

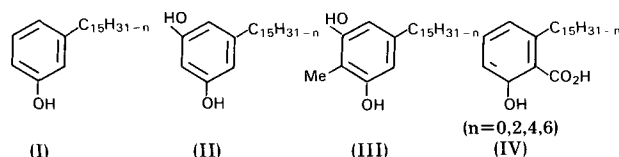
Practical Liquid Chromatographic Separation of the Phenols in Technical Cashew Nutshell Liquid from *Anacardium occidentale*¹

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The practical separation of cardanol from technical cashew nutshell liquid or its distillate has been effected by liquid chromatography on Silica Gel H 60 (TLC type) with solute/adsorbent in the range 1:5–1:6. Concentrates of the monoene, diene and triene constituents of cardanol have been prepared by argentation liquid chromatography on Silica Gel H 60 with dry incorporation of 15% silver nitrate. The present use of pressurized columns was made prior to the advent of flash chromatography. *Lipids* 21, 241–246 (1986).

Cardanol (I) the principal component of technical cashew nutshell liquid (CNSL) together with cardol (II) and 2-methylcardol (III) is formed industrially (2,3) by the hot decarboxylation of the anacardic acid (IV) in natural CNSL in the cashew nut (*Anacardium occidentale*).



The production of the cashew nut industry, which has grown steadily in the last two decades, has been projected (4) to be in excess of 10⁶ ton/yr by the early 1990s and theoretically should yield 25% of by-product technical CNSL though processing losses result in smaller yields. While the established use of technical CNSL in friction dusts involves no purification stage, increasing interest in chemical uses has led to various distillation procedures (5–7) for obtaining cardanol. Cardol also has a potential chemical utility due to its greater side chain unsaturation and reactivity in the aromatic ring than cardanol, but because it is not recoverable by these methods due to its higher boiling point and greater sensitivity than cardanol to thermal deterioration, it is best obtained by column chromatography.

In the present work cardanol and cardol have been separated by this technique with thin layer chromatographic Silica Gel H type 60 at much higher solute/adsorbent ratios than previously (8,9) with the additional objectives of effecting solvent recovery and column reuse.

The conditions we have found valuable are similar to those described in the technique of flash chromatography (10), although our experiments with the pressurized technique were done prior to that description. The important factors in preparative liquid chromatography of sample load and resolution (11), of large samples of solute (12)

and theoretical aspects (13) have not been examined in the field of phenolic lipid separation.

Argentation methods are necessary (14) for resolving the monoene, diene and triene constituents of the component phenols as fractional crystallization procedures are unduly slow (15), although for some applications (16) complete resolution of the constituents is not necessary. Argentation columns have been prepared previously by slurring aqueous (17) or aqueous methanolic solution of silver nitrate with Silica Gel G (18) and by the use of silver nitrate dissolved in acetonitrile (19). We have examined the novel method of dry incorporation of finely powdered silver nitrate into Silica Gel H 60 and much higher solute/adsorbent ratios for the separation of the constituents of cardanol.

All fractions obtained in chromatographic separations have been monitored by thin layer chromatography (TLC) followed by gas liquid chromatography (GLC) examination (20) of the combined fractions. Fractions from argentation columns were analyzed subsequently by high performance liquid chromatography (HPLC) (21). Quantitative analysis has not been used previously (8,22,23).

EXPERIMENTAL PROCEDURES

Materials. Technical CNSL was obtained from British Coco Mills (Hull, United Kingdom), Tar Residuals Ltd. (London, S.E.I., United Kingdom) and Minnesota 3M Research Ltd. (Harlow, United Kingdom) Natural CNSL was extracted as described (9) as were the recovered cardol, 2-methylcardol and cardanol after removal of anacardic acid used for the separation in Table 2. Technical CNSL was molecularly distilled in a single stage wiped-wall still to remove polymeric materials. Vacuum-distilled CNSL was isolated as described (5).

