Journal of Chromatography, 324 (1985) 343–353
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 17 558

GAS CHROMATOGRAPHY OF HOMOLOGOUS ESTERS

XXIX*. PROPANOYL AND MONOCHLORPROPANOYL ESTERS OF LOWER SATURATED BRANCHED-CHAIN AND UNSATURATED ALCOHOLS

J. K. HAKEN*
Department of Polymer Science, University of New South Wales, Box 1, Kensington, N.S.W., 2033 (Australia)
and
I. O. O. KORHONEN
Department of Chemistry, University of Jyväskylä, Kyllikinkatu 1-3, SF-40100 Jyväskylä 10 (Finland)
(Received January 17th, 1985)

SUMMARY

The gas chromatographic retention behaviour of the propanoyl and monochloropropanoyl esters of saturated C_3–C_5 branched-chain and unsaturated C_3–C_6 alcohols on SE-30 and OV-351 capillary columns at several temperatures is reported. Retention index increments at 80 and 120°C show the effect of branching in the alkyl chain and also the effect of unsaturation and of its position in the chain with chlorination at the two possible positions in the acyl chain. The various incremental effects are discussed and compared with the behaviour of the corresponding *n*-alkyl esters.

INTRODUCTION

The gas chromatographic retention behaviour of branched-chain aliphatic esters has not been extensively reported, with studies seemingly restricted to methylethyl, 2-methylpropyl and 3-methylbutyl alkanoates[2]. Straight-chain propanoates and their monochlorinated derivatives have been examined and programmed studies to optimize the separations[3] and retention increment studies from isothermal operation[4] have been reported, while more recently programmed capillary gas chromatography of the propanoyl esters and their monochlorinated derivatives of C_3–C_5 branched-chain alcohols have appeared[5].

The gas chromatography of unsaturated esters has similarly received little attention. Some lower esters with unsaturation in both the alkyl and acyl chains have been examined by Ashes and Haken[6], and studies of isomeric butenoic acid esters have been reported[7]. More recently, the separation of the propanoyl esters and their monochlorinated derivatives of some unsaturated C_3–C_6 alcohols on SE-30 and OV-351 capillary columns has been reported[8].

* For Part XXVIII, see ref. 1.

0021-9673/85/$03.30

This paper describes the isothermal capillary gas chromatography at several temperatures of the propanoyl and monochloropropanoyl esters of saturated C_3–C_5 branched-chain and unsaturated C_3–C_6 alcohols. Retention index increments at 80 and 120°C on SE-30 and OV-351 show the effect of branching in the alkyl chain and similarly the effect of unsaturation and of its position in the chain with chlorination at the two possible positions in the acyl chain. The various incremental effects are discussed in relation to the behaviour of the corresponding *n*-alkyl esters[4].

EXPERIMENTAL

Materials

The branched-chain alcohols and 3-buten-1-ol, 4-penten-2-ol, 4-penten-1-ol and 2-propyn-1-ol were obtained from Fluka (Buchs, Switzerland) and 2-propen-1-ol and a mixture of *cis*- and *trans*-3-hexen-1-ols from Merck-Schuchardt, (Darmstadt, F.R.G.). Alkenyl and alkynyl propanoates, 2-chloropropanoates and 3-chloropropanoates were prepared from the appropriate alcohol and propanoyl chloride or its chlorinated homologues as described previously[3,7].

Gas chromatography

A Perkin-Elmer Sigma 3 gas chromatograph was used under the following operating conditions: injector and flame-ionization detector temperatures, 275°C; nitrogen carrier gas flow-rate, 1 ml min^{-1}; splitting ratio, 1:50; and chart speed, 10 mm min^{-1}. The columns used were a vitreous-silica SE-30 wall-coated open-tubular (WCOT) column (25 m × 0.33 mm I.D.), supplied by SGE (North Melbourne, Australia), and a fused-silica OV-351 WCOT column (25 m × 0.32 mm I.D.), supplied by Orion Analytica (Espoo, Finland). The measurements were made isothermally at the temperatures shown in the Tables.

The chromatographic data were recorded with a Hewlett-Packard Model 3390A reporting integrator. Retention times were measured from the time of sample injection and the retention indices were determined off-line using a Vector M2 microprocessor system, the dead volume first being determined by regression analysis from a series of *n*-alkanes using the procedure of Grobler and Balizs[9].

