

# EXPERIMENTAL ANALYSIS OF THE INFRARED SPECTRUM OF SOME PYRROLIZIDINE ESTERS

V. P. GUPTA, S. K. HANDOO

*Department of Physics, University of Jammu, Jammu*

AND

R. S. SAWHNEY

*Regional Research Laboratory (C.S.I.R.), Jammu*

## ABSTRACT

Infrared absorption spectra of some 25 pyrrolizidine esters and their corresponding acids have been recorded in the 400–4000  $\text{cm}^{-1}$  range on Spectrophotometer Perkin-Elmer 521. A complete interpretation of the absorption peaks in terms of the types of vibrations has been provided and the characteristic frequencies isolated. It is found that the absorption peaks in the 740–760; 800–950; 960–980 and 1075–1130  $\text{cm}^{-1}$  could be assigned to ring deformation modes. Bands at around 610, 750, 965  $\text{cm}^{-1}$  can be used for identifying the presence of five membered nitrogen containing saturated ring. An inverse relationship has been observed between the C=O and C–O stretch frequencies.

## INTRODUCTION

PYRROLIZIDINE derivatives are well known for their physiological activity such as the anaesthetic and anti tumour action<sup>1</sup>. Some chemical investigations have been undertaken in the literature to establish the geometrical structure of these compounds. However no systematic work is reported on the structural study of these compounds using the spectroscopic methods, in particular the methods of vibrational spectroscopy. Evans and Wahr<sup>2</sup> have studied the infrared and Raman spectra of pyrrolidine molecule by giving assignments to various vibrations in the 300–3500  $\text{cm}^{-1}$  range. No such investigations for pyrrolizidine esters are reported in the literature. Culvenor *et al.*<sup>3,4</sup> have studied the carbonyl stretching frequencies of some pyrrolizidine alkaloids. Leisegang and Schuler<sup>5</sup> studied the existence of intermolecular hydrogen bond in platynecine and retronecine molecules. In the present communication, we have extended our studies to a detailed analysis of the infrared spectra of some pyrrolizidine esters in the 400–4000  $\text{cm}^{-1}$  range for finding out the spectra-structure relationship and the characteristic vibrations of the pyrrolizidine nucleus.

## EXPERIMENTAL

Platynecine, retronecine and their esters (III–XVII) were prepared by the method reported in our earlier communication<sup>6</sup>. The compounds were purified by column chromatography using alumina as adsorbent. The purity of the compounds was finally checked by t.l.c.

The spectra of most of the compounds were recorded in nujol mull because of their poor solubility. The spectra of platynecine (III) and retronecine (X) were recorded in KBr. pellets.

The spectra of acids constituting the esters were recorded for comparison purposes. All the spectra were recorded on infrared spectrophotometer Perkin-Elmer 521 in the 400–4000  $\text{cm}^{-1}$  range. The infrared spectra of pyrrolizidine (II) in carbon tetrachloride was kindly supplied to us by Dr. Bjorn Lunning of the University of Stockholm, Sweden. For pyrrolidine (I) the spectral data of Evans and Wahr has been used.

## RESULTS AND DISCUSSION

*OH-stretch vibrations.*—Platynecine and retronecine absorb at 3332 and 3315  $\text{cm}^{-1}$  respectively (Table I). Leisegang *et al.*<sup>4</sup> have interpreted this

