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LONG-CHAIN PHENOLS

XII[*]. COMPOSITIONAL STUDIES: THE POLYMERIC MATERIAL IN THE UNSATURATED PHENOLS OF *ANACARDIUM OCCIDENTALE*

J. H. P. TYMAN

School of Chemistry, Brunel University, Uxbridge, Middlesex (Great Britain)

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SUMMARY

By the use of *n*-alkane internal standards the proportions of the non-volatile and volatile material in the unsaturated phenols of natural and technical cashew nut-shell liquids (CNSL; *Anacardium occidentale*) have been determined by gas–liquid chromatography. For the analyses the hydrogenated and methylated natural and technical products were used and also the acetylated (unsaturated) technical material. With the hydrogenation/methylation procedure the natural product was found to contain approximately 20% polymeric material and technical CNSL 24% in a higher state of polymerisation. The acetylated unsaturated technical CNSL contained about 32% of polymeric material showing that in the thermal conditions of GLC analysis further polymerisation occurs, unless the hydrogenated material is used. Polymerisation mechanisms are discussed and comparisons briefly made with other unsaturated natural products.

INTRODUCTION

Previously, gas–liquid chromatography (GLC) of the constituents[1] of the component phenols[2] of the volatile portion of natural (*Anacardium occidentale*) and of technical cashew nut-shell liquid (CNSL) has been studied. The non-volatile part of technical CNSL was estimated by thin-layer chromatography (TLC) and by molecular distillation[3]. The volatile portion of natural CNSL contains a majority of the monomeric phenolic acid, anacardic acid (I; $R_1=CO_2H$, $R_2=R_3=H$, $n=0,2,4,6$), cardol (I; $R_3=OH$, $R_1=R_2=H$, $n=0,2,4,6$), cardanol (I; $R_1=R_2=R_3=H$, $n=0,2,4,6$) and

		$n = 0$
	8 (Z)	$n = 2$
	8 (Z), 11 (Z)	$n = 4$
	8 (Z), 11 (Z), 14	$n = 6$

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* Part XI: ref. 3. Part X: *Lipids*, in press.

2-methylcardol (I; R_3=OH, R_2=CH$_3$, R_1=H, n=0,2,4,6) and in technical CNSL, cardanol is the principal phenol formed through the decarboxylation[4] of anacardic acid.

In Part IX[5], preliminary results were described on the use of n-alkane internal standard with the natural and technical products. This work has now been extended to determine more accurately the proportions of non-volatile (polymeric) and volatile materials in hydrogenated (15:0) methylated natural and technical CNSL, as an alternative procedure to TLC and molecular distillation. The same materials were used as in Part VI[2]. It was found necessary to use the n-C$_{26}$ and n-C$_{28}$ alkanes as internal standards for natural and technical CNSL, respectively.

An uncertainty in the GLC analysis of unhydrogenated acetylated technical CNSL[3] has been the influence of column and pre-heated temperatures, usually 230° and 280°, respectively, in possibly causing further polymerisation since both are considerably above that reached in the hot decarboxylation process[4]. The analytical results have been compared with the hydrogenation and methylation method.

The percent non-volatile material of hydrogenated and methylated products was higher than found by TLC or molecular distillation and greater still in the case of the unhydrogenated acetylated technical CNSL, indicating the susceptibility of the highly unsaturated materials to polymerisation (and probably cyclisation) under various physical as distinct from chemical conditions. The findings suggest the existence of distinct thermal and photochemical mechanisms. Rules have been formulated[6] to predict the course of certain cyclisation reactions proceeding under these two conditions. The highly unsaturated glycerides and vitamin A are analogous to the phenolic lipids in their thermal and photochemical reactions and the probable course with the latter materials is briefly discussed.

EXPERIMENTAL

Materials

Hydrogenated and methylated natural and technical cashew nut-shell liquid were as previously described[2]. These materials had been kept under aseptic conditions and GLC demonstrated them to be unaltered. Acetylated technical CNSL was obtained by the acetylation of technical CNSL with acetic anhydride–pyridine as described[3]. (15:0) Phenolic methyl ethers were as previously used[2]. GLC examination on 3% SE-30 and on 3% Dexsil showed the absence of phenolic material in the methyl ethers and the acetates.