RESULTS AND DISCUSSION

Retention indices of saturated branched-chain and unsaturated acohols, the corresponding alkyl propanoates and their monochlorinated derivatives determined on SE-30 and OV-351 are shown in Tables I and II, respectively. Relatively few compounds within homologous series are included and the retention plots are not significant, although it is evident from the results on the non-polar stationary phase that the alcohols have the lowest retention and the 2-chloro and 3-chloro esters have increasing retention.

With the corresponding normal esters[4] retention index increments for the methylene group in the alcohol chains were given previously, but here insufficient compounds of any one series were available.

The incremental effect of the alcohols is shown in Table III by the retention indices on esterification at 80 and 120°C on SE-30. The retention increase of the

TABLE I

RETENTION INDICES OF SATURATED C_3–C_5 BRANCHED-CHAIN AND UNSATURATED C_3–C_6 ALCOHOLS AND THEIR PROPANOYL AND MONOCHLOROPROPANOYL ESTERS ON SE-30

Type	*Compound*	*Temperature (°C)*					
		60	*80*	*100*	*120*	*140*	*160*
Alcohols	2-Propanol	491	453	508			
	2-Methyl-2-propanol	531	500	548			
	2-Butanol	605	577	615	622		
	2-Methyl-2-butanol	644	628	652	662	642	
	2-Methyl-1-propanol	629	609	629	641	620	
	3-Methyl-2-butanol	683	668	683	690	699	
	2-Pentanol	697	683	692	701	704	
	3-Methyl-1-butanol	733	721	723	727	738	
	2-Propen-1-ol		546	576	558		
	4-Penten-2-ol		679	673	675	687	734
	3-Buten-1-ol		640	640	641	620	663
	4-Penten-1-ol		757	739	730	764	794
	2-Propyn-1-ol		552	576	559	369	402
	trans-3-Hexen-1-ol		853	831	824	853	873
	cis-3-Hexen-1-ol		859	836	829	855	873
Alkyl propanoates	Methylethyl	751	739	739	739	747	
	Dimethylethyl	790	781	776	776	780	
	1-Methylpropyl	845	838	829	825	845	
	1,1-Dimethylpropyl	893	887	847	873	888	
	2-Methylpropyl	862	856	880	842	860	
	1,2-Dimethylpropyl	915	910	901	893	913	
	1-Methylbutyl	932	926	916	908	928	
	3-Methylbutyl	961	950	947	937	958	
	2-Propenyl		796	774	767	793	818
	1-Methyl-3-butenyl		926	902	891	913	929
	3-Butenyl		889	864	855	877	894
	4-Pentenyl		990	969	958	978	986
	2-Propyl		809	784	773	797	818
	trans-3-Hexenyl		1090	1071	1063	1080	1085
	cis-3-Hexenyl		1092	1074	1066	1085	1090
2-Chloropropanoyl esters	Methylethyl	885	880	873	866	886	
	Dimethylethyl	921	917	911	905	926	
	1-Methylpropyl	979	975	967	960	984	
	1,1-Dimethylpropyl	1025	1023	1016	1011	1035	
	2-Methylpropyl	994	990	983	976	999	
	1,2-Dimethylpropyl	1046	1044	1037	1032	1054	
	1-Methylbutyl	1063	1059	1050	1045	1067	
	3-Methylbutyl	1092	1089	1080	1075	1097	
	2-Propenyl		935	914	904	928	949
	1-Methyl-3-butenyl		1057	1040	1032	1054	1062
	3-Butenyl		1024	1007	998	1020	1030
	4-Pentenyl		1122	1106	1101	1123	1128
	2-Propynyl		948	924	914	933	953

(*Continued on p. 346*)

