Journal of Chromatography, 87 (1973) 576–580

CHROM. 6972

Note

Gas chromatographic examination of some diesters of normal aliphatic dicarboxylic acids

CHRISTOPHER ROY STRAUSS
The Australian Wine Research Institute, Private Bag, Glen Osmond, South Australia 5064 (Australia)
(Received July 26th, 1973)

Diesters of normal aliphatic dicarboxylic acids have been identified in a variety of sauces[1], essences[2,3], and alcoholic beverages. Sherries[4,5], muscats, ports[6], and brandies[7] have been shown to contain diethyl succinate. Two other diethyl esters, the malonate and the azelate, have also been reported in whisky[8].

Previous workers who have examined the dimethyl esters[9–12] and the dipropyl esters[13] by packed column gas chromatography (GC) have concentrated on the separation of the individual components of one homologous series of esters only. However, any diesters which may occur in wines and brandies could be expected to incorporate one or two esterified alcohols from a number of different alcohols present in the beverages. Some of these alcohols include methanol, ethanol, *n*-propanol, isobutanol, isoamyl alcohol, 2-methyl-*n*-butanol and β-phenethanol. Because of the predominance of ethanol in the beverages it would be expected that of the diesters present, the diethyl ones would be present in the greatest concentrations. It would not be unreasonable, however, to expect trace quantities of other diesters to occur.

In this work, a series of dimethyl, methyl ethyl, diethyl and dipropyl esters of the homologous normal aliphatic diacids from malonic to sebacic were gas chromatographed, to assist in the identification of any such diester which may be present in Australian wines and brandies.

Any diesters in these beverages would be expected to exist in very small quantities along with several other organic compounds, many of which have been identified as simple esters[14–16] of monobasic aliphatic acids. Because wines and brandies contain such a large number of trace volatile constituents, many of them with essentially similar chemical properties, there was a need for a very efficient chromatographic separation of the diesters, so capillary[17] columns were used.

EXPERIMENTAL

Preparation of derivatives

Many of the reference dimethyl and diethyl esters were commercial "analytical grade" products checked for purity by GC. Any other diesters were prepared by the usual synthetic procedures.

Gas chromatography

A Varian Model 1400 instrument (Varian, N. Springvale, Australia) fitted with stainless-steel capillary columns and a flame ionisation detector was used. The chromatography was carried out on two separate liquid phases of differing polarity, Apiezon M (column dimensions 50 m × 0.5 mm I.D.) and Ucon oil LB-550X (column dimensions 30 m × 0.5 mm I.D.), at column temperatures of 130° and 120°, respectively, and nitrogen carrier gas pressures of 30 p.s.i. and 25 p.s.i., respectively. The injector and detector temperatures were 240°. Further work was done on the Ucon oil LB-550X column at an oven temperature of 100°, nitrogen carrier gas pressure of 25 p.s.i. and injector and detector temperatures as above.

RESULTS AND DISCUSSION

Chromatographic data for the diesters on the two columns used are shown in Table I. The Ucon oil column proved more satisfactory than the Apiezon M column,

TABLE I

CHROMATOGRAPHIC DATA

Ester	*GC peak No. in Figs. 2 and 3*	*Adjusted retention time (min)*		
		Ucon oil LB-550X		*Apiezon M*
		120°	*100°*	*130°*
Dimethyl malonate	1	1.5	3.4	2.3
Dimethyl succinate	3	2.6	6.3	4.1
Dimethyl glutarate	6	5.0	12.3	7.8
Dimethyl adipate	10	9.3	26	15
Dimethyl pimelate	14	17	48	24
Dimethyl suberate	18	32	93	48
Dimethyl azelate	22	58	183	85
Dimethyl sebacate		108	348	150
Methyl ethyl malonate	2	2.1	5.0	2.7
Methyl ethyl succinate	5	3.8	9.5	5.2
Methyl ethyl glutarate	8	6.9	18	9.8
Methyl ethyl adipate	12	13	35	18
Methyl ethyl pimelate	16	25	70	32
Methyl ethyl suberate	20	45	133	60
Methyl ethyl azelate	24	81	260	110
Methyl ethyl sebacate		155	—	200
Diethyl malonate	4	2.8	7.1	3.6
Diethyl succinate	7	5.3	14	7.1
Diethyl glutarate	11	9.8	27	14
Diethyl adipate	15	19	52	25
Diethyl pimelate	19	35	101	48
Diethyl suberate	23	63	190	82
Diethyl azelate		115	382	150
Diethyl sebacate		212	—	260
Dipropyl malonate	9	7.9	22	11.5
Dipropyl succinate	13	16	44	24
Dipropyl glutarate	17	29	84	40
Dipropyl adipate	21	55	174	71
Dipropyl pimelate		98	327	129
Dipropyl suberate		180	—	246
Dipropyl azelate		335	—	402
Dipropyl sebacate		640	—	800

