

Volatile Constituents of *Carphephorus corymbosus* and *Carphephorus paniculatus*

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The volatile fractions obtained from the leaves of *Carphephorus corymbosus* and *Carphephorus paniculatus* are shown to be small and complex. More than one hundred and thirty compounds, the majority of which were common to both species, were identified using GLC-MS as the main tool. These include mono- and sesquiterpenoids, norisoprenoids, α,β -unsaturated straight chain aldehydes and ketones, saturated aldehydes and fatty acids. The chemotaxonomical significance of these compounds is discussed.

The genus *Carphephorus* presently comprises seven species since the only recognized representatives of the genus *Trilisa*, *T. odoratissima* and *T. paniculata*, have been transferred to the former genus. Botanically *Carphephorus* and *Liatris* are closely related and both belong to the natural tribe Eupatorieae of the family Compositae.¹

Of the *Carphephorus* species, the coumarin-containing *C. odoratissimus* (*T. odoratissima*) is of a certain commercial interest and its dried leaves are commonly used in the flavouring of tobacco. We have previously examined the nonvolatile^{2,3} as well as the volatile⁴ constituents of the leaves and have encountered a great number of aroma components which, besides coumarin, obviously contribute to the attractive aroma properties of this plant.

This investigation has now been extended to the volatile fractions obtained from acetone extracts of dried leaves of *C. corymbosus* (Nutt.) T. and G. and *C. paniculatus* (Walter Ex. J. F. Gmel) Cass (*T. paniculata*) in order to provide information on the odouriferous components of these plants and to allow a chemical comparison. The latter is desirable since it may well provide chemotaxonomical data useful in the classification of the *Carphephorus* species.

RESULTS

Low-pressure distillation of the acetone extracts of *C. corymbosus* and *C. paniculatus* afforded only small amounts of volatiles having typical "green

leaf" aromas. The distillates were partitioned between pentane and water and the pentane-soluble fractions were subsequently divided into neutral and acidic components which were examined separately.

Neutrals

As is evident from the gas chromatograms shown in Figs. 1–3, the neutral fractions derived from the two plants were complex and similar to that of *C. odoratissimus*, included for comparison. It was therefore necessary to fractionate them further by chromatography on ordinary and AgNO₃ impregnated silica gel to facilitate the GLC and GLC–MS analyses. Since the present examination was performed on a very small scale, the identifications of the compounds enumerated in Table I were based primarily on comparison of mass spectra and, when possible, retention times with those of authentic samples. Only one component could be isolated and conclusively identified (*vide infra*).

In conformity with *C. odoratissimus*, the neutral volatile fraction of *C. paniculatus* contained predominantly sesquiterpene hydrocarbons, while oxygenated compounds of terpenoid and non-terpenoid origin were present in minor quantity only. The neutral material from *C. corymbosus*, on the other hand, had a considerably lower concentration of sesquiterpene hydrocarbons and a greater number of oxygenated compounds. The most striking difference between the three plants, however, lay in the varying concentrations of

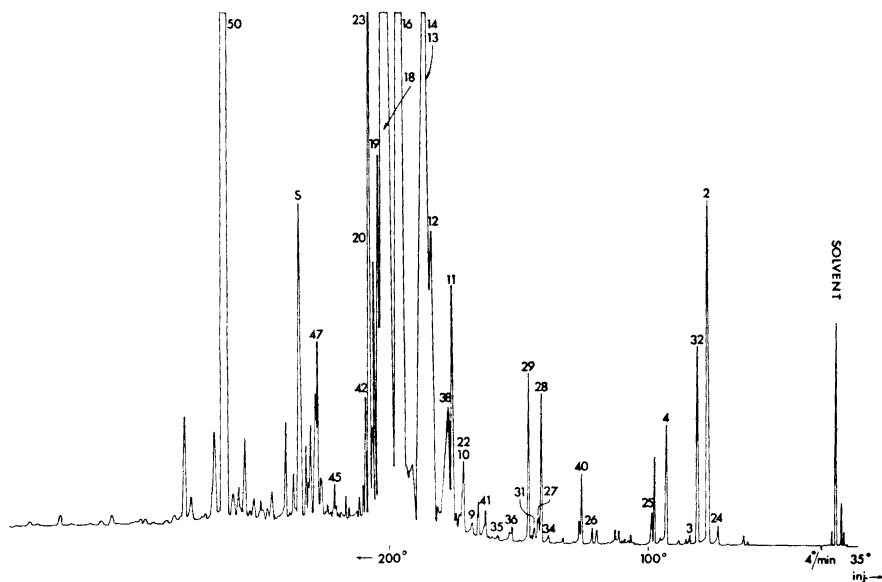


Fig. 1. Gas chromatogram of the neutral fraction from *C. odoratissimus*. Column: HB 2000 50 m \times 0.35 mm.

