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7[1]. MASS SPECTROMETRIC FRAGMENTATION OF DIPHENYLPENTANERESINOLS

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The diphenylpentaneresinols agatharesinol, hinokiresinol and sugiresinol (cf. Figs. 1-3), recently isolated from conifers of several different botanical orders, appear to be of widespread occurrence in the Coniferae. Further work on Agathis species[2] and on the Sequoia phenols[3,4] has increased the number of compounds in the group and widened the range of structures found but all the compounds so far known are closely related to agatharesinol and present either variations in the original oxygenation pattern or products of subsequent conversions. Mass spectrometry is a useful and convenient tool for recognition and assignment of structure in this series, especially when only small amounts of material are available, and the fragmentation of these compounds has therefore been studied further. (Evidence of configuration required for complete structural determination can be obtained on a small scale from ORD measurements[1,5]). The present paper discusses the mass spectra of these compounds and the structural evidence obtainable from them.

The three main naturally occurring compounds appear to be representative of the types of structure liable to occur in this series. Although chemically and biogenetically closely related they give mass spectra which are rather different. However, they can all be converted by hydrogenation into compounds with a saturated aliphatic chain which offer a convenient basis for comparison and interrelationship.

The spectrum of agatharesinol (Fig. 1)[6], which is typical of the pent-1-ene derivatives, displays three prominent peaks. These are unaffected by variation of the saturated C(3) fragment ($-CH(OH)CH_2OH$, $-CH(\overline{O)CH_2O}C(CH_3)_2$, $-CH_2CH_3$, $-CH_2OH$ or

-CHOOH), while methylation of the phenolic groups shifts the base peak by 28 mass units and the other two peaks by 14 mass units. It follows that the main species is formed from the molecular ion by cleavage of the C(3)-C(4) bond and can be depicted as ion a or as the corresponding styryltropylium ion (metastable ions observed are indicated in these diagrams by m*). Although no evidence is available from metastable ions the two abundant species of lower mass number are most probably formed from ion a; the m/e 107 species can be formulated as the hydroxytropylium ion c and the m/e 131 species as the corresponding ethynyl derivative b or as a hydroxyindenyl ion[7].

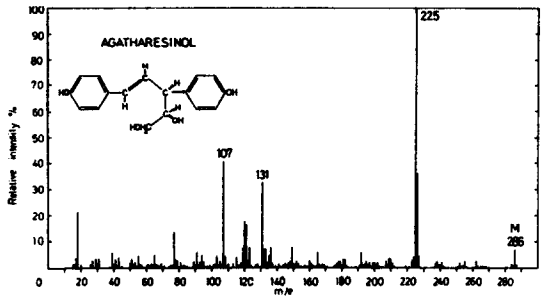
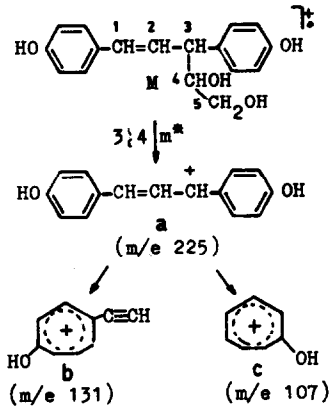


Figure 1



In the spectrum of agatharesinol tetraacetate[8] the occurrence of ion a is now shown by three prominent peaks (m/e 309, 267 and 225) due to the successive loss of two molecules of ketene from the initial species and it therefore offers an additional way of determining the number of aromatic acetate groups present. There is also a fairly abundant M-60 peak corresponding to the loss of acetic acid and indicating the presence of an aliphatic acetate group. However, the ion due to the loss of two molecules of acetic acid from the molecular ion does not give a peak of useful intensity.

The mass spectra of these compounds thus offer a good indication of the presence of the diphenylpropenyl moiety and of the nature of the substituents on the aromatic rings and on the C(4)-C(5) unit. When the aromatic rings are different the peaks associated with ions b and c will be doubled, but it is not possible on the basis

of the present results for this group of compounds to say whether a particular phenolic substituent is at C(1) or C(3).

