

IDENTIFICATION OF TRIMER AND DIMER OF 4-HYDROXY-3-METHOXY BENZALDEHYDE IN CRYSTAL STRUCTURE OF VANILLIN

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ABSTRACT

The effect of intermolecular hydrogen bonding on the molecular structure of vanillin has been studied using negative ion chemical ionization (NICI) mass spectrometry methods. The [Trimer-H₂O] and [Dimer-H₂O] were observed at m/z 438 and 286 respectively in NICI (CH₄) mass spectrum of vanillin. The NICI (Cl) mass spectrum of vanillin differs where deprotonated molecular ion peak, [monomer-H] at m/z,151 was the second most abundant ion peak. The base ion peak was observed at m/z,187 due to the presence of monomer+³⁵Cl. The [Trimer-H₂O] and [Dimer - H₂O] were not detected due to the presence of chloride ion. The results obtained support that the crystal of vanillin consists of trimer and dimer of 4-hydroxy-3-methoxy benzaldehyde.

Keywords 4-hydroxy-3-methoxy benzaldehyde, vanillin, intermolecular hydrogen bonding.

INTRODUCTION

Vanillin (4-hydroxy-3-methoxy benzaldehyde) is a degradation product of lignin, which is one of the constituents of wood (Glasser, 1990). It is also an industrial raw material for the production of papavarine, a constituent of opium (Cram and Hammond, 1964). Further, the vanillin thiosemicarbazone, one of its derivatives has been used as metal chelating agent (Akinchan and Abram, 2000, Akinchan et. al, 1996). The molecular structure of vanillin is not known, whereas X-ray crystallographic data on Ni(vtsc)₂ 4C₂H₅OH (vtscH=Vanillin thiosemicarbazone) has been reported (Akinchan and Abram, 2000). The presence of four ethanol molecules in the unit crystal suggests intermolecular hydrogen bonding involving uncoordinated hydroxy group of vanillin moieties. Further the crystal structure data reported earlier on phenol indicated, its trimeric nature due to strong intermolecular hydrogen bonding (Fabio et. al, 1995). The chemical ionization mass spectrometry has been found useful for solving stereochemical problems (Harrison, 1992, Akinchan, 2001). The Negative-ion chemical ionization mass spectrometric data have been reported on 'cis-diols, (Winkler and Stahl, 1978, 1979) hydroxy coumarin (Madhusudanan et al, 1990) and semicarbazone (Akinchan, 2002) derivatives. The present article describes the negative-ion

chemical ionization (NICI) mass spectral studies, which were undertaken to know the structure of vanillin.

MATERIALS AND METHODS

The negative Ion Chemical Ionization, NICI(CH₄) and Negative Ion Chemical Ionization, NICI(Cl) mass spectra were recorded at Regional Sophisticated Instrumentation Centre at Central Drug Research Institute, Lucknow, India. The reagent gases used were CH₄ and a mixture of CHCl₃ and MeOH in 1:10 molar ratio. The Spectrometer used was JEOL-SX-102.

RESULTS AND DISCUSSION

NICI(CH₄) mass spectrum of 4-hydroxy-3-methoxy benzaldehyde (vanillin)

The negative-ion Chemical Ionization (NICI(CH₄) mass spectrum of vanillin is summarized in Table1 and shown in Figure1. The [trimer-H₂O] and [dimer-H₂O] were observed at m/z 438 and 286 respectively but deprotonated monomer, [monomer-H] ion was absent. The reported X-ray data on phenol indicated that unit cell of the crystal contains three crystallographically independent phenol molecules. These are connected via O-H...O-H hydrogen bonds. (Fabio et al, 1995). One could assume similar hydrogen bonded dimeric