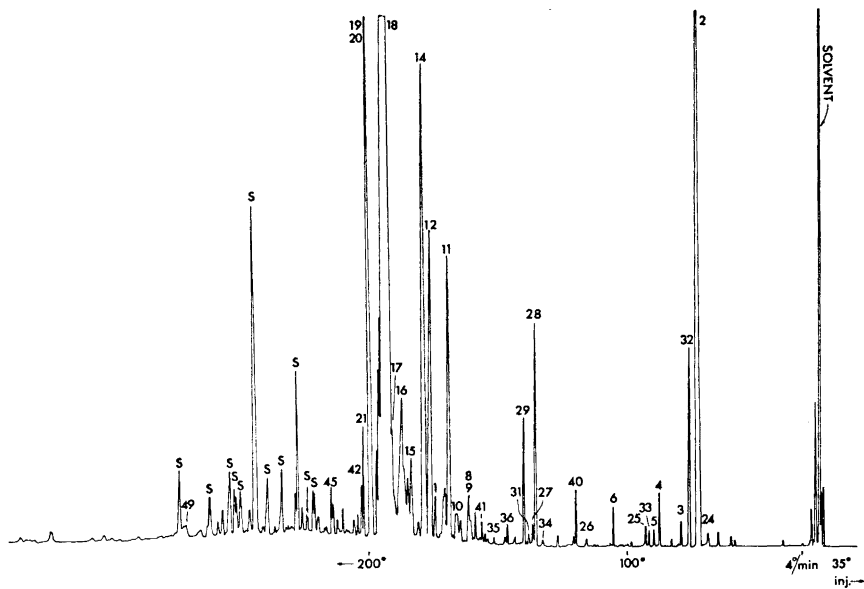


Fig. 2. Gas chromatogram of the neutral fraction from *C. paniculatus*. Column: HB 2000 50 m \times 0.35 mm.

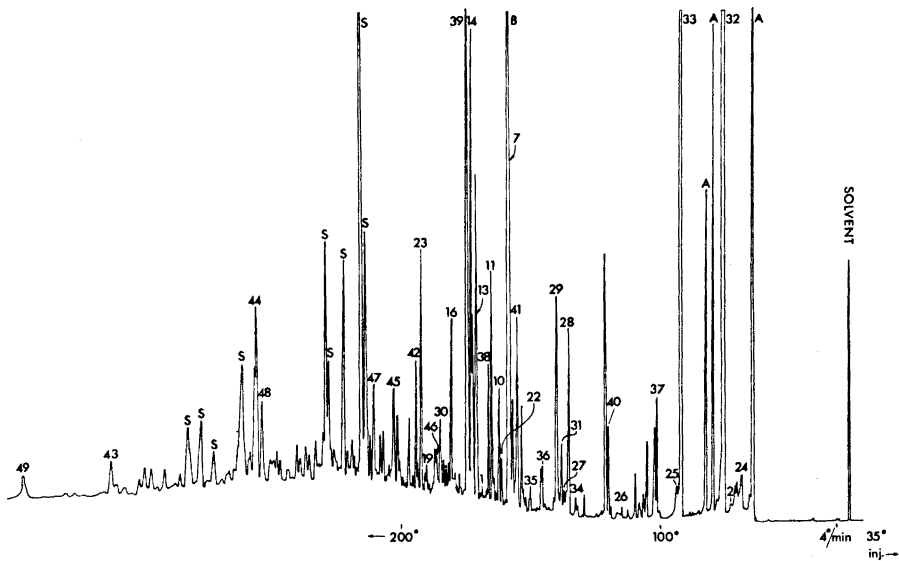


Fig. 3. Gas chromatogram of the neutral fraction from *C. corymbosus*. A = Ketones $C_6H_{10}O$, B = A dimethylcyclohexenone. Column: HB 2000 50 m \times 0.35 mm.

