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Mass Spectral Fragmentations. I. *Mass Spectral Date on the Synthetic Intermediates Related to the Preparation of Linaloyl Oxide*

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Synopsis

This paper describes mass spectral data from synthetic intermediates of linaloyl oxide. The fragmentation of sulfur functional groups including compounds 1-8 would provide fruitful evidences for structural assignment of acyclic and alicyclic monoterpenoid precursors. Since, 1,3-dithianyl group in 1, 2, and 3 can provide a base peak and the elimination of the sulfinyl group from 7 and 8 is considered to occur at the initial stage of the fragmentation.

I. Introduction

Along with the synthetic works of linaloyl oxide[1] from 2-(2-hydroxy-2,6-dimethyl-5-heptenyl)-1,3-dithiane (1) and methyl 1-methylthio-3-hydroxy-3,7-dimethyl-6-octenyl sulfoxide (8), we paid much attention to the structural assignment on the basis of mass spectral fragmentation data. Despite of the necessity of the accumulation of graphical data of mass spectrum on reactive sulfur compounds very few have been reported.[2] Therefore, it is believable that typical fresh graphic data of mass spectrum of the compounds 1-10 would provide additional evidences for structural elucidation in the monoterpenoid field in addition to expectations toward thermal stability and reactivity arising from sulfur function moiety.

II. Results and Discussion

Mass spectra were measured at 70 eV with a Hitachi RMS-4 mass spectrometer by indirect insertion method. Injection temperatures are 80 °C for compounds 2, 6, 7, and 8 and 100 °C for compounds 1, 3, 4, and 5. The spectral charts are shown in Fig. 1-10 and parent peaks, their relative intensities, and base peaks for 1-8 are listed in Table 1. Analysis of each fragmentation is carried out by grouping the compounds as follows: Group A Compounds 1, 2, and 3; Group B Compounds 4,

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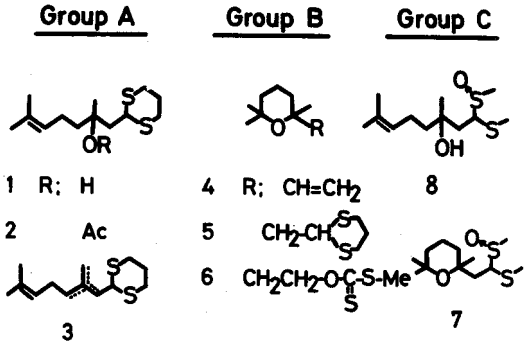
5, and 6; Group C' Compounds 7 and 8. Group A provides a base peak m/e 119 corresponding to 1,3-dithianyl group. Both alcohol 1 and its acetate 2 afford a peak m/e 242, indicating that dehydration and/or deacetoxylation takes place at the initial fragmentation stage giving olefin 3 followed by elimination of prenyl, thiomethyl (CH_2SH), and 1,3-dithianyl groups.



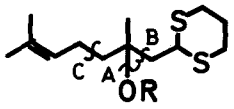
Group B displays molecular ions and their intensities significantly depend on complexity of their molecular structure. A typical fragmentation from the tetrahydropyranyl function is shown in scheme 2 and the elimination of water from the ion affords an olefinic fragment (2-methyl-2,5-heptadiene) which is subjected to eliminate prenyl group.

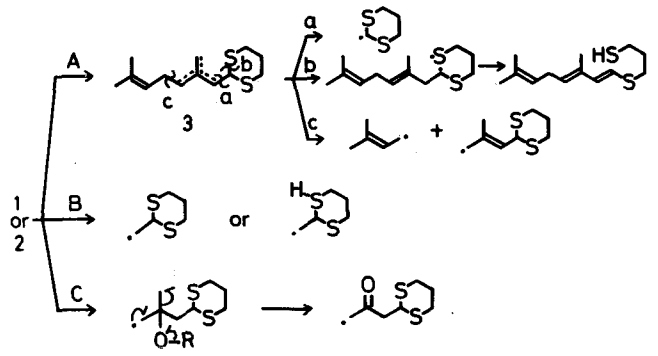
Group C exhibits no parent peak, but a base peak at m/e 69 corresponding to prenyl group. A characteristic peak from the Group C is the peak at m/e 200 due to the elimination of methyl sulfenic acid (CH_3SOH) from the corresponding mother ion, which is comparable with the pyrolitic olefin synthesis from sulfoxides.[3] A tentative assignment for the fragments derived from the Group A, B, and C are summarized in Schemes 1, 2, and 3.

