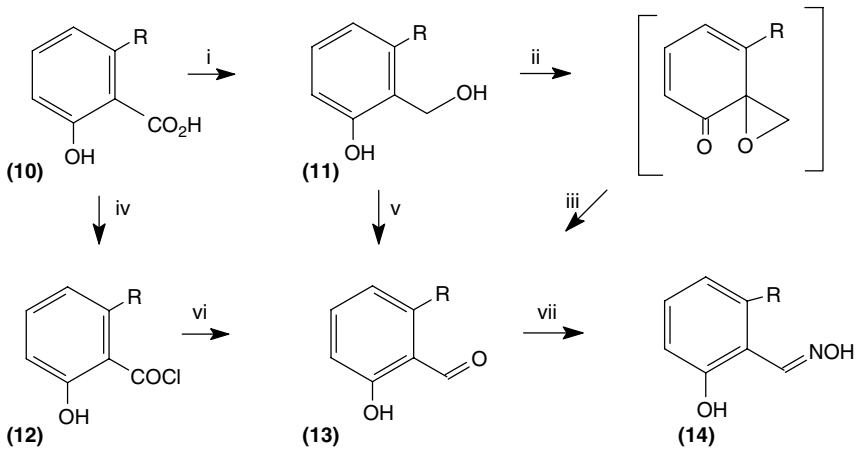


Figure 1. Formulae of phenolic Lipids and structures of unsaturated side chains of **(1)**, **(2)** and **(3)**, $n = 0$, pentadecyl; $n = 2$, pentadeca-8(z) -enyl; $n = 4$, pentadeca- (8z) (11z)-dienyl; $n = 6$, pentadeca-(8z), (11z, (14)-trienyl).



Scheme 1. Synthesis of isoanacardic aldoximes (C_{15}) and other 2-hydroxy-4-alkyl and alkenylbenzaldoximes (**7**, $C_{15}H_{31}$, $C_{15}H_{31-n}$, for C_8 and C_{11} aldoximes, R = C_8 and C_{11}, steps i and ii).



Scheme 2. Synthesis of anacardicaldoximes (2-hydroxy-6-pentadecyl and 2-hydroxy-6-pentadec(en)ylbenzaldoxime, R = $C_{15}H_{31}$, $C_{15}H_{31-n}$).

available lower chain length fatty acids, particularly octanoic acid and C_7 methyl ketones provided other sources of alkyl side chains for C_8 oximes in this work.

The role of chain length, the position of the alkyl group in the benzene ring, branching and unsaturation in the alkyl side chain have been studied in this work. In previous work[11] on aldoximes, only a series of homologous *p*-alkylphenolic aldoximes appears to have been examined.

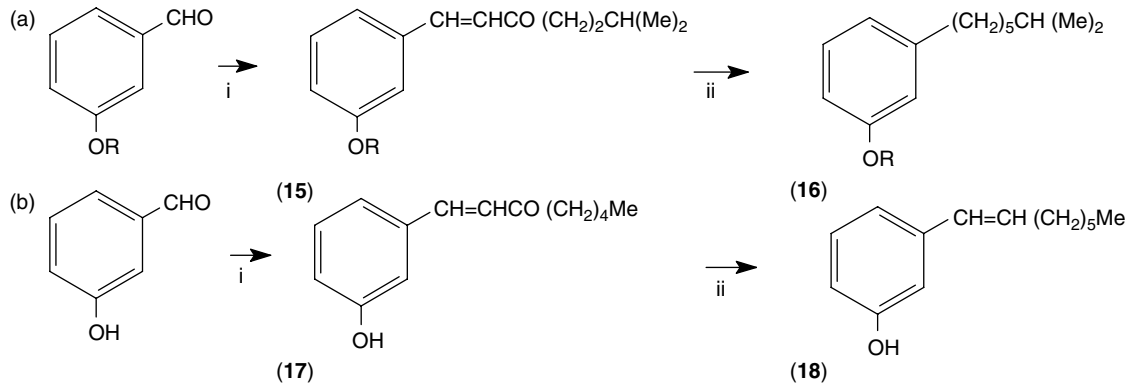
Apart from their replenishability, an advantage of phenolic and alkanoic sources is their biodegradability.[12]

The aldoximes synthesised from natural sources are depicted in Scheme 1 (from semi-synthetic C_8, C_{11}, and C_{15} 3-alkylphenolic lipids), in Scheme 2 (from C_{11} and C_{15} anacardic acids), in Scheme 3 (from branched and unsaturated chain 3-alkylphenols derived from C_8 ketonic intermediates), in Scheme 4 (from *o*- and *p*-substituted C_8 *n*-alkylphenols). In Scheme 5 ketoximes have been synthesised from a C_{15} phenolic lipid. Scheme 6 depicts *p*-substituted reference compounds prepared from petrochemical intermediates.