Table 1. Neutral constituents.

Peak No.	Compound	Method of identification		Ref.
		<i>C. corymbosus</i>	<i>C. paniculatus</i>	
<i>Hydrocarbons</i>				
	Decane	MS ^b		^a
	Undecane	MS ^b		^a
	Dodecane	MS ^b		^a
	Tridecane	MS ^b		^a
	Hexadecane	MS ^b		^a
	Heptadecane	MS ^b		^a
	Octadecane	MS ^b		^a
	Nonadecane	MS ^b		^a
1	Naphthalene	MS ^b	MS	^a
	2-Methylnaphthalene	MS ^b	MS	^a
	Dimethylnaphthalene	MS ^b		24
2	α -Pinene	MS ^b	MS, GLC	25
3	Camphene		MS, GLC	25
4	β -Pinene		MS, GLC	25
5	Sabinene		MS	25
6	Limonene		MS, GLC	25
	<i>p</i> -Cymene	MS ^b	MS, GLC	25
7	α -Guaiene	MS		26
8	α -Cubebene		MS, GLC	26
9	α -Ylangene		MS, GLC	27
10	α -Copaene	MS, GLC	MS, GLC	26
11	β -Bourbonene	MS, GLC	MS, GLC	26
	α - <i>trans</i> -Bergamotene	MS, GLC		28
12	β -Ylangene		MS, GLC	^a
13	Sativene	MS, GLC	MS, GLC	^a
14	Caryophyllene	MS, GLC	MS, GLC	29
	β -Copaene		MS, GLC	^a
15	Alloaromadendrene		MS	26
16	α -Humulene	MS, GLC	MS, GLC	26
17	γ -Muurolene		MS, GLC	26
18	Germacrene D	MS, GLC	MS, IR	^a , 6
	α -Amorphene		MS	^a
	α -Muurolene		MS, GLC	26
	β -Selinene	MS, GLC		29
	α -Selinene	MS		29
19	δ -Cadinene	MS, GLC	MS, GLC	26
20	γ -Cadinene		MS, GLC	26
	4,10-Dimethyl-7-isopropyl-bicyclo[4,4,0]-1,4-decadiene		MS, GLC	26
21	Calamenene		MS, GLC	^a
	α -Calacorene		MS, GLC	^a
<i>Ethers</i>				
	1,8-Cineol		MS, GLC	^a
22	Thymol methyl ether	MS ^b	MS, GLC	^a
23	Thymohydroquinone dimethyl ether	MS, GLC	MS, GLC	^a
	Dibenzofuran		MS ^b	^a
<i>Aldehydes</i>				
24	Hexanal	MS, GLC	MS, GLC	^a
	Heptanal	MS, GLC	MS, GLC	^a

Table 1. Continued.

