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AN APPLICATION OF ION-MOLECULE REACTION WITH VINYL METHYL ETHER: DIRECT LOCATION OF DOUBLE BOND IN C₂₅ TO C₃₅ MONOOLEFINS OF ANT CUTICULAR EXTRACTS.

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INTRODUCTION

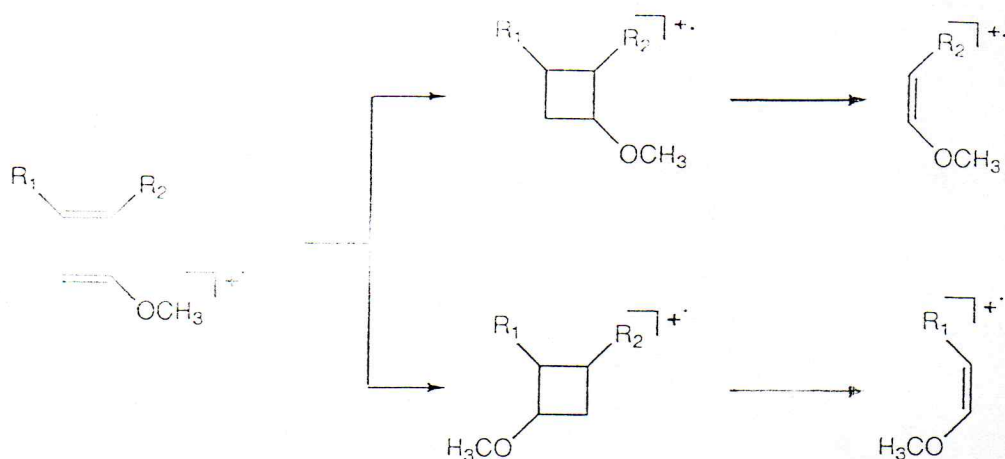
Recognition between different ant species is due to components present on the cuticle of the insects. Analysis of cuticular extracts exhibit components commonly identified as long chain branched or unbranched alkanes and alkenes. Until recently, liquid phase prederivatization followed by GC/MS analysis was a typical method [1] for determination of the double bond position in the long chain alkenes. For direct location of the double bonds, gas phase ion-molecule reactions induced by the vinyl methyl ether (VME) radical cation are utilized conveniently towards the olefinic substrates herein investigated.

EXPERIMENTAL

Cuticular extracts were obtained by washing with pentane whole ant bodies of different species (*Myrmica alaskensis*, *Cataglyphis cursor*). CI-VME-MS data were obtained using a R-30-10 Nermag quadrupole analyser with Vinyl Methyl Ether (Air liquide) at 5 10⁻⁵ Torr (measured in the source housing). Components were separated by GC (oven temperature conditions depending on the substrates).

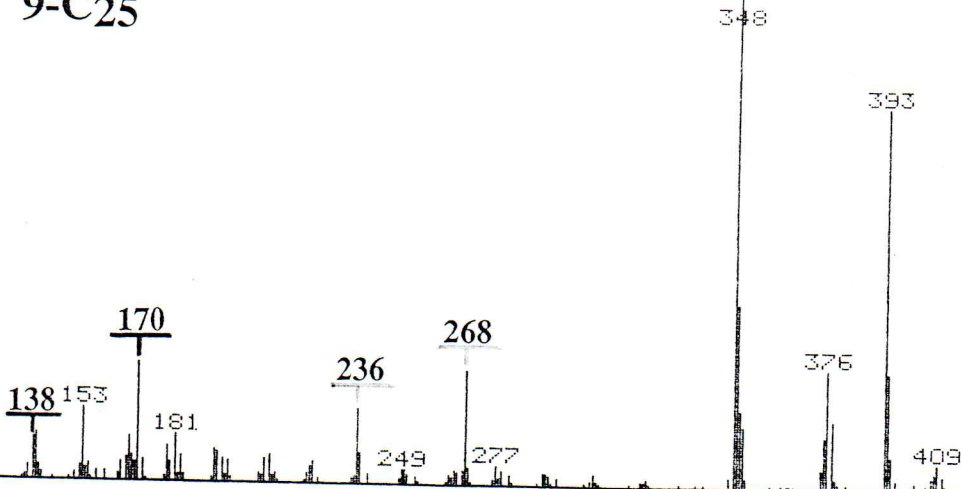
RESULTS

Besides the molecular species, [M+HVME]⁺, [(M+HVME)-15]⁺, [M-2H]⁺, substituted vinyl methyl ether radical cations are produced. All spectra exhibit two couples of 32 amu distant ions clearly related to the position of the double bond in the initial alkenes (Fig.1). These diagnostic-ions are presumably formed via an initial [2+2] cycloaddition reaction according to Jennings et al. [2] assessments (scheme), and in agreement with our studies using a deuterated reagent (Fig.2).