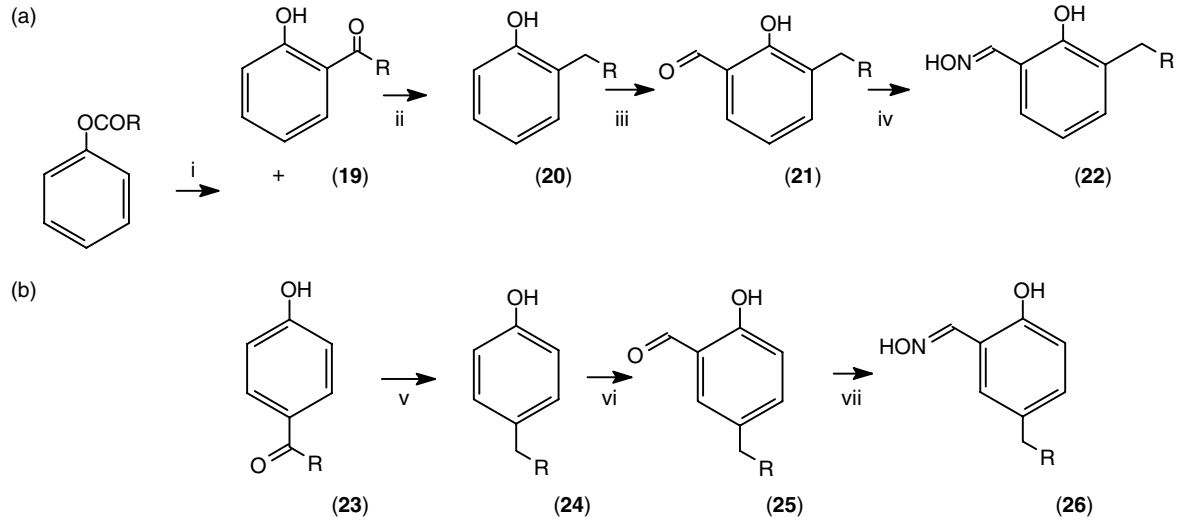
EXPERIMENTAL

Materials

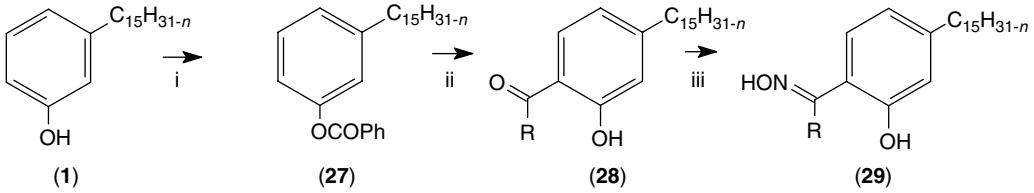
Raw cashew nuts were obtained from Gill, Duffas and Landauer, London SE1 and half shells from Buhler-Miag, Barnet, London. Technical CNSL



Scheme 3. Synthesis of (a) 3-iso-octylphenol and (b) 3-iso-octenylphenol.



Scheme 4. Synthesis of (a) 2-hydroxy-3-*n*-alkyl- and (b) 5-*n*-alkyl benzaldoximes.



Scheme 5. Synthesis of 2-hydroxy-4-pentadecylbenzophenone ketoximes [(a) R = Me and (b) R = Ph].

was supplied by 3M Research Ltd, Harlow, Essex. Chemicals were obtained from Aldrich Chemical Co. *t*-Nonyl and *t*-octylphenols were obtained from ICI Ltd. *Anacardeum giganteum* was made available from Prof T Pastore, University of Brasilia.

Acorga 5100 (50% with *t*-nonylphenol), SME 529 (neat) and LIX 65N (containing 15% volatile which was removed *in vacuo* to constant weight) were obtained from ICI, Shell and Henkel respectively.

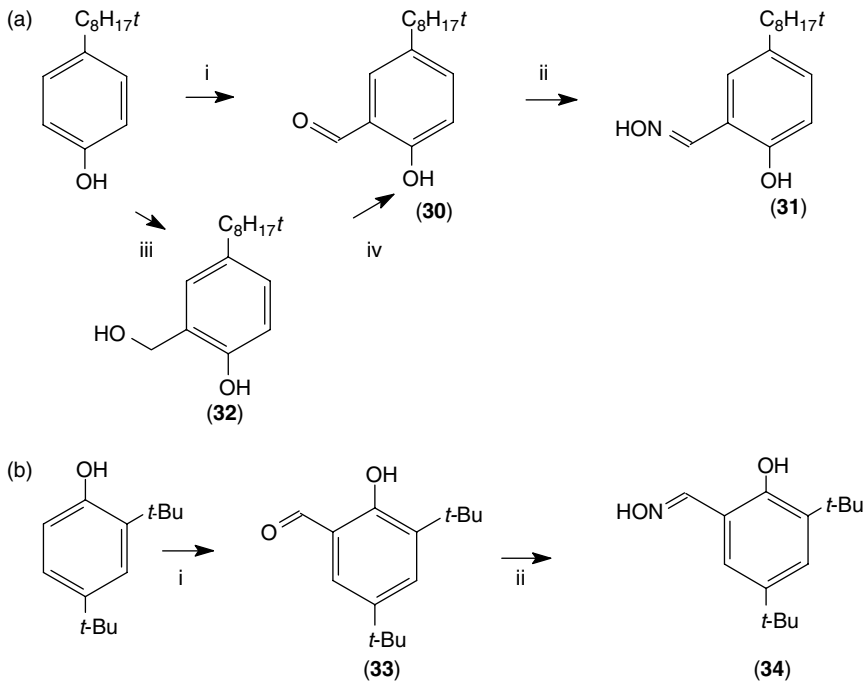
Microanalyses were carried out by Butterworth's Laboratories, Teddington, Middlesex, UK.

Chromatography

Analytical thin layer chromatography (TLC) was effected with Whatman silica gel 60 AMK6F plates ($1'' \times 3''$) with a 250 μm layer and preparative TLC with Merck silica gel 60GF plates (20×20 cm) with a 1 mm layer.

Column chromatography was carried out with BDH silica gel, particle size 0.13–0.25 mm. For flash chromatography, Merck kieselgel 60 (230–400 mesh) was used.

High performance liquid chromatography was carried out with a chromatograph consisting of a Perkin-Elmer spectrophotometer (set at 275 nm) (model LC55). This was equipped with an 8cm flow-through cell, an Altex (Anachem) metering pump (model 110A), a Rheodyne injection system (model 7120) with a 20cm loop, a Servoscribe recorder (model 1s) and a Chemtronics Supergrator 3A programmable computing integrator. Gradient elution was effected with a second similar Altex pump and an Altex programmer (model 420). Stainless steel columns



Scheme 6. Synthesis of (a) 2-hydroxy-5-*t*-octylbenzaldoxime and of (b) 2-hydroxy-3, 5-di-*t*-butylbenzaldoxime.

(25 cm × 0.46 cm) were packed with ODS Spherisorb of particle size 5 µm. Operating pressures were in the range 77–153 atm with acetonitrile/water (33/17 v/v) and a flow rate 1–3 cm^3 min^{-1}.

Spectroscopy

Infrared spectra were recorded on a Perkin Elmer 1420 spectrophotometer. Proton NMR spectra were determined with Varian T60 (60 mHz) and CFT20 instruments with tetramethylsilane as internal standard.

Mass spectra were obtained on a modified AEI MS920 instrument and accurate mass determinations were made by the Physico Chemical Measurement Unit, Harwell, UK.

Preparation of semi-synthetic phenolic lipids

*Saturated, (15:0)-cardanol (**1**; n = 0)*

This compound was obtained by (a) catalytic hydrogenation in ethanol solution of **1** with 5% palladium–carbon catalyst and hydrogen and by (b) chemical reduction of **1**. Cardanol (96 g) in methylated spirit (300 cm^3) was mixed with hydrazine hydrate (61.30 g) in methylated spirit (200 cm^3) and the stirred mixture warmed at 40 °C for 7 days with continuous aeration. After this time, argentation TLC monitoring indicated almost complete reduction to the saturated compound and the solution was concentrated *in vacuo* to approximately 150 cm^3, cooled, acidified with hydrochloric acid (50 cm^3) and extracted with diethyl ether (3 × 200 cm^3). The ethereal extract was washed with sodium chloride solution, dried (sodium sulfate), and the ether evaporated to leave a solid which was crystallised (60–80 °C light petroleum) to give pale cream crystals (65 g).