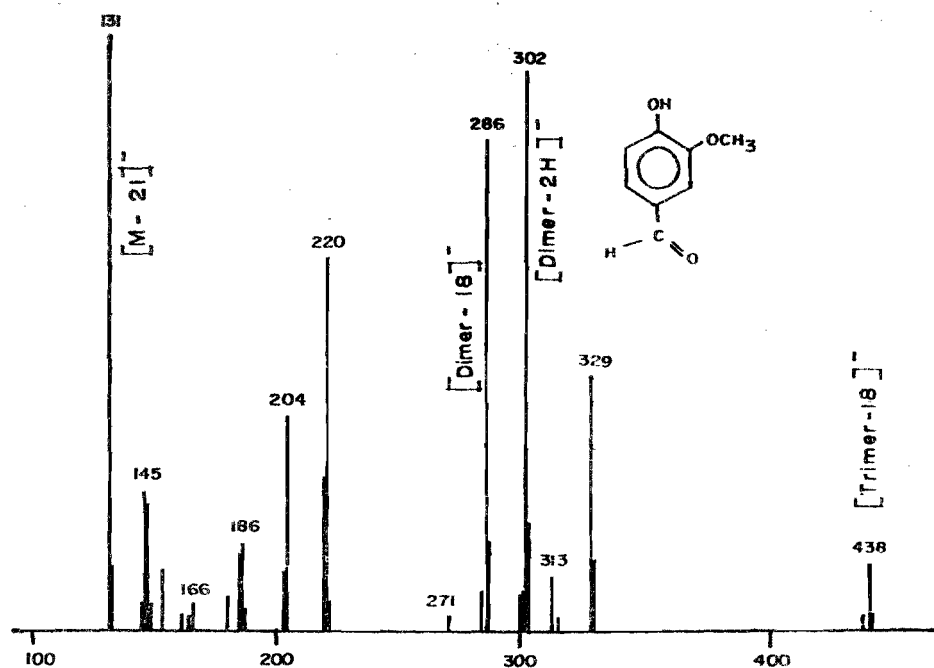


Figure 1 $\text{NICl}(\text{CH}_4)$ mass spectrum of 4-hydroxy-3-methoxy benzaldehyde

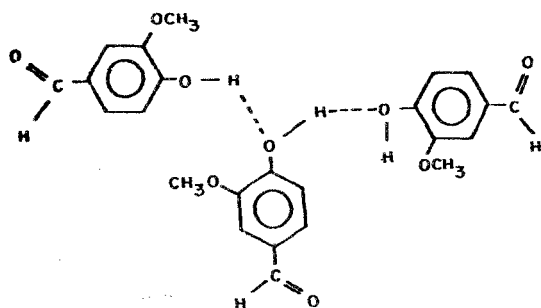


Figure 2 Hydrogen bonded trimer of vanillin

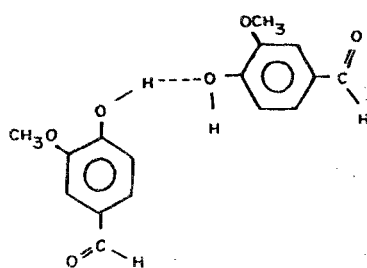


Figure 3 Hydrogen bonded dimer of vanillin

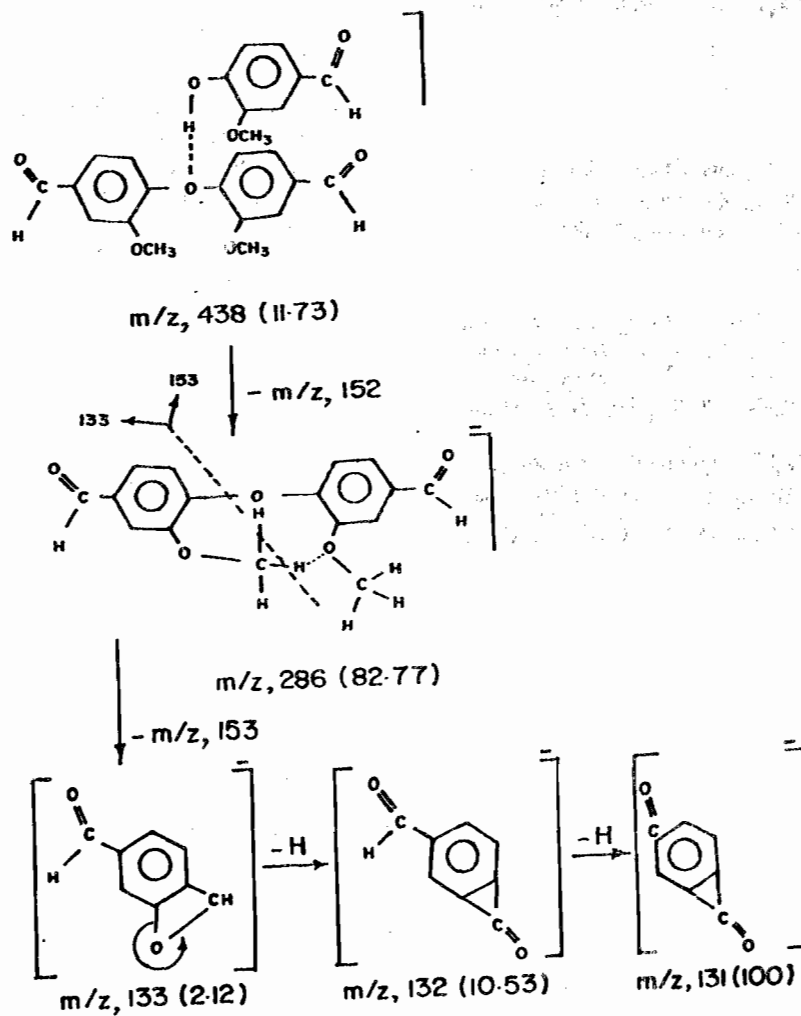
(Figure 3) and trimeric (Figure 2) structures for vanillin. The central molecule could have greater stretch than the other two in the trimeric form. Here central molecule acts as both donor and acceptor for hydrogen bonding. As a result one molecule of water is eliminated and the ion peak is observed at m/z 438. The