TLC was carried out on silica gel G as described[7] and was used as a check on purity. In chloroform and in chloroform–light petroleum (b.p. 40°–60°) (30:70), the following R_F values were found: (15:0) cardanol methyl ether (0.74, 0.67), (15:0) cardol dimethyl ether (0.72, 0.42), 2-methylcardol dimethyl ether (0.72, 0.50), (15:0) dimethylanacardate (0.61, 0.17), (15:0) methyl anacardate (0.67, 0.29). In the same two solvents the following R_F values were found for (15:0) cardanol acetate (0.62, 0.32), (15:0) cardol diacetate (0.43, 0.13) and 2-methylcardol diacetate (0.42, 0.27).

Gas–liquid chromatography

GLC was carried out on a Pye Unicam GCD apparatus equipped with flame ionisation detector (FID), computing integrator DP88 and AR55 linear recorder.

Glass columns (5 ft. × 3/16 in.) were used with acid-washed and silanised diatomite M as support and 3% Dexsil 300 as stationary phase. The column temperature was 230° and the injector and detector were maintained 50° higher. The gas pressures and flow-rates were: nitrogen 17 p.s.i., 45 ml/min; hydrogen 20 p.s.i.; air 5 p.s.i., 225 ml/min. Some determinations were made using a Pye 104 chromatograph under the conditions previously given[2]. The relative response factors (RRF) of the phenolic methyl ethers were found to be identical for the FID in several different Pye 104 instruments and in the GCD apparatus. Peaks were recorded at a chart speed of 60 sec/cm. Injections were made with approximately 5% benzene solutions up to sample sizes of 2 μl. Attenuation adjustments were made to obtain all the components with approximately similar peak size wherever possible. Triangulation and integration were found to give comparable results. All results were the average of at least six determinations and standard deviations were calculated in the usual way.

Spectroscopic determinations and molecular distillation

^{1}H Nuclear magnetic resonance (NMR) spectra were determined on a Varian T60 instrument with tetramethylsilane as internal standard and indicated the absence of OCH_3 (aliphatic) (no dimethyl sulphate present) and $HO\cdots CO_2H$ (hydrogen-bonded) due to anacardic acid[8]. Mass spectra were carried out on an RMS 4 Perkin-Elmer–Hitachi instrument and by the PCMU, Harwell. The presence of n-C_{28} alkane in the n-C_{26} material was confirmed in this way. Molecular distillations were carried out in a Ridgeway-Watt 10-stage molecular still. Microanalyses and molecular weight determinations were carried out by BMAC, Teddington, Middlesex.

Preparation of standard solution

The C_{26} n-alkane was used for hydrogenated and methylated natural CNSL and the C_{28} for hydrogenated and methylated technical CNSL and also for acetylated unsaturated technical CNSL.

Internal standards and reference compounds. For the (15:0) phenolic methyl ethers, standards 1 and 2 were prepared. All weighings were made on a 5-place balance and the materials used have been summarised in Tables III and IV.

Standard 3 contained (15:0) cardol dimethyl ether (0.06755 g), n-C_{26} alkane (0.0949 g; corrected weight 0.0910 g) and n-C_{28} alkane (0.07340 g; corrected weight 0.07692 g) and the percent composition from the peak areas was 24.34% ± 0.394%, 41.44 ± 0.323% and 34.19 ± 0.376%, respectively.

For the (unsaturated) technical CNSL, a standard was prepared based on cardanol (containing saturated monoene, diene and triene constituents) (0.20388 g), cardol (0.13697 g) and n-C_{28} alkane (0.11635 g) which was then acetylated with acetic anhydride–pyridine reagent (5 ml) to effect complete reaction. The percent composition from the average peak areas was 44.06 ± 0.187%, 32.14 ± 0.332% and 32.80 ± 0.253%, respectively. Samples were withdrawn and used for GLC examination without preliminary recovery of the acetates.

The (15:0) phenolic methyl ethers and the relevant internal standard were made up in hot benzene solution, the only satisfactory solvent for all the materials. The unsaturated phenolic acetates were more soluble and the excess acetylation reagent mixture was a satisfactory solvent which prevented slight reversion of the acetates to the phenols.

Internal standards and CNSL samples. After the appropriate number of determinations with the standards, the relevant *n*-alkane was incorporated with the particular hydrogenated and methylated CNSL sample being examined.

For unsaturated technical CNSL the *n*-C_{28} alkane was added and the mixture acetylated. This step was necessary because of complications in the work-up of acetylated technical CNSL.

All internal standards and CNSL samples were made up in benzene solution to approximately 5 ml in graduated flasks.

