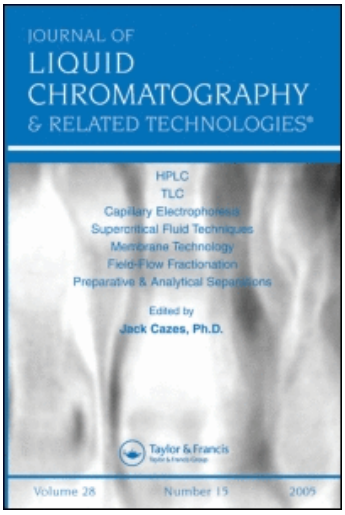

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PREPARATIVE HPLC SEPARATION OF THE UNSATURATED CONSTITUENTS OF CARDANOL AND CARDOL

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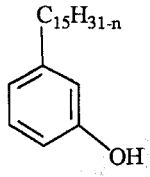
Abstract The analytical and preparative separation of the saturated, monoene, diene and triene constituents of cardanol and cardol have been achieved by reverse phase HPLC on a C_{18} column using gradient elution.

Introduction

Technical Cashew Nutshell Liquid (CNSL), an important natural feedstock of phenolic lipids, is a mixture of unsaturated and saturated pentadecyl phenols (cardanols) and dihydric phenols (cardols). Its principal components, 3-pentadecyl (1a), 3-[(Z)-pentadec-8-enyl] (1b), 3-[(Z,Z)-pentadec-8,11-dienyl] (1c), 3-[(Z,Z)-pentadec-8,11,14-trienyl] (1d) phenols and 1,3-dihydroxy-5-[(Z)-pentadec-8-enyl] (2a), 1,3-dihydroxy-5-[(Z,Z)-pentadec-



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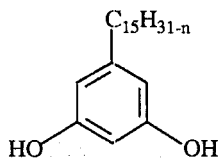
1b n=2
1c n=4
1c n=6



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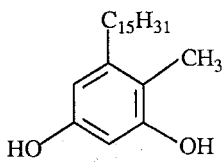
2c n=6



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8,11-dienyl] (2b), and 1,3-dihydroxy-5-[(Z,Z)-pentadec-8,11,14-trienyl) (2c) benzenes, are accompanied by small amounts of 1,3-dihydroxy-4-methyl-5-pentadecyl benzene (2-methyl cardol) (3) and some polymeric material.

Various methods have been employed to determine the composition of CNSL, such as gas chromatography and gas-liquid chromatography of the methyl ethers[1-3], argentation TLC combined with UV spectrophotometry[4], and analytical high performance liquid chromatography[5,6].

Tyman and co-workers[7,8] obtained good yields of pure unsaturated cardanols on a preparative scale using argentation TLC on silica gel plates and argentation column chromatography. These methods are time-consuming as TLC plates of silica gel impregnated with 20% silver nitrate are not commercially available and moreover only 10-20mg can be loaded on to each plate although the use of 'Chromatotron' equipment can accelerate the process. Argentation column chromatography is also laborious since

up to 100 fractions need to be collected and the method is costly.

The only related preparative HPLC separation was carried out by Lloyd et al[9] who achieved reasonable separation of the anacardic acids, the carboxylated precursors of cardanol, using a C_{18} column and isocratic elution with methanol/acetic acid (85:15). Skopp and Schwenker[10] have descibed a preparative HPLC separation of the olefinic cardanols but little information about methodology or sample purity were discussed, while Nakatsu and Kubo[11] reported some success by a recycling HPLC technique.

Recently we required the individual pure unsaturated cardanols and cardols for synthetic work so we decided to look at HPLC as a simpler, more rapid preparative technique. We found that the system described previously[6] using a C_{18} reverse phase column and acetonitrile:water-THF gradients gave baseline analytical separation of the constituents of cardanol and cardol. The method was extended to the preparative scale separation of the monoenes, dienes and trienes of both cardanol and cardol.

EXPERIMENTAL

The assembly used was a Gilson Autoprep system containing 2 model 303 25ml pumps, a model 803 manometric module, a model 811 dynamic mixer, a model 201 fraction collector and a holochrome variable wavelength detector set at 275nm. A Rheodyne injector with a 20µl sample loop was

used for analytical work, while for preparative scale injections a Gilson model 303 auto-injector. The analytical column was a Spherisorb C-18 100x4.6mm I.D. while preparative scale separations were carried out on a Spherisorb C-18 250x22.4mm I.D. column.