Silica Gel H (TLC grade, type 60, article 7736, E. Merck, Darmstadt, West Germany) or Silica Gel (article 9385) and/or Silica Gel MFC was used. Silica Gel G would be equally effective.

Chromatography. Preparative column chromatography for the experiments in Table 1 was carried out with a wide bore (id 6.5 cm × 50 cm length) glass column of known volume, equipped with a sintered disc (porosity 2), a stopcock with a PTFE key at the lower end and a tightly fitting rubber bung at the upper end having a glass entry tube for pumped solvent or for attachment of a hand-operated double rubber bulb, air pressurized (scent bottle type), which was invaluable in the absence of a compressed air supply.

The column was packed by slurring the silica gel with a known volume of light petroleum and consolidation by light tapping during filling. From the volume of solvent collected when the solvent and adsorbent levels were equal, the dead space was found. Three closely fitting circles of filter paper were placed on the adsorbent to ensure even passage of the solute solution (in light

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petroleum 60–80 C). A hand-actuated air pressure ensured a practical rate of development and elution; in the absence of this, a small reciprocating pump (Hyflo model B, Metcalf Bros., London, United Kingdom) was useful for step-wise elution, although it was practicable to remove the bung and add the new solvent when the adsorbent was almost exposed.

Light petroleum (60–80 C) with the progressive addition of diethyl ether was preferred to light petroleum/ethyl acetate to assist solvent recovery by distillation. Chloroform/ethyl acetate (Table 3) was an alternative solvent with which TLC experience could be related to that of column chromatography. All fractions were monitored by analytical TLC on Silica Gel G type 60 (commercial plates) with the solvent, light petroleum (40–60 C) diethyl ether (70:30, v/v) and visualization of bands with 0.1% ethanolic rhodamine 6G or 50% aqueous sulphuric acid followed by charring at 150 C. For fraction volumes of 20 ml or less, a fraction collector was used of the turntable type with 84 tubes (Central Ignition Co., London, N.I., United Kingdom). Fractions were combined appropriately into six groups and concentrated and the phenolic material was weighed.

The comparative separations with Silica Gel MFC were performed with glass columns packed as before and usable without pressurization (i.e., 2.5 cm × 65 cm length) equipped with a PTFE stopcock.

Dry incorporation argentation columns (Table 3) were prepared from Silica Gel H (type 60, article 7736) by mixing with dry, finely ground silver nitrate of particle size distribution as indicated in Table 3, followed by a brief activation of the mixture at 110 C and then packed as before. Control wet incorporation columns were prepared using a concentrated aqueous solution of silver nitrate with the Silica Gel H and by drying, grinding and activa-

tion of the mixture in subdued light at 110 C. Columns were protected from the light by wrapping with foil and were used with pressurization. The solvent light petroleum (60–80 C) diethylether was preferred to light petroleum/ethyl acetate. Fractions eluted with light petroleum/ether were free of silver nitrate; it was removed from methanolic eluates by evaporation and aqueous washing of the ethereal extract, which was then dried and weighed. All fractions were monitored by analytical TLC as described (5) with reference samples of the cardanol constituents.

GLC on the fractions from argentation columns was conducted at 190 C with 4% (w/w) polyethyleneglycol adipate on silanized 60–100 mesh chromosorb W and apparatus as described (20). Fractions from column separations on Silica Gel 4 type 60 were analyzed on 3% SE 30 as described (20).

HPLC of fractions from argentation columns was effected more recently by the reversed phase procedure on 5 μm ODS Spherisorb with equipment and the gradient elution program as described (21).

The following unsaturated constituents had the retentions (min) indicated, (15:3)-cardol (2.26), (15:3)-cardanol (3.37), (15:2)-cardanol (4.07), (15:1)-cardanol (7.63) and polymer (14.16).