RESULTS AND DISCUSSION

Retention of (15:0) component phenolic methyl ethers and acetylated phenols in relation to n-alkanes

The average retention distances determined over a lengthy period, relative retentions and log (retention distances) of the principal (15:0) phenolic methyl ethers and unsaturated acetates determined on 3% Dexsil at 230° in relation to the C_{20}–C_{32} *n*-alkanes are shown in Table I.

TABLE I

RETENTION DISTANCES (*RD*) OF METHYL ETHERS OF (15:0) PHENOLS AND PHENOLIC ACETATES IN RELATION TO THE *n*-ALKANE

RR = relative retention.

(15:0) Component phenolic methyl ether or acetate	RD (mm)	RR	log RD	n-Alkane	RD (mm)	log RD
Cardanol methyl ether	79.7 ± 4.85	1.000	1.901	C_{20}	16.7	1.222
Cardol dimethyl ether	161.5 ± 2.76	2.026	2.208	C_{22}	29.85*	1.475*
2-Methyl cardol dimethyl ether	184.3	2.312	2.265	C_{24}	54.33*	1.735*
Methyl anacardate	199.2 ± 3.67	2.499	2.299	C_{26}	114.6	2.058
Dimethyl anacardate	208.5 ± 1.07	2.616	2.319	C_{28}	216.6	2.335
Cardanol acetate	116.9 ± 2.60	1.467	2.067	C_{30}	411.1	2.613
Cardol diacetate	337.3 ± 6.69	4.232	2.528	C_{32}	799.6	2.902
2-Methyl cardol diacetate	374.1 ± 2.92	4.694	2.573	—	—	—

* By extrapolation from a plot of log *RD*/carbon number.

Only the *n*-C_{26} member (hexacosane) fulfilled the requirement of an internal standard to possess a retention intermediate between the two principal components. The *n*-C_{30} compound and higher *n*-alkanes would have been satisfactory for both the saturated methyl ethers and unsaturated acetates but their relatively greater insolubility was a disadvantage. However the *n*-C_{26} hydrocarbon was more useful for hydrogenated and methylated natural CNSL since the C_{28} member was close in retention to (15:0) dimethyl anacardate with *R* (resolution[9]) 0.69. The *n*-C_{26} standard would have been appropriate for hydrogenated and methylated technical CNSL (*R* of the *n*-C_{26} alkane with respect to (15:0) cardanol methyl ether, was 1.37) but was not used on account of *n*-C_{28} impurity (3.7% by GLC) which entailed a correction in the procedure.

With the unsaturated phenolic acetates the resolution *R* of cardanol acetate and the *n*-C_{26} standard was 0.145 and therefore the *n*-C_{28} alkane was used.

TABLE II

RMR VALUES OF COMPONENT PHENOLIC METHYL ETHERS DETERMINED FROM RRF VALUES RELATIVE TO n-C_{28} ALKANE

Component phenolic methyl ether or dimethyl ether	RRF	M.W.	RMR relative to n-C_{28}
Cardanol methyl ether	6.564	318	0.792
Cardol dimethyl ether	5.794	348	0.765
2-Methylcardol dimethyl ether	5.476	362	0.752
Dimethyl anacardate	5.7465	376	0.820
Methyl anacardate	3.103	362	0.426
n-C_{28} alkane	6.688	394	1.000

Determination of the RMR values

Two procedures were used, the first based on the former relative response factor (*RRF*) values found[2,5] and the second on the present internal standard procedure.

Hydrogenated and methylated component phenolic methyl ethers. From the *RRF* values and the relevant molecular weights the *RMR* values shown in Table II with respect to the n-C_{28} alkane (*RMR*, 1.000) as the internal standard were obtained.

In the second procedure the GLC results for the standards 1, 2 and 3 were used and the *RMR* values relative to n-C_{26} or C_{28} alkane calculated from the usual expression[10]. By this means the *RMR* values for three phenolic methyl ethers relative to n-C_{28} alkane were determined for standard 1 and are given in Table III. Similarly for standard 2 the *RMR* values relative to C_{26} are shown in Table IV, in the final column of which the figures derived from *RRF* information are given for comparison.

With standard 3 the *RMR* values of (15:0) cardol dimethyl ether relative to n-C_{28} and n-C_{26}, respectively, were 0.716 and 0.756. The reason for the low value (0.716) compared with the values given in Table IV is obscure since the other values indicate reasonably close agreement by the two procedures used. The *RMR* of n-C_{26} (0.948) relative to n-C_{28} (1.000) or conversely of n-C_{28} (1.055) in relation to n-C_{26} (1.000) enabled the *RMR* values of the (15:0) phenolic methyl ethers to be expressed in terms of either standard by simple proportionation.

