Compositional Studies on Technical Cashew Nutshell Liquid (CNSL) by Chromatography and Mass Spectroscopy[1]

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ABSTRACT

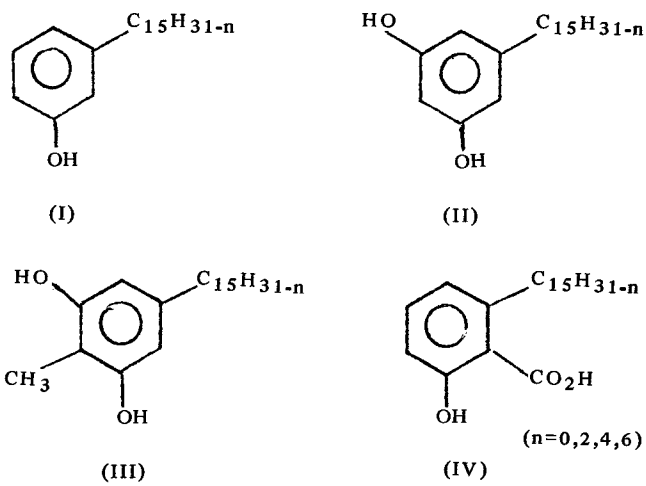
The composition of technical cashew nutshell liquid (CNSL), *Anacardium occidentale,* from four different sources has been examined. The C15 component phenols cardanol, cardol, 2-methyl cardol, and traces of anacardic acid have been determined by gas liquid chromatography (GLC), after hydrogenation and methylation, on the stationary phases Dexsil 300, SE52, SE30, and OV17, or alternatively the acetylated (unsaturated) phenols on Dexsil 300, SE52, or SE30. After thin layer chromatographic (TLC) separation of the component phenols, their saturated (15:0), monoene (15:1), diene (15:2), and triene (15:3) constituents have been determined by mass spectrometry (MS). In both the GLC and the MS procedures, the results have been corrected for differing relative responses. The more highly polymeric material present in technical CNSL from different sources has been determined by molecular distillation and by TLC. The fractions obtained by molecular distillation have been analyzed by GLC, the results of which show there is present some low polymeric material less volatile than the C15 component phenols, but the major portion of technical CNSL is volatile and can be analyzed by GLC.

INTRODUCTION

The industrial decarboxylation of natural cashew nutshell liquid (CNSL) from the shell of the cashew nut, *Anacardium occidentale,* by the roasting process (1) produces technical CNSL (sometimes termed commercial CNSL), a dark brown phenolic liquid rich in cardanol (I), (2), containing smaller amounts of cardol (II), (3), 2-methyl cardol (III) (4), and a trace of residual anacardic acid (IV), (5), the main component phenolic acid of natural CNSL. Technical CNSL is widely used throughout the world primarily as the raw material for friction dusts and other surface applications (6).

Traditionally, technical CNSL has been assessed on the basis of physical tests such as viscosity, time of polymerization under thermal and acidic conditions, and by its iodine value (7). Such information is of less value where different sources are concerned and in predicting the behaviour of this complex product towards formaldehyde polymerization or other reaction conditions. Potentiometric titration and some chromatographic work (8) have been described. Solvent extraction, alkali extraction, and standard phenol/phenolic acid separation have been examined (9), but no detailed information obtained. Early work based on thin layer chromatorgraphy (TLC) combined with ultraviolet spectrophotometry for the analysis of component phenols of natural CNSL proved difficult to apply quantitatively to technical CNSL (10). Gas liquid chromatography (11) of the hydrogenated and methylated component phenols was found useful for natural and technical CNSL, and the four constituents (n = 0,2,4,6,I,II,III,IV) of each component phenol, separated by preliminary TLC, were then determined by GLC (12) and later by mass spectroscopy (13). Cardanol in technical CNSL and anacardic acid in natural CNSL are accompanied by small proportions of the respective C17 homologues and the corresponding unsaturated constituents. The preceeding methods were directed more toward natural CNSL, and the quantitative analysis of technical CNSL has been found in some respects more complicated because of the presence of polymeric and degraded material.

