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CHEMISTRY OF LICHEN CONSTITUENTS. PART IV[‡]

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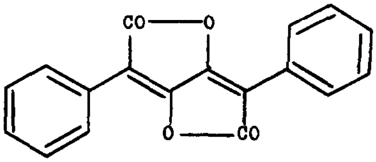
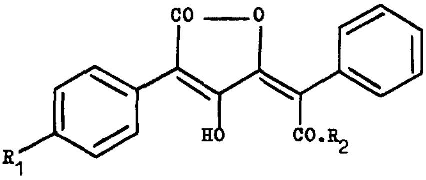
Skeletal rearrangement under electron impact conditions is of particular significance in the application of mass spectrometry to structure elucidations. In the course of our investigation of the mass spectra[*] of pulvic acid derivatives [I - V], certain characteristic rearrangements were observed.



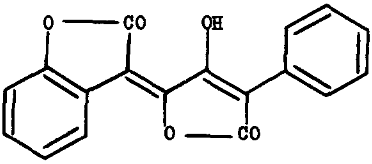
I Pulvic Acid Lactone



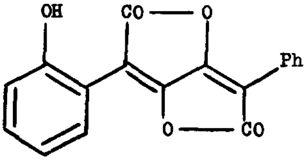
II Vulpinic Acid, $R_1 = H$; $R_2 = OCH_3$

III Pinastric Acid, $R_1 = OCH_3$; $R_2 = OCH_3$

IV Rhizocarpic Acid, $R_1 = H$;
$R_2 = NH.CH(CH_2Ph).CO_2CH_3$



V Calycin

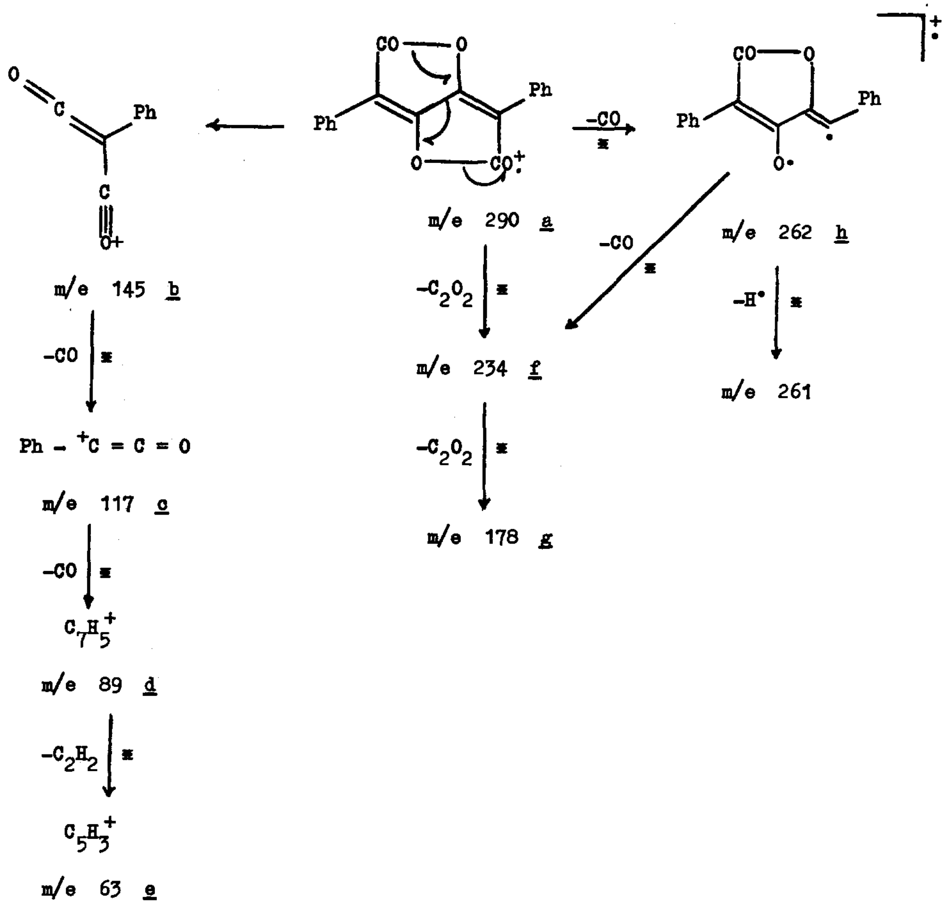


VI

[‡] Part III in press.
Part II. S.H. Harper and R.M. Letcher, Chem. & Ind., 419 (1966).