TABLE I

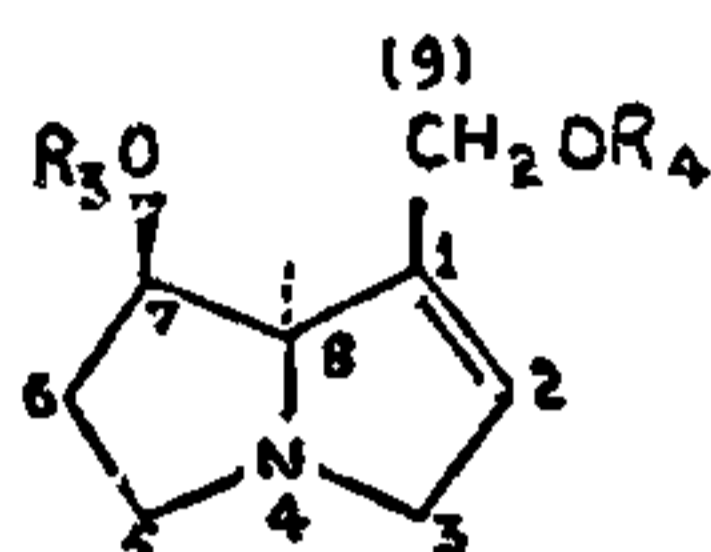
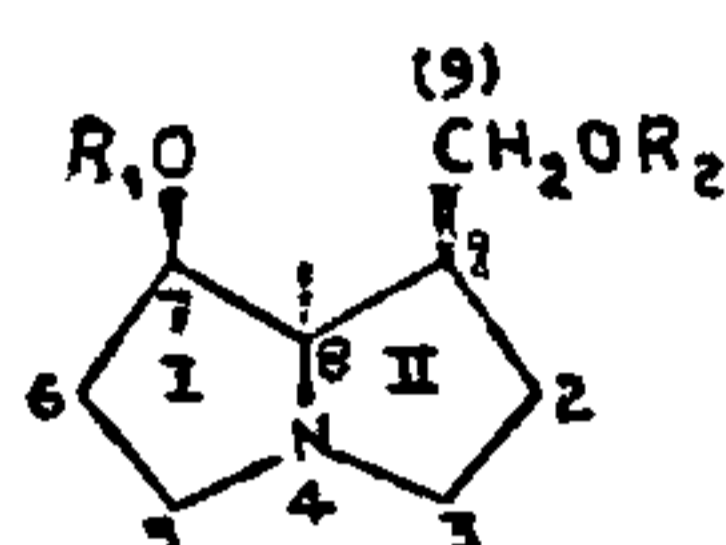
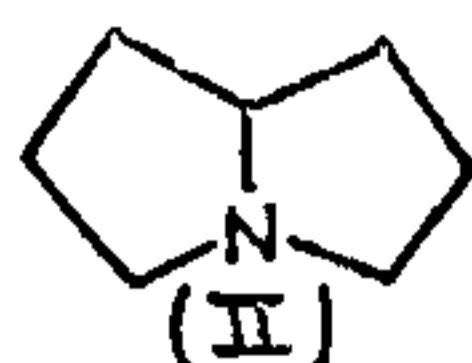
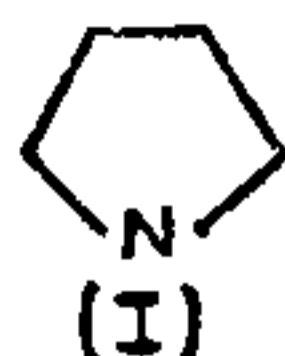
*OH stretch and deformation vibration*

Compound	$\nu_{\text{OH}}$ ( $\text{cm}^{-1}$ )	$\delta_{\text{CH}}$ ( $\text{cm}^{-1}$ )	$\gamma_{\text{OH}}$ ( $\text{cm}^{-1}$ )
III	3332 (3340)*	635, 655	1250
IX	3410	632	1265
X	3315 (3320)	630, 665	1250
XVI	3380	658	1240
XVII	3400	638	1258

\* Figures given in parentheses correspond to the data of Leisegang *et al.* (Ref. 5).

band as indicative of the intermolecular hydrogen bond formation. The mono-substituted esters (IX, XVI, XVII) were found to absorb at 3410, 3380 and 3400  $\text{cm}^{-1}$  respectively. Thus the replacement of one of the OH groups in platynecine and retronecine by an ester group results in a higher frequency shift of the OH stretch vibration. This

increase in the frequency is perhaps caused by the reduction in the chain of molecules connected through hydrogen bonds.



