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LONG-CHAIN PHENOLS

V*. GAS CHROMATOGRAPHIC ANALYSIS OF CASHEW NUT-SHELL LIQUID (*ANACARDIUM OCCIDENTALE*)

J. H. P. TYMAN
School of Chemistry, Brunel University, Kingston Lane, Uxbridge, Middlesex (Great Britain)
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SUMMARY

Cashew nut-shell liquid (CNSL) of natural origin or as the technical product obtained by industrial decarboxylation, has been analysed by gas–liquid chromatography. Requirements of the method are the use of a relatively non-polar stationary phase at a high temperature, the need to avoid tailing by initial conversion of the unsaturated constituents into the common saturated member by hydrogenation and to obtain anacardic acid, the principal component of natural CNSL, in the form of the volatile methyl ester.

INTRODUCTION

In previous work[1] the phenols in cashew nut-shell liquid (CNSL) from *Anacardium occidentale* have been analysed by a combined thin-layer chromatographic–spectroscopic procedure with elution of the bands or directly by scanning[2] the chromatographic plate. Such methods were however not so easily applied to technical CNSL, the industrial product formed by the hot decarboxylation of the natural product.

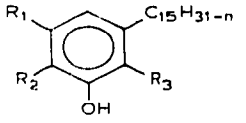
A method was sought, therefore, which would be readily applicable to both natural and technical CNSL and in principle to other long-chain phenolic natural products[3]. Liquid chromatography has been used for larger scale separation[1,4,5] but has limitations when attempted quantitatively. It seems very likely however that high-pressure columns could prove useful for the small scale relevant to analytical work and experiments are being carried out with this technique.

In view of the time-consuming nature of the preceding methods, total analysis of natural and technical CNSL has been examined by a gas–liquid chromatographic (GLC) procedure. The majority of the present investigation was carried out some years ago and work on a method for the analysis of the unsaturated constituents of the

* Parts III and IV of this series: see refs. 5 and 6, respectively.

component phenols[6] makes it desirable to place on record earlier results on the latter materials.

The component phenols of natural CNSL are cardanol (I with $R_1=R_2=R_3=H$, $n = 0, 2, 4, 6$); cardol (I with $R_2=R_3=H$, $R_1=OH$, $n=0, 2, 4, 6$); 2-methylcardol (I with $R_1=OH$, $R_2=CH_3$, $R_3=H$, $n=0, 2, 4, 6$) and anacardic acid (I with $R_1=R_2=H$, $R_3=CO_2H$, $n=0, 4, 6$).



Technical CNSL simply contains cardanol, cardol and 2-methylcardol. The main problems in the total analysis of the component phenols are their poly-unsaturated nature, relative non-volatility, and the decarboxylation of anacardic acid at temperatures suitable for GLC. On polar columns (*e.g.* Dexsil) the dihydric phenols did not elute even up to 310° while even with non-polar columns some tailing and lack of resolution were found. Accordingly to avoid this it was desirable to work with the saturated material obtained by hydrogenation of natural or technical CNSL. To overcome the difficult volatilisation of the phenols a variety of derivatives was examined including the acetates, the trimethylsilyl and the methyl ethers. On silanised supports the stationary phase SE-30 was found to give comparatively little tailing and methylation of the hydrogenated phenols was not required. Hydrogenated anacardic acid was rendered volatile by selective and quantitative conversion to methyl anacardate with ethereal diazomethane at 0°, conditions which led to no methylation of phenolic groups. By this procedure, GLC analysis of natural and technical CNSL has been effected for the first time. Owing to the differing response of the flame ionisation detector (FID) towards the hydrogenated component phenols, calibration was required for each material.