HPLC grade acetonitrile, water and THF were obtained from May & Baker Ltd, U.K.. Acetic acid was laboratory grade obtained from BDH Ltd, U.K.. All solvents were filtered and degassed with helium before use. It was found that the solvent systems used in the previous work[6] were satisfactory for use in this current investigation. These were: Solvent A - acetonitrile, water, acetic acid (66:33:2), Solvent B - THF. All samples were made up in hexane.

Samples of pure cardanol and cardol were obtained using the method described[6].

PROCEDURE

The pure samples of cardanol and cardol were obtained by column chromatography of Technical CNSL using a silica gel stationary phase and elution with petroleum ether/diethyl ether as described[6]. These samples of cardanol and cardol were dissolved in hexane. Flow rates of 1ml/min and 20ml/min were used for the analytical and preparative work respectively. A gradient of 0-100% B over a 20 minute period was found to give the best resolution and peak shape followed by reequillibration of the column in readiness for the next injection. For each sample

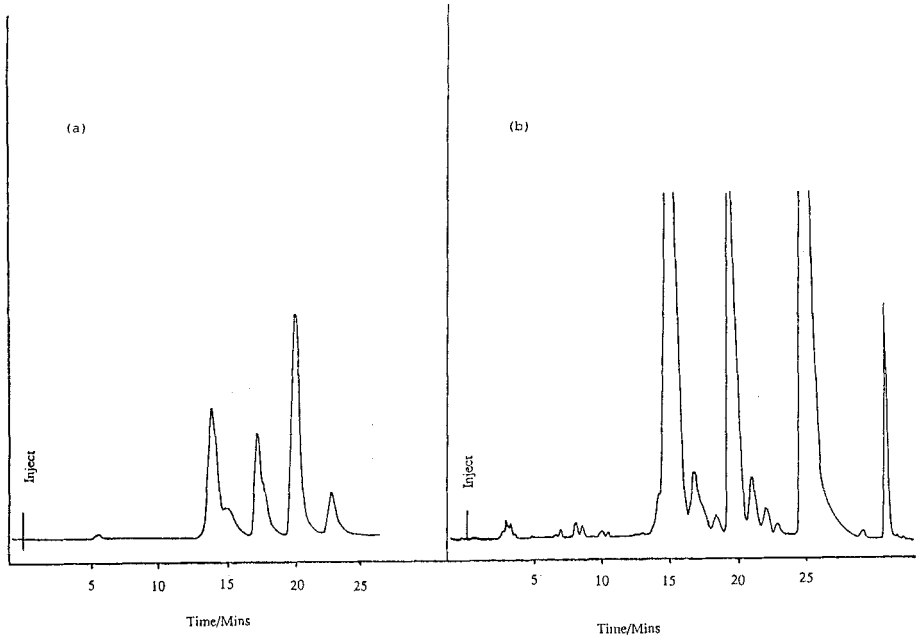

Figure 1. HPLC separation of cardanols on (a) column : Spherisorb ODS 100x4.6mm, gradient : 0-100%B over 20min., flow rate : 1ml/min., UV detector, 275nm, Load 2µg in 2µl of hexane, (b) column : Spherisorb ODS 250x22.4mm, gradient as (a), flow rate : 20ml/min., UV detector, 275nm, Load 0.35g in 1ml of hexane.

collected, the THF and acetonitrile were removed under reduced pressure, the acetic acid neutralised with sodium bicarbonate and the remaining water extracted with chloroform and dried to constant weight under high vacuum at room temperature. All residual products were reexamined by HPLC, a 240XA Elemental C,H,N Analyser, an MS-902 and a Jeol FX-200 ^{1}H nmr spectrometer.