The present work has been concerned with the quantitative analysis of technical CNSL from several different industrial sources. GLC analysis of the hydrogenated and methylated component phenols, and of the acetylated unsaturated materials, TLC separation of the component phenols followed by mass spectroscopy and the use of TLC and of molecular distillation for the polymeric substance have been studied. The objective has been to devise chromatographic procedures based on TLC and GLC which could be carried out in an instrumentally equipped industrial laboratory.



EXPERIMENTAL PROCEDURES

Materials

Technical CNSL representing selected types from three different sources referred to as source A, source B, and source C was obtained from BP Chemicals International Ltd., Penarth, Glam. S. Wales. A fourth material referred to as technical CNSL (reference) was from Mozambique. All materials were stored in tightly stoppered bottles in the dark, or cans, at ambient temperature.

Preparation of Derivatives of the Component Phenols

Hydrogenation: Hydrogenation of technical CNSL samples (2% in ethyl acetate) was carried out as described (17) in an atmospheric pressure glass apparatus of the constant pressure type with vigorous mechanical agitation of the hydrogenation flask. Completion of the hydrogenation was ensured by disappearance of olefinic signals in the ^{1}H-NMR absorption spectrum.

Methylation: Methylation was carried out as described (11). The filtered reaction mixture was thoroughly washed

[1]Part XI: Phenolic Lipids.

TABLE I

Retention Distances (RD in mm) of Component Phenols in Technical CNSL Phenols, Acetates, and (Hydrogenated and Methylated) Phenols

Stationary phase	Temp. (C)	Phenol/derivative	Cardanol (C15) RD	Cardanol (C17) RD	Cardol RD	2-Methyl cardol RD	Anacardic acid RD	R[a]	α[a]
OV17 (3%)	220 (250)[b]	(i) Hydrogenated methylated	83.1	157.8	189.8	211.2	287.4	0.936	1.12
	220 (250)	(ii) acetylated[f] (unsaturated)	(108.0) (119.8)	(205.3) (225.8)	413.0	---	-----	---	---
		(iii) phenol[f] (unsaturated)	(94.2) (103.2)	(182.1) (200.9)	349.1	-----	---	---	---
SE52 (5%)	220 (250)	(i)	56	(101.2)[d]	106.4	122.4	133.6	1.89	1.15
		(ii)	77.5	136.7	202.8	226.6	---	1.31	1.12
		(iii)	65.2	116.8	162.1	182.3	---	0.86	1.12
SE52 (5%)	200	(i)	122.9	(237)[d]	252.6	297.9	---	---	1.18
	200	(ii)	172.7	329.8	---	---	---	---	1.18
Dexsil (3%)	220 (350)	(i)	70.4 (66.9)[c]	131.7 (130.6)[c]	141.6 (140.8)[c]	159.8 (161.0)[c]	174.2 (181.7)[c]	1.41	1.12
		(ii)	96.1	179.1	289.1	322.8	(362)	1.12	1.12
SE30 (3%)	220 (250)	(i)	64.3	(103.4)[d]	114.7	132.9	---	1.41	1.16
		(ii)	74.6	(132.3)[d]	183.6	206.6	---	0.96	1.12
		(iii)	63.4	110.7	141.9	162.9	---	0.90	1.15
PEGA (3%)	190 (200)	(i)	96.0	173.7	307.1	266.2	---	1.23	0.87
		(ii)	(261.4)[e] (324.1)[e] (399.8)[e]	---	---	---	---	---	---
APL	220 (250)	(i)	181.6	---	371.8	414.4	---	0.93	1.11
	240	(ii)	85.1	---	165.8	182.8	---	---	1.09
	240	(iii)	99.0	187.6	240.2	248.1	---	---	1.03

[a]Resolution (R) and separation factor (α) between cardol and 2-methyl cardol calculated as described in reference 16.
[b]Maximum column temperature recommended.
[c]These values determined by another observer one year later.
[d]C17 peak retention time approximate.
[e]Values for the (15:), and (15:2), and (15:3), cardanol acetates.
[f]Partial resolution of unsaturated constituents.

with water and concentrated to give an approximately 10% solution of the methyl ether.