*Saturated, (15:0)-isoanacardic acid (**2**, n = 0), 2-hydroxy-4-pentadecylbenzoic acid*

Isoanacardic acid **(2)** was obtained by carboxylation of cardanol[13] and (150 g) was reduced with a total of hydrazine hydrate (126 g) in methylated spirit (950 cm^3) at 40 °C with aeration over 10 days to give the saturated acid by crystallisation (light petroleum, 40–60 °C) as white crystals, 34.2 g.

*Saturated, (15:0)-anacardic acid (**3**, n = 0), 2-hydroxy-6-pentadecylbenzoic acid*

Anacardic acid **(3)**,(135.4 g,) in methylated spirit (975 cm^3) was reduced[14] with a total of hydrazine hydrate (103.9 g), in methylated spirit (1180 cm^3) at 50 °C over 4 days to give after crystallisation (light petroleum 40–60 °C), mp 80–83 °C.

*3-Undecylphenol **(5)***

Anagigantic acid **(4)** essentially the saturated constituent, was extracted as described[15] and decarboxylated as for anacardic acid[16] by heating with 2% calcium hydroxide at 130–140 °C for 1 h until evolution of carbon dioxide ceased. The cooled mixture was extracted with light petroleum, filtered and concentrated to give a brown oil which was purified by preparative TLC to give 3-undecylphenol, R_f 0.35 ($CHCl_3$), identical chromatographically and spectroscopically with synthetic material.[15]

Synthesis of oximes

*Unsaturated, isoanacardic aldoxime [2-hydroxy-4-pentadec(en)ylbenzaldoxime] (**7**, R = $C_{15}H_{31-n}$ (n = 0, 2, 4, 6)) (Scheme 1)*

Three methods were employed for the preparation of the aldehyde **(6)**. By adaptation from a formylation

method,[17] from isoanacardic acid **(8)** by reduction to isoanacardic alcohol **(9)**[15] and oxidation with pyridinium chlorochromate or, by sodium periodate[14] (to the dienone), followed by irradiation, and by a method,[18] comprising formation of a Mannich base oxidation to a Schiff's base and final acid hydrolysis. The first procedure was the best and gave,[8] after flash chromatography, isoanacardic aldehyde (**6**, R = $C_{15}H_{31-n}$) in 78% yield, R_f 0.75 ($CHCl_3$/EtOAc, 95:5), containing a trace of the 6-isomer and cardanol; δ_H (CCl_4) 0.75–1.05 [m, Me], 1.1–1.65 [m, $(CH_2)_n$], 1.8–2.35 [CH_2CH=], 2.4–2.95 [$CH_2(CH=)_2$, CH_2Ar, m], 4.7–5.55 [CH=CH, CH_2=, m], 6.30–7.40 [HAr, m], 9.7 [1H, CHO, s], 10–11 [1H, bs, H-bonded OH]. Repetition afforded similar yields.

(a) Isoanacardic aldehyde (19.8 g) in pyridine (200 cm^3) containing hydroxylamine hydrochloride (37.6 g) was refluxed for 2h (TLC monitoring). The cooled mixture was diluted with water, acidified with dilute hydrochloric acid (150 cm^3), washed with 6% sodium hydrogen carbonate (50 cm^3) and aqueous sodium chloride to neutrality and ethereally extracted. The combined extracts were dried (sodium sulfate), filtered and concentrated to give the product, 18.52 g (85.6%) (**7**, R = $C_{15}H_{31-n}$); R_f 0.48 ($CHCl_3$/EtOAc, 95:5); δ_H (CCl_4), 0.78–1.05 [t,Me], 1.08–1.65 [m, $(CH_2)_n$], 1.80–2.30 [m, CH_2CH=], 4.80–5.55 [m, CH=CH, CH_2=], 6.68–7.32 [m, HAr], 8.20 [CH=N], 8.30–9.0 [bs H-bonded OH, D_2O exch].

(b) Isoanacardic aldehyde (2.04 g) in ethanol (75 cm^3) containing potassium acetate (1.44 g) and hydroxylamine hydrochloride (1.01 g) was refluxed for 8h. Work-up as before, afforded an oil (1.84 g, 82.6%) identical with the product from (a).

*(15:0)-Isoanacardic aldoxime (**7**, R = $C_{15}H_{31}$), 2-hydroxy-4-pentadecylbenzaloxime (Scheme 1)*

This was prepared[8] (a) from (15:0)-isoanacardic aldehyde, obtained from (15:0)-isoanacardic acid and (b) from (15:0)-cardanol.[8]

Isoanacardic aldehyde, 4-pentadecylsalicylaldehyde (**6**, R = $C_{15}H_{31}$), was obtained as pale yellow crystals, mp 50–54 °C (0.61 g); δ_H (CCl_4), 0.7–1.1 [3H, t, Me], 1.2–1.65 [26H, m, $(CH_2)_{13}$], 2.55–2.85 [2H, t, CH_2Ar], 7.15–7.98 [3H, m, HAr], 10.85 [1H s, H-bonded CHO], 12.1 [1H, s, OH, D_2O exch], identical with the oxidation product of isoanacardic alcohol with pyridinium chlorochromate and that (b) from reaction of (15:0)-cardanol by formylation.

Reaction of isoanacardic aldehyde with hydroxylamine hydrochloride in pyridine solution at 100 °C gave isoanacardic aldoxime (**7**, R = $C_{15}H_{31}$); *m/z*, M^+; found: 347.2819; $C_{22}H_{37}NO_2$ requires 347.2815.

*Saturated anacardic aldoxime (**14**, R = $C_{15}H_{31}$) (Scheme 2)*

Anacardic aldehyde (**13**, R = $C_{15}H_{31}$) was prepared by three different methods (a) oxidation of anacardic alcohol with pyridinium chlorochromate,[15] (b) through the dienone[14] and by the preferred method (c) from anacardic acid chloride,[8] and was identical with the product from the alcohol by oxidation; ν_{max} (film, cm^{-1}), 2950 (H-bonded OH), 1680 (C=O); δ_H (CCl_4), 0.8–1.0 [3H, t, Me], 1.06–1.55 [26H, m $(CH_2)_{13}$], 2.7–3.0 [2H, t, CH_2Ar], 6.55–7.24 [3H, m, HAr], 10.55 [1H, s, CHO], 12.2 [1H, s, H-bonded OH, D_2O exch]. The oxime was prepared and characterised as described previously.[8]

*Anacardic aldoxime (**14**, R = $C_{15}H_{31-n}$) (Scheme 2) (prepared by SPS Ahdan)*

Anacardic alcohol was prepared by reduction of unsaturated anacardic acid with lithium aluminium hydride and converted to the aldehyde (**13**, R = $C_{15}H_{31-n}$), by (a) oxidation, (b) from the acid chloride by hydride reduction[9] and (c) from the acid chloride by Rosenmund reduction.