In hinokiresinol (Fig. 2), the sole representative of the pent-1,3-diene type, the presence of the C(4)-C(5) double bond largely inhibits the formation of ion a and increases the stability of the molecular ion. This now undergoes a fragmentation entirely different from that of agatharesinol. The more important processes involve loss from the molecular ion of a methyl radical (m/e 237), a phenol molecule (m/e 158) or a p-hydroxybenzyl radical (m/e 145) and the formation of a hydroxytropylium ion (m/e 107). These processes are confirmed by metastable ions and appropriate shifts on methylation of the phenolic groups. They may all be rationalized as a migration of the C(3) hydrogen to the vinyl or p-hydroxystyryl moieties accompanied by ring closure and elimination of a substituent attached to the newly formed ring and are in agreement with results[9] recently obtained for 1,3-diphenylpropene that show the occurrence of hydrogen rearrangements and minimal disintegration of the aromatic rings on electron impact.

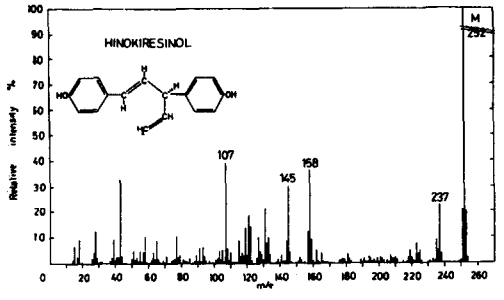


Figure 2

The mass spectrum of sugiresinol (Fig. 3), representing a tetrahydropyrane type, shows a richer array of ions, mostly rather different from those in the

TABLE 1. Mass numbers of main fragments from sugiresinol derivatives. (R = para substituent on aromatic rings. After correction for isotopic inhomogeneity, the deuterium label transfer or retention is essentially quantitative except where indicated by a ~ 80%, b ~ 70% or c ~ 60%).

Labelling	R	M	d	e	f	g	h	i	j	k	l
None	-OH	286	226	192	149	148	136	123	121	120	107
None	$-OCH_3$	314	254	206	163	162	150	137	135	134	121
$4\text{-}d_1$-	$-OCH_3$	315	254	207	163	162	151	137	135	134	121
$3,3,5\text{-}d_3$-	$-OCH_3$	317	255	209	164	163	151	137	135[b]	135[a]	122[c]
$4\text{-}O\text{-}d_1$-	$-OCH_3$	317	254	207	164	162	151	138	135	134	121[a]

agatharesinol and hinokiresinol spectra. Many of the abundant ions represent readily recognisable structural units and the main fragmentation processes, supported by metastable ions and by the results from labelled derivatives given in table 1, may be visualised as shown on the next page, although mechanistically alternative routes may readily be invoked.

Cleavage of the C(3)-C(4) and C(1)-O bonds in the molecular ion gives the m/e 226 species which may be formulated as ion d (and other forms in equilibrium with it, cf. ref. 9). Elimination of a molecule of phenol from the molecular ion gives rise to the m/e 192 species, which by further fragmentation gives the m/e 149 och 148 ions. The first fragment can be formulated as ion e, formed by loss of an aromatic substituent and the C(2) hydrogen with a 1,3-hydrogen shift to give the more stable conjugated system. The smaller fragments can be visualised as the ions f and g formed by retro-Diels-Alder fragmentation, accompanied in the first case by transfer of the hydroxyl hydrogen to the ether oxygen. The production of these ions may also be accounted for by ring contraction with formation of a C(3)-oxygen bond and then successive loss of a phenol molecule and the C_2-fragment as before.