Acetylation: Acetic anhydride (1 vol) with AR anhydrous pyridine (2 vol) was found the most useful reagent. The CNSL (1.0 g) and acetylation reagent (20 ml) were warmed on the steam bath for 2 hr, protected from the atmosphere, or simply kept at ambient temperature overnight. Rate studies indicated that acetylation was complete within a short period. It was found convenient to use the reaction mixture directly (1.0 μl samples). For isolation, the reaction mixture was poured into ice water, thoroughly stirred to hydrolyze the acetic anhydride, extracted with light petroleum ether (bp 40-60 C), the combined extracts washed with water to remove pyridine and acetic acid, and dried. The acetates were examined by analytical GLC (SE30) to ensure complete conversion and absence of the phenol.

Preparation and Examination of Calibration Standards for Determination of Relative Response Factors

Cardol, 2-methyl cardol, and cardanol were separated from technical CNSL (ref. sample) by preparative TLC on ordinary Silica Gel G plates with 5% ethyl acetate-95% chloroform followed by repurification of each (15,17).

Cardanol acetate after hydrogenation gave (15:0) cardanol acetate, identical with the acetylation product of (15:0) cardanol, and obtained as prisms from light petroleum, mp 40-41 C. Found C, 80.35: H, 11.04: required for $C_{23}H_{38}O_2$, C, 79.77: H, 10.98%. (15:0) Cardol diacetate was similarly obtained mp 56-57 C (lit. (14) 55.5-56.5 C). Found C, 74.96: H, 10.19: calc. for $C_{25}H_{40}O_4$, C, 74.25: H, 9.90%. Anacardic acid O-acetate, (light petroleum/benzene) had mp 63-64 C. These compounds had the following ^{1}H-NMR absorption spectral properties (15:0) Cardanol acetate, δ (CCl_4), 6.83-7.43 (4H, m HAr), 2.50-2.77 (2H, t, CH_2Ar), 2.23, (3H, s, CH_3CO), 1.27 (26H, m, $(CH_2)_{13}$), 0.80-0.97 (3H, t, CH_3). (15:0) Cardol diacetate, δ (CCl_4), 6.80 (3H, m, HAr), 2.47-2.73(2H, t, CH_2Ar), 2.23, (6H, s, $2CH_3CO$), 1.26 (26H, m, $(CH_2)_{13}$), 0.77-0.94, (3H, t, CH_3). (15:0) Anacardic acid O-acetate, δ(CCl_4), 11.30 (1H, bs, CO_2H), 6.80-7.57 (3H, m, HAr), 2.67-2.93 (2H, t, CH_2Ar), 2.26, (3H, s, CH_3CO), 1.23 (26H, m, $(CH_2)_{13}$), 0.73-0.97 (3H, t, CH_3). The unsaturated cardol and cardanol acetates showed additional bands due to olefinic absorption (-CH=CH, -CH=CH_2) at ca. 4.90-5.60, (CH_2CH=). 2.0-2.26, and (=CH-CH_2-CH=) 2.62-2.85. The (15:0) methyl ethers were used as described (11).

In the determination of relative response factors of the phenolic (unsaturated) acetates, the GLC peaks of cardol diacetate and 2-methyl cardol diacetate slightly overlapped, and accordingly two separate standards were made up. Standard 1 consisted of cardanol acetate (0.27208 g) and cardol diacetate (0.26060 g) and Standard 2 cardanol acetate (0.08080 g) with 2-methyl cardol diacetate (0.05458 g). The two were interrelated subsequently. All samples were weighed on a five place balance and the mixtures of acetates made up to 2 ml in benzene solution.

Thin Layer Chromatography

Thin layer chromatography was carried out as described (11,13) on Kieselgel G (Merck). All separated component phenols for GLC or MS examination were stored until required in tightly stoppered containers at -20 C.

Gas Liquid Chromatography

A Pye Unicam model 104 gas chromatograph with Fisons Vitatron recorder was used equipped with a flame ionization detector and mass/flow controllers. Glass columns were 5 ft by 3/16 in., and the following were used: (% stationary phase, support, mesh); 3% SE30, Diatomite

