



CHAPTER IV

DISCUSSION

According to recent study on the chemical constituents of *Piper ribesoides* Wall. (aerial parts) from Kanchanaburi Province, nine substances are reported (Table 7, p. 129-130) (Kijjoa *et al.*, 1989). The present work had led to isolated of two phenylpropanoids from the fruits, two benzenoids from the stems and four unidentified substances from the stems. One of the phenylpropanoids namely bornyl *p*-coumarate is reported for the first time in *Piper* species.

FP-1 was identified to be hinokinin by comparison with the IR absorption, proton NMR and mass spectra with the published data of hinokinin (Belletire and Fry, 1987 ; Jakupovic, 1986).

Hinokinin was obtained as a viscous liquid, its IR absorption spectrum (Fig.30) showed a characteristic band for a γ -lactone carbonyl at 1776 cm^{-1} . Its proton NMR spectrum (Fig.31) displayed signals characteristic of a diaryl butyrolactone. Signals for methylenedioxy protons were observed as a singlet at $\delta 5.95$ (4H). Aromatic protons were observed as a multiplet at $\delta 6.46$ (2H) for 3-H and 5-H, a doublet of doublets at $\delta 6.60$ (1H) for 5'-H, a doublet at $\delta 6.63$ (1H) for 3'-H, a doublet at $\delta 6.70$ (1H) for 6-H and a doublet at $\delta 6.75$ (1H) for 6'-H. Methyleneoxy protons were observed as a doublet of doublets at $\delta 3.86$ (1H) for 9₂-H and a doublet of doublets at $\delta 4.12$ (1H) for 9₁-H. Two methine protons of the butyrolactone system were observed along with two protons of benzylic group that is far from carbonyl group centered at $\delta 2.50$ as a multiplet. Two protons of

benzylic group that is near carbonyl group were observed as a doublet of doublets at $\delta 2.84$ (1H) for 7_2^1-H and a doublet of doublets at $\delta 2.99$ (1H) for 7_1^1H . The mass spectrum showed the base peak at m/z 135, molecular peak at m/z 354. The proposed fragmentation pattern was shown in Fig.22.

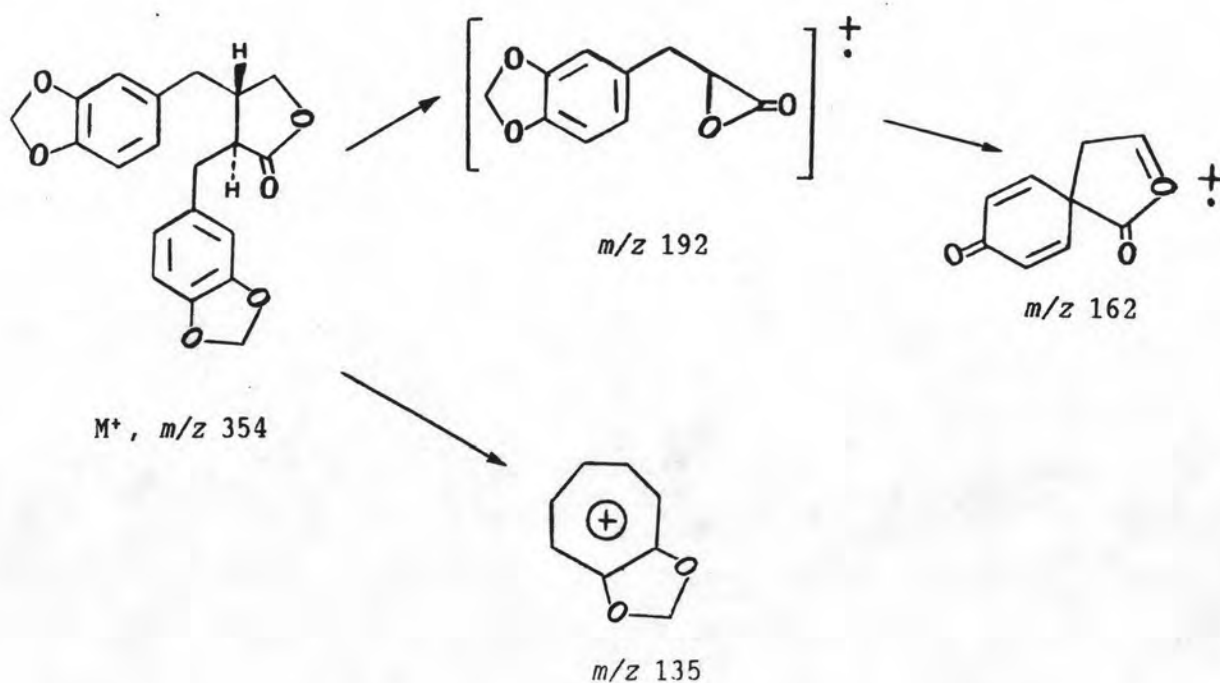


Fig.22 The proposed fragmentation pattern of hinokinin

Hinokinin is a widely distributed lignan whose structure was firmly established by Haworth (1950). Hinokinin has been isolated from *Piper clusii* Cass DC. (Koul *et al.*, 1983), *Piper cubeba* (Prabhu and Mulchandani, 1985), *Piper trichostachyon* DC (Koul *et al.*, 1988) and *Piper ribesoides* Wall. (Kijjoa *et al.*, 1989).

FP-2 was identified to be bornyl p-coumarate by comparison with the IR absorption, proton NMR and mass spectra with the published data of bornyl p-coumarate (Hernandez *et al.*, 1986).