hydrogen bond energy decreases due to the strong covalent bond between oxygen and two aromatic rings. The loss of one molecule of vanillin gave [dimer- H_2O] ion peak at m/z 286 (Scheme 1). The $\text{NICl}(\text{CH}_4)$ spectrum also shows ion peaks at m/z 303 and 302 due to the presence of [dimer-H] and [dimer-2H] respectively. This is probably due to gradual deprotonation of vanillin dimer (Figure 1). The other most abundant ion peaks are at m/z 220 and 204. The base ion peak was detected at m/z 131 probably due to fragmentation of m/z 286. The ion peak at m/z , 286 could be alternatively formed due to loss of one molecule of water from the dimer. $\text{NICl}(\text{Cl})$ mass spectrum of 4-hydroxy-3-methoxy benzaldehyde (Vanillin).

The negative-ion Chemical ionization ($\text{NICl}(\text{Cl})$), mass spectrum of vanillin is reported in table 1. The [monomer-H] was observed at m/z 151 but molecular ion peak was absent. The spectrum appears to be completely different from the $\text{NICl}(\text{CH}_4)$ mass spectrum having fewer numbers of ion peaks. The ion peaks at m/z 189 and 187 correspond to [monomer- ^{37}Cl] and [monomer- ^{35}Cl] respectively with characteristic isotopic pattern. The base ion peak at m/z 187 is due to the adduct formation between monomer and ^{35}Cl involved in hydrogen bonding. (Madhusudanan et al, 1990). Similar

Table 1: $\text{NICl}(\text{CH}_4)$ and $\text{NICl}(\text{Cl})$ mass Spectra of 4-hydroxy-3-methoxy-benzaldehyde

Ion*	$\text{NICl}(\text{CH}_4)$		$\text{NICl}(\text{Cl})$	
	m/z	rel. int.	m/z	rel. int.
[trimer- H_2O]	438	11.73		
[dimer-H]	303	18.24		
[dimer-2H]	302	93.49		
[dimer- H_2O]	286	82.77		
[dimer- H_2O -66]	220	62.83		
[dimer- H_2O -82]	204	35.85		
[monomer- ^{37}Cl]			189	34.94
[monomer- ^{35}Cl]			187	100.00
[monomer-H]			151	61.29
[m/z 286-(152+H)]	133	02.12		
[m/z 286-(152+2H)]	132	10.53		
[m/z 286-(152+3H)]	131	100.00		

**Scheme I** $\text{NICl}(\text{CH}_4)$ fragmentation of m/z, 438

observations were reported for $\text{NICl}(\text{Cl})$ spectra of a number of cyclic diols. (Winkler and Stahl 1979).

CONCLUSIONS

The Negative Ion Chemical ionization ($\text{NICl})\text{CH}_4$ mass spectral study demonstrates that the Crystal structure of vanillin probably consists of hydrogen bonded trimer and dimer. Further supports came from the Negative ion chemical ionization ($\text{NICl}(\text{Cl})$ mass spectrum, where [monomer-H] at m/z 151 and adducts with isotopic chloride ions at m/z , 189 and 187 respectively were detected. Here trimeric and dimeric structures are not possible for vanillin due to the presence of chloride ion capable of forming strong hydrogen bond.

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