EXPERIMENTAL

Gas–liquid chromatography

A Pye 104 gas chromatograph was used, equipped with an FID and a Vitatron-Fisons recorder/integrator. Glass columns were 5 ft. × 3/16 in. In general, a nitrogen flow-rate of 45 ml/min was used, corresponding to 7 p.s.i. A chart speed of 0.5 cm/min was generally used. Injections of 0.5–1.0 μl of benzene solutions of materials were made. To revive columns which produced asymmetrical peaks it was found useful to inject 5 μl of water and subsequently hexamethyldisilazane. Triangulation and integration were carried out; generally, since integration required a high chart speed, the former method of quantification was preferred. All triangulations were carried out in the usual way and the peak areas of the component phenols normalised. The results were the average of six determinations in most cases; standard deviations were calculated.

Preparation of materials

Natural CNSL was extracted as described[4,5]. Technical CNSL was obtained

through British Cocoa Mills, Hull, Great Britain. Saturated natural and technical CNSL were obtained by hydrogenation in ethyl acetate with palladised charcoal and after a number of experiments the following procedure was found to be convenient.

Technical CNSL (10.0 g) in ethyl acetate (75 ml) containing 10% palladised charcoal (Pd/C, 1.0 g) was hydrogenated at ambient temperature and a pressure of 20 p.s.i. in a Parr apparatus. After a series of rechargings (and total pressure drop of 146.5 p.s.i.) a second addition of catalyst (0.5 g) was made and (following a pressure drop of 50.5 p.s.i.) finally a third addition of catalyst (0.25 g) led to a negligible further uptake. The filtered and recovered product was examined for unsaturation by ^{1}H nuclear magnetic resonance spectroscopy (NMR).

Saturated cardanol* was obtained by the molecular distillation of technical CNSL at 10^{-3} torr in a Ridgway–Watt molecular still and the fractions monitored by thin-layer chromatography (TLC), followed by complete hydrogenation (Pd/C) and spectroscopic examination. For final purification, the hydrogenated material was crystallised from light petroleum. It gave a single peak on GLC examination (m.p. 44–45°; ref. 7: 51.5–52.5°)**.

Saturated anacardic acid (H anacardic acid) was obtained by the hydrogenation (Pd/C, ethyl acetate) of anacardic acid separated by a modified lead salt method[7] and crystallisation from light petroleum (b.p. 40–60°) (m.p. of final product was 84.5–85.5°; ref. 7:91.5°).

The methyl ester of saturated anacardic acid was prepared by the addition of a cold ethereal solution (0°) of diazomethane to an ice-cold ethereal solution of the acid. An excess of the reagent was used and the methylated mixture was allowed to stand for two hours before recovery of the methyl ester, which was examined by NMR spectroscopy and by GLC (single peak) to ensure that no methyl ether had been formed; m.p. 41–42°.

Saturated cardol (H cardol) was prepared by the hydrogenation (Pd/C, ethyl acetate) of cardol which was obtained by preparative TLC (ethyl acetate–chloroform, 5:95) of the filtrate from the lead salt separation followed by crystallisation from benzene–light petroleum (m.p. 86–87°; ref. 7: 95.5–96°). The saturated cardol was examined by NMR spectroscopy; it was found to give a single peak on GLC examination.

Saturated 2-methyl cardol (H 2-methyl cardol) was prepared by hydrogenation of 2-methyl cardol separated by preparative TLC from the filtrate from the lead salt procedure. The saturated product was crystallised from benzene–light petroleum (m.p. 98–100°, ref. 5).

Preparation of derivatives of the component phenols

Methyl ethers of the component phenols (saturated phenols) were prepared as described[6] by methylation with dimethyl sulphate of the phenols in benzene solution containing anhydrous potassium carbonate by refluxing the mixture on a steam bath.

* To distinguish unsaturated from saturated cardanol, the former has been termed cardanol and the latter H cardanol.

** Throughout this work the m.p.'s of the H phenols have been found to be 6° lower than those recorded[7].

Acetates of the phenols were prepared in the usual way by interaction of the phenols with excess of acetic anhydride–pyridine (1:5) reagent on a steam bath. At the conclusion of the acetylation, the reaction mixtures were cooled and diluted with ice-cold water. The acetates were isolated by filtration and thorough washing with water, if solid, or if liquid, by ethereal extraction, acid washing and drying, followed by evaporation of the solvent. The O-acetyl derivative of H methyl anacardate was prepared preferably by acetylation after methylation. The physical properties of all the derivatives will be described in a forthcoming publication on their NMR absorption spectra.