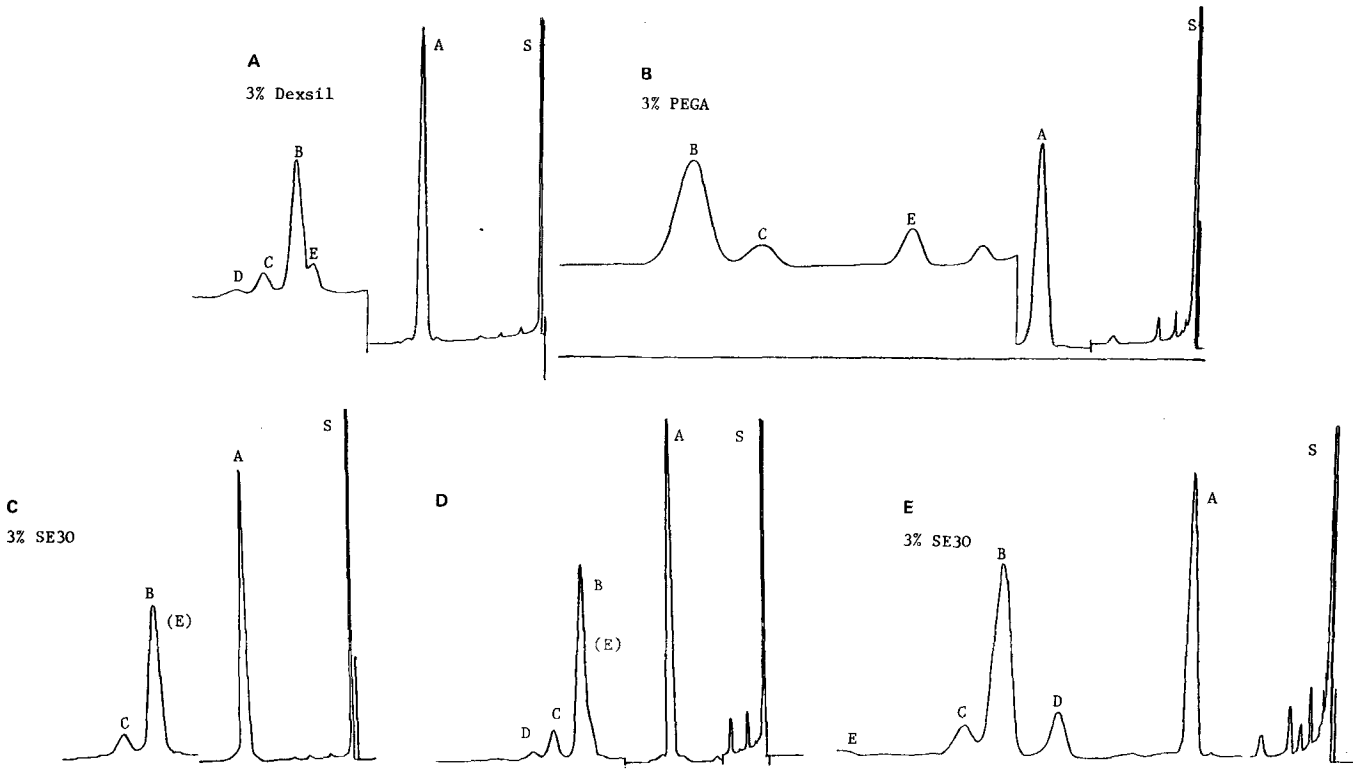


FIG. 1. GLC on hydrogenated and methylated technical CNSL. (a) 3% Dexsil (220 C), (b) 3% PEGA (190 C), (c) 3% SE30 (220 C), (d) 3% OV17 (220 C), (e) 5% SE52 (220 C). Vertical lines or breaks indicate changes of attenuation. A, (15:0) cardanol methyl ether; B, (15:0) cardol dimethyl ether; C, (15:0) 2-methyl cardol dimethyl ether; D, (15:0) dimethyl anacardate; E, (17:0) cardanol methyl ether; S, solvent.

C, 100-120; 5% SE52, Diatomite C, 100-120; 3% OV17, Diatomite M, 60-80; 3% Dexsil 300, Diatomite M, 60-80; 3% PEGA, Diatomite M, 60-80; 5% APL, Diatomite M, 60-80. All supports were acid washed and silanized. Nitrogen flow rate was 45 ml/min, and the preheater and detector heaters were 50 C higher than the oven temperature. Chart speed of 0.5 cm/min was used (and sometimes 1 cm/min). Sample injection and procedures were as described. Attenuation adjustments had been confirmed to be linear (15) and were made so as to produce comparable size large peaks; changes were made appropriately so that a straight base line was obtained. Peak areas were measured by a triangulation procedure which had been checked by integration. At least four chromatograms were carried out on each sample and standard deviations obtained in the usual way.

