It has been shown [1,5] that if, for each oxygen atom bonded to two molybdenum atoms, the sum of the two Mo-O distances are plotted against the difference between these, the points fall close to one and the same curve for all molybdenum oxides for which accurate atomic distances are known. Some points corresponding to distances in Mo_4O_{11} (o-rh.) showed the greatest deviation from this curve. Calculated from the new values of interatomic distances these points fit to the curve much better.

It was also found previously [5] that a logarithmic relation, according to Pauling, between bond distance and bond number could be formulated which corresponds to the above-mentioned curve assuming that the sum of bond numbers to each oxygen atom is 2. With the aid of this formula the sum of the bond numbers was calculated for the metal atoms in some molybdenum oxides. A systematic variation in the values thus obtained was observed for Mo_8O_{23}, Mo_4O_{11} (mon.) and Mo_4O_{11} (o-rh.). Rather high values were, however, obtained for the atoms 1 and 2 in the last of these structures, *viz.*, 6.40 and 6.36, respectively, compared to an expected maximum value of 6. Calculations based on the new interatomic distances give the values 5.94, 5.74, 5.17, and 4.80 for the atoms 1, 2, 3, and 4, respectively, (mean value 5.41, expected 5.50), which are all below the expected maximum and close to the corresponding values calculated for the monoclinic form.

A complete list of interatomic distances and angles in this structure as well as the observed and calculated structure factors is given in a separate document [6] copies of which may be obtained on request from the secretary of this institute.

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Mass Spectra and Organic Analysis IV[1] Some Comments on the Mass Spectra of Monoterpene Alcohols

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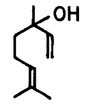
A recent publication of the mass spectra of some monoterpene alcohols [2] which were obtained by a method which we have already criticized [1] has led us to examine the differences between our results and those of the Swedish group in more detail.

As we have mentioned,[2] the main differences between the methods are in the energy of the bombarding electrons (70 eV in our case and 20 eV in the Swedish work [3]) and the presence of a large amount of helium with the sample in the latter case. The first of these differences accounts for the higher proportion of light fragments (particularly below *m/e* 60) that we observe, and is illustrated in Figs. 1 and 2 (linalool) and Figs. 3 and 4 (sabinol), which we measured at both 20 eV (Figs. 1 and 3) and 70 eV (Figs. 2 and 4). This, however, is not sufficient to explain all the differences observed. In the case of linalool, for instance, von Sydow shows fragments of significantly greater intensity at *m/e* 155, 93, 68, 67, and 59, and his fragments at *m/e* 43 and 41 would fit better with bombarding electrons at 70 eV rather than 20 eV. We considered at first the possibility of reaction of $He^{\oplus}$ ions with the substance under examination, but we could detect no difference in our spectra even when measured in the presence of a 4-fold excess of helium. Since only

Linalool



20 eV

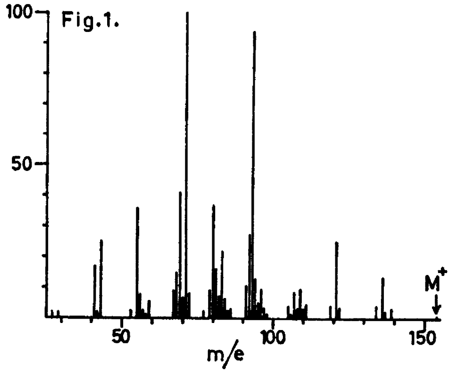


Fig.1.

70 eV

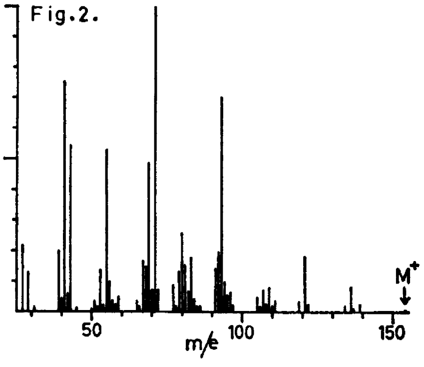
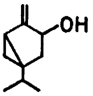


Fig.2.

Sabinol



20 eV

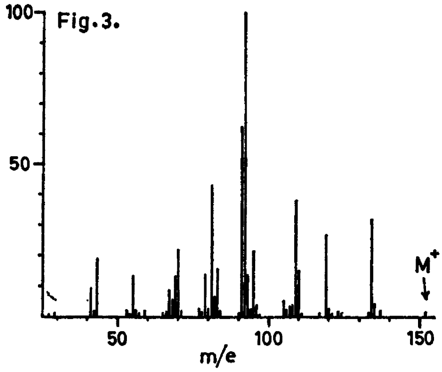


Fig.3.