(a) Anacardic alcohol (3.3 g) in dichloromethane (125 cm^3) was treated with pyridinium chlorochromate complex (6.50 g) and the mixture stirred for 90min at ambient temperature (TLC monitoring). After filtration and washing of the filtrate with water, decolourising charcoal was added, the solution was dried (sodium sulfate) and evaporated to give the aldehyde as a pale yellow oil (2.51 g, 76%); R_f 0.81 ($CHCl_3$/EtOAc (95:5); ν_{max} (film, cm^{-1}), 3300 (OH), 1600 (C=O, H-bonded).

(c) Anacardic acid (**10**, R = $C_{15}H_{31-n}$) (3.44 g) was suspended in light petroleum (19 cm^3) containing pyridine (0.02 g) and reacted with thionyl chloride (0.62 cm^3) at 30 °C for 2 h. The mixture was filtered and the filtrate evaporated to leave the acid chloride **(12)** as an oil; ν_{max} (film, cm^{-1}), 3100 (OH), 2825 (CH_2), 1770 (COCl), 1570 (C=C).

Anacardic acid chloride (**12**) (5.0 g) in dry xylene (9.2 cm^3) containing palladium–barium sulfate catalyst (0.276 g) and thiourea catalyst poison (0.055 g) was heated at 140–150 °C and hydrogen was passed into the mixture. The hydrogen chloride evolved was passed into water and the resulting solution titrated with standard sodium hydroxide to determine the extent of reaction. The cooled mixture was treated with decolourising charcoal, filtered and the xylene removed *in vacuo* to leave anacardic aldehyde (4.6 g, 92%); R_f 0.78; ν_{max} (film, cm^{-1}), 3300 (OH), 2950 (CH_2), 1600 (C=O, H-bonded); δ_H (CCl_4), 0.76–1.06 [3H, t, Me], 1.06–1.58 [m, $(CH_2)_n$], 1.58–2.14 [CH_2CH=], 2.6–3.08 [CH_2Ar, $CH_2(CH=)_2$], 5.0–5.58 [CH=CH], 6.48–7.38 [3H, m, HAr], 10.55 [1H, s, CHO], 12.12 [1H, s, OH, D_2O exch].

Anacardic aldehyde (1.0 g), with hydroxylamine hydrochloride (1.0 g) in ethanol (10 cm^3) containing pyridine (1 cm^3) was refluxed for 1h. The mixture was filtered, the filtrate was washed with water, dried and evaporated to give the oxime (**14**, R = $C_{15}H_{31-n}$) as an oil (0.59 g, 57%);) R_f 0.30; ν_{max} (film, cm^{-1}), 2950 (OH), 1620 (C=N), 980 (N–O); δ_H (CCl_4), 0.75–1.08 [3H, t, Me], 1.08–1.72 [m,

$(CH_2)_n$], 1.76–2.38 [CH_2CH=CH, m], 2.40–3.18 [CH_2Ar, $CH_2(CH=CH)_2$ m], 4.76–5.58 [CH=CH, m], 6.4–7.52 [HAr, m], 8.0–9.0 [br s, CH=N–, OH, D_2O exch].

A mixture of anacardic and isoanacardic aldehydes together with some of the *p*-isomer was formed in the unselective Gattermann, Hoesch and in Reimer–Tiemann reactions. In our work, (15:0)-cardanol with either chloroform or bromoform with sodium hydroxide solution gave a 31% yield of the *o*-aldehyde. The reaction in unreported yield has also been described.[19]

2-Hydroxy-4-undecylbenzaldoxime (7, R = $C_{11}H_{23}$) (Scheme 1)

By the general formylation procedure, 3-undecylphenol (**5**, R = $C_{11}H_{23}$) (0.55 g) gave crude 2-hydroxy-4-undecylbenzaldehyde (0.44 g), which was purified by column chromatography to give an oil, 0.14 g (**6**, R = $C_{11}H_{23}$), R_f 0.78 ($CHCl_3$). The aldehyde (0.40 g) in ethanol (50 cm^3) containing potassium acetate (0.20 g) and hydroxylamine hydrochloride (0.22 g) was refluxed for 5h. The cooled mixture was diluted with water (100 cm^3) extracted with ether (50 cm^3), the ethereal extract dried and concentrated to give a yellow oil (0.33 g), the oxime (7, R = $C_{11}H_{23}$), R_f 0.27, which solidified to afford a creamy crystalline solid; δ_H ($CDCl_3$), 0.72–0.98 [3H, t, Me], 1.05–1.4 [18H, m, $(CH_2)_{11}$], 2.30–2.72 [2H, t, CH_2Ar], 6.72–7.30 [3H, m, HAr], 8.20 [1H, s, CH=N–], 8.4–9.4 [2H, bs, H-bonded OH, D_2O exch]. *m/z*, M^+; found: 291.2193; $C_{18}H_{29}NO_2$ requires 291.2191.

2-Hydroxy-4-n-octylbenzaldoxime (7, R = n-C_8H_{17}) (Scheme 1)

3-*n*-Octylphenol (**5**, R = C_8H_{17}) was used, prepared as described[20] by the reaction of 3-benzyloxybenzaldehyde with 1-bromoheptane and lithium followed by hydrogenolysis of the benzyl and secondary hydroxyl groups, and by ozonolysis of cardanol **(1)** followed by reduction.[20]

By the general formylation method, 3-*n*-octylphenol gave a pale yellow golden oil (0.35 g), which upon column purification afforded 2-hydroxy-4-*n*-octylbenzaldehyde (**6**, R = C_8H_{17}) as an oil, R_f 0.82 ($CHCl_3$).

The aldehyde (0.06 g) in pyridine (7.0 cm^3), containing hydroxylamine hydrochloride (0.26 g), was refluxed and then maintained at 50 °C for 16h and gave upon work-up, as before, a pale brown oil which solidified; R_f 0.26 (found: C, 72.69; H, 9.50; N, 5.48; $C_{15}H_{23}NO_2$ requires C, 72.29; H, 9.24; N, 5.62%); *m/z*, M^+; found: 249.1726; $C_{15}H_{23}O_2N$ requires 249.1723.