TABLE I *(continued)*

Type	*Compound*	*Temperature (°C)*					
		60	*80*	*100*	*120*	*140*	*160*
	trans-1-Hexenyl		1223	1209	1204	1225	1228
	cis-3-Hexenyl		1226	1213	1208	1229	1232
3-Chloropropanoyl esters	Methylethyl	952	947	939	930	951	
	Dimethylethyl	991	987	980	973	996	
	1-Methylpropyl	1043	1042	1033	1038	1050	
	1,1-Dimethylpropyl	1095	1093	1085	1081	1105	
	2-Methylpropyl	1062	1058	1049	1045	1067	
	1,2-Dimethylpropyl	1115	1112	1104	1100	1123	
	1-Methylbutyl	1132	1128	1119	1114	1135	
	3-Methylbutyl	1160	1156	1148	1144	1166	
	2-Propenyl		997	977	968	989	1004
	1-Methyl-3-butenyl		1124	1107	1102	1123	1128
	3-Butenyl		1088	1071	1066	1085	1085
	4-Pentenyl		1189	1176	1170	1192	1196
	2-Propynyl		1011	989	978	998	1008
	trans-3-Hexenyl		1286	1275	1272	1290	1293
	cis-3-Hexenyl		1289	1279	1276	1295	1298

propanoate esters is approximately 256 and 206 retention index units over the range of esters studied. The hydroxy group has little influence with a low-polarity phase and replacement with the larger group with both a carboxyl group and an alkyl chain explains the substantial increase. The values at the higher temperature are lower than that at the lower temperature, as previously observed[4] with the *n*-alkyl esters, and is to be expected as the increments are simply a type of separation factor and the earliest work showed that such factors decrease with increasing temperature[10,11]. At the same temperature common as in the earlier work[4] on the *n*-alkyl esters, *i.e.* 120°C, the average increment value of 206 retention index units for the branched-chain esters is lower than the value of 230 units observed for the straight-chain compounds. The lower value is, as expected, with the branched-chain alkyl groups, where retention is usually reduced. From Table III it is also apparent that little variation is observed with the unsaturated alkenyl homologues or the single alkynyl derivative on the non-polar stationary phase. At 80°C the 2-chloro- and 3-chloropropanoyl esters show retention enhancements of 136 and 205 units with the saturated esters and 134 and 198 units with the alkenyl esters, again indicating little effect of unsaturation. At 120°C the values are little affected, with values of 135 and 204 units with the saturated esters and 141 and 209 units with the introduction of a double bond. These values are in the same range as previously found with the straight-chain 2- and 3-chloropropanoyl esters (139 and 207 units)[4].

The corresponding values on the OV-351 column are shown in Table IV and the increased retention of the alcohols is indicative of the operation of polar effects. The variable effect of interactions rather than the regular one with the straight-chain

TABLE II

RETENTION INDICES OF SATURATED C_3–C_5 BRANCHED-CHAIN AND UNSATURATED C_3–C_6 ALCOHOLS AND THEIR PROPANOYL AND MONOCHLOROPROPANOYL ESTERS ON OV-351

Type	*Compound*	*Temperature (°C)*					
		60	*80*	*100*	*120*	*140*	*160*
Alcohols	2-Propanol	949	957	981			
	2-Methyl-2-propanol	930	942	981			
	2-Butanol	1038	1036	1048	1114	1206	
	2-Methyl-2-butanol	1028	1026	1048	1114	1206	
	2-Methyl-1-propanol	1100	1094	1108	1153	1241	
	3-Methyl-2-butanol	1100	1094	1108	1153	1241	
	2-Pentanol	1129	1121	1130	1172	1254	
	3-Methyl-1-butanol	1212	1203	1208	1238	1315	
	2-Propen-1-ol		1128	1130	1167	1245	
	4-Penten-2-ol		1154	1159	1184	1263	
	3-Buten-1-ol		1185	1187	1209	1283	
	4-Penten-1-ol		1308	1305	1305	1370	
	2-Propyn-1-ol		1352	1343	1334	1395	
	trans-e-Hexen-1-ol		1368	1366	1361	1423	
	cis-3-Hexen-1-ol		1387	1385	1382	1442	
Alkyl propanoates	Methylethyl	986	996	1028	1092	1206	
	Dimethylethyl	986	996	1028	1092	1206	
	1-Methylpropyl	1067	1070	1092	1145	1241	
	1,1-Dimethylpropyl	1087	1089	1108	1153	1241	
	2-Methylpropyl	1100	1094	1108	1153	1241	
	1,2-Dimethylpropyl	1125	1121	1130	1172	1254	
	1-Methylbutyl	1148	1145	1159	1202	1283	
	3-Methylbutyl	1198	1196	1206	1238	1315	
	2-Propenyl		1128	1130	1167	1245	
	1-Methyl-3-butenyl		1196	1197	1225	1301	1364
	3-Butenyl		1200	1203	1230	1301	1364
	4-Pentenyl		1300	1302	1305	1370	1419
	2-Propynyl		1312	1305	1305	1370	1419
	trans-3-Hexenyl		1384	1383	1382	1443	1486
	cis-3-Hexenyl		1392	1391	1390	1451	1487
2-Chloropropanoyl esters	Methylethyl	1229	1226	1233	1264	1337	
	Dimethylethyl	1223	1220	1229	1264	1337	
	1-Methylpropyl	1312	1311	1315	1335	1402	
	1,1-Dimethylpropyl	1326	1327	1333	1353	1421	
	2-Methylpropyl	1342	1340	1344	1363	1428	
	1,2-Dimethylpropyl	1369	1366	1368	1386	1447	
	1-Methylbutyl	1387	1385	1389	1404	1460	
	3-Methylbutyl	1443	1443	1444	1458	1514	
	2-Propenyl		1387	1385	1382	1443	1486
	1-Methyl-3-butenyl		1438	1436	1434	1496	1512
	3-Butenyl		1458	1454	1453	1514	1543
	4-Pentenyl		1552	1554	1546	1604	1625
	2-Propynyl		1588	1580	1575	1632	1648