[*] Spectra were recorded on an AEI-M.S.-9 mass spectrometer at an ionizing voltage of 70eV, using the direct insertion technique.

All compounds show prominent molecular ions. The fragmentation of I (Fig. 1) may be rationalised as follows:-



Formation of the base peak at m/e 145 (ion b) from ion a could be rationalised on the basis of the original charge residing on one of the carbonyl groups in a. Ion b fragments further through successive losses of two molecules of CO, and acetylene to provide ions c, d and e. The ion f is of particular interest. A metastable peak at 188.8 indicates that this ion is, in part, formed by a one-step loss of two molecules of carbon monoxide. This demands

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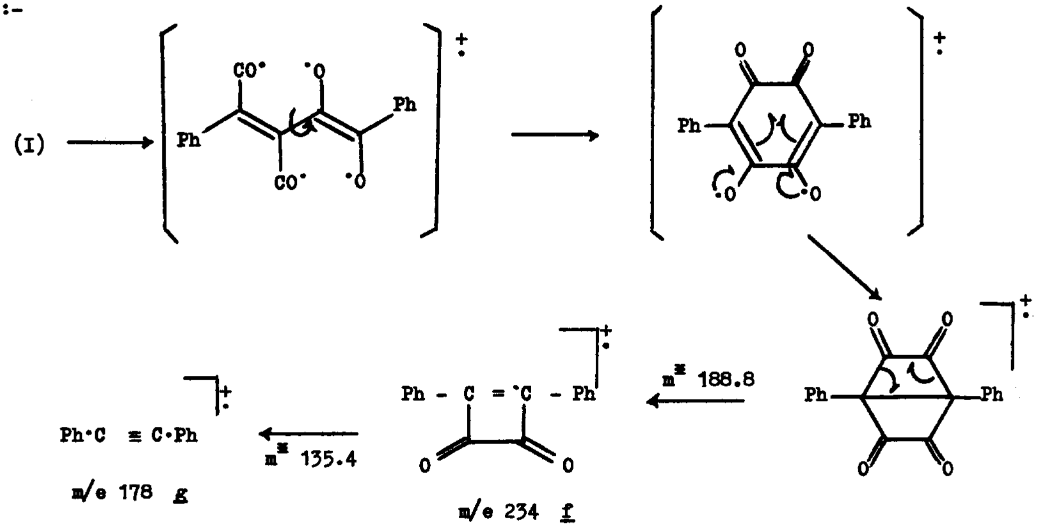
* Appropriate metastable peaks were observed for these transitions.

a skeletal rearrangement, probably to a polyporic acid type of intermediate which could lose C_2O_2:-



A metastable ion at 135.4 indicates a further loss of C_2O_2 from ion f to g. Similar concurrent losses of two molecules of carbon monoxide have been reported for monocyclic 2-pyrones (1), and several pyrono(5',6' : 3,4) coumarins (2). Metastable peaks at 236.7 and 209 indicate that ion f is also formed through a two-step process via h by consecutive losses of two molecules of carbon monoxide.

Vulpinic acid (II) shows a molecular ion at m/e 322 (Fig. 2). The remainder of the spectrum is virtually identical with that of pulvic acid lactone which is presumably formed after primary elimination of the elements of methanol.

The contribution of peaks arising from pulvic acid lactone can easily be recognised in the mass spectrum of pinastric acid (III), (Fig. 3). Elimination of methanol from the molecular ion (m/e 352) affords the base-peak at m/e 320. Subsequent loss of formaldehyde from the -OMe group yields the pulvic lactone (m^* 262.8, 320 → 290) which fragments as outlined before. Peaks at m/e 264 and m/e 208 arise through consecutive losses of C_2O_2 from the ion m/e 320 (m^* 217.8, 320 → 264; m^* 163.8, 264 → 208). The process leading to ion b in I should in this instance provide two distinct ions differing by 30 mass units due to the additional methoxyl group. Both ions are observed, viz. at m/e 145 and m/e 175, the latter suffering two further losses of carbon monoxide to provide ions m/e 147 and m/e 119 as indicated by the appropriate metastable peaks at 123.5 and 96.3.

FIG 1.