TABLE 1 Mass Spectral Data of Compounds 1 ~ 8

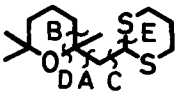
Compound	1	2	3	4	5	6	7	8
Parent P.	M^+	M^+ – AcOH	M^+	M^+	M^+	M^+	M^+ – MeSOH	M^+ – MeSOH
Rel. Int. (%)	21	8	4	1	68	0.2	4	2
Base P.	119	119	119	71	159	69	69	69

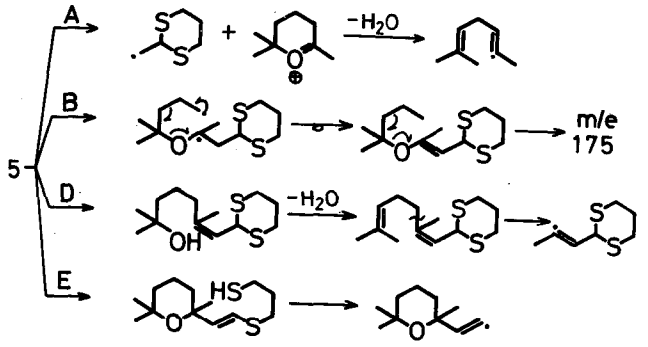
Scheme 1



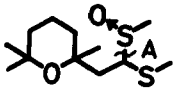


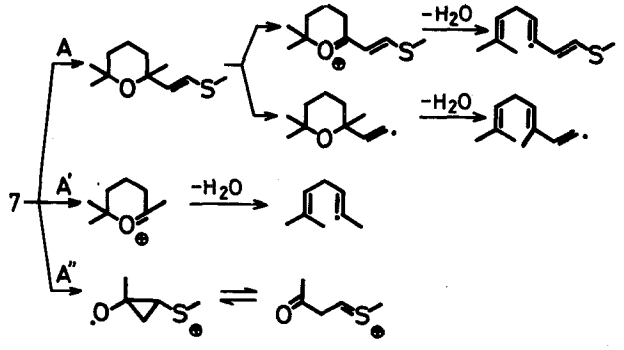
Scheme 2





Scheme 3





References

1) S. Torii, K. Uneyama, and M. Ishihara, J. Org. Chem., 39, (24) (1974) in press.
2) H. Budzikiewicz, C. Djerassi, and D. H. Williams,"Mass Spectrometry of Organic Compounds", Holden-Day, Inc., (1967).
3) C. A. Kingsbury and D. J. Cram, J. Amer. Chem. Soc., 82, 1810 (1960).

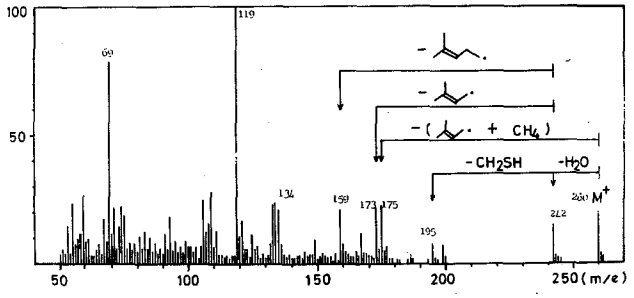
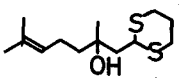


Fig 1



$C_{13}H_{24}OS_2$ MW 260

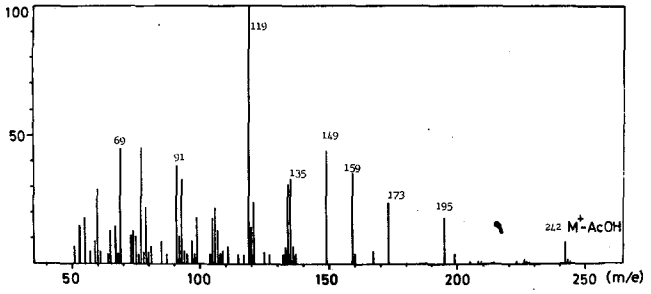
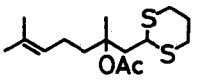
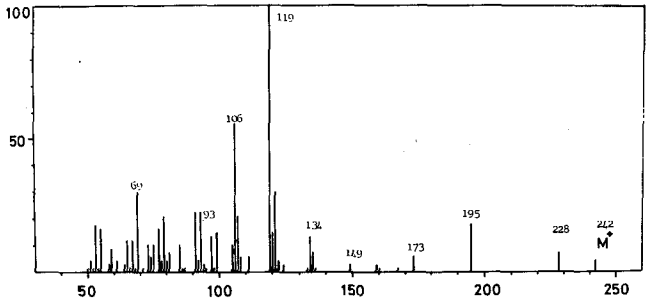