2-Hydroxy-4-iso-octylbenzaldoxime (7, R = iso-C_8H_{17}) (Schemes 1 and 3)

The use of either 3-methoxy or 3-hydroxybenzaldehyde was adapted from related work.[21]

3-Methoxybenzaldehyde (1.40 g) and methyl isoamylketone (3.42 g) were reacted in the presence of 2 mol dm^{-3} sodium hydroxide solution (10 cm^3) and stirred and warmed at 70–80 °C for 4 h (TLC monitoring). Column chromatography afforded the Claisen condensation product (**15**, R = Me) as an oil {δ_H,CCl_4, 0.82–0.96 [6H, d, 2Me], 1.14–2-68 [3H, m, CH, CH_2], 2.36–2.5.8 [2H, t, CH_2CO], 3.65 [3H, s, MeO], 6.42–7.52 [2H, d, $\mathcal{J}$16Hz, CH=CH], 6.86–7.12 [4H, m, HAr]}, 2.0 g of which was catalytically hydrogenated in ethanol containing 5% palladium–carbon (0.70 g) until absorption of hydrogen (198 cm^3) occurred and TLC monitoring indicated reduction of the double bond. The mixture was filtered and the ethanol removed *in vacuo* to afford an oil, the keto intermediate (1.78 g, 88%) {δ_H,CCl_4, 0.84–0.96 [6H, d, 2Me], 1.08–1.88 [m, 5H], 2.08–2.36 [2H, t, CH_2CO], 2.56–2.74 [2H, t, CH_2Ar], 3.72 [3H, s, MeO], 6.36–7.24 [4H, m, HAr]}, which was reduced by the Wolff–Kishner method to give 3-methoxy-iso-octylbenzene (**16**, R = Me). The carbonyl compound (1.1 g) in digol (9 cm^3) containing potassium hydroxide (0.5 g) and hydrazine hydrate (20 cm^3) was refluxed at 150 °C for 2h. The mixture was cooled, diluted with water and extracted with ether (100 cm^3), the ethereal extract was washed with water, dried (sodium sulfate) and evaporated to give an oil (0.80 g, 77%) consisting of 3-methoxy-iso-octylbenzene. This was separated chromatographically from the simultaneously formed phenol, 3-iso-octylphenol (**16**, R = H) {δ_H $CDCl_3$, 0.68–0.92 [6H, d, 2Me], 1.04–1.92 [9H, m, $4CH_2$, CH], 2.42–2.72 [t, CH_2Ar], 6.54–7.42 [4H, m, HAr]}, resulting from partial demethylation; **16** was also obtained by demethylation of the methyl ether with boron tribromide.

*2-Hydroxy-4-iso-octylbenzaldehyde (**6**, R = C_8H_{17}) (Scheme 1)*

By the general formylation method, 3-iso-octylphenol (0.70 g) gave 2-hydroxy-4-iso-octylbenzaldehyde (TLC monitoring) which was purified by preparative TLC to give the aldehyde as a pale brown oil; R_f 0.92 (found: C, 75.90; H, 9.25; $C_{15}H_{22}O_2$ requires: C, 76.92; H, 9.40%).

2-Hydroxy-4-iso-octylbenzaldehyde (0.70 g), potassium acetate (0.71 g) and hydroxylamine hydrochloride (0.45 g) were refluxed in ethanol for 16h (TLC monitoring) and upon work-up, as before, gave an oil, the oxime (7, R = iso-C_8H_{17}) which was purified (TLC); R_f 0.56 (found: C, 72.30; H, 9.43; C_{15} $H_{23}NO_2$ requires: C, 72.29; H, 9.24%).

2-Hydroxy-4-(oct-1-enyl)benzaldoxime (7, R = C_8H_{15})

3-Hydroxybenzaldehyde (5.47 g), and heptan-2-one (16.02 g) with 3 mol dm^{-3} sodium hydroxide (50 cm^3) were heated and stirred for 16h (TLC monitoring). The cooled mixture was diluted with water (100 cm^3) and extracted with ether (3 × 50 cm^3). The aqueous layer was acidified, extracted with ether (3 × 100 cm^3), the extract dried (sodium sulfate) and the solvent

evaporated to give a brown oil (9.11 g). Column purification afforded the Claisen condensation product **(17)** as an oil (4.74 g), 3-(3-oxo-oct-1-enyl)phenol. Clemmensen reduction of the carbonyl group with amalgamated zinc in hydrochloric acid solution afforded 3-(oct-1-enyl)phenol **(18)** as an oil.

By the general formylation procedure, 3-(oct-1-enyl) phenol (0.26 g) gave a pale brown oil (0.50 g), 2-hydroxy-4-(oct-1-enyl)benzaldehyde (**6**, R = C_8H_{15}). The product (0.29 g) in ethanol containing potassium acetate (0.24 g) and hydroxylamine hydrochloride (0.17 g) was refluxed for 9h and after work-up afforded the oxime, as an oil, which was purified by preparative TLC (found: C, 72.9; H, 8.45; $C_{15}H_{21}NO_2$ requires: C, 72.87; H, 8.50%).

*2-Hydroxy-5-n-octylbenzaldoxime **(26)** (Scheme 4)*
Phenyl *n*-octanoate: redistilled thionyl chloride (21.07 g) was slowly added to a mixture of phenol (15.01 g) and octanoic acid (24.50 g) over 1h and hydrogen chloride removed by warming, after which the mixture was distilled to give the product, bp 210–230 °C/16–19mm Hg (32.24 g, 91.8%).

4-Octanoyl- and 2-octanoylphenol: phenyl octanoate (14.05 g) in tetrachloroethane (50 cm^3) was treated with anhydrous aluminium chloride (11.22 g) over 1h and the mixture was then heated to reflux for 5h (TLC monitoring). To the cooled mixture water (75 cm^3) was added and on standing gave an aqueous brown oily mixture which was extracted with ether. The ethereal extract was washed with 1 mol dm^{-3} sodium hydroxide (3 × 50 cm^3) until the extract was colourless. The ethereal layer was dried (sodium sulfate) and evaporated *in vacuo* to give a pale brown oil, which was distilled, bp 120–130 °C/1 mm Hg to give 2-octanoylphenol (**19**, R = C_7H_{15}) (5.31 g); R_f 0.51. Acidification of the alkaline solution afforded a brown oil which solidified. Filtration, and drying of the solid followed by crystallisation (60–80 °C light petroleum) gave 4-octanoylphenol (**23**, R = C_7H_{15}); R_f 0.25 ($CHCl_3$/EtOAc, 95:5); mp 61–62 °C, (2.82g).