RESULTS AND DISCUSSION

Adsorption chromatography of cashew phenols. Following earlier experiments in which Davison grade silica gel 60–120 mesh had been used with an adsorbent/solute ratio of 50:1, it seemed feasible to effect practical separations with TLC type silica gel having considerably greater surface area and uniformity of particle size. Table 1 summarizes two experiments of the series in which two grades

TABLE 1

Adsorption Chromatography of Technical CNSL on Silica Gel H TLC Type

Technical CNSL (g)	Silica Gel H (g)	Combined fraction	Wt (g)	%	Solvent ^a	Volume (ml)	Component phenol
Experiment 1 (25.6)	Article 7736; 4th reuse of column (125)	1	17.68	69.1	P; P/E (12:1); P/E (10:1)	650; 650; 650	Cardanol pure
		2	0.90	3.5	P/E (7:1)	650	Cardanol/2-methylcardol
		3	0.98	3.9	P/E (3:1)	650	Cardanol/2-methylcardol
		4	0.80	3.1	P/E (1:1)	650	2-methylcardol/cardol
		5	2.84	11.1	P/E (1:1)	650	Cardol (pure)
		6	2.40	9.3	M	650	Polymer
Experiment 2 (50.0)	Article 9385 (250)	1 (1–80) ^c	34.42	61.0	P; P/E (12:1); P/E (10:1) P/E (7:1)	1000; 500; 500; 500	Cardanol (98.5%) ^b
		2 (82–89)	1.04	3.7	P/E (3:1)	500	Cardanol (87.5%), 2-methylcardol
		3 (90–97)	2.34	4.2	P/E (3:1); P/E (1:1)	500; 500	Cardanol (61.5%), 2-methylcardol (36.4%)
		4 (98–106)	4.17	7.4	P/E (1:1)	500	2-methylcardol (52.3%), cardol (40.8%)
		5 (107–122)	9.19	16.3	P/E (1:1)	650	Cardol (98.8%)
		6 (128–141)	5.24	9.3	M	2000	Polymer

^aLP, light petroleum (60–80); E, diethylether; M, methanol.

^bGLC analyses of trimethylsilylether.

^cFigures in brackets show the ranges of subfractions of eluant collected.

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of Silica Gel (type 60) were used. The vertical columns show the combined phenolic fractions, the weight and percent of the bulked fractions, the compositional assignment of the fraction and the relevant solvent and its volume for that part of the chromatogram. In a preliminary experiment with semipurified technical CNSL, Silica Gel H type 60 (article 7736) was used, after which the column then was reused four times with the same solvent system. For the first three runs, 30.20 g, 34.97 g and 35.60 g, respectively, of semipurified CNSL were used; in the fourth, 25.60 g of technical CNSL was used, as shown in the table. The amount of solute was increased in the first three because the resolution was sustained in the series. Visual examination alone of the final array of fractions clearly indicated the demarcation between the main component phenols. Figure 1 shows a typical chromatogram by analytical TLC of alternate samples in which a total of 141 fractions was collected. Figure 2 gives the results from combining fractions. It was convenient to combine fractions into six groups in the two experiments, the first representing pure cardanol and the fourth or fifth being pure cardol, while 2-methylcardol containing some cardanol or cardol was present in intermediate fractions. Polymeric material was eluted with methanol and tenaciously held colored

material (in the case of technical CNSL) with a small volume of acetic acid, following the removal of which the column could be reused for other separations. That complete separations of the two main component phenols, cardanol and cardol, were achieved was confirmed by GLC (20) as shown for experiment 2 (Table 1). For six experiments, the recoveries of cardanol were 77.5, 77.5, 81.0 and 76.0% from single stage molecularly distilled CNSL and 69.1 and 61.0% from technical CNSL; recoveries of cardol were 17.7, 14.2, 8.6, 10.2, 11.9 and 16.3%.