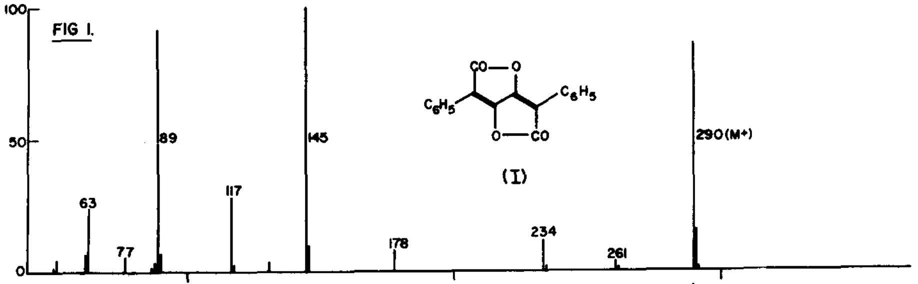


FIG 2.

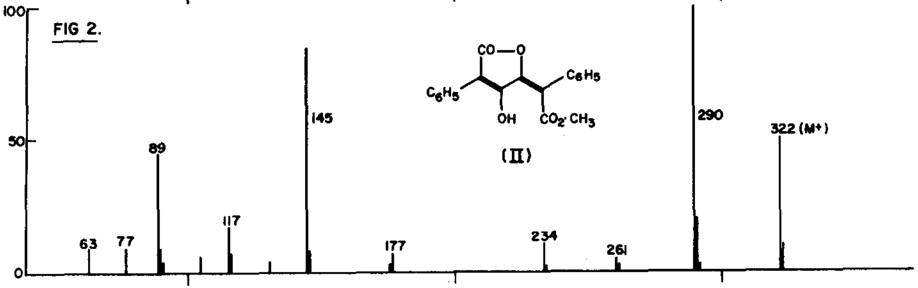


FIG 3.

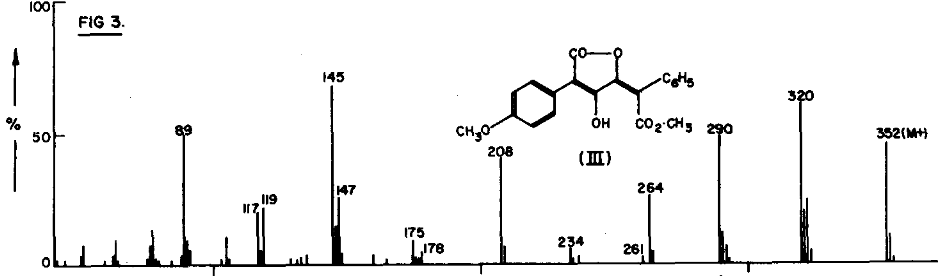


FIG 4.

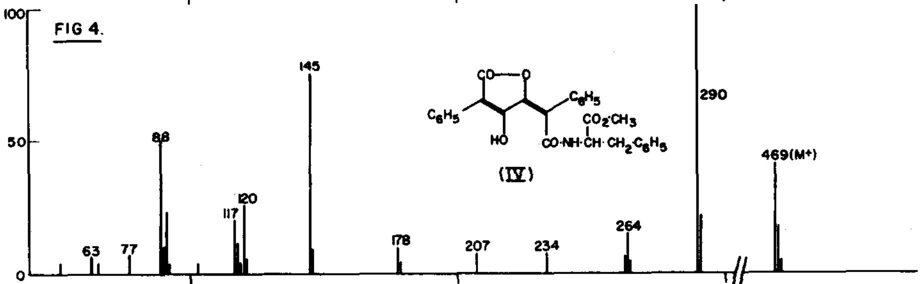
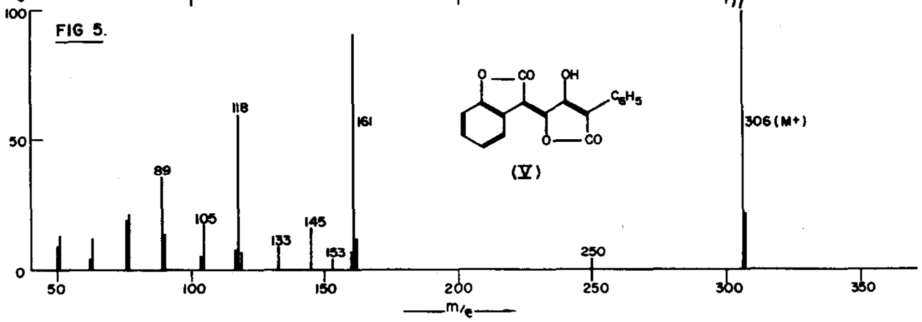