In this way the *RMR* values for (15:0) cardanol methyl ether (0.836) and (15:0) 2-methylcardol dimethyl ether (0.794) relative to n-C_{26} were calculated from the fourth column of Table II and the appropriate conversion factor.

TABLE III

RMR VALUES FOR (15:0) PHENOLIC METHYL ETHER WITH C_{28} INTERNAL STANDARD (STANDARD 1)

(15:0) Material	Weight (g)	Percentage from peak area	RMR values*
Cardanol methyl ether	0.03938	46.287 ± 1.806	0.785
Cardol dimethyl ether	0.00648	6.782 ± 0.137	0.766
Methylanacardate	0.01418	7.952	0.427
n-C_{28} alkane	0.02656	32.104 ± 1.124	1.000

* Calculated from sample containing internal standard.

TABLE V

C_{15} PHENOLIC COMPOSITION OF HYDROGENATED METHYLATED NATURAL CNSL (WITH C_{26} INTERNAL STANDARD)

(15:0) Materials*	Weight (g)	Percentage from peak area	RMR value	Percent composition	Normalised (%)	Percentage by direct GLC**	Percentage of theory (col. 5/col. 7)
Cardanol methyl ether	(0.08159)	0.665	0.836***	1.20	1.50	1.59	75.22
Cardol dimethyl ether	hydrogenated methylated natural CNSL	5.179 ± 0.096	0.745	11.31	14.23	13.95	81.09
2-Methyl cardol dimethyl ether		0.957	0.794***	2.04	2.57	2.65	77.09
Dimethyl anacardate		30.888 ± 0.776	0.837	64.93	81.84	81.84	79.34
n-C_{26} alkane	0.09264	63.879 ± 0.751	1.000	—	—	—	—

* Materials present as component phenols in hydrogenated and methylated natural CNSL.

** Values from Part VI.

*** Values from RRF sources and others from Table IV.

TABLE IV

RMR VALUES FOR (15:0) CARDOL DIMETHYL ETHER AND (15:0) DIMETHYL ANA-CARDATE WITH C_{26} INTERNAL STANDARD (STANDARD 2)

(15:0) Material	Weight (g)	Percentage from peak area	RMR values*	RMR values**
Cardol dimethyl ether	0.05226	27.674 ± 0.555	0.745	0.760
Dimethyl anacardate	0.04926	27.105 ± 0.944	0.837	0.834
n-C_{26} alkane	0.0694***	45.221 ± 0.949	1.000	1.000

   * Calculated from sample containing internal standard.
   ** Calculated from *RRF* values.
   *** True weight (0.0694 × 0.963) g.

Acetylated (unsaturated) phenols. The *RMR* values for cardanol acetate, cardol diacetate and 2-methylcardol diacetate relative to n-C_{28} were found to be 0.596, 0.501 and 0.503. No individual values for the acetates of the constituents are yet available as they are for the unsaturated methyl ethers[5], in order to be able to derive the *RMR* values of the mixtures by prior calculation. It is of interest that *RMR* values of long chain phenolic derivatives follow the order, ArOMe > ArOAc > ArOH, taking into account previous *RRF* values[5].

Determination of the percent volatile material in natural and technical CNSL

Hydrogenated and methylated natural CNSL. The results of incorporating a n-C_{26} internal standard are given in the fifth column of Table V. The results were obtained using the expression shown in which $RMR_{(15:0)p.m.e.}$ (p.m.e. = phenolic methyl ether) and W_2 the weight of the internal standard are known. The percent composition was obtained from the known weight of hydrogenated and methylated natural CNSL taken,

$$W_1 = \frac{\text{peak area}_{p.m.e.} \times \text{M.W.}_{p.m.e.} \times W_2}{\text{peak area}_{n\text{-alkane}} \times \text{M.W.}_{n\text{-alkane}} \times RMR_{(15:0)p.m.e.}}$$

For comparison the percent composition by direct GLC[2] is given in the seventh column which compares favourably with normalised figures. The total material accounted for was 79.68% and thus 20.32% was non-volatile and represented oligomeric and polymeric material.

Hydrogenated and methylated technical CNSL. The results of GLC analysis are given in the fifth column of Table VI. The total volatile material was found to be 76.19% and 23.81% was non-volatile. The seventh column in the table gives the composition found by direct GLC examination[2].