The m/e 136 ion corresponds to the smaller fragment originating from the molecular ion on rupture of the C(2)-C(3) and C(4)-C(5) bonds which may occur by a cyclic process giving ion h. Further loss of a CHO radical from this ion gives the hydroxytropylium ion l, but as shown by the labelling results given in table 1, ion l must to some extent also be formed by other routes. Although no supporting metastable ions were found the m/e 123 and 121 species are apparently formed from the molecular ion by cleavage of the C(1)-C(2) and C(5)-O linkages accompanied by hydrogen transfer giving ions i and j. The m/e 120 ion corresponds to a fragment produced either by the cyclic process shown or by stepwise cleavage of the C(1)-C(2) and C(3)-C(4) bonds and may hence be formulated as ion k.

Loss of the C(4) hydroxyl group as water in sugiresinol and its dimethyl ether is negligible, but elimination is markedly facilitated by acetylation. The upper part of the spectrum of sugiresinol dimethyl ether acetate is thus dominated by the M-60 ion, formed by elimination of the acetate group together with the C(3) hydrogen, and

by the diene fragment (m/e 160) formed from it by a retro-Diels-Alder fragmentation. The position of the strong peak due to the diene fragment offers a further guide to the substitution on the C(3) aromatic ring and should be useful when this differs from that of the aromatic ring at C(1). The only other significant peak in the upper part of the spectrum is that due to ion a which is formed here in preference to ion d.

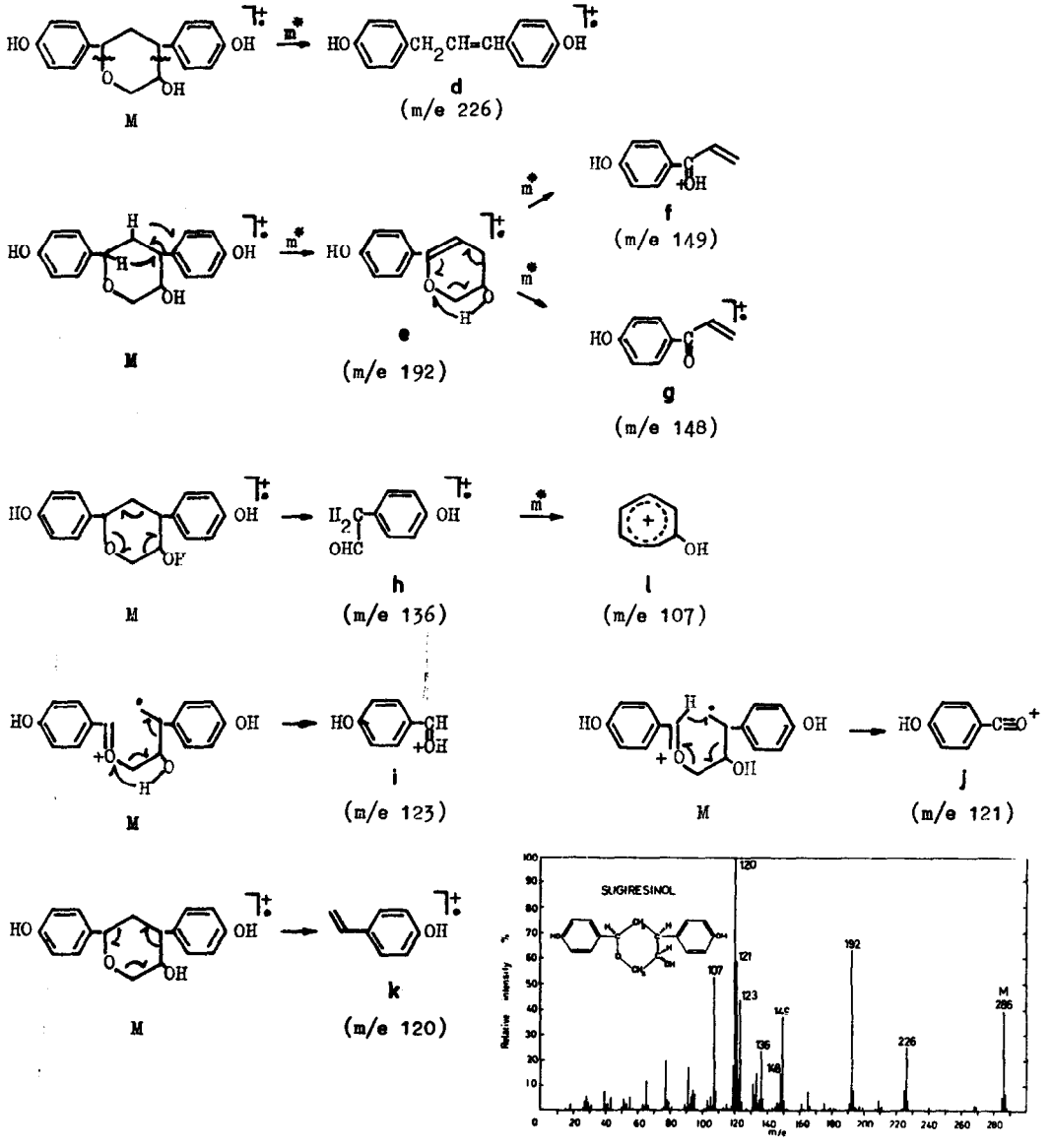
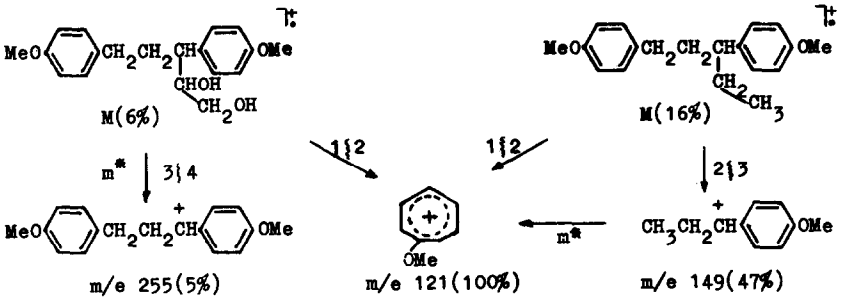