70 eV

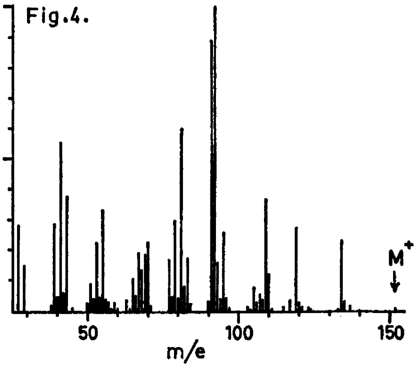
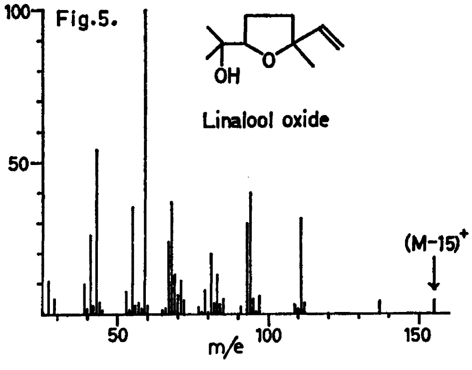
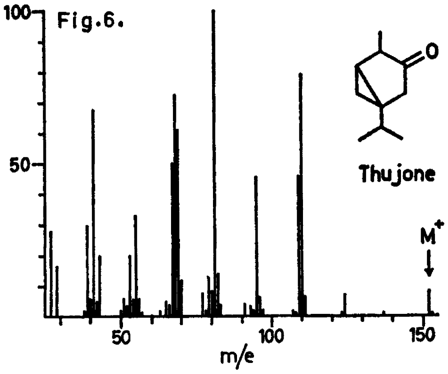


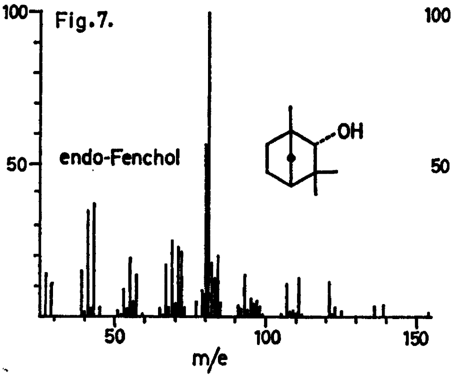
Fig.4.

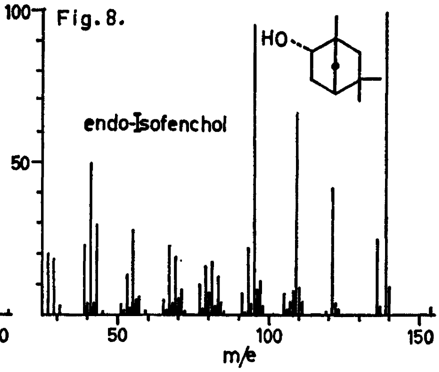
an impurity can be responsible for the fragment at *m/e* 155, we examined several of our own samples of gas-chromatographically purified linalool, and found that the fragment at *m/e* 155 was nearly always greater than the isotopic contribution from the molecular ion at *m/e* 154, but, more significantly, varied from one sample to another. A possible impurity that fits most of these facts is linalool oxide, the mass spectrum of which (at 70 eV) is shown in Fig. 5. This substance has approximately the same retention time as linalool on silicone oil columns.

We feel that most of the additional or enhanced fragments observed by von Sydow in sabinol, notably, those at *m/e* 150, 110, 95, 81, 69, 68, and 67 may be accounted for by the presence of 1-thujone (Fig. 6, 70 eV) in his sample (though at least one other impurity must be present to explain the fragment at *m/e* 150). Finally









the extraneous fragments reported in the mass spectrum of fenchol at *m/e* 139, 109, and 95 are characteristic of isofenchol (fenchol and isofenchol are shown in Figs. 7 and 8, respectively, both as endo-isomers). About 10 % isofenchol would give the spectrum of von Sydow.

All the pairs we quote here have very similar retention times on silicone oil columns.

It is pertinent to query von Sydow's use of the term "parent", which is customarily employed to designate the peak arising from the molecular ion. We are furthermore of the opinion that a formula with a dotted line across it and a figure (*e.g.* "69", occurring on von Sydow's Fig. 12, terpine-4-ol) which represents the mass of a minor fragment might lead to confusion, since it could appear that this is a mode of fission of the molecule.

In these laboratories, we are at present making a detailed study concerning the mass spectra of certain terpene alcohols and ketones using deuterium labelling, and we shall publish the results in due course.

Experimental. Except in the cases stated, all mass spectra were determined at an energy of 70 eV, source temp. about 260° in an Atlas mass spectrometer model CH 4.

The compounds mentioned in the text were made by known methods in the case of linalool oxide [4] and fenchol.[5] The linalool oxide was a mixture of *cis*- and *trans*-isomers. Isofenchol was made by lithium aluminium hydride reduction of isofenchone, the latter having been purified by crystallization of the semicarbazone.[6] We presume that the reduction will yield principally the endoisomer as is the case with fenchone.[5]

Sabinol, 1-thujone and linalool were from our collection; all compounds were purified by distillation and gas chromatography using 5 metre columns packed with carbowax on chromosorb W.

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