Mass Spectroscopy

Mass spectra were determined on an MS902 instrument by courtesy of ULIRS scheme at the School of Pharmacy, University of London, and on an RMS4 Hitaci-Perkin-Elmer instrument at Brunel University. Sample preparation, technique of examination by repeated scanning, and processing of the results were carried out as described (13).

Molecular Distillation

Molecular distillation was carried out in a Vitamins-Watt 10 stage molecular still equipped with its own diffusion pump. A charge of ca. 5 g of technical CNSL was used in the boiler, and after degassing by evacuation under rotary pump vacuum, the latter was reduced to 10^{-3} torr and distillation commenced. A temperature range of ca. 180 to 240 C was necessary, after which distillation had almost stopped. The residue in the boiler was weighed. All fractions and the rinsings from the condenser and the upper wall of the boiler were examined by GLC on an SE30 column.

RESULTS AND DISCUSSION

Retention Distances (RD) of the (15:0) Phenolic Methyl Ethers, the Unsaturated Phenols, and Phenolic Acetates

The unsaturated phenols, their acetates, and the (15:0) phenolic methyl ethers were examined by GLC on the semipolar stationary phases OV17, Dexsil 300, and PEGA and on the nonpolar stationary phases SE52, SE30, and APL, since the use of the more polar stationary phases led to excessively long retention times. The results for the retention distances (RD in mm) for each stationary phase have been summarized in Table I in which R, the resolution, and α, the separation factor, (between cardol and 2-methyl cardol) have been calculated in the usual way (16). Figures 1 and 2 show GLC tracings of the (15:0) phenolic methyl ethers and unsaturated acetates respectively of technical CNSL on a number of different stationary phases.

In previous work (15:0) dimethyl anacardate (from residual nondecarboxylated acid) was not detected, but on OV17, SE52, Dexsil 300 it appeared as a small peak of longest retention. In the earlier work (11) on 2% PEGA, the R values (0.92 at 190 C and 0.85 at 180 C) were less than on 3% PEGA (1.23 at 190 C). The alternatives of SE52, Dexsil 300, SE30, and 3% PEGA were superior to OV17 and APL, on both of which a small diminution in performance would lead to nonresolution of the cardol and 2-methyl cardol derivatives. Although (17:0) cardanol methyl ether was not adequately resolved from (15:0) cardol dimethyl ether, Dexsil represented the best choice generally since at 220 C it was being used well within its upper temperature limit. 3% PEGA (and 2% PEGA) were satisfactory, but the need to use them near the maximum recommended temperature was a disadvantage. PEGA can also be used for the analysis of the methyl ethers of the unsaturated constituents of the component phenols (12).

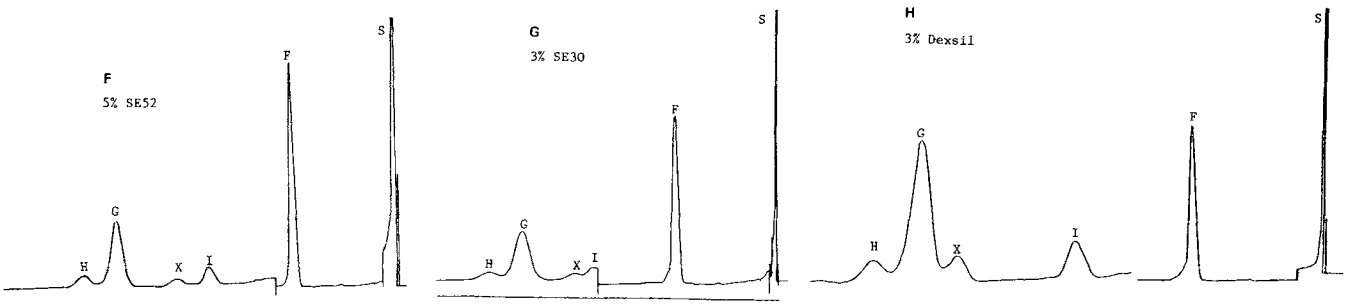


FIG. 2. GLC on acetylated technical CNSL. (f) 5% SE52 (220 C), (g) 3% SE30 (220 C), (h) Dexsil (220 C). Vertical lines or breaks indicate changes of attenuation. F, cardanol acetate; G, cardol diacetate; H, 2-methyl cardol diacetate; (I) (17:0) cardanol acetate; X, unidentified peak; S, solvent.