Calibration experiments

Owing to the slight overlap of the H cardol and H 2-methyl cardol peaks on SE-30 columns (see Results and discussion) it was desirable to make up two separate standard solutions, one comprising H 2-methyl cardol, H cardanol and H methyl anacardate and the other H cardol and H cardanol. The materials were weighed, using a five-place balance, and made up in 5-ml graduated flasks in benzene solution. Portions of 1.0 μl were used and at least six peak area determinations carried out with each standard solution. Response factors for the four saturated components were obtained by relating the two series (from H cardanol which was common to both standards). Standard deviations were obtained as before.

RESULTS AND DISCUSSION

Relative retentions of the component phenols and their derivatives on different stationary phases

The averaged relative retentions of the parent component (C_{15}) phenols, the saturated phenols, the methyl ethers and the acetates are summarised together with column conditions in Table I.

The results indicated are the average of the retention distances found in experiments carried out at different times. The standard deviations were often negligible. Sometimes, as with H cardol (260 $\pm$ 6.2) and H methyl anacardate (195 $\pm$ 3) the values were higher.

SE-30 and OV-17 columns tended to give similar results. The advantage of these two stationary phases is that they can be used at higher temperatures than most others and thus, as the table shows, the component phenols can be volatilised as a basis for analysis of natural and technical CNSL. Due to internal hydrogen bonding methyl anacardate is more volatile than cardol and 2-methyl cardol. It was found advantageous to use the hydrogenated component phenols on account of the considerably reduced tailing compared with the unhydrogenated phenols. The reduced tailing and symmetrical peaks formed made the methyl ether and acetate particularly useful. Unfortunately methylation of hydrogenated CNSL (natural and technical) resulted in coincidence of the peaks for H methyl anacardate O-methyl ether and H 2-methyl cardol dimethyl ether, while acetylation was not sufficiently quantitative for analytical purposes which precluded its use for the unhydrogenated component phenols. By silanisation of the glass column and the support, the tailing (with SE-30) was reduced. The possible advantage of OV-17 compared with SE-30 lay in its use at a higher temperature with speeding up of the analysis. However, attempts to use

TABLE I

RELATIVE RETENTIONS OF THE COMPONENT PHENOLS OF CNSL AND THEIR DERIVATIVES ON SE-30 AND OV-17 GLC COLUMNS

Nitrogen carrier-gas pressure, 7 p.s.i.; retention distance of 5 mm = 1 min. The SE-30 column support was 100–120 mesh acid-washed and silanised diatomite C; the OV-17 support was 80–100 mesh diatomite C, similarly treated.

Compound	*Retention distance (mm)*	*Relative retention*
Support, SE-30; temperature, 220°		
Cardanol	96	0.91*
Cardol	235	2.24
2-Methyl cardol	263	2.50
Methyl anacardate	181	1.72
H Cardanol	105	1.00
H Cardol	260	2.48
H 2-Methyl cardol	291	2.77
H Methyl anacardate	195	1.86
H Cardanol methyl ether	88	0.84
H Cardol dimethyl ether	167	1.59
H 2-Methyl cardol dimethyl ether	194	1.84
H Methyl anacardate O-methyl ether	207	1.97
Cardanol acetate	114	1.09
Cardol diacetate	295	2.81
2-Methyl cardol diacetate	352	3.35
H Methyl anacardate O-acetate	276	2.63
H Cardanol acetate	125	1.19
H Cardol diacetate	326	3.10
H 2-Methyl cardol diacetate	374	3.56
Support, SE-30; temperature, 235°		
Cardanol	62	0.59*
Cardol	139	1.32
2-Methyl cardol	—	n.r.**
Methyl anacardate	112	1.07
Support, SE-30; temperature, 250°		
Cardanol	50	0.48*
Cardol	84	0.80
2-Methyl cardol	—	n.r.**
Methyl anacardate	67	0.64
Support, OV-17; temperature, 220°		
Cardanol	98	0.93*
Cardol	243	2.31
Methyl anacardate	181	1.72
Cardanol***	59	0.56
Cardol	142	1.35
2-Methyl cardol	—	n.r.**
Methyl anacardate	105	1.00
Cardol diacetate	170	1.62
2-Methyl cardol diacetate	197	1.88