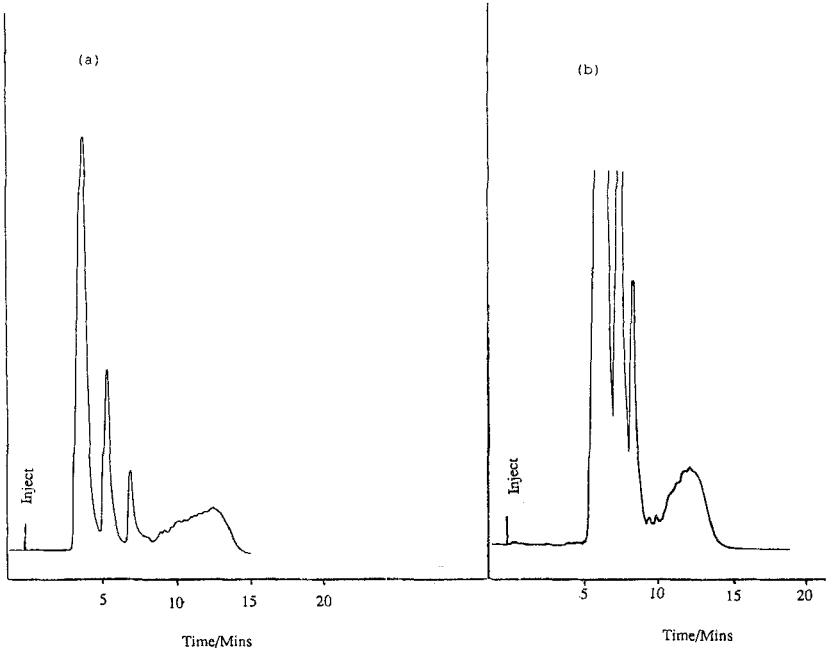

Figure 2. HPLC separation of cardols using the same conditions as in Figure 1, but loading on B was 0.33g in 1ml of hexane.

RESULTS AND DISCUSSION

Of the various gradients we investigated, the best resolution was achieved with a gradient of 0-100% THF in acetonitrile over a 20 minute period. Using this system the saturated, mono-, di- and trienes separated with baseline resolution in the analytical runs. Typical elution patterns for both cardanol and cardol are shown in Figures 1 and 2. Shoulders and slight fronting of the main peaks is probably due to additional components in

Table 1 Composition of the cardanol fractions

Fraction	Wt/g (%)	Compound
1	0.103(29.4)	Triene
2	0.048(13.7)	Diene
3	0.107(30.6)	Monoene
4	0.058(16.6)	Saturated
5	0.029(8.2)	Polymer
Total	0.345(98.5)	

Table 2 Composition of the cardol fractions

Fraction	Wt/g (%)	Compound
1	0.187(56.6)	Triene
2	0.081(24.5)	Diene
3	0.027(8.1)	Monoene
4	0.034(10.3)	Polymer
Total	0.329(99.6)	

the mixture such as small amounts of the C_{13} to C_{17} side chain homologues. The weight and composition of the materials isolated from the various fractions are given in Tables 1 and 2; over 97% of the materials injected were recovered.

The values in Tables 1 and 2 compare well with those already reported[4]. All products had the expected spectroscopic properties by MS and ^1H nmr examination.

In conclusion, we report a fast, high throughput method for obtaining the pure saturated, monoenes, dienes and trienes of both cardanol and cardol.

3-(pentadecyl) phenol (1a)

Expected; C=82.89%, H=11.84%, Found; C=82.67%, H=11.71%

MS m/e=304.1

3-[(Z)-pentadec-8-enyl] phenol (1b)

Expected; C=83.44%, H=11.26%, Found; C=83.19%, H=11.51%

MS m/e=302.1

3-[(Z,Z)-pentadec-8,11-dienyl] phenol (1c)

Expected; C=83.94%, H=10.73%, Found; C=83.72%, H=11.01%

MS m/e=300.2

3-[(Z,Z)-pentadec-8,11,14-trienyl] phenol (1d)

Expected; C=84.51%, H=10.13%, Found; C=84.26%, H=10.33%

MS m/e=298.1

1,3-dihydroxy-5-[(Z)-pentadec-8-enyl] benzene (2a)

Expected; C=79.25%, H=10.69%, Found; C=79.11%, H=10.84%

MS m/e=318.1

1,3-dihydroxy-5-[(Z,Z)-pentadec-8,11-dienyl] benzene (2b)

Expected; C=79.75%, H=10.12%, Found; C=79.54%, H=9.96%

MS m/e=316.1

1,3-dihydroxy-5-[(Z,Z)-pentadec-8,11,14-trienyl) benzene (2c)

Expected; C=80.25%, H=9.55%, Found; C=80.06%, H=9.31%

MS m/e=314.2

Acknowledgements

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