TABLE II

Composition (%) of the C15 and C17 Component Phenols in Different Sources of Technical CNSL by GLC (Dexsil) of Hydrogenated and Methylated Materials (1) and (SE30) of the Unsaturated Acetates (2)

Source and parameter	Cardanol		Cardol	2-Methyl cardol	Anacardic acid
	C15	C17			
Technical CNSL (reference)					
(1)	82.4	---	13.58	2.92	1.09
(2)	82.11	2.28	11.89	3.71	---
Source A					
(1)	82.56	---	13.39	2.78	1.27
(2)	82.18	2.29	11.63	3.89	---
Source B					
(1)	77.14	---	18.63	3.04	1.23
(2)	74.69	2.42	17.86	5.03	---
Source C					
(1)	83.14	---	12.93	2.17	1.75
(2)	80.99	2.35	13.02	3.63	---
Technical CNSL (reference)					
(1)	83.31	---	13.73	2.95	---
(2)	84.03	---	12.17	3.80	---
Source A					
(1)	83.62	---	13.56	2.82	---
(2)	84.11	---	11.90	3.98	---
Source B					
(1)	78.10	---	18.86	3.08	---
(2)	76.54	---	18.30	5.15	---
Source C					
(1)	84.62	---	13.16	2.21	---
(2)	82.95	---	13.33	3.72	---
Relative response factors					
(1)	1.0000	1.0000	0.8822	0.8341	0.8754
(2)	1.0000	---	0.7676	0.6443	---

The unsaturated phenolic acetates are less volatile and polar than the phenols, as shown by the longer relative retentions and symmetrical peaks observed. For the unsaturated phenolic acetates, SE52, Dexsil 300, and SE30 all gave satisfactory results with R values for cardol diacetate and 2-methyl cardol diacetate in a decreasing order.

For the unsaturated phenols, Dexsil 300 produced tailing peaks, and only SE30 and SE52 gave resolution of the cardol and 2-methyl cardol peaks. Anacardic acid O-acetate could not be detected. The GLC analysis of hydrogenated technical CNSL on SE30 has been described (17) showing agreement with the phenolic acetate method, although the main disadvantage was a tendency toward tailing peaks and rather short column life.

Composition of the C15 Component Phenols in Different Sources of Technical CNSL by GLC

Use of hydrogenated and methylated materials: In the GLC analytical procedure for natural and technical CNSL (11) 2% PEGA and 3% Dexsil were used. The results for 3% Dexsil are summarized in Table II for source A, source B, source C, and technical CNSL (reference). The four steps in the processing were (a) calculation of the uncorrected normalized % composition for (15:0) dimethyl anacardate, (15:0) cardol dimethyl ether, (15:0) 2-methyl cardol dimethyl ether, and (15:0) cardanol methyl ether; (b) correction and normalization of the % composition by the use of relative response factors, (a)/RRF; (c) calculation and normalization of the results in terms of the (15:0) phenols, anacardic acid, cardol, 2-methyl cardol, and cardanol; and (d) expression of the results shown in the table as the unsaturated phenols.

Normalization of the results excluding the % anacardic acid, gives the figures in the lower half of Table II, and those for technical CNSL (ref.) show good agreement with the previous analysis (11) on 2% PEGA. The three sources show differences, particularly source B which contains ca. 40% more cardol and 6% less cardanol than the others.

3% Dexsil was a more satisfactory column for technical CNSL than for natural CNSL since the resolution of (15:0) dimethyl anacardate was considerably improved when the latter was present in minor amount.

The results reveal the presence of a small % of anacardic acid in all the sample, indicating that the industrial processing has effected a good compromise between the simultaneous reactions of decarboxylation and polymerization.