	Octanal	MS, GLC	MS ^b	^a
	Nonanal	MS, GLC	MS ^b	^a
	Decanal	MS, GLC	MS ^b	^a
25	2-Hexenal	MS, GLC	MS, GLC	^a
26	<i>trans</i> -2-Heptenal	MS	MS	30
27	<i>trans</i> -2-Octenal	MS	MS	18
28	2,4-Heptadienal	MS	MS	^a
29	2,4-Heptadienal	MS	MS	^a
	2- <i>trans</i> -4- <i>cis</i> -Heptadienal	MS	MS	^a
	2,4-Octadienal		MS	Tentative
	2,4-Nonadienal	MS	MS	Tentative
30	2,4-Decadienal	MS	MS	31
	2,4-Decadienal	MS	MS	31
	2,6-Dimethylhept-5-enal	MS	MS	32
31	Benzaldehyde	MS, GLC	MS, GLC	^a
	2-Phenylethanal		MS	18
	3-Phenylpropanal		MS, GLC	33
	Veratrumaldehyde		MS	^a
	α -Campholene aldehyde		MS, GLC	34
	β -Cyclocitral	MS, GLC	MS, GLC	^a
	Safranal	MS, GLC	MS ^b	^a
	Myrtenal		MS ^b	35
	<i>Ketones</i>			
	Pentan-2-one	MS, GLC	MS ^b	36
	Pentan-3-one	MS ^b	MS, GLC	36
32	Mesityloxide	MS, GLC	MS, GLC	^{a,c}
33	Hex-3-en-2-one	MS	MS	Tentative
34	Oct-3-en-2-one	MS		37
35	Non-3-en-2-one	MS	MS	37
	Hepta-3,5-dien-2-one	MS		Tentative
36	Octa-3,5-dien-2-one	MS	MS	16
	Octa-3,5-dien-2-one	MS	MS	16
	Nona-3,5-dien-2-one	MS		Tentative
37	5-Methylhex-3-en-2-one	MS	MS	37
	2,6,6-Trimethylcyclohexanone	MS, GLC	MS, GLC	^a
38	Isophorone	MS, GLC	MS, GLC	^a
39	2,6,6-Trimethylcyclohex-5-enone	MS	MS	38
	6-Methylheptanone	MS ^b	MS ^b	^a
40	6-Methylhept-5-en-2-one	MS, GLC	MS, GLC	37
41	6-Methylhepta-3- <i>trans</i> -5- <i>trans</i> -dien-2-one	MS, GLC	MS, GLC	^a
	6-Methylhepta-3,5-dien-2-one	MS	MS	Tentative
42	Geranylacetone	MS, GLC	MS, GLC	39
	Tetrahydrogeranylacetone	MS ^b	MS, GLC	^a
43	Farnesylacetone	MS ^b	MS, GLC	^a
44	Hexahydrofarnesylacetone	MS, GLC	MS, GLC	40
45	β -Ionone	MS, GLC	MS, GLC	41
46	Damascenone	MS, GLC	MS, GLC	42
	<i>trans</i> - β -Damascone	MS, GLC		^a
	Verbenone		MS, GLC	35
47	Humuladienone	MS ^b		7
	Acetophenone	MS, GLC		^a
	1-Phenylpropan-2-one	MS	MS	Tentative
	<i>Esters and lactones</i>			
	Methyl palmitate	MS, GLC	MS, GLC	^a
	Ethyl palmitate	MS, GLC	MS, GLC	^a

Table 1. Continued.

	Isopropyl laurate		MS, GLC	^{a,c}
	Isopropyl myristate	MS	MS, GLC	^{a,c}
	Isopropyl palmitate		MS, GLC	^{a,c}
	<i>cis</i> -3-Hexenyl caproate	MS		17
48	Dihydroactinidiolide	MS, GLC	MS, GLC	43
	2,3-Dimethyl-4-hydroxy- -2-nonenic acid lactone	MS, GLC		44
	Benzyl acetate	MS, GLC		^a
	Pentyl benzoate		MS	Tentative
	Hexyl benzoate		MS, GLC	^a
49	Benzyl benzoate	MS, GLC	MS, GLC	^a
50	Coumarin	MS, GLC	MS, GLC	^a
	<i>Alcohols</i>			
	Pentan-2-ol	MS ^b	MS, GLC	36
	Pentan-3-ol	MS, GLC	MS ^b	36
	2-Methylbutan-2-ol		MS	24
	Benzyl alcohol	MS ^b		^a
	2-Phenyl ethanol	MS ^b	MS, GLC	^a
	2- <i>cis</i> -Pentenol	MS		18
	Linalooloxide		MS	40

^a Mass spectrum of an authentic sample. ^b The fraction was too small to permit repeated injections for GLC-retention times studies. ^c Probably an artefact formed from the acetone used in the extraction.

coumarin. This compound, which was by far the most abundant volatile constituent of *C. odoratissimus*, was present in trace amounts only in the other two *Carphephorus* species.

The macrocyclic sesquiterpene germacrene D, identified after isolation, proved to be the major neutral constituent of the distillate from *C. paniculatus*. All other sesquiterpenes identified in this plant, except for α -humulene and caryophyllene, were found to belong to the germacrene class, *i.e.* δ - and γ -cadinene, α - and γ -muurolene, α -amorphene, 4,10-dimethyl-7-isopropylbicyclo[4,4,0]-1,4-decadiene, alloaromadendrene, α - and β -copaene, α - and β -ylangene, α -cubebene, sativene, β -bourbonene, calamenene, and α -calacorene.⁵ These results accord with current views on sesquiterpene biogenesis which postulate germacrene D as a key intermediate in its class.^{5,6} However, as discussed previously, some of the representatives can be formed non-biologically from the labile germacrene D.^{4,6} While this cannot be totally excluded in the present case, the fact that germacrene D is quantitatively so predominant demonstrates that such alterations could not have occurred to any great extent.