4-Octanoylphenol (1.42 g) in digol (20 cm^3) containing 98% hydrazine hydrate (1.0 cm^3) and potassium hydroxide (0.90 g) was refluxed for 5h (TLC monitoring) and then at 180 °C for 40h after removal of volatile material. Water (50 cm^3) was added to the cooled mixture which, after acidification, was extracted with ether, the ethereal extract was dried and the solvent evaporated to give an oil (1.17 g) which solidified and was purified by preparative TLC to afford 4-*n*-octylphenol (**24**, R = C_7H_{15}); δ_H (CCl_4), 0.80–1.10 [3H, t, Me], 1.16–1.80 [12H, m, $(CH_2)_6$], 2.36–2.74 [(2H, t, CH_2Ar], 5.05 [1H, s, OH, D_2O exch], 6.78–7.28 [4H, dd, J8Hz, HAr],

By the general formylation method, 4-*n*-octylphenol (1.10 g) afforded an orange oil (1.09 g) which was purified by preparative TLC to give 2-hydroxy-5-*n*-octylbenzaldehyde (**25**, R = C_7H_{15}); R_f 0.70 (found: C, 76.98; H, 9.86; $C_{15}H_{22}O_2$ requires: C, 76.92; H, 9.40%); δ_H (CCl_4), 0.68–0.95 [3H, t, Me], 1.05–1.66 [12H, m, $(CH_2)_6$], 2.33–2.72 [2H, t, CH_2], 6.78–7.42 [3H,dd, J8Hz, m, HAr], 9.65 [1H, s, CHO], 10.90 [1H, s, OH, D_2O exch].

2-Hydroxy-5-*n*-octylbenzaldehyde (0.33 g) in ethanol (50 cm^3) containing hydroxylamine hydrochloride (0.28 g), and potassium acetate (0.39 g) was refluxed for 26h (TLC monitoring) and worked up to give the crude product which was purified by column chromatography to give the oxime, as pale yellow cubic crystals (**26**, R = C_7H_{15}) (0.26 g). R_f 0.40 (found: C, 72.40; H, 9.37; N, 5.33; $C_{15}H_{23}NO_2$ requires: C, 72.29; H, 9.24; N, 5.62%).

2-Hydroxy-3-n-octylbenzaldoximes (22) (Scheme 4)
2-Octanoylphenol (1.45 g) in digol (28 cm^3) containing hydrazine hydrate (1.3 cm^3) and potassium hydroxide (1.45 g) was refluxed for 2h and water then distilled to raise the temperature to 180 °C (TLC monitoring). After 4h at this temperature, the cooled mixture was worked up similarly to give an oil (0.75 g) which was purified by column chromatography to yield 2-octylphenol (**20**, R = C_7H_{15}); R_f 0.78.

By the general formylation procedure, 2-*n*-octylphenol (1.02 g) gave an orange oil (1.13 g), which was purified by preparative TLC to give 2-hydroxy-3-*n*-octylbenzaldehyde (**21**, R = C_7H_{15}) (found: C, 77.3; H, 9.99; $C_{15}H_{22}O_2$ requires: C, 76.92; H, 9.40%).

2-Hydroxy-3-*n*-octylbenzaldehyde (0.29 g) in ethanol (50 cm^3) containing hydroxylamine (0.23 g), and potassium acetate (0.36 g) was refluxed for 20h (TLC monitoring). Work-up as before gave an oil which was purified by column chromatography to afford the oxime (**22**, R = C_7H_{15}) as a pale brown solid (0.16 g); R_f 0.53 (found: C, 72.81; H, 9.87; $C_{15}H_{23}NO_2$ requires: C, 72.29; H, 9.24%).

*2-Hydroxy-4-pentadecylbenzophenone ketoxime (**29**, R = Ph, n = 0) (Scheme 5)*
Cardanol (1, $n = 0$) (2.0 g) in dry pyridine (5 cm^3) was treated with benzoyl chloride (1.5 cm^3) and the mixture warmed for 5h. The cooled mixture was diluted with water, basified with sodium hydroxide solution and the precipitate worked up to give 3-pentadecyl benzoate (2.785 g) **(27)**. The dry product (1.366 g) was mixed with finely pulverised anhydrous aluminium chloride (0.616 g) and, after HCl evolution at 165 °C had ceased (15min), the cooled mixture was worked up to give the crude product, 2-benzoyl-5-pentadecylphenol (**28**, R = Ph, $n = 0$) (1.348 g) which was purified by chromatography and crystallised (light petroleum) to give needles, mp 46–47 °C. Reaction in pyridine with hydroxylamine hydrochloride afforded the ketoxime (**29**, R = Ph, $n = 0$), mp 51–53 °C.

In a similar way from cardanyl acetate, the acetyl analogue (**29**, R = Me, $n = 0$) was prepared. Cardanol (**1**, $n = 0$) (4.0 g) and acetic anhydride (10 cm^3) were treated with conc sulfuric acid (1 drop) and the mixture reacted at ambient temperature for 1h (TLC monitoring) and then heated at 80 °C for 5 h. Work-up gave the acetate (3.948 g). Cardanyl acetate

(1.0 g) and finely powdered aluminium chloride (0.628 g) heated to 120 for 1h and then to 180 (15 min) (TLC monitoring) upon work-up gave yellow crystals of 2-acetyl-5-pentadecylphenol (**28**, R = Me, $n = 0$), which was converted in pyridine solution with hydroxylamine hydrochloride to the oxime, 2-hydroxy-5-pentadecyl ketoxime (**29**, R = Me, $n = 0$).

2-Hydroxy-5-(1,1,3,3-tetramethylbutyl)benzaldoxime ***(31)*** *(Scheme 6)*
This reference compound was synthesised by the formylation of 4-*t*-octylphenol, and by hydroxymethylation to **32** as described[15] followed by oxidation with pyridinium chlorochromate, and oximation of the aldehyde, **30**.

By the general formylation method, *t*-octylphenol (9.76 g) afforded a pale green brown oil (9.53 g), which was column-purified to give the aldehyde, 2-hydroxy-5-(1,1,3,3-tetramethylbutyl)benzaldehyde **(30)** (found: C, 77.18; H, 9.79; $C_{15}H_{22}O$ requires: C, 76.92; H, 9.40%).