Bornyl p-coumarate was obtained as a white amorphous powder, its IR spectrum (Fig.32) showed an absorption band for an unsaturated ester carbonyl at 1684 cm^{-1} , an absorption band for CH_3 stretching at 2869 cm^{-1} and an absorption band for CH and CH_2 stretching at 2942 cm^{-1} . From proton NMR spectrum (Fig.33), aromatic protons were observed as a doublet of doublets at $\delta 6.85$ (2H) for 5^{r}-H and 9^{r}-H and a doublet of doublets at $\delta 7.45$ (2H) for 6^{r}-H and 8^{r}-H . Two 1H doublets at $\delta 6.33$ and $\delta 7.62$ due to proton on a *trans*-double bond (2^{r}-H and 3^{r}-H respectively). Carbinyl proton was observed as a doublet of triplets at $\delta 5.01$ (1H) for 1-H. Beside these, the proton NMR spectrum of bornyl p-coumarate showed three quaternary methyl proton signals at $\delta 0.88$, $\delta 0.90$ and $\delta 0.94$ and 7H signals at $\delta 1.05$ to $\delta 2.42$ due to methylenes and a methine. The mass spectrum showed the base peak at m/z 147, molecular peak at m/z 300. The proposed fragmentation pattern was shown in Fig.23.

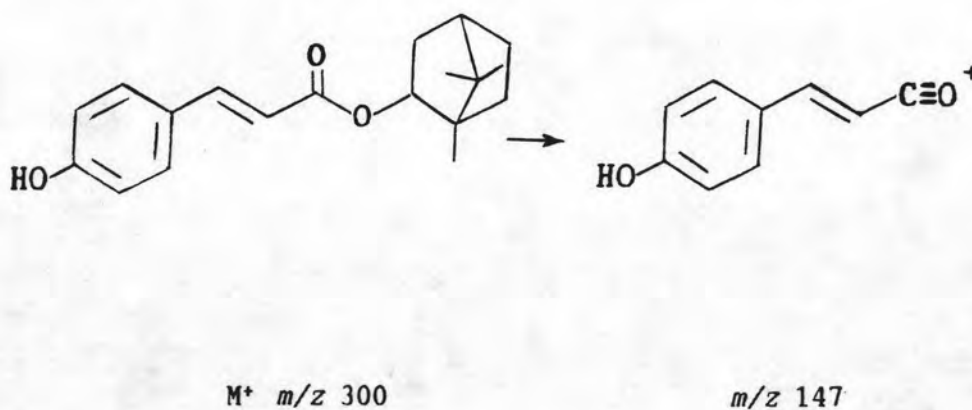


Fig.23 The proposed fragmentation pattern of bornyl p-coumarate

This appears to be the first time that bornyl p-coumarate has been isolated from a *Piper* species., although it was previously found in *Verbesina rupestris* (Box and Chan, 1975) and *Eupatorium deltoideum* (Hernandez *et al.*, 1986).

SP-1 was identified to be methyl 2E,4E,6E-7-phenyl-2,4,6-hepta-trienoate by comparison with the IR absorption, proton NMR and mass spectra with the published data of methyl 2E,4E,6E-7-phenyl-2,4,6-heptatrienoate (Asokan *et al.*, 1985 ; Kijjoa *et al.*, 1989).

Methyl 2E,4E,6E-7-phenyl-2,4,6-heptatrienoate was obtained as a yellow amorphous powder. Its IR absorption spectrum showed a characteristic band for ester carbonyl at 1703 cm^{-1} . From proton NMR spectrum (Fig.35), olefinic protons were observed as a doublet at $\delta 5.92$ (1H) for 2-H, a doublet of doublets at $\delta 6.44$ (1H) for 4-H, a doublet and a doublet of doublets at $\delta 6.72$ (2H) for 5-H and 7-H, a doublet of doublets at $\delta 6.87$ (1H) for 6-H and a doublet of doublets at $\delta 7.39$ (1H) for 3-H. Aromatic protons were observed as a multiplet at $\delta 7.27$ (1H) for 4¹-H, a broad triplet at $\delta 7.38$ (2H) for 3¹-H and 5¹-H and a doublet of doublets at $\delta 7.43$ (2H) for 2¹-H and 6¹-H. Methoxy protons were observed as a singlet at $\delta 3.76$ (3H).

Methyl 2E,4E,6E-7-phenyl-2,4,6-heptatrienoate has been synthesized by Asokan *et al.* (1985), and by Vedejs and Bershas (1975). It has never been reported as a natural product until it was isolated from *Piper ribesoides* Wall. by Kijjoa *et al.* (1989).

SP-2 was identified to be methyl piperate by comparison with the IR absorption, proton NMR and mass spectra with the published data of methyl piperate (Kijjoa *et al.*, 1989).

Methyl piperate was obtained as a yellow amorphous powder, its IR absorption spectrum exhibited characteristic band for a ester carbonyl at 1738 cm^{-1} (Fig.37). From proton NMR spectrum (Fig.38), olefinic protons were observed as a doublet at $\delta 5.95$ (1H) for 2-H, a doublet of doublets at $\delta 6.70$ (1H) for 4-H, a doublet at $\delta 6.81$ (1H) for 5-H and a doublet of doublets at $\delta 7.42$ (1H) for 3-H. Aromatic protons were observed as a doublet at $\delta 6.79$ (1H) for 5'-H, a doublet of doublets at $\delta 6.91$ (1H) for 6'-H and a doublet at $\delta 7.00$ (1H) for 2'-H. Signals for methylenedioxy protons were observed as a singlet at $\delta 5.99$ (2H) and methoxy protons were observed as a singlet at $\delta 3.76$ (3H).

Methyl piperate has been isolated from *Piper officinarum* Cass. DC. (Gupta, Atal and Gaiind, 1972 b) and *Piper ribesoides* Wall. (Kijjoa *et al.*, 1989).

Owing to the time limit the structure elucidation of the isolated components SP-3, SP-4, SP-5 and SP-6 could not be carried out.