Although germacrene D was a minor component of *C. corymbosus*, a few members of the germacrane class (*cf.* Table 1) were encountered in addition to α -humulene and caryophyllene of the humulane class and α -transbergamotene of the bisabolane class.

Both plants also contained a number of oxygenated sesquiterpenoids (S in Figs. 1–3) but, due to the lack of proper reference material, only one, humuladienone,⁷ could be identified as a constituent of *C. corymbosus*.

C. paniculatus proved to contain both a greater variety and a higher concentration of monoterpenoids than *C. corymbosus*. Thus, while α -pinene was a main neutral component of the former plant, it occurred only in minute quantities in the latter. Moreover, several odouriferous monoterpenoids, although less abundant, were found in *C. paniculatus* alone, *i.e.* β -pinene, camphene, sabinene, limonene, 1,8-cineol, α -campholene aldehyde, myrtenal, verbenone and linalooloxide; only α -pinene, p-cymene, β -cyclocitral, safranal, thymol methyl ether, and thymohydroquinone dimethyl ether were common to both species. The presence of the last two compounds seems to be characteristic of the *Compositae*.

Consistent with the results for *C. odoratissimus*, several of the constituents encountered in *C. corymbosus* and *C. paniculatus* are nor-isoprenoids, in all probability formed on degradation of carotenoids and higher terpenoids.^{4,9-11} They are represented in both species by the acyclic compounds 6-methylheptanone, 6-methylhept-5-en-2-one, 6-methylhept-3,5-dien-2-one, geranylacetone and farnesylacetone and their corresponding perhydro derivatives. Similarly, the cyclic compounds β -ionone, damascenone, dihydroactinidiolide, 2,6,6-trimethylcyclohexanone, isophorone, and 2,6,6-trimethylcyclohex-5-enone were found in both plants, while *trans*- β -damascone¹² was present in *C. corymbosus* alone. Although most of these compounds were of fairly low abundance, 2,6,6-trimethylcyclohex-5-enone was in fact one of the main constituents of the neutral volatile fraction derived from *C. corymbosus*. This fraction also contained a number of relatively low-molecular compounds, which on the basis of their mass spectra were tentatively identified as polymethyl-substituted cyclohexenones. However, since they could not be isolated, it has not been possible to characterize them fully at the present stage.

Several of the above nor-isoprenoids constitute important aroma components and this is also true for the series of straight-chain diunsaturated aldehydes and ketones of the types $R_1CH=CHCH=CHCHO$ and $R_2CH=CHCH=CHCOCH_3$ ($R_1 = C_2H_5 \rightarrow C_5H_{13}$ and $R_2 = CH_3 \rightarrow C_3H_7$) found in these two plants. Some of them are present as mixtures of stereoisomers.

Similarly, several of the less unsaturated oxo compounds encountered as minor constituents in both plants, $R_1CH=CHCHO$, $R_2CH=CHCOCH_3$, and R_3CHO ($R_1 = C_3H_7 \rightarrow C_5H_{11}$, $R_2 = C_2H_5 \rightarrow C_5H_{11}$, and $R_3 = C_5H_{11} \rightarrow C_9H_{19}$), also have flavour properties. These compounds have previously been found in *C. odoratissimus*.⁴

Acids

The acidic fractions, examined after methylation were considerably less complex than the volatile neutral fractions. As expected, all $C_6 - C_{18}$ straight-chain saturated fatty acids were found in both species, palmitic acid being the main constituent (*cf.* Table 2). Of somewhat greater interest was the identification of two isoprenoid acids in *C. paniculatus*, the monoterpene geranic acid¹³ and the diterpene eperuic acid.^{14,15} According to the mass spectral results, this plant also contains other, hitherto unidentified, diterpene acids which are being investigated.

Table 2. Acidic constituents.