The aldehyde (2.32 g) in ethanol (80 cm^3) containing hydroxylamine hydrochloride (91.53 g) and potassium acetate (2.35 g) was refluxed for 6h (TLC monitoring) and worked up to give the oxime **(31)** as a colourless solid, which was purified by crystallisation (1.81 g, 73%) (found: C, 72.69; H, 9.55; N, 5.20; $C_{15}H_{23}NO_2$ requires: C, 72.29; H, 9.24; N, 5.62 %).

2-Hydroxy-5-*t*-nonylbenzaldoxime was prepared in a similar way and from 2-hydroxymethyl-4-*t*-nonylphenol, by oxidation to the aldehyde and oximation.

2-Hydroxy-3,5-di-t-butylbenzaldoxime ***(34)*** *(Scheme 6)*
By the formylation method, 2,4-di-*t*-butylphenol (15.1 g) gave an oil which was purified by column chromatography to give the aldehyde **(33)**, 14.28 g (84%); δ_H ($CDCl_3$), 1.28, 1.42 [18H, 2s, 2 *t*-Bu], 7.08–7.42 [3H, m, HAr], 9.84 [1H, s, CHO], 11.83 [1H, s, OH, D_2O exch].

The aldehyde (7.82 g) in ethanol (200 cm^3) containing potassium acetate (12.4 g) and hydroxylamine hydrochloride (8.4 g) was heated at 80 °C for 8h and left for 18 h. The cooled mixture was diluted with water (200 cm^3) and extracted with light petroleum (3 × 50 cm^3), the extract was washed with water, dried (sodium sulfate) and the solvents evaporated to leave a pale yellow viscous oil which crystallised with light petroleum to afford pale yellow crystals, 7.31 g (88%) of the oxime, 2-hydroxy-3,5-di-*t*-butylbenzaldoxime **(34)**, δ_H ($CDCl_3$), 1.28, 1.42 [18H, 2s, 2 *t*-Bu], 6.92–7.42 [3H, m, HAr], 8.34 [1H, s, CH=N–], 10.46 [2H, s, OH, D_2O exch].

RESULTS AND DISCUSSION

Synthesis of *o*-hydroxybenzaldehydes and *o*-hydroxyoximes

Scheme 1 depicts the general route to **7**, 2-hydroxy-4-alkyl and alk(en)ylbenzaldoximes which commence with *m*-substituted phenols such as the readily available cardanol **(1)** and the acid **(2)**. More recently, a procedure (Tyman and Payne, unpublished work), to be described elsewhere, has been found for avoiding the use of hexamethylphosphoramide (HMPA). For the C_8 aldoximes and the C_{11} aldoxime only steps (i) and (ii) were used in syntheses.

Scheme 1

Reagents: (i) EtMgBr, $(CH_2O)_n$, HMPA,
(ii) $NH_2OH.HCl$, py, (iii) KOH,
CO_2, 180 °C, (iv) $LiAlH_4$, (v) $NaIO_4$,
(vi) hν, (vii) $PyClCrO_4$(R = $C_{15}H_{31}$,
$C_{15}H_{31-n}$; i,ii, only for C_8 and C_{11} oximes)

Scheme 2 illustrates the synthesis of **14**, anacardic aldoxime, 2-hydroxy-6-pentadec(en)yl benzaldoxime and the C_{11} analogue from the less available sources (**3** and **4**). Selective catalytic hydrogenolysis avoided the use of hydride reductions. A C_8 sidechain analogue is also available from ozonolysis of anacardic acid[20] and by alkylation of 6-methyl-2-hydroxybenzoic acid.[15]

Scheme 2

Reagents: (i) $LiAlH_4$, (ii) $NaIO_4$, (iii) hν,
(iv) $SOCl_2$, py, (v) $PyClCrO_4$, (vi) H_2, Pd–$BaSO_4$
or $LiAlH_4$, *t*-BuOH, (vii) $NH_2OH.HCl$
(R = C_8H_{17}, $C_{11}H_{23}$, $C_{15}H_{31}$, $C_{15}H_{31-n}$)

Scheme 3 gives routes from certain long chain 2-alkanones, to the *m*-substituted intermediates (**16** and **18**), required for the *m*-iso-octyl and *m*-octenyl compounds **(7)**, R = C_8H_{17} and iso-C_8H_{15} respectively.

Scheme 3

Reagents : (a) (R = Me), (i) KOH,MeCO
$(CH)_2CH(Me)_2$, (ii) H_2, Pd–C; N_2H_4, KOH
(b) (i) KOH, $MeCO(CH_2)_4Me$, (ii) Zn/Hg, HCl

Scheme 4 depicts the use of readily available octanoic acid to provide routes to **22**, 2-hydroxy-3-*n*-octyl-, and **26**, 2-hydroxy-5-*n*-octyl-benzaldoximes, based on 2-octyl- and 4-octylphenol respectively. The proportion of 2- and 4-hydroxy isomers is solvent- and temperature-dependent, solvent and low temperature affording the *p*-isomer and high temperature, in the absence of solvent, the *o*-isomer.[22] In the present work the conditions were selected to obtain both compounds for the synthesis of the final compounds, **22** and **26**.

Scheme 4

Reagents: (a) (b) (i) $AlCl_3$; HCl, (ii), (v) N_2H_4,
KOH, (iii),(vi) EtMgBr, $(CH_2O)_n$, HMPA,
(iv) (vi) $NH_2OH.HCl$

Scheme 5 shows the route to ketoximes **(29)** (R = Ph and Me) from saturated cardanol. The nature of the conditions involving evolution of HCl, precluded the use of unsaturated cardanol.

Scheme 5

Reagents: (a) (i) **1**, $n = 0$, PhCOCl, py, (ii) $AlCl_3$; HCl, (iii), $NH_2OH.HCl$

(b) **1**, $n = 0$, (i)Ac_2O, H_2SO_4, (ii) $AlCl_3$; HCl, (iii) $NH_2OH.HCl$

Scheme 6 gives routes to reference compounds (a) *p-t*-octylbenzaldoxime **(31)**, its *p-t*-nonyl analogue and (b) to a readily available isomer, the 3,5-di-*t*-butylbenzaldoxime **(34)**.