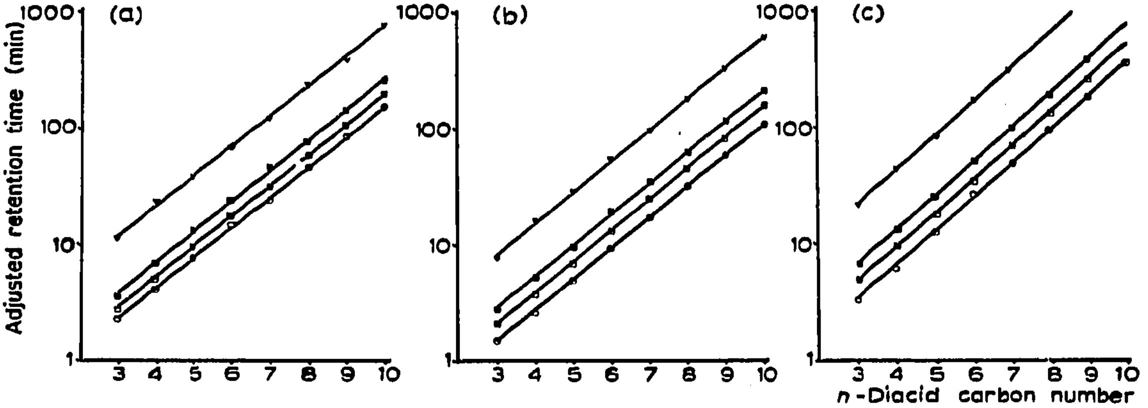

Fig. 1. Semilog plots of adjusted retention times against *n*-diacid carbon number for each series of diesters examined. Columns: (a) Apiezon M at 130°; (b) Ucon oil LB-550X at 120°; (c) Ucon oil LB-550X at 100°. ○, Dimethyl; □, methyl ethyl; ■, diethyl; ▼, dipropyl esters.

the chromatograms featuring higher resolution and, generally, narrower peaks with less tailing.

Conventional semilog plots of retention time against *n*-diacid carbon number (see Fig. 1) yielded straight lines for each of the dimethyl, methyl ethyl, diethyl and dipropyl series of esters chromatographed. Portions of chromatograms on the Ucon oil LB-550X column at 120° and 100° are shown in Figs. 2 and 3. Assignments for

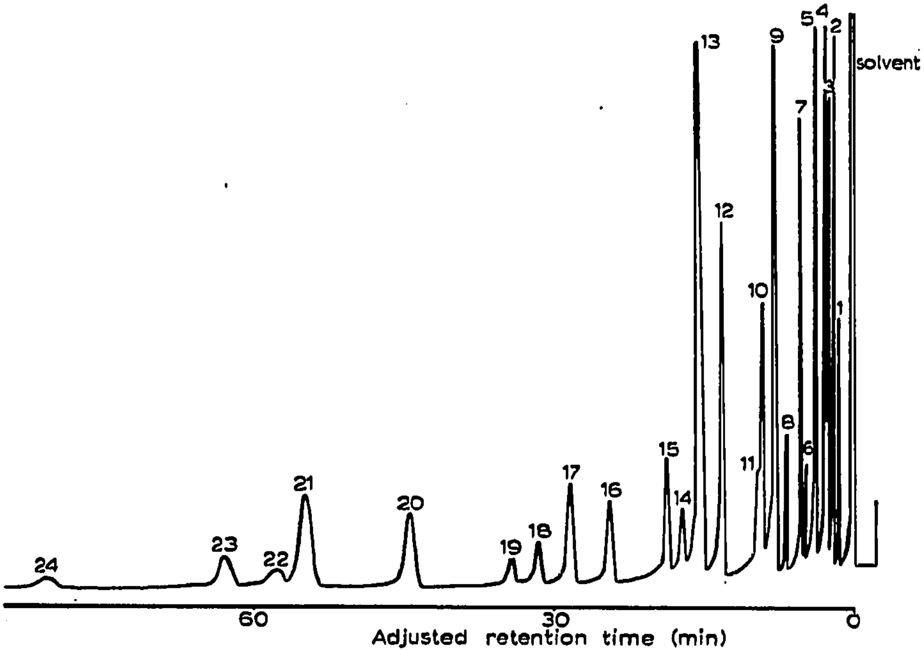

Fig. 2. Portion of a chromatogram of a mixture of dimethyl, methyl ethyl, diethyl, and dipropyl esters of normal aliphatic diacids. The column coating was Ucon oil LB-550X at 120°. Peak assignments are shown in Table I.