Figure 3

Sugiresinone dimethyl ether gives a spectrum corresponding to that of sugiresinol but devoid of peaks due to processes blocked by the carbonyl group (e → f, e → g and M → i).

While the mass spectra of the groups of compounds described above differ considerably, the spectra of the saturated pentane derivatives obtained by hydrogenation of these compounds are quite similar and offer not only a convenient basis for the assignment of relationship and structure, but also a ready and general means of distinguishing between the aromatic rings when these carry different substituents. In agreement with expectation dihydroagatharesinol dimethyl ether gives rise to a single high intensity peak at m/e 121, which, as shown by the nearly complete shift (90 %) to m/e 122 for the 1-d_1-derivative and the absence of shift for the 4-d_1-derivative, is due almost entirely to the methoxytropylium ion formed on cleavage of the C(1)-C(2) bond. The only prominent peaks in the upper half of the spectrum are the molecular peak and the m/e 255 peak due to the larger fragment formed by cleavage between C(3) and C(4).



In the spectrum of tetrahydrohinokiresinol dimethyl ether the base peak also occurs at m/e 121. The only other prominent peaks are the molecular peak and the m/e 149 peak, formed by benzylic cleavage, this time between C(2) and C(3). The m/e 149 peak thus shows the nature of the aromatic substituent at C(3) and hence indirectly the nature of the C(1) substituent. The m/e 149 ion undergoes further fragmentation and as shown by a metastable ion gives rise to the methoxytropylium ion at m/e 121 which in

this case must therefore derive from both aromatic rings and hence when these are different will appear as two peaks. Depending on the substituents, the m/e 121 and m/e 149 ions should thus give a good indication of the nature of the aromatic substituents at C(1) and C(3).

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