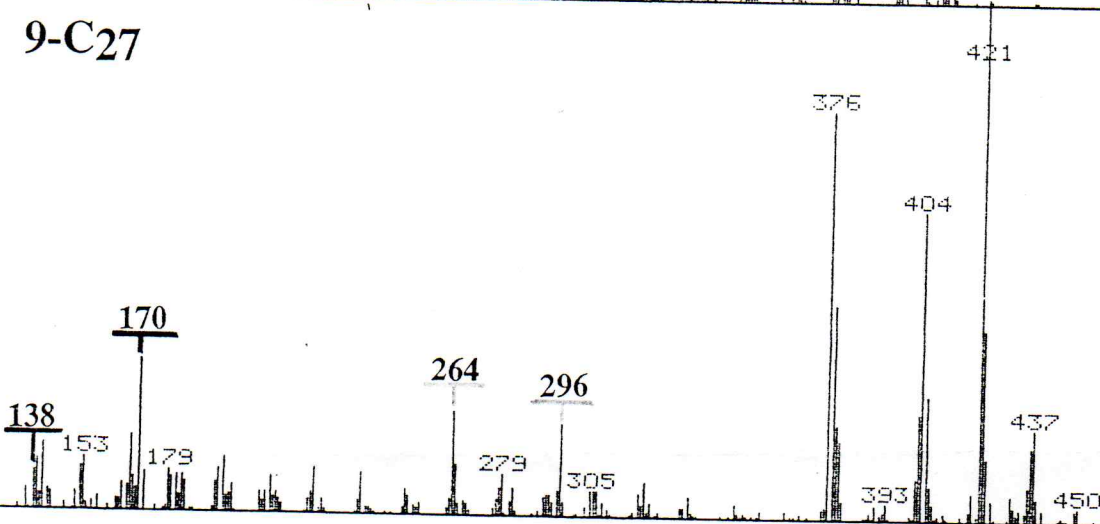
9-C25

a



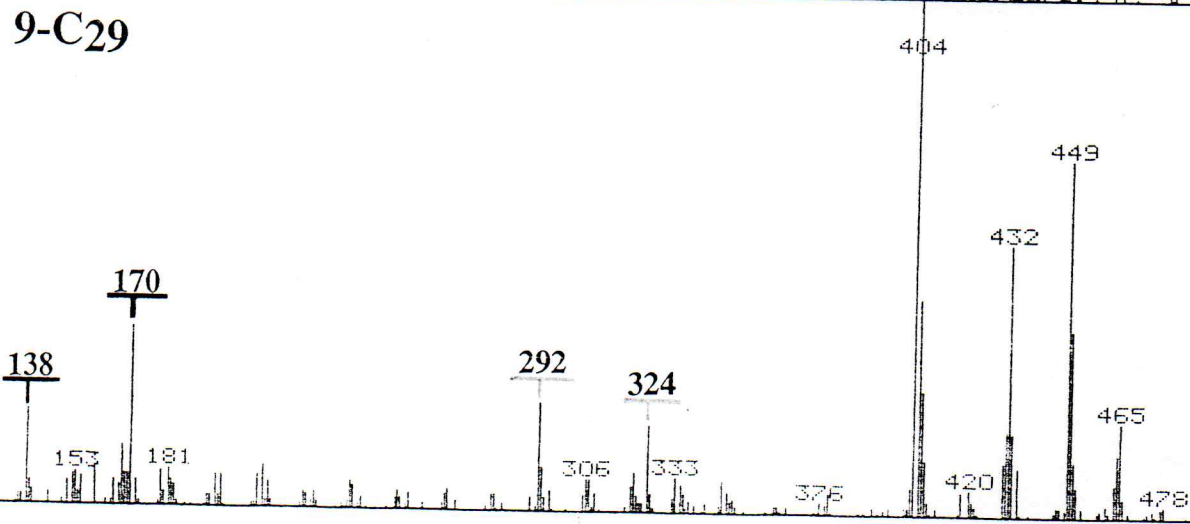
9-C27

b



9-C29

c



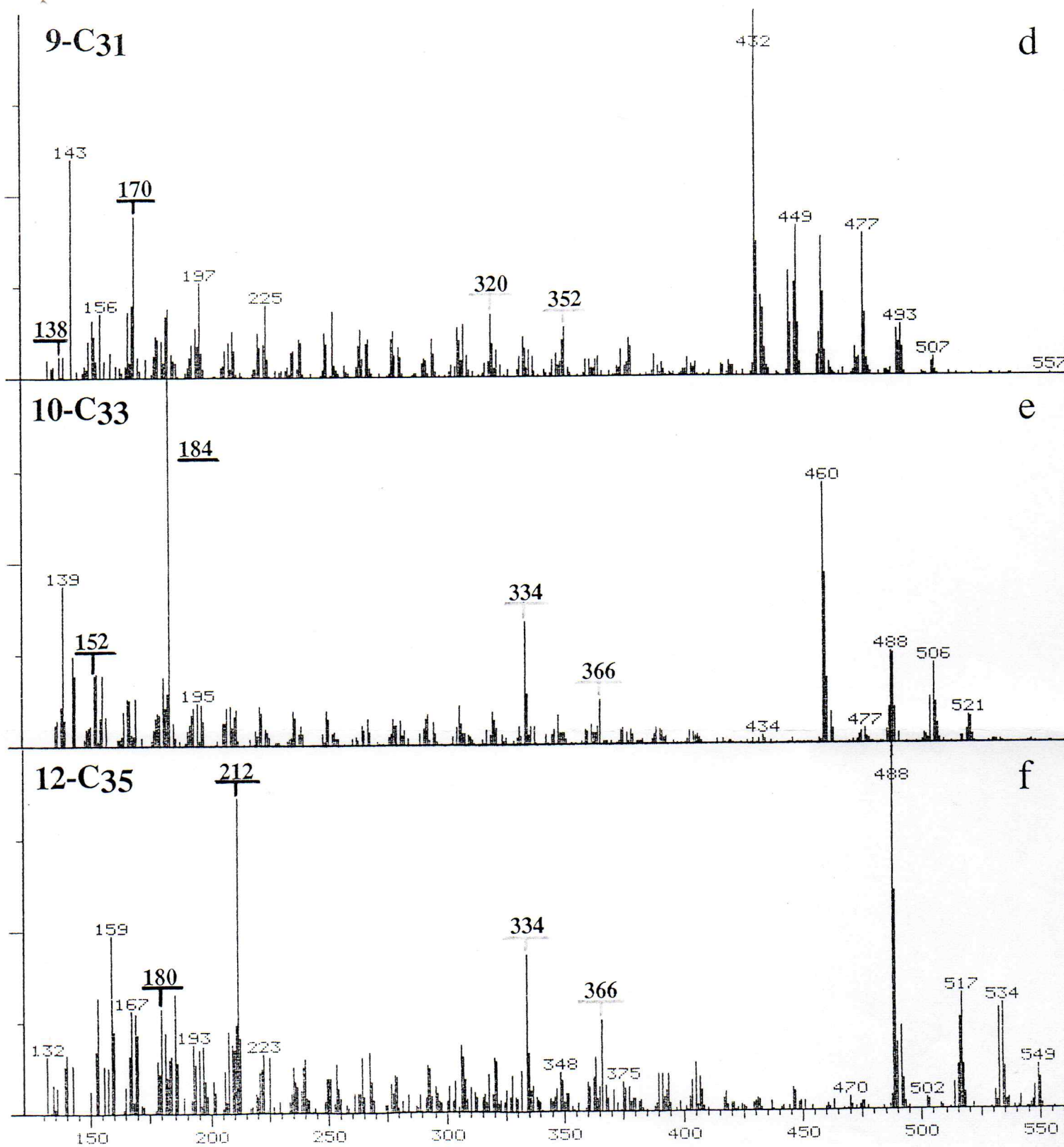


Fig. 1: CI-VME mass spectra of natural monoolefins : a, b ,c (*Myrmica alaskensis*) and d, e ,f (*Cataglyphis curvis*)