The small difference between the natural and technical CNSL and moreover the high percentage of non-volatile material by GLC in the former is remarkable. It seems most probable that in the natural product the non-volatile substances are dimeric or oligomeric, while in the technical material as shown by the results of TLC and molecular distillation, the level of polymerisation is appreciably higher.

Acetylated technical CNSL. The results obtained by GLC analysis are given in column four of Table VII. The total volatile material accounted for was 68.42% and 31.59% was non-volatile, and the normalised results agree with those obtained by direct GLC.

TABLE VI

C_{15} PHENOLIC COMPOSITION OF HYDROGENATED METHYLATED TECHNICAL CNSL (WITH C_{28} INTERNAL STANDARD)

(15:0) Materials*	Weight (g)	Percentage from peak area	RMR value	Percent composition	Normalised (%)	Percentage by direct GLC**	Percentage of theory (col. 5/col. 7)
Cardanol methyl ether		56.785 ± 0.920	0.785	62.86	82.50	82.36	76.32
Cardol dimethyl ether	0.13323 hydrogenated methylated	9.055 ± 0.296	0.766	11.25	14.76	14.88	75.58
2-Methyl cardol dimethyl ether	Tech. CNSL	1.584	0.752***	2.08	2.73	2.76	75.47
n-C_{28} alkane	0.04788	33.382 ± 0.817	1.000	—	—	—	—

* Materials present as component phenols in hydrogenated and methylated tech. CNSL.

** Values from part VI.

*** Value from RRF sources and others from Table III.

TABLE VII

C15 PHENOLIC COMPOSITION OF ACETYLATED TECHNICAL CNSL (WITH C28 INTERNAL STANDARD)

Material	Weight (g)	Percentage from peak area	RMS value	Percent composition	Normalised (%)	Percentage by GLC[a]	Percentage of theory (col. 5/col. 7)
Cardanol acetate		39.964 ± 1.091	0.596	58.59	85.64	84.03	69.7
Cardol diacetate	0.1932 Tech. CNSL	4.212 ± 0.253	0.501	7.68	11.22	12.17	63.1
2-Methyl cardol diacetate		1.132 ± 0.097	0.503	2.15	3.14	3.79	56.7
n-C28 alkane	0.12066	54.709 ± 0.803	1.000	—	—	—	—

[a] Calculated (disregarding C17) from Table III in ref. 4.

It is apparent that the column and preheater temperatures, some 40° and 90°, respectively, above that of the decarboxylation stage in the preparation of cardanol, are sufficient to cause some polymerisation of the unsaturated constituents of the component phenols to the extent of about 8%. The lower percentage cardol compared with the hydrogenation/methylation procedure indicates the greater susceptibility of this component to polymerisation.

General analytical observations

For the analysis of hydrogenated and methylated natural and technical CNSL the internal standard was incorporated after the two reactions while it was present from the beginning in the case of the acetylated material. This was partly due to the intractability of the acetylation reaction mixture due to the separation of polymeric material from technical CNSL during the isolation of the product. Pyridine–acetic anhydride solutions were therefore used immediately following the rapid acetylation stage. The unsaturated derivatives undergo some autoxidation and polymerisation reactions upon storage although the parent phenols are somewhat more stable probably due to inherent auto-antioxidant properties.

Since some polymerisation occurs with acetylated technical CNSL it must be assumed that the standards are similarly affected and the *RMR* values are subject to some inaccuracy through a consequent slight decrease in their value, leading in turn to an overestimate in the percent composition.

For the hydrogenated and methylated products the *RMR* values were not subject to errors of chemical origin. The effect of taking average values was found to make a negligible difference to the final results which were still within the standard deviations found. An average value of 0.788 for (15:0) cardanol methyl ether gave 62.57% rather than 62.86 ± 0.92. With (15:0) cardol dimethyl ether an average value of 0.741 (0.766 from Table III and 0.716) gave a composition 11.62% in place of $11.25 \pm 0.29\%$.

Nature of the polymeric material in natural and technical CNSL

Distribution. The previous determinations[3] of the non-volatile material in technical CNSL by TLC (7.1%) and molecular distillation (8.7%) were considerably lower than found by the GLC method. The earlier figures represented highly polymeric material isolated as an intractable solid while the present results reveal the existence of a greater percentage of less highly polymerised, oligomeric material.