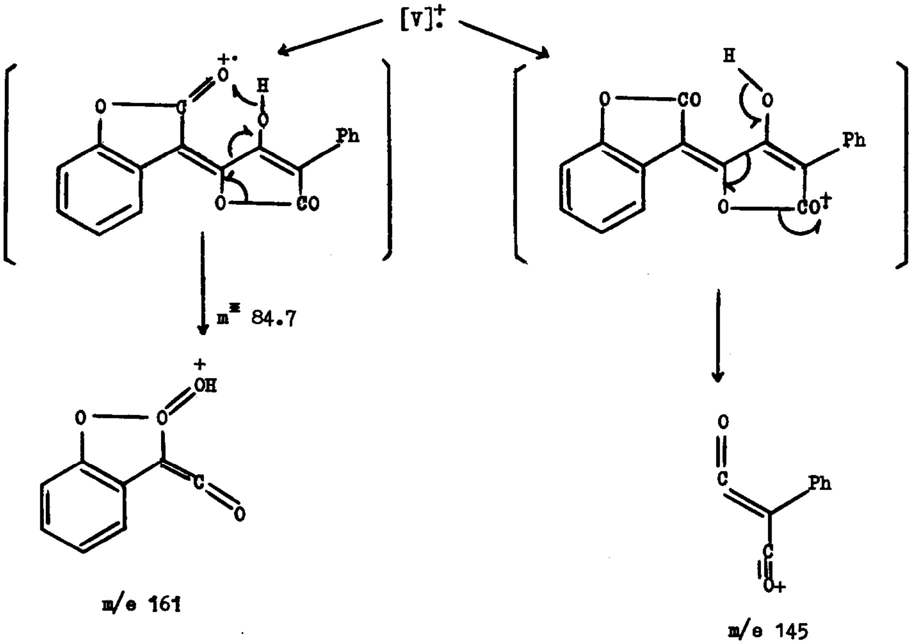
FIG 5.



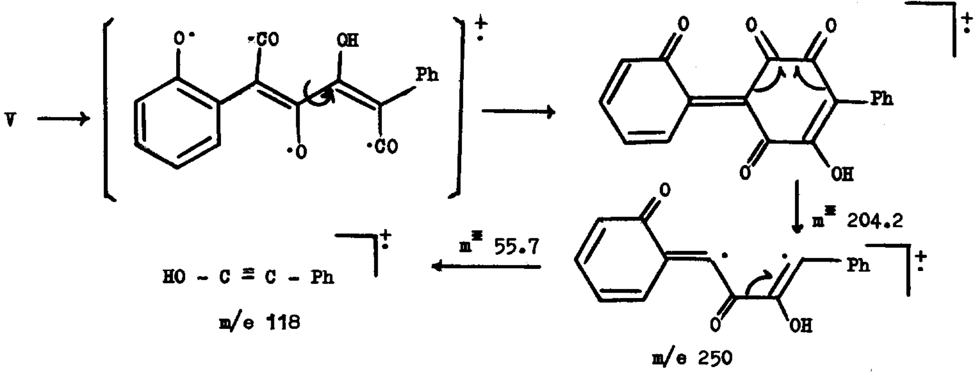
The mass spectrum (Fig. 4) of rhizocarpic acid (IV) is essentially the superimposition of the spectrum of phenylalanine methyl ester (3) on that of pulvic acid lactone. A metastable peak at 179.2 (469 → 290) establishes the electron-impact induced formation of the lactone from the molecular ion, through elimination of the methyl ester.

The fragmentation of calycin (V) is somewhat similar to that of pulvic acid lactone. The spectrum (Fig. 5) can be rationalised more readily on the basis of the recently accepted structure V (4), than on the previous structure VI (5).

Formation of the ions at m/e 161 and m/e 145 may be explained as follows:



A metastable peak at 204.2 corresponds to loss of C_2O_2 from the molecular ion, which must in this instance also undergo a rearrangement:



Structure VI would be expected to yield an m/e 161 ion, but formation of the m/e 118 fragment would be difficult to rationalise on the basis of this structure. Furthermore, there is only one concurrent elimination of C_2O_2 as opposed to two such losses observed in the spectra of the other four substances. It would thus appear that the mass spectrum provides further evidence in favour of structure V.

From the above observations it is clear that mass spectrometry can be put to good use in this field, in spite of skeletal rearrangements. It may also be of assistance in distinguishing between structural isomers such as pinastric and isopinastric acids.

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