(*Continued on p. 348*)

TABLE II *(continued)*

Type	*Compound*	*Temperature (°C)*					
		60	*80*	*100*	*120*	*140*	*160*
	trans-3-Hexenyl		1635	1627	1623	1678	1694
	cis-3-Hexenyl		1645	1637	1634	1690	1706
3-Chloropropanoyl esters	Methylethyl	1374	1371	1372	1388	1447	
	Dimethylethyl	1365	1364	1368	1386	1447	
	1-Methylpropyl	1461	1459	1460	1471	1523	
	1,1-Dimethylpropyl	1475	1475	1477	1490	1542	
	2-Methylpropyl	1493	1492	1492	1503	1554	
	1,2-Dimethylpropyl	1517	1517	1516	1527	1576	
	1-Methylbutyl	1540	1538	1537	1548	1594	
	3-Methylbutyl	1594	1594	1595	1605	1652	
	2-Propenyl		1528	1521	1516	1574	1596
	1-Methyl-3-butenyl		1596	1581	1567	1615	1630
	3-Butenyl		1602	1594	1590	1647	1666
	4-Pentenyl		1708	1698	1695	1749	1763
	2-Propynyl		1742	1723	1712	1757	1765
	trans-3-Hexenyl		1780	1770	1767	1819	1829
	cis-3-Hexenyl		1790	1780	1779	1833	1844

esters illustrates the particular effect of each alcohol, depending on its individual structure. In addition to the effect with the alcohols, the overall retention of the chlorinated esters and the separation between the three series of homologues is greatly increased. At 80°C the 2- and 3-chloro esters show retention enhancements of 239 and 388 retention index units with the saturated esters and minimal increases to 253 and 401 units with the olefinic esters. The sole acetylenic ester, however, shows significantly increased retention. The pattern is as previously observed with fatty esters, where some reduction in retention might be expected with unsaturation on a non-polar column but a greater increase is observed with polar columns[10]. The values at 120°C are comparable to those in our earlier work[4] and the values with the branched chain esters are lower, as expected.

Table V shows the separation between the groups of 2- and 3-chloro esters, and at both 80 and 120°C it is apparent that the separation is slightly more than doubled on the polar stationary phase. Ratios of the retention increments on the two stationary phases are shown in Table VI and, as expected, for all three types of compounds the ratio of the 3-chloro esters is higher than that of the 2-chloro esters. High values of these ratios have been shown previously to indicate maximization of polar effects with the influence of steric hindrance reducing the retention on the polar phase and accordingly the ratio[12]. In agreement with the results for the corresponding *n*-alkyl esters[4], a greater steric effect is observed with proximity of the carbonyl and chlorine atom in the α-position due to the –C(O)–C(Cl)–C– structure compared with the –C(O)–C–C(Cl)–structure with chlorine in the β-position.

It is further evident that the polar effects are increased with those compounds containing olefinic and, in one instance, acetylenic unsaturation.