* Relative retention referred to H cardanol at 220° on SE-30.
** n.r. = not resolved; mixture of cardol and 2-methyl cardol used.
*** Carrier-gas pressure, 12 p.s.i.

higher temperatures (235°) led to poor resolution of the H cardol and H 2-methyl peaks. Accordingly analysis of natural and technical CNSL was carried out at 220° on SE-30 columns, with the hydrogenated materials, after conversion of H anacardic acid to H methyl anacardate with ethereal diazomethane.

Calibration of the FID towards the hydrogenated components phenols

Two different standards were made up, the first comprising H cardol and H cardanol, and the second H cardanol, H methyl anacardate and H 2-methyl cardol.

The percentage component phenol from peak areas (with standard deviations), the average areas, the weights and the response factors[8] are given in Table II for the first standard, and in Table III for the second standard.

TABLE II

RELATIVE RESPONSE FACTORS FOR H CARDOL AND H CARDANOL

Parameter	*H cardol*	*H cardanol*
Percentage component from peak area	22.46 ± 1.97	77.53 ± 2.33
Average peak area × 10^{-4}	0.2009	0.6802
Weight taken (g)	0.4158	0.8302
Relative response factor	0.4832	0.8793

TABLE III

RELATIVE RESPONSE FACTORS FOR H CARDANOL H 2-METHYL CARDOL AND H METHYL ANACARDATE

Parameter	*H 2-methyl cardol*	*H methyl anacardate*	*H cardanol*
Percentage component from peak area	12.23 ± 0.49	46.73 ± 0.51	41.14 ± 0.32
Average peak area × 10^{-4}	0.09522	0.3642	0.3214
Weight taken (g)	0.1171	0.4123	0.2321
Relative response factor	0.8728	0.8823	1.384

Interrelating these two sets of results leads to relative response factors of 1.384 for H cardanol, 0.8823 for H methyl anacardate, 0.8162 for H cardol and 0.8128 for H 2-methyl cardol. The reason for the higher standard deviations in the results shown in Table II is obscure but it was not considered likely to have much effect on the final calculated results.

Composition of the component phenols in technical and natural CNSL

The results for technical CNSL are shown in Table IV. The uncorrected percentage composition from the normalised peak areas of C_{15} H cardanol, H cardol,

TABLE IV

COMPOSITION OF THE C_{15} COMPONENT PHENOLS OF TECHNICAL CNSL

Parameter	*H cardanol*	*H cardol*	*H 2-methyl cardol*
Uncorrected composition (%)	88.56 ± 0.56	8.603 ± 0.77	2.819 ± 0.30
Relative response factor	1.384	0.8162	0.8728
Corrected composition (%)	82.15	13.71	4.148

and H 2-methyl cardol, the relative response factors and the corrected results are given.

After allowance for the differing unsaturation in the component phenols[6] which shows that cardanol and anacardic acid are predominantly dienoid while cardol and 2-methyl cardol are trienoid, the final composition of technical CNSL can be calculated as 82.22 cardanol, 13.64% cardol and 4.13% 2-methyl cardol.

In a similar way the composition of natural CNSL is given in Table V. The last line shows the correction to enable the composition to be expressed in terms of H anacardic acid rather than H methyl anacardate obtained by diazomethane methylation.

TABLE V

COMPOSITION OF THE C_{15} COMPONENT PHENOLS OF NATURAL CNSL

Parameter	*H cardanol*	*H methyl anacardate*	*H cardol*	*H 2-methyl cardol*
Uncorrected composition (%)	3.615 ± 0.32	77.97 ± 1.09	15.08 ± 0.82	3.43 ± 0.66
Relative response factor	1.384	0.8833	0.8162	0.8128
Corrected composition (%) (normalised)	2.298	77.69	16.26	3.715
Corrected result (expressed as H anacardic acid)	2.370	77.02	16.77	3.832

Conversion of the results expressed in terms of H phenols to the unsaturated component phenols present in natural CNSL gives a final composition of 2.37% cardanol, 77.14% anacardic acid, 16.67% cardol and 3.81 % 2-methyl cardol.