Scheme 6

Reagents: (a) (i) EtMgBr, $(CH_2O)_n$, HMPA, (ii) $NH_2OH.HCl$, (iii) NaOH, CH_2O, (iv) $PyClCrO_3$

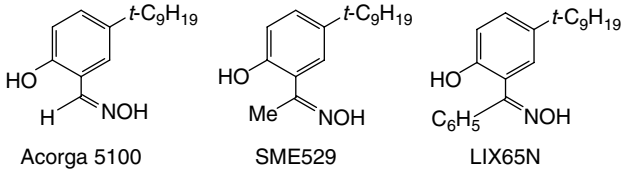
(b) (i) EtMgBr, $(CH_2O)_n$, HMPA, (ii) $NH_2OH.HCl$

Evaluation of new aldoximes and ketoximes for the solvent extraction of copper(II) with recovery by acidic stripping

Anacardic aldoxime (**14**, R = $C_{15}H_{31}$) and 2-hydroxy-5-*t*-nonylacetophenone ketoxime (SME529) have been compared on an equimolar basis and the results described.[8] Promising results were indicated although **14** proved less soluble than the SME529. The mixed unsaturated anacardic aldoxime overcame this but it was relevant to experiment with an aldoxime derived from a more readily available raw material such as cardanol and the derived isoanacardic aldoxime (**7**, R = $C_{15}H_{31-n}$). This was compared with the reagents shown in Fig 2, 2-hydroxy-5-*t*-nonylaldoxime (Acorga), 2-hydroxy-5-*t*-nonylacetophenone ketoxime (SME 529) and 2-hydroxy-5-*t*-nonylphenylbenzophenone ketoxime (LIX 65N) in equimolar solutions.

The results have been described[9] and again were promising except that phase separation at the stripping stage fell outside the desired specification. Equally, the C_{11} aldoxime (**7**, R = $C_{11}H_{23}$) gave excellent extraction but unsatisfactory phase separations.

The C_{15} and C_{11} linear chains are homogeneous and believed to be the cause of slow separation by comparison with that found for commercial reagents, where the linearity is probably on average between C_5 and C_6 and the oximes are complex mixtures[3] resulting in more soluble copper chelates. Similarly the pure compounds **31** and **34** from petrochemical sources were less effective than Acorga 5100.



Acorga 5100 SME529 LIX65N

Figure 2. Structures of current and former extraction reagents.

By contrast with the longer side chain compounds, the C_8 isomeric aldoximes, 2-hydroxy-3-*n*-octylbenzaldoxime **(22)**, 2-hydroxy-4-*n*-octylbenzaldoxime **(7)**, 2-hydroxy-5-*n*-octylbenzaldoxime **(26)**, when compared with Acorga 5100, by the same procedure,[9] exhibited promising extraction, recovery and notably phase separations, (particularly with the *o*-compound, **22**), which were not markedly different from that of the commercial reagent.

Compared with the linear C_8 compounds, 2-hydroxy-4-oct-1-enylbenzaldoxime (**6**, R = C_8H_{15}) and 2-hydroxy-5-*t*-octylbenzaldoxime (**31**, R = C_8H_{17}) were less effective extractants.

The low solubility of the saturated ketoximes (**35**, R = Me and R = Ph, $n = 0$) in petroleum, precluded their evaluation on the same basis but the synthesis of more soluble unsaturated versions was problematic.

The Acorga reagent originally contained approximately 50% *p-t*-nonylphenol which has now been replaced by tridecanol, but from the aspect of renewability, the nature of the remaining diluent constituting 90% of the extraction system is probably more relevant. Isooctane, octane, cyclohexane, petroleum, xylene, and dichloroethane[23] have all been examined rather than a replenishable source, for example of terpenoid or other biological origin.

Structure of copper complexes and stability of oximes

The complexes in the extraction of copper(II) with oximes are considered[24] to be initially 1:1, with a hexahydrated copper cation, proceeding to a tetrahydrated structure and eventually to a 2:1 structure shown (Fig 3) in the hypothetical instance of copper chloride. The position of attachment of the alkyl group in the case of C_8 isomeric aldoximes is shown as (.....) for the complexes from *para*- (compound **26**), *meta*$_1$- (compound **7**), *meta*$_2$- (compound **14**), and *ortho*-isomers (compound **22**), in the four types of oxime depicted. While combined electronic and steric influences in oxime complexation are likely, a steric effect could result in a rate order, *para* > or = *meta*$_1$ > or = *meta*$_2$ > *ortho* isomer (the most hindered member) which was found in practice for the relative extractions.

In the stripping stage, the oximino group is susceptible to acidic cleavage and partial reversion to the aldehyde can occur. From TLC experiments on the recovered isomeric C_8 oximes from extractions, the *o*-compound appeared less subject to reversion than either the *m*- and *p*-isomers or the commercial Acorga reagent.

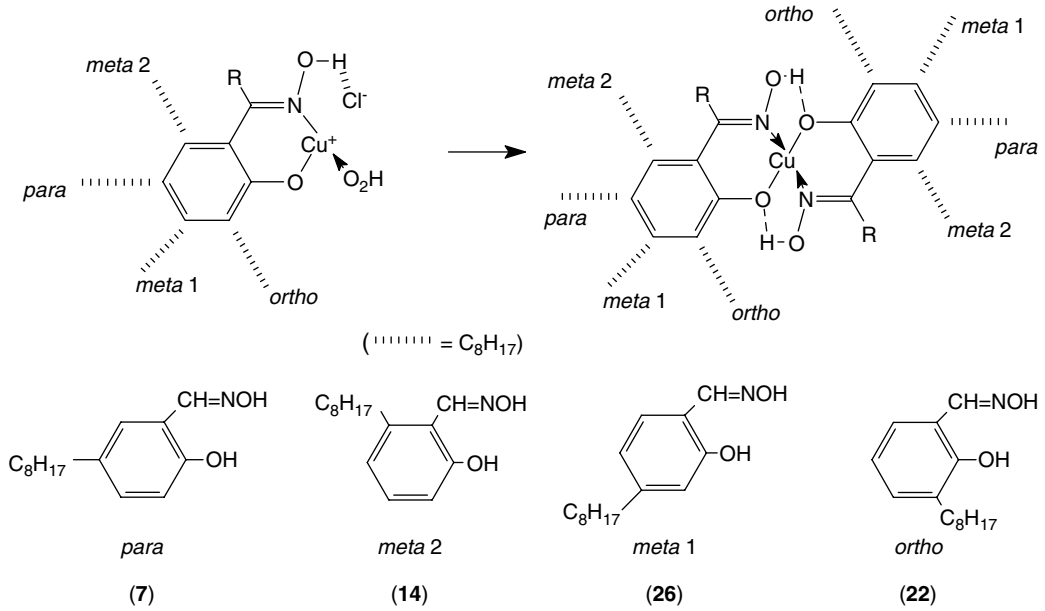


Figure 3. 1:1 and 2:1 chelated structures of Cu(II) chloride with aldoximes from C_8 *o*-, *m*-, or *p*-alkylphenols (R = H).

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