TABLE III

Composition (%) of the Unsaturated Constituents of the Component Phenols of Technical CNSL from Different Sources, by TLC/Mass Spectrometry

Component and parameter	Constituent 15:3 (Triene)	15:2 (Diene)	15:1 (Monoene)	15:0 (Saturated)
Technical CNSL (reference)				
Cardanol	47.97 (39.53)[a] (1.50)	16.12 (13.28) (0.50)	31.97 (26.34) (1.00)	3.94 (3.25)
Cardol	56.81 (3.77)	27.84 (1.85)	15.07 (1.00)	0.27
2-Methyl cardol	50.23	23.63	24.80	1.34
Source A				
Cardanol	50.87 (41.99) (1.81)	16.80 (13.87) (0.59)	28.08 (23.18) (1.00)	4.24 (3.50)
Cardol	56.46 (3.73)	28.25 (1.86)	15.15 (1.00)	2.70
2-Methyl cardol	49.82	24.36	24.73	1.08
Source B				
Cardanol	58.99 (45.50) (2.72)	15.36 (11.85) (0.71)	21.64 (16.69) (1.00)	4.01 (3.09)
Cardol	67.18 (7.97)	24.20 (2.87)	8.43 (1.00)	0.19
2-Methyl cardol	62.20	20.56	16.27	0.96
Soruce C				
Cardanol	45.23 (37.60) (1.40)	18.22 (15.15) (0.57)	32.20 (26.77) (1.00)	4.35 (3.62)
Cardol	56.56 (3.97)	28.92 (2.03)	14.25 (1.00)	0.26
2-Methyl cardol	50.48	23.07	25.27	1.17

[a]Figures in parentheses obtained by multiplying % unsaturated component times cardanol content from Table II.

Table I shows that OV17, SE52, and SE30 are alternative stationary phases for the analysis of hydrogenated and methylated technical CNSL. In other experiments single determinations gave results on 3% Dexsil, 3% OV17, 5% SE52, 2% PEGA, and 3% PEGA that were identical and illustrated the principle that % composition is independent of the stationary phase used.

Use of the unsaturated phenolic acetates: With technical CNSL, SE52, Dexsil 300, and SE30 proved useful stationary phases for the quantitative analysis of the unsaturated phenolic acetates.

The relative response factors (RFF) for the acetates of the three main component phenols were determined by the GLC examination of standards 1 and 2. By GLC on 3% SE30, standard 1 contained cardanol acetates, 57.63 ± 2.82% and cardol diacetate, 42.37 ± 2.73%; and standard 2 contained cardanol acetate, 69.68 ± 0.78% and 2-methyl cardol diacetate, 30.33 ± 1.35%. The RRF values (peak area/wt x 10^3) found, namely 2.1181, 1.6259 for standard 1, and 0.86241, 0.55567 for standard 2, respectively, were interrelated giving relatively 1.00000 (cardanol acetate), 0.7676 (cardol diacetate), and 0.6443 (2-methyl cardol diacetate) for the principal acetates. The RRF values for the acetates of cardanol, cardol, and 2-methyl cardol from each source cannot strictly be assumed to be the same owing to minor differences in the unsaturation (15).

The compositional results for the acetylation method, applied to technical CNSL (reference) and the three different sources, are shown in Table II. The steps in the processing of results were (a) calculation of the uncorrected normalized % composition from the peak areas by GLC, (b) the correction and normalization of the % composition [(a)/RRF], and (c) the expression of the results from (b) as the unsaturated component phenols (e.g., cardanol, average dienoid, MW 300, gives the acetate, MW 342; cardol, average trienoid, MW 314 gives the diacetate, MW 398; 2-methyl cardol, MW 328, mainly trienoid, gives the diacetate, MW 412).

The results are comparable with those by the hydrogenation and methylation procedure with source B substantially higher in cardol although in general because of the decreased resolution (R) of the diacetates of cardol and 2-methyl cardol the method is inherently less accurate.

The difference between the % cardanol in the two methods, particularly in the case of technical CNSL (reference), could be due to the decarboxylation (at 220 C) of undetected traces of anacardic acid 0-acetate formed in the acetylation. From the % anacardic acid found (by GLC on Dexsil 300) and the equivalent cardanol produced by decarboxylation, the calculated % of cardanol was 83.08% (originally, Table II, 84.03%) leading to a normalized % composition, cardanol (83.88%), cardol (12.29%), and 2-methyl cardol (3.84%), which brings the results nearer to those for the hydrogenation and methylation procedure.