Compound	Method of identification		Ref.
	<i>C. corymbosus</i>	<i>C. paniculatus</i>	
Hexanoic acid	MS, GLC	MS, GLC	<i>a</i>
Heptanoic acid	MS, GLC	MS, GLC	<i>a</i>
Octanoic acid	MS, GLC	MS, GLC	<i>a</i>
Nonanoic acid	MS, GLC	MS, GLC	<i>a</i>
Decanoic acid	MS, GLC	MS, GLC	<i>a</i>
Undecanoic acid	MS, GLC	MS, GLC	<i>a</i>
Dodecanoic acid	MS, GLC	MS, GLC	<i>a</i>
Tridecanoic acid	MS, GLC	MS, GLC	<i>a</i>
Tetradecanoic acid	MS, GLC	MS, GLC	<i>a</i>
Pentadecanoic acid	MS, GLC	MS, GLC	<i>a</i>
Hexadecanoic acid	MS, GLC	MS, GLC	<i>a</i>
Heptadecanoic acid	MS, GLC	MS, GLC	<i>a</i>
Octadecanoic acid	MS, GLC	MS, GLC	<i>a</i>
<i>cis</i> -2-Pentenoic acid	MS		10
Oleic acid		MS, GLC	<i>a</i>
Linoleic acid	MS, GLC	MS, GLC	<i>a</i>
Linoleic acid	MS, GLC	MS, GLC	<i>a</i>
Benzoic acid	MS, GLC		<i>a</i>
Geranic acid		MS, GLC	41
Eperuic acid		MS	45

^a Mass spectrum of an authentic sample.

Concluding remarks

The compositions of the volatile fractions obtained from the three *Carphephorus* species examined, particularly those of *C. odoratissimus* and *C. paniculatus*, are strikingly similar (*cf.* Tables 1 and 2). It seems somewhat premature at the present stage, however, to draw any chemotaxonomical conclusions from these results. This is partly due to the fact that several of the compounds, *e.g.* the nor-isoprenoids and the α,β -unsaturated aldehydes and ketones, have been found in widely different and thoroughly examined plant materials such as tea,¹⁶⁻²⁰ tomato,^{11,21} and tobacco.²² In view of their probable biogeneses, it may be that many of them are very widely distributed in the plant kingdom, but have escaped detection on account of their low concentrations.

EXPERIMENTAL

Analytical GLC was performed on a Varian 1700 instrument equipped with a capillary injector and a flame-ionization detector. The temperature of the injection block was kept at 220° and that of the detector at 250°. Stainless steel columns (50 m × 0.5 mm) coated with Apiezon L and Emulphor, and a glass column (50 m × 0.35 mm) coated with HB 2000 were used in the experiments. The carrier gas flow was 3 ml N₂/min (i.d. 0.5 mm) and 2 ml N₂/min (i.d. 0.35 mm) and the samples were injected with a split ratio of 1:20.

GLC in combination with mass spectrometry was carried out on a modified LKB 9000 instrument. The columns described above were used also in the GLC-MS studies but helium was substituted for nitrogen as carrier gas. The temperature of the separator was 260° and that of the ion source 290°. An electron energy of 70 eV was employed.

The solvents, silica gel and drying agents used in all operations were carefully purified as previously described.⁴

Extraction and separation. Dried leaves of *C. corymbosus* * (781 g) were crushed and extracted with acetone in a Soxhlet apparatus for 24 h to give a green viscous extract (204 g).** This was distilled at reduced pressure (90°, 0.1 mmHg), using carbon dioxide as a carrier gas,²³ to yield a small distillate (~4 g) and a distillation residue (194 g). The distillate, containing residual acetone, was diluted with pentane (1000 ml) and subsequently extracted with water. The pentane-soluble material was separated into acids (1.1 g) and neutral constituents (1.8 g). No bases were present.

The volatile pentane-soluble neutral (1.7 g) and acidic (0.9 g) fractions from dried leaves of *C. paniculatus* (800 g) were isolated as described above for *C. corymbosus*.

The neutral fractions from the two plants were initially chromatographed on silica gel (pentane-ether) to give subfractions 1-9 and 1-8, respectively, which were studied by GLC and GLC-MS.

Subfraction 1 from *C. paniculatus*, consisting of hydrocarbons, was rechromatographed on AgNO₃-impregnated silica gel (pentane-ether) furnishing six new fractions. The last of these consisted of pure germacrene D (MS, IR).

The acidic fractions from both plants were reacted with ethereal diazomethane overnight and subsequently examined by GLC and GLC-MS.

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** Since the solvent was not removed completely to avoid losses of volatile material, the weights given for the various fractions are necessarily inexact.

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