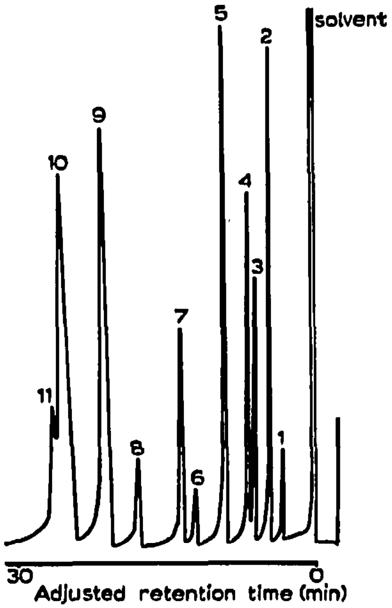

Fig. 3. Portion of a chromatogram of a mixture of dimethyl, methyl ethyl, diethyl and dipropyl esters of normal aliphatic diacids. Peak assignments are indicated in Table I. The column coating was Ucon oil LB-550X and the oven temperature 100°.

peak numbers of these chromatograms are indicated in Table I. The peaks for the remaining eight diesters in Table I, not included in Fig. 2, were well resolved, as their retention time data indicate. The poorest resolution obtained between neighbouring peaks was that between peaks 10 and 11 (dimethyl adipate and diethyl glutarate), which remained only partially resolved under all GC conditions used.

CONCLUSIONS

The results indicate that, generally, individual compounds of various series of diesters of normal aliphatic dicarboxylic acids can be separated by capillary GC. The GC technique gives a comparatively high order of resolution, and, with the aid of a coupled mass spectrometer, may be used to provide confirmatory evidence for the presence of one or more of these compounds in Australian wines and brandies.

REFERENCES

1 S. Morimoto and M. Murakami, *Hakko Kogaku Zasshi (J. Ferment. Technol.)*, 44 (1966) 476.
2 H. Bohnsack, *Riechst. Aromen, Körperpflegem.*, 17 (1967) 358.
3 R. K. Creveling, R.-M. Silverstein and W. G. Jennings, *J. Food Sci.*, 33 (1968) 284.
4 A. D. Webb, R. E. Kepner and W. G. Galetto, *Amer. J. Enol. Viticult.*, 15 (1964) 1.
5 A. D. Webb, R. E. Kepner and L. Maggiora, *Amer. J. Enol. Viticult.*, 18 (1967) 190.
6 A. K. Rodopulo, A. A. Bezubov and I. A. Egorov, *Prikl. Biokhim. Mikrobiol.*, 6 (1970) 214.
7 J. F. Guymon and E. A. Crowell, *Amer. J. Enol. Viticult.*, 23 (1972) 114.
8 J. H. Kahn, *J. Ass. Offic. Anal. Chem.*, 52 (1969) 1166.
9 Y. Suzuki and T. Takeuchi, *Kogyo Kagaku Zasshi*, 67 (1964) 902.
10 S. Mori and T. Takeuchi, *J. Chromatogr.*, 46 (1970) 137.

11 B. E. Sharpless, *J. Chromatogr.*, 12 (1963) 401.
12 F. Falk, *J. Chromatogr.*, 17 (1965) 450.
13 A. J. Appleby and J. E. O. Mayne, *J. Gas Chromatogr.*, 5 (1967) 266.
14 D. W. Connell and C. R. Strauss, *J. Sci. Food Agr.*, in press.
15 J. Schaefer and R. Timmer, *J. Food Sci.*, 35 (1970) 10.
16 A. D. Webb, R. E. Kepner and L. Maggiora, *Amer. J. Enol. Viticult.*, 20 (1969) 16.
17 L. S. Ettre, *Open Tubular Columns in Gas Chromatography*, Plenum Publ., New York, 1965, p. 55.