

## Gas chromatography of long-chain $\alpha,\omega$ -diols and related compounds

Long-chain  $\alpha,\omega$ -diols in waxes have been identified by gas chromatography of their diacetates<sup>1</sup> or of the hydrocarbons derived from them by reduction of the corresponding iodides or tosylates<sup>2</sup>. In the present work, the behaviour of free diols (even-numbered homologues,  $C_{10}$ – $C_{26}$ ) has been compared with that of their diacetates, the dimethyl esters of the corresponding diacids, and the *n*-paraffins. The corresponding mono-alcohols, their acetates, and the methyl esters of the saturated fatty acids have also been examined.

### Experimental

**Materials.** The  $C_{10}$ ,  $C_{12}$  and  $C_{14}$   $\alpha,\omega$ -diacids were obtained commercially, and were esterified by boiling with 1% sulphuric acid in methanol. These acids were subjected to the enamine method of chain extension by six carbon atoms at each end<sup>3</sup>, and the resulting  $C_{22}$ ,  $C_{24}$  and  $C_{26}$  diacids were esterified in the same way. The  $C_{24}$  and  $C_{26}$  compounds contained traces of the  $C_{18}$  and  $C_{20}$  products resulting from chain extension at one end only.

A mixture of the methyl esters of saturated fatty acids,  $C_{16}$ – $C_{30}$ , was isolated from hydrolysed carnauba wax as described by DOWNING *et al.*<sup>2</sup>

The individual diols, and mixed mono-alcohols, were prepared by reducing the methyl esters with lithium aluminium hydride. The melting points of the pure diols agreed with those reported by MURRAY *et al.*<sup>4</sup> Their acetates were prepared in the conventional way. A series of homologous *n*-paraffins was obtained by reducing the tosylates of the mixed mono-alcohols with lithium aluminium hydride.

**Gas chromatography.** All the materials were chromatographed at 245° in a glass column, 120 cm  $\times$  0.4 cm I.D., packed with a stationary phase of 10% Silicone Elastomer E 301 (Griffin and George Ltd., London) on acid-washed celite (72–85 mesh). Nitrogen, inlet pressure 15 p.s.i., flow rate 40 ml/min, was used as carrier gas. Samples, 0.2–1.0  $\mu$ l, were applied directly on the column. The detector was a gas-density balance (Abbotsbury Laboratories, Elstree, Herts., Great Britain).

### Results and discussion

Under these conditions, the peaks corresponding to diols and mono-alcohols are as well resolved and symmetrical as those of the other classes of compounds studied. Fig. 1 shows the parallel straight-line plots of log retention times against carbon numbers (of the parent compounds) for the seven homologous series. Though GLC of the free hydroxy compounds has the advantage that their retention times are shorter than those of the ester derivatives, the direct determination of the chain lengths of diols and mono-alcohols, with a column kept at a constant temperature of 245°, is still limited to 26 and 28 carbon atoms respectively. Higher homologues have retention times longer than about 2 h, leading to broad peaks that are difficult to observe. The range might be extended by programmed heating, but this technique has not been used in the present work. A few experiments with trimethylsilyl ethers<sup>5</sup> have shown that these derivatives do not have any particular advantages in this system, as their retention times are intermediate between those of the two types of esters. The lower line in Fig. 1 clearly shows the advantage of using the derived hydrocarbons to define the chain lengths of diols.

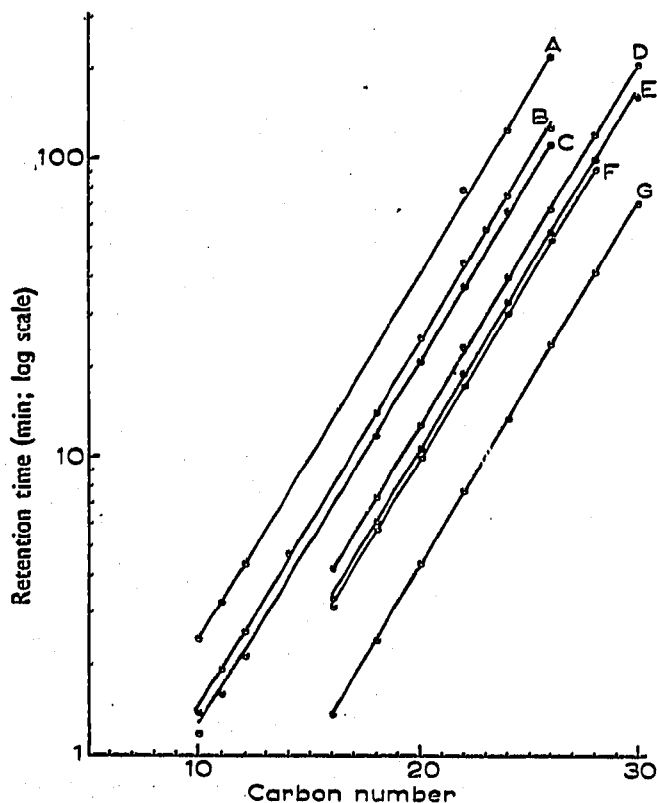


Fig. 1. Gas chromatography of  $\alpha,\omega$ -diols and derivatives. A = Diacetates; B = dimethyl esters; C = diols; D = monoacetates; E = monomethyl esters; F = monoalcohols; G = *n*-paraffins.

These methods have been used to establish the chain length of the diol, m.p.  $108.3^\circ$ , a product of the hydrolysis of some hydroxycinnamoyl esters from oats<sup>6,7</sup>. Single peaks of retention times, 117, 214 and 138 min, respectively, were observed on chromatograms of the diol, its diacetate, and the dimethyl ester of the derived diacid, corresponding to a chain length of 26 carbon atoms. Two peaks, of retention times 24 and 41 min (ratio of areas, 2:1 approximately) were observed in chromatograms of the derived hydrocarbon, suggesting that the natural diol is a mixture of the  $C_{26}$  and  $C_{28}$  diols in this proportion. This finding accounts for its lower melting point,  $108.3^\circ$  compared with the synthetic  $C_{26}$  diol (m.p.  $109.6^\circ$ , mixed m.p.  $108.5^\circ$ ).

This investigation was financed in part by the U.S. Department of Agriculture under the authority of U.S. Public Law 480, 83rd Congress.

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Received August 13th, 1965