A number of purely comparative separations of technical CNSL were carried out on Silica Gel MFC. In the three experiments at the adsorbent/solute ratios of 45:1, 30:1 and 16:1, the recoveries of cardanol were 71.8, 66.4 and 71.07 and of cardol were 16.7, 12.0 and 17.0%, respectively. In the first two experiments the main component phenols were resolved, as shown by analytical TLC and GLC while separations were inadequate in the final experiment. Generally, therefore, Silica Gel MFC is only effective compared with Silica Gel H (type 60) if used in a 10-fold greater proportion. In a final experiment with a 3:1 mixture of Silica Gel H (type 60) and MFC grade and an adsorbent/solute ratio of 3.2:1, the quality of the recovered cardanol (66.9%) and cardol (5.79%) was diminished and the presence of a number of intermediate mixed fraction rendered the separation much less effective.

Natural CNSL is a useful source of the component phenols, cardol and 2-methylcardol, after removal of anacardic acid. Table 2 shows a separation on Silica Gel G (type 60) with an adsorbent/solute ratio of 25:1, in which cardol (61.2%), 2-methylcardol (4.9%) and cardanol (25.8%) were recovered. Both analytical TLC and a plot of fraction weight/fraction number or volume eluant indicated three distinct stages in the separation. Comparison with an earlier separation on Silica Gel MFC type (adsorbent/solute, 40:1) confirmed the remarkable effectiveness of Silica Gel G type 60.

Plots of both fraction weight/fraction number and fraction weight/volume of eluant for the experiment given in Table 1 with Silica Gel H type 60 showed that the separations were optimal. Below an adsorbent/solute ratio of 5:1 with Silica Gel H type 60, it appears likely that the elu-

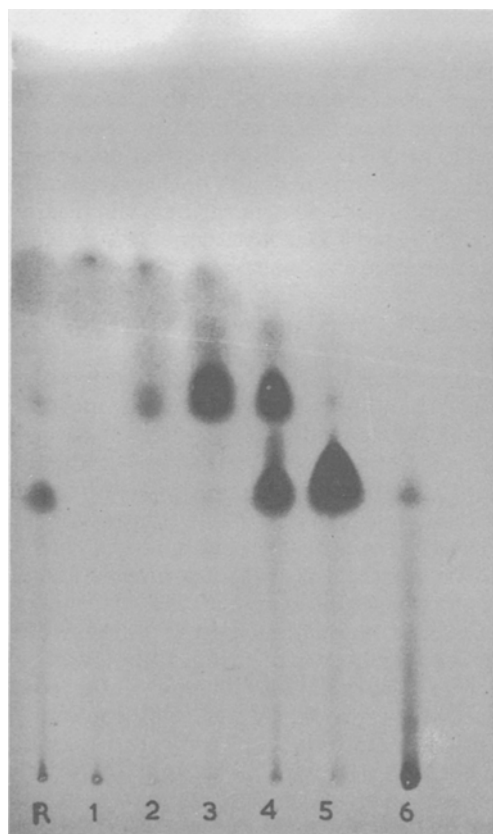


FIG. 1. Analytical TLC on combined fractions from experiment 2, Table 1. R (ref. technical CNSL), alternate fractions examined to fraction 121, then every fourth fraction to fraction 141, A frn. 10, B frn. 30, C frn. 50, D frn. 70, E frn. 90 (X frn. 81), F frn. 110, G frn. 130.



FIG. 2. Analytical TLC on fractions 1-141 from experiment 2, Table 1, on Silica Gel G type 60. Fraction 81 was a fraction collected after the column had been left overnight in the middle of a separation. It shows a trace of cardol and 2-methylcardol to be present. R (ref. technical CNSL), combined phenolic fractions 1, 2, 3, 4, 5 and 6.