From Table I, Dexsil 300 and SE52, but not OV17 or PEGA, would be alternative stationary phases for the analysis of the phenolic acetates. The results of single determination of 3% Dexsil, and 5% SE52 showed close agreement.

Composition of the Unsaturated Constituents of the Component Phenols in Technical CNSL from Difference Sources

The original GLC procedure (11) for quantitative analysis of the unsaturated constituents of the component phenols as methyl ethers on 2% PEGA is more time consuming for the examination of a range of samples than a recently developed procedure (13) based on mass spectroscopy (MS) which shows close agreement (15).

It consists of a preliminary TLC separation of the component phenols followed by MS analysis with a repeated scanning technique. The results are summarized in Table III for the four samples, technical CNSL (reference) and sources A, B, and C. The steps in the procedure are (a) calculation of the normalized % composition from the peak heights of the relevant molecular ion (P) in the mass spectrum, (b) normalization of the % composition corrected for the (P + 2) contribution, (c) normalization of the % composition corrected for relative response differences (b x RRF) (13). The relative proportions of the (15:1), (15:2), and (15:3) constituents are shown in the lower bracket [on the basis in each case of (15:1) = 1]. Alongside the cardanol in each source the % constituent is shown in terms of the total % cardanol component found in the source (Table II).

TABLE IV

% Nonvolatile (Polymeric) and Volatile Materials in Technical CNSL from Different Sources

Source	% Nonvolatile (polymeric) materials		% (Average) of (1) and (2)	% Volatile material	Volatile material[a] % composition (C15 and C17 phenols)			
	(1) By TLC	(2) By mol distn.			C15 Cardanol	C17 Cardanol	C15 Cardol	C15 2-Methyl
Technical CNSL (reference)	7.13	8.74	7.935	92.065	87.2	1.80	9.87	2.20
Source A	7.30	8.94	8.12	91.88	88.25	1.81	8.03	1.61
Source B	8.95	10.97	9.96	90.04	77.32	5.37	11.56	5.75
Source C	6.43	7.88	7.155	92.845	86.55	1.74	7.25	2.46

[a]These compositional figures are uncorrected.

The relative proportions of unsaturated constituents [on the basis of (15:1) = 1] indicated a similarity between technical CNSL (reference) and source C, while source A is rather different and source B markedly different with a considerably greater proportion of (15:3) constituent present.

These results are relevant to the acidic polymerization step used in a number of applications of technical CNSL. The triene (15:3) is the most reactive constituent, and CNSL from source B would be expected to be faster in reaction.

Polymeric Substances in Technical CNSL

Prolonged thermal treatment ($\geqslant$ 200 C) of anacardic acid and of technical CNSL results in gradual polymerization, presumably by a succession of autocatalyzed reactions in which (15:3) cardanol disappears, although the diene, and certainly the monoene, are less susceptible in this process. Industrial decarboxylation would therefore be expected, however efficiently carried out, to result in some polymerization. Dimeric and trimeric as well as more highly polymeric material is considered to be present.

The latter material has been determined by TLC and by molecular distillation. Multiple development enabled all the monomeric and oligomeric phenols to be separated from the polymer which remained as the base line of the TLC plate and was eluted with a polar solvent followed by gravimetric determination.

In the molecular distillation, all volatile monomeric material was removed up to 240 C/10^{-4} torr and collected in a series of fractions which were then analyzed by GLC (SE30), and the summed values (uncorrected) of the component obtained. The residual polymeric material in the still was weighed. The results for the two methods are shown in Table IV. The heating in molecular distillation may be the reason for the slightly higher % polymer compared with the TLC method. With regard to the composition of the molecular distillate, relative response factors are not available for the unsaturated phenols. The % cardol was generally slightly lower than found with the GLC analysis of the phenolic acetates and confirms the greater susceptibility of this component to polymerization.

Examination of the highest fractions from the molecular distillation indicated the presence of less volatile (oligomeric) materials representing some 10 to 15% of the latter. These migrated by TLC unlike the more highly polymeric materials which remained at the base line. GLC studies of the more volatile methylated/hydrogenated and of trimethylsilylated technical CNSL have indicated the existence of some extremely long retention peaks. These are the subject of further quantitative work concerned with the use of internal standards, the determination of the molecular weight, and total composition (by GLC and MS) of technical CNSL and its molecularly distilled fractions.

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