Fig 2



$C_{15}H_{26}O_2S_2$ MW 302



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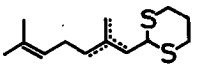
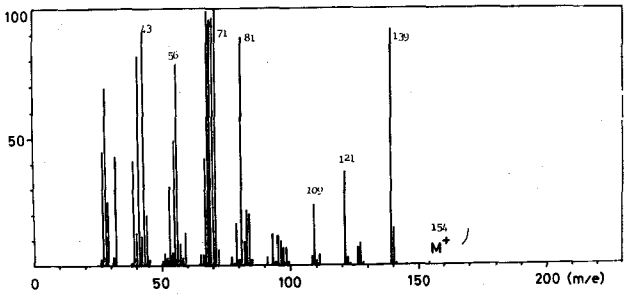


$C_{13}H_{22}S_2$ MW 242



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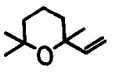
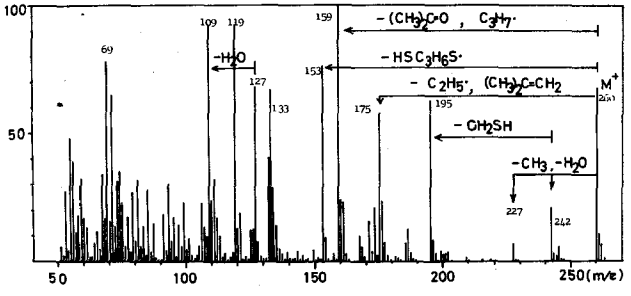


$C_{10}H_{18}O$ MW 154



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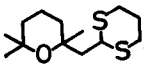

$C_{13}H_{24}OS_2$ MW 260

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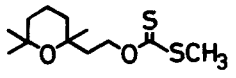
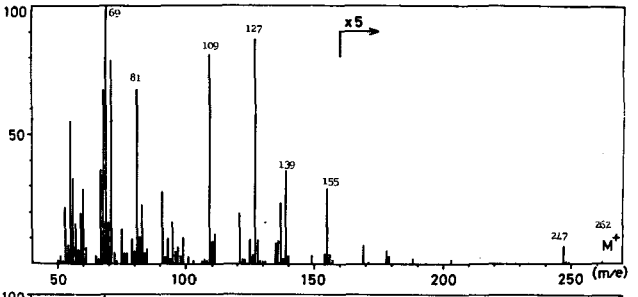


$C_{12}H_{22}O_2S_2$ MW 262



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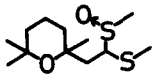
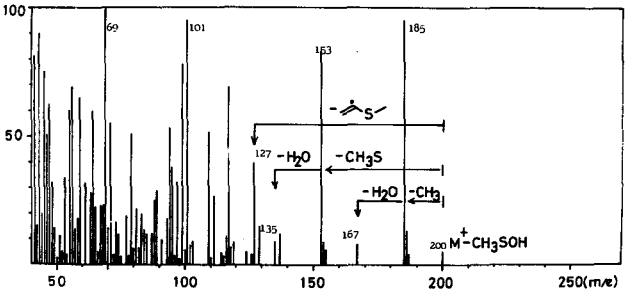


$C_{12}H_{24}O_2S_2$ MW 264



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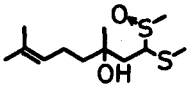
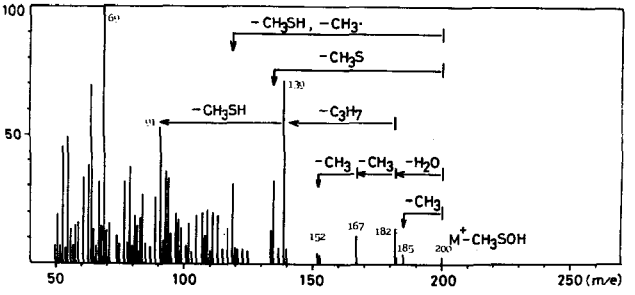


$C_{12}H_{24}O_2S_2$ MW 264



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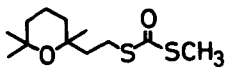


$C_{12}H_{22}O_2S_2$ MW 262

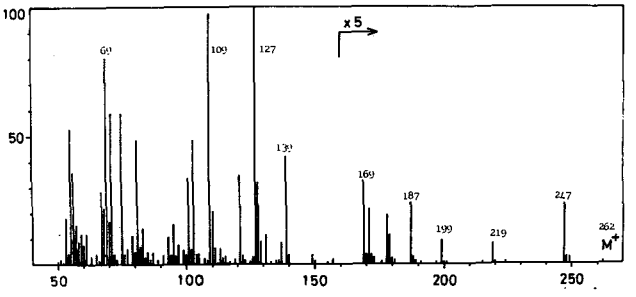
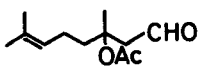


Fig 10



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