The GLC results for the composition of natural CNSL compare favourably with those obtained by the TLC–ultraviolet spectrophotometric method[1] which indicated the presence of 73.5% anacardic acid, 19.1% cardol, 2.8% 2-methyl cardol and 4.8% cardanol. The two materials were of different origin.

The GLC procedure for technical CNSL shows general agreement with the gravimetric results obtained by preparative TLC. In this method 80.00% of volatile non-polymerised material contained 76.43% cardanol, 16.99% cardol and 6.58% 2-methyl cardol (contaminated with some cardanol) and 20.00% of non-volatile polymeric material was present.

Although it was not possible to obtain samples of the natural CNSL used for preparing the technical CNSL, both nevertheless originated from Mozambique, and it is instructive to calculate the theoretical yield derivable by decarboxylation from the natural product having the composition shown in the last line of Table V. The total cardanol obtainable is slightly increased by the natural presence of 2.37% and the composition of the theoretical unsaturated product would be 77.27% cardanol, 18.49 % cardol and 4.22% 2-methyl cardol. The actual heated product shows a slightly higher proportion of cardanol which indicates that the 20% of non-volatile material present in the technical product contains approx. 40% polymerised cardol (together with 2-methyl cardol) and 60% polymerised cardanol.

In all the GLC tracings the presence of small amounts of C_{17} cardanol and considerably less C_{13} homologue were observed in technical CNSL, and of a C_{17} anarcardic

acid in natural CNSL. The retention times of these constituents agreed precisely with synthetic samples[9] and the plot of log (retention) against chain length was linear in each case. Considerable proportions of homologous materials have been described in other work[10], but in the present case, relative to the C_{15} materials, natural CNSL contained 4.62% of C_{17} anacardic acid and technical CNSL 5.89% of C_{17} cardanol. The compositions expressed in Tables IV and V relate to the C_{15} component and thus the total homologous anacardic acid and total homologous cardanol in both products is slightly higher.

CONCLUSION

GLC analyses of hydrogenated natural CNSL and technical CNSL have been carried out conveniently on SE-30 as a stationary phase after conversion of H anacardic acid in the case of the natural product to H methyl anacardate. These initial results show that technical CNSL contains (as C_{15} phenols) 82.2% cardanol, 13.7% cardol and 4.1% 2-methyl cardol together with a small proportion of C_{17} cardanol. Natural CNSL contains (as C_{15} phenols) 77.1% anacardic caid, 16.7% cardol, 2.4% cardanol and 3.8% 2-methyl cardol together with a small proportion of C_{17} anacardic acid.

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REFERENCES

1 J. H. P. Tyman and L. J. Morris, *J. Chromatogr.*, 27 (1967) 287.
2 J. H. P. Tyman, unpublished results.
3 J. H. P. Tyman and C. H. Khor, *Chem. Ind. (London)*, (1974) 526.
4 B. G. K. Murthy, M. A. Siva Samban and J. S. Aggarwal, *J. Chromatogr.*, 32 (1968) 529.
5 J. H. P. Tyman, *J. Chem. Soc. (Perkin I)*, (1973) 1639.
6 J. H. P. Tyman, *J. Chromatogr.*, 111 (1975) 277.
7 H. J. Backer and N. H. Haack, *Rec. Trav. Chem.*, 60 (1941) 661.
8 H. McNair and E. J. Bonelli, *Basic Gas Chromatography*, Varian Aerograph, Walnut Creek, Calif., 1965, p. 151.
9 A. A. Durrani and J. H. P. Tyman, *Chem. Ind. (London)*, (1971) 934.
10 J. L. Gellerman and H. Schlenk, *Anal. Chem.*, 40 (1968) 239.