TABLE 2

Adsorption Chromatography of Natural CNSL Phenols (After Removal of Anacardic Acid) on Silica Gel G (TLC Type)

Natural CNSL (g)	Silica Gel G (g)	Combined main fractions	Wt (g)	%	Solvent ^a	Volume (ml)	Component phenol
9.8	250	1	0.07	0.71	C	1000	Minor components
		2	2.54	25.8	C/EA (50:1)	1200	Cardanol (pure)
		3	0.10	1.02	C/EA (50:1)	400	Cardanol, 2-methylcardol
		4	0.48	4.90	C/EA (19:1)	800	2-Methylcardol (pure)
		5	0.08	0.82	C/EA (9:1)	500	2-Methylcardol, cardol
		6	6.02	61.2	C/EA (9:1)	2000	Cardol (pure)

^aC, chloroform; EA, ethyl acetate.

tion program would have to be modified to achieve an equivalent resolution. It is of interest that the volumes of eluant/g technical CNSL in two experiments with Silica Gel MFC and in experiment 2 (Table 1) were ca. 500 ml, 200 ml and 100 ml, respectively, and the use of Silica Gel H type already results in an economy of solvent.

The range of the particle size and its distribution appear in our experience to be particularly significant, although the influence of solute load on resolution (11) and of large samples of solute (12) and the effect of tamping compared to natural settlement of the adsorbent slurry (25) are important. Silica Gel H (type 60, article 7736) has probably more than 20 times the surface area/g compared with the MFC type if the particle size in the middle of the ranges of 0.01–0.04 mm and 0.075 mm, respectively, is compared. Silica Gel (article 9385), by contrast, with a particle size range of 0.040–0.063 mm may be intermediate in surface area/g but probably is more uniform. Silica Gel H or G, type 60 has a considerable potential use for the column separation of various synthetic or natural product mixtures.

Argentation column chromatography of cardanol. For synthetic purposes pure constituents of phenolic lipids are required, whereas in other work, concentrates of an excess of one constituent are adequate (16). Cardanol methyl ether has been separated on alumina into its 15:1, 15:2 and 15:3 constituents (26). These cannot be easily demethylated (27) to the corresponding cardanol compounds, although the trimethylsilyl ether (28) probably could be used because it is readily reconverted to cardanol, itself not resolvable on such a column. Argentation column chromatography (17) appeared to be the method of choice with Silica Gel type 60 as the adsorbent with higher solute/adsorbent ratios than previously used (8). To avoid the lengthy procedure involved with aqueous solutions of silver nitrate and Silica Gel G, we adopted for column work the novel expedient of dry incorporation of the finely divided salt. Table 3 summarizes two experiments of the series on the separation of cardanol with a pressurized column packed with Silica Gel H type 60 containing 15% (w/w) silver nitrate, 10% having proved insufficient. The initial experiments were carried out with dry incorporation and adsorbent/solute ratios of 16:1, 20:1 and 10:1, giving total recoveries of 55.0, 76.7 and 77.2%, respectively, of main constituents (monoene, diene and

triene), with the remaining material representing mixed fractions. The percent in the first experiment was low, probably due to its being a preliminary run. For comparative purposes only, two control experiments were conducted on columns prepared by wet incorporation of silver nitrate with adsorbent/solute ratios of 28:1 and 18:1. The total recoveries of cardanol constituents were 85.0 and 75.1%, the last giving a comparable separation to experiment 1 in Table 3. All fractions were monitored by analytical TLC with visualization by the acidic charring method and then were combined to give the main fractions described in the table. Plots of fraction weight/fraction number or of fraction weight/volume of eluant for the experiments showed that an adsorbent/solute ratio of 25:1 is probably optimal and that below this, unresolved intermediate fractions begin to increase. Experiment 1 was carried out with the lowest adsorbent/solute ratio in the series and, although both analytical TLC and GLC had indicated good separations, the lack of resolution of the 15:0- and 15:1-constituents led us to use HPLC analysis some time after the fractions had been collected. Fractions 3, 7 and 9 (Table 4) contain concentrates of the 15:1-, 15:2- and 15:3-constituents, respectively.