TABLE III

INCREMENTAL EFFECT OF CONVERSION OF ALCOHOL TO PROPANOYL ESTER AND CHLORINATION TO THE 2-CHLOROPROPANOYL AND 3-CHLOROPROPANOYL ESTERS ON SE-30

Compound	*80°C*			*120°C*		
	*ΔP−ΔA**	*Δ2C1P−ΔP**	*Δ3C1P−ΔP**	*ΔP−ΔA**	*Δ2C1P−ΔP**	*Δ3C1P−ΔP**
Methylethyl propionate	286	141	208	–	127	191
Dimethylethyl propionate	281	136	206	–	129	197
1-Methylpropyl propionate	261	137	204	203	135	213
1,1-Dimethylpropyl propionate	259	136	206	211	138	208
2-Methylpropyl propionate	247	134	202	201	134	203
1,2-Dimethylpropyl propionate	242	134	202	203	139	207
1-Methylbutyl propionate	243	133	202	207	137	206
3-Methylbutyl propionate	229	139	206	210	138	207
Average:	259	136	205	206	135	204
2-Propenyl propionate	250	139	201	209	137	201
1-Methyl-3-butenyl propionate	247	131	198	216	141	211
3-Butenyl propionate	249	135	199	214	143	211
4-Pentenyl propionate	233	132		228	143	212
trans-3-Hexenyl propionate	237	133	196	239	141	209
cis-3-Hexenyl propionate	233	134	197	237	142	210
Average:	242	134	198	224	141	209
Acetylenic unsaturation						
2-Propynyl	257	139	202	214	141	205

* Retentions of propanoyl esters (*Δ*P), alcohols (*Δ*A), 2-chloropropanoyl esters (*Δ*2C1P) and 3-chloropropanoyl esters (*Δ*3C1P).

TABLE IV

INCREMENTAL EFFECT OF CONVERSION OF ALCOHOL TO PROPANOYL ESTER AND CHLORINATION TO THE 2-CHLOROPROPANOYL AND 3-CHLOROPROPANOYL ESTERS ON OV-351

Compound	*80°C*			*120°C*		
	*ΔP−ΔA**	*Δ2C1P−ΔP**	*Δ3C1P−ΔP**	*ΔP−ΔA**	*Δ2C1P−ΔP**	*Δ3C1P−ΔP**
Methylethyl propionate	39	230	375	–	172	296
Dimethylethyl propionate	54	224	368	–	172	294
1-Methylpropyl propionate	34	241	389	31	190	326
1,1-Dimethylpropyl propionate	63	238	386	39	200	337
2-Methylpropyl propionate	0	246	398	0	210	350
1,2-Dimethylpropyl propionate	27	245	396	19	214	355
1-Methylbutyl propionate	24	240	393	30	202	346
3-Methylbutyl propionate	– 7	247	398	0	220	367
Average:		239	388		198	334
2-Propenyl propionate	0	259	400	0	215	349
1-Methyl-3-butenyl propionate	42	242	400	41	209	342
3-Butenyl propionate	15	258	402	21	223	360
4-Pentenyl propionate	– 8	252	408	0	241	390
trans-3-Hexenyl propionate	16	251	396	21	241	385
cis-3-Hexenyl propionate	5	253	398	8	244	389
Average:		253	401		229	369
Acetylenic unsaturation						
2-Propynyl	−40	276	430	−29	270	407

* See Table III.

TABLE V

SEPARATION BETWEEN GROUPS OF ESTERS AT 80 AND 120°C ON SE-30 AND OV-351

Esters	*Temperature (°C)*	*Stationary phase*					
		SE-30			*OV-351*		
		3-Chloro esters	*2-Chloro esters*	*3-Chloro esters – 2-chloro esters*	*3-Chloro esters*	*2-Chloro esters*	*3-Chloro esters – 2-chloro esters*
Branched-chain	80	205	136	69	388	239	149
	120	204	135	69	334	198	136
Olefinic	80	198	134	64	401	253	148
	120	209	141	68	369	229	140
Acetylenic	80	202	139	63	430	276	154
	120	205	141	64	407	270	137

The individual effect of the shape of the alkyl group is shown for the saturated branched-chain esters in Table VII. For the 3-chloro esters the polar effects are maximized by the terminal chlorine substituent and accordingly the values of the increment ratios are higher than with the 2-chloro esters, where the proximity of the chlorine substituent to the carbonyl group is of importance. It is apparent for both series of esters that steric effects are most apparent with methyl or dimethyl substitution in the α-position.