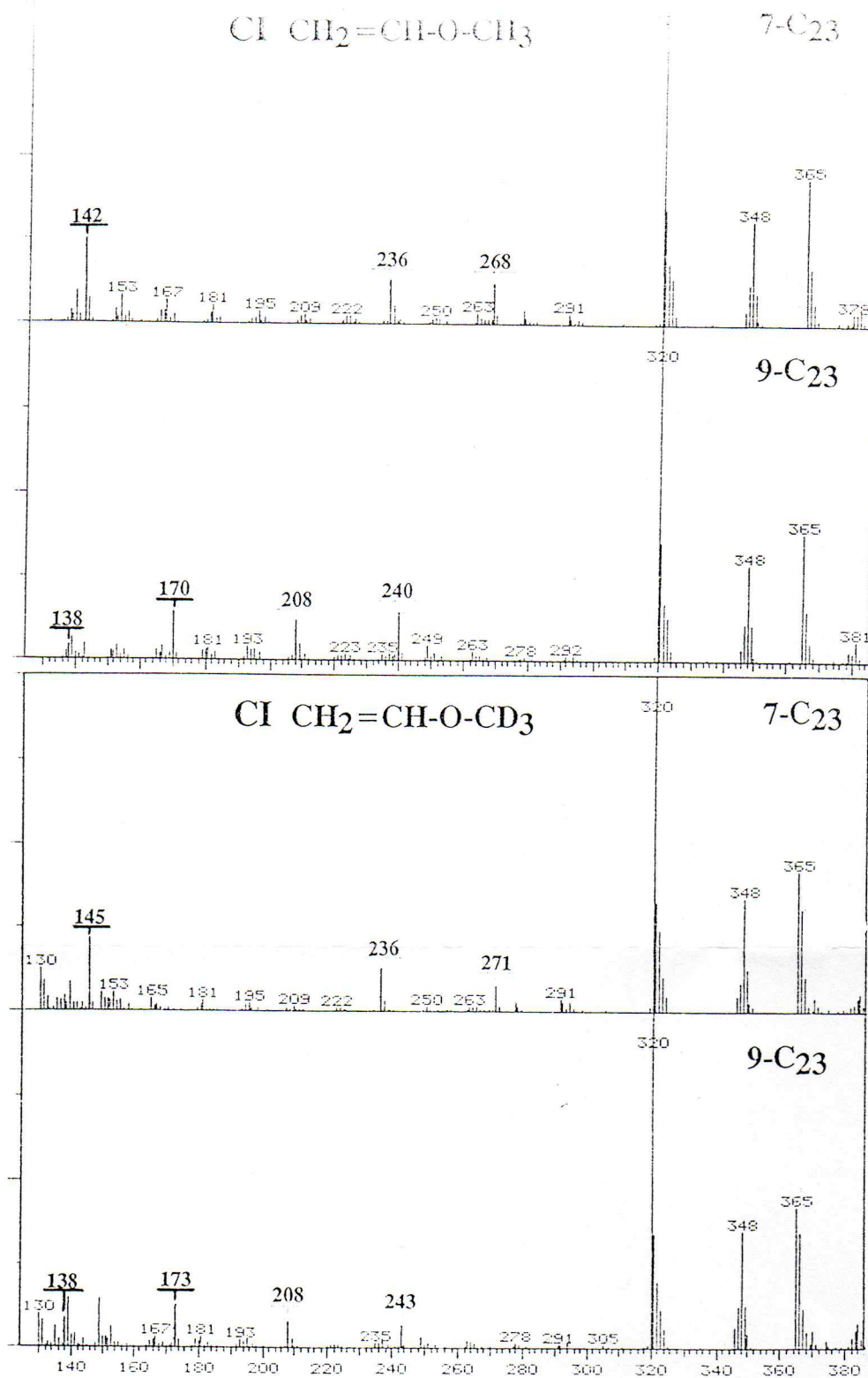


Fig. 2: Cl-VME and Cl-deuterated VME (CH₂=CH-OC(D)₃) of 7-C₂₃ and 9-C₂₃.

CONCLUSION

Various reagent gases such as isobutane [3], amines [3], vinyl ethers [2] and nitric oxide [3,4] have been already proposed last years for direct location of the double bond in the case of monofunctional olefins. VME as reagent gas represents an useful and appropriate alternative to initiate ion-molecule reactions for structural determinations in the case of long chain (>C₂₅) alkenes.

REFERENCES

- [1]-Francis G.W. and Veland K., *J. Chromat.*, 219, 379, 1981.
- [2]-Greathead R.G. and Jennings K.R., *Org. Mass Spectrom.*, 15, 431, 1980.
- [3]-Budzikiewicz H. and Busker E., *Tetrahedron*, 36, 255-266, 1980.