By comparison, at the much greater adsorbent/solute ratio of 900:1 on Silica Gel (60–120), which is larger in particle size than Silica Gel MFC containing 100% silver nitrate, complete resolution of cardanol with virtually 100% recovery of solute was effected (8). The resolution $2d/(w_1 + w_2)$ can be readily found to be 5 from the information given; both the adsorbent/solute proportion and the percent of silver nitrate could have been considerably lowered. The present described experiments had to be concluded before the full scope of the dry incorporation technique could be examined in the higher adsorbent/solute ratio range between 25:1 and 40:1. Similar separations of other cashew phenols have been effected at higher adsorbent/solute ratios by the wet method. Methyl anacardate, the methyl ester of (IV) (2.5 g), was readily resolved into the 15:0, 15:1, 15:2 and 15:3 constituents on Silica Gel H type 60 (170 g) impregnated with silver nitrate (340 g) by the slurry method. Cardol (II) contains more than 65% of the 15:3 constituent and on Silica Gel H type 60 (200 g) containing 15% silver nitrate, with an adsorbent/solute ratio of 48:1, it very readily was obtained pure.

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TABLE 3

Argentation Adsorption Chromatographic Separation of Mixed Cardanol on Silica Gel H TLC Type Containing 15% Dry Incorporated Silver Nitrate^a

Cardanol (g)	Silica Gel H (g)	Combined main fractions	Wt (g)	%	Cardanol constituents	Solvent ^b	Volume (ml)
12.5	250	1	0.6	6.0	15:0, 15:1	P; P/E (20:1)	100; 500
		2	1.22	12.2	15:1	P; (15:1)	300
		3	1.36	13.6	15:1	P/E (12:1)	300
		4	0.52	5.2	15:1	P/E (10:1)	400
		5	0.75	7.5	15:1, 15:2	P/E (8:1)	300
		6	0.91	9.1	15:2, 15:1	P/E (5:1)	1000
		7	1.28	12.8	15:2	P/E (2:1)	400
		8	0.52	5.2	15:2, 15:3	P/E (2:1)	100
		9	2.34	23.4	15:3	P/E (2:1)	100
10	100	1 (33-64) ^c	6.48	42.30	Monoene	P; P/E (20:1) for fractions (1-12)	100; 500
		2 (65-82)	2.27	14.82	Monoene, diene	P/E (15:1) (13-24)	300
		3 (83-104)	2.04	13.32	Diene, monoene	P/E (12:1) (25-46)	300
		4 (105-122)	0.99	6.46	Triene, diene	P/E (10:1) (47-70)	400
		5 (123-140)	1.00	6.50	Triene	P/E (8:1) (71-90)	300
		6 (141-166)	2.54	16.60	Triene	P/E (5:1) (91-146) P/E (2:1) (147-166)	1000 600

^aParticle size sieve distribution: 94.6% passed through 500 μm , 87.1% through 355 μm , 68.1% through 210 μm and 9.4% through 53 μm .

^bP, light petroleum (60-80); E, diethylether.

^cFigures in parentheses show the ranges of subfractions of eluant collected.

TABLE 4

Composition (%) by HPLC Analysis of Fractions from Argentation Adsorption Chromatography of Cardanol^a

Fractions	Wt (g)	%	% Composition of cardanol constituents			
			15:3 (Triene)	15:2 (Diene)	15:1 (Monoene)	15:0 (Saturated)
1	0.60	6.0	—	—	—	—
2	1.22	12.2	2.95	0.62	81.35	—
3	1.36	13.6	2.29	4.26	85.19	8.26
4	0.52	5.2	4.27	4.90	89.31	1.52
5	0.75	7.5	5.83	13.54	80.03	0.60
6	0.91	9.1	18.99	45.78	35.22	0.0
7	1.28	12.8	3.06	82.21	13.17	1.55
8	0.52	5.2	32.03	65.00	2.77	—
9	2.34	23.4	96.54	1.99	1.47	—

^aThe cardanol had the composition 15:3-cardanol (43.43%), 15:2-cardanol (18.20%), 15:1-cardanol (25.11%), 15:0-cardanol (3.01%), cardol (1.15%), polymer (7.32%), and was used for the separation on 100 g Silica Gel G (Table 3).

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