The same ratios are shown in Table VIII for the olefinic esters and the same trends exist as regards the 2- and 3-chloro esters, and again the lowest ratios are experienced with a methyl substituent in the α-position. The 2-propynyl esters show considerably higher values owing to the acetylenic unsaturation and possibly the terminal position of unsaturation. A further study of representative alkynyl esters would be of interest.

TABLE VI

AVERAGE RETENTION INCREMENT RATIOS (ΔOV-351/ΔSE-30) OF SATURATED AND UNSATURATED CHLORINATED ESTERS AT 80 AND 120°C

Temperature (°C)	*Acyl group*	*Alkyl group*		
		Saturated	*Olefinic*	*Acetylenic*
80	3-Chloro esters	1.89	2.03	2.13
	2-Chloro esters	1.76	1.89	1.99
120	3-Chloro esters	1.64	1.77	1.99
	2-Chloro esters	1.47	1.62	1.91

TABLE VII

RETENTION INCREMENT RATIOS FOR BRANCHED-CHAIN 3-CHLORO- AND 2-CHLORO-PROPANOATES AT 120°C

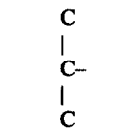
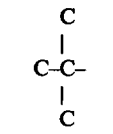
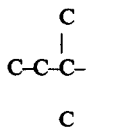
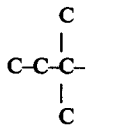
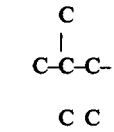
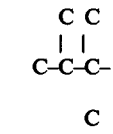
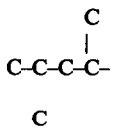
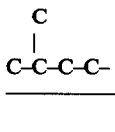
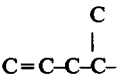
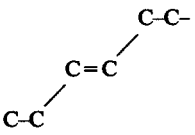
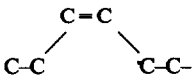
Alcohol structure	*3-Chloro esters*	*2-Chloro esters*
	1.55	1.35
	1.49	1.33
	1.53	1.41
	1.62	1.45
	1.72	1.57
	1.71	1.54
	1.68	1.47
	1.77	1.59

TABLE VIII

RETENTION INCREMENT RATIOS FOR UNSATURATED 3-CHLORO- AND 2-CHLOROPROPANOATES AT 120°C

Alcohol structure	*3-Chloro esters*	*2-Chloro esters*
C=C–C–	1.74	1.57
	1.62	1.48
C=C–C–C–	1.71	1.56
C=C–C–C–C–	1.84	1.69
	1.84	1.71
	1.85	1.72
C≡C–C–	1.99	1.91

ACKNOWLEDGEMENTS

I. O. O. Korhonen gratefully acknowledges the Kalle and Dagmar Välimaa Foundation (Cultural Foundation of Finland), the Medica Corporation Research Foundation, the Alfred Kordelin Foundation and the Academy of Finland for financial support.

REFERENCES

1 J. K. Haken and I. O. O. Korhonen, *J. Chromatogr.*, 320 (1985) 325.
2 J. R. Ashes and J. K. Haken, *J. Chromatogr.*, 101 (1974) 103 and references cited therein.
3 I. O. O. Korhonen, *J. Chromatogr.*, 268 (1983) 229.
4 J. K. Haken and I. O. O. Korhonen, *J. Chromatogr.*, 319 (1985) 131.
5 I. O. O. Korhonen, *J. Chromatogr.*, 270 (1983) 171.
6 J. R. Ashes and J. K. Haken, *J. Chromatogr.*, 111 (1975) 171 and references cited therein.
7 J. R. Ashes and J. K. Haken, *J. Chromatogr.*, 62 (1971) 39.
8 I. O. O. Korhonen, *J. Chromatogr.*, 270 (1983) 181.
9 A. Grobler and G. Balizs, *J. Chromatogr. Sci.*, 12 (1974) 57.
10 A. T. James and A. J. P. Martin, *Biochem. J.*, 63 (1956) 144.
11 R. A. Landowne and S. R. Lipsky, *Biochim. Biophys. Acta*, 47 (1961) 589.
12 J. K. Haken, J. R. Chretien and C. Lion, *J. Chromatogr.*, 217 (1981) 125.