TLC examination of hydrogenated and methylated technical CNSL and natural CNSL showed the presence of substances of lower R_F values than (15:0) dimethylanacardate. Streaking of bands was observed consistent with probable presence of dimeric substances corresponding to each component. With the polystyrenes, the R_F of the dimer is slightly lower than that of the monomer and progressively decreases with the extent of polymerisation[11,12].

Molecular weight determinations on fractions obtained by molecular distillation of unhydrogenated technical CNSL and GLC–mass spectroscopic (GLC–MS) examination of the same fractions converted to trimethylsilyl derivatives have both indicated the likely presence of dimeric material. The molecular weight of the penultimate fraction was 358 compared with 312 for the total starting material. With 85% of cardanol (M.W. 300; dienoid) and 15% of cardol (M.W. 314; trienoid) present

(average M.W. 302), 19% dimeric material (M.W. 604) and 81% monomer would be present. Some depolymerisation in the molecular distillation as found[13] for "Kitol" the dimer of vitamin A[14] seems likely to be the reason for the relatively low percentage of dimer in the fraction studied in the present work.

GLC–MS examination of the TMS fraction indicated peaks attributable to dimeric substances in the mass ranges 740–750 (cardanol triene TMS ether M.W. 370, dimer M.W. 740) and 910–920 (cardol triene TMS ether M.W. 358, dimer M.W. 916). The molecular distillation of hydrogenated and methylated natural and technical CNSL, followed by precise mass measurements is currently being examined. GLC of hydrogenated and methylated technical CNSL on new Dexsil columns with 3% stationary phase at 220° has revealed a long retention peak (relative retention 11.2), (15:0) cardanol methyl ether 1.00, (15:0) cardol dimethyl ether 2.05. The uncorrected peak area contribution was 23%, showing some similarity to the non-volatile percentage found by the use of an internal standard.

Structure of polymerisation products. The polymerisation of technical CNSL is largely brought about by thermal processing and is quite different from that occurring under acidic conditions. By contrast the presence of oligomeric material in natural CNSL is likely to originate by a photochemical (or biochemical) mechanism. Both thermal[15,16] and photochemical mechanisms occur with the highly unsaturated glycerides which have a structural similarity to the constituents of CNSL. Experiments on the thermally catalysed conjugation and isomerisation of technical CNSL[17] resulted in extensive polymerisation suggesting that these two stages are relevant. Conjugated *trans* polyethenoid fatty esters polymerise many times faster than their non-conjugated *cis* isomers[15]. Since trienes are the major constituents of cardol and to a lesser extent of cardanol and anacardic acid, the ready polymerisation of the former particularly suggests the following probable scheme (N is a non-conjugated and C a conjugated molecule). Isomers with conjugated *trans* double bonds then probably dimerise to Diels-Alder adducts which in turn may react further.
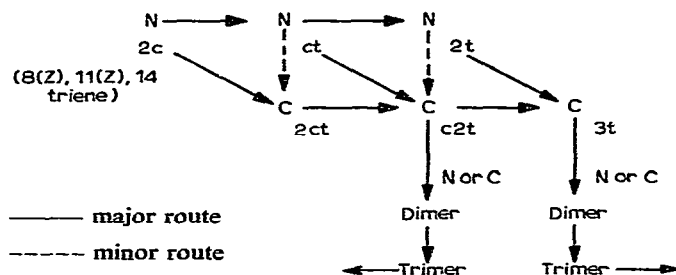
Thermal cyclisation[16], photoisomerisation[18] and photodimerisation[19] of 9(E), 11(E) 13(E) octadecatrienoic acid and the dimerisation of vitamin A to "Kitol" have been described and it seems most likely that the 8(Z), 11(Z), 14 double bonds in the trienoid constituents of CNSL undergo isomerisation to 8(E), 10(E), 12(E), as well as other structures, prior to polymerisation. Evidence for the existence of isomeric constituents in technical CNSL has appeared from recent studies[20] on the unsaturated members. Oxidation of the hydroxylated materials produced other aldehydes in addition to the expected formaldehyde, *n*-butanal, and *n*-heptanal. Ex-

periments are being carried out to determine the structure of the oligomeric materials in technical and natural CNSL.

CONCLUSION

The polymeric non-volatile material in natural and technical CNSL has been determined by GLC with an internal standard present after hydrogenation and methylation of the phenolic material. Some further polymerisation occurs in the GLC analysis of the acetylated unsaturated technical CNSL at 230°.

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