- (III)  $R_1 = R_3 = H$   
 (IV)  $R_1 = R_3 = C_6H_5-CH=CH-CO$   
 (V)  $R_1 = R_2 = C_6H_5-CH_2-CO$   
 (VI)  $R_1 = R_2 = (CH_3)_2CH-CH_2-CO$   
 (VII)  $R_1 = R_2 = CH_3(CH_2)_{16}-CO$   
 (VIII)  $R_1 = R_3 = (CH_3)_2C=CH-CO$   
 (IX)  $R_1 = H, R_3 = p-CH_3O-C_6H_4-CO$   
 (X)  $R_3 = R_4 = H$   
 (XI)  $R_3 = R_4 = CH_3-(CH_2)_{16}-CO$   
 (XII)  $R_3 = R_4 = (CH_3)_2C=CH-CO$   
 (XIII)  $R_3 = R_4 = C_6H_5-CH=CH-CO$   
 (XIV)  $R_3 = R_4 = p-Cl-C_6H_4-CO$   
 (XV)  $R_3 = R_4 = CH_3-(CH=CH)_2-CO$   
 (XVI)  $R_3 = H, R_4 = CH_3-(CH=CH)_2-CO$   
 (XVII)  $R_3 = H, R_1 = p-CH_3O-C_6H_4-CO$

**$CH_2$  stretch vibrations.**—A number of absorption bands with medium to strong intensity were observed in 2800–3000  $cm^{-1}$  range which can be assigned to the  $CH_2$  stretch vibrations. Pyrrolizidine absorbs at 2817, 2865 and 2912, 2941  $cm^{-1}$ , due to symmetric and asymmetric  $CH_2$  stretch vibrations<sup>2</sup> respectively. Pyrrolizidine, platynecine and retronecine were found to absorb at nearly the same frequencies as pyrrolizidine (Table II). The

TABLE II  
 $CH_2$  stretch vibrations

Compound	Symmetric ( $cm^{-1}$ )	Asymmetric ( $cm^{-1}$ )
I	2817, 2865	2912, 2941
II	2810 (M), 2872 (M)	2905 (W), 2945 (S), 2965 (S)
III	2815 (W), 2870 (S)	2925 (WM), 2940 (WM), 2965 (W), 2988 (W)
X	2825 (W), 2850 (WM), 2870 (WM)	2915 (W), 2975 (W)

band near 2810  $cm^{-1}$  has been assigned<sup>7,8</sup> to symmetric stretch of  $CH_2$  attached to the nitrogen atom. Though it appears as a medium strong band in pyrrolizidine, it is only a weak band in platynecine and retronecine. In pyrrolizidine it is noticed that the intensity of the asymmetric stretch at about 2940 and 2960  $cm^{-1}$  is more than that of the symmetric stretch near 2870  $cm^{-1}$ . However reverse is the case in platynecine and retronecine where  $CH_2$  symmetric stretch bands are more intense than the asymmetric stretch bands. This reversal in the intensity could be attributed to the presence of an electron donating group OH adjacent to the  $CH_2$  in platynecine and retronecine.

**C—O and C=O stretch vibrations.**—Platynecine and retronecine absorb strongly at 1017 (VS), 1050 (S)  $cm^{-1}$  and 1010 (S), 1040 (MS)  $cm^{-1}$  respectively. The 1017 and 1010  $cm^{-1}$  absorption bands could be assigned<sup>9</sup> to C—O stretch of secondary alcohol (—COH) and 1050 and 1040  $cm^{-1}$  bands to C—O stretch of primary alcohol (—CH<sub>2</sub>OH). In the case of disubstituted esters, because of the presence of two more C—O bonds (due to ester group) four absorption bands are observed as listed in Table III; the additional bands appearing in the 1100–1300  $cm^{-1}$  range. In almost all the pyrrolizidine esters a band of medium to strong intensity corresponding to C=O stretch has been observed in the 1715–1740  $cm^{-1}$  range. It is found in a series of compounds that the C—O stretch frequency around 1270  $cm^{-1}$  decreases gradually while the C=O stretch frequency increases (Table III). A plot of C=O vs. C—O stretch frequencies is given in Fig. 1. It is evident from the figure that there exists a linear relationship between these frequencies which could be mathematically expressed as :

$$\nu_{C-O} = 4136 - 1.666 \nu_{C=O} \quad (1)$$

This relation however does not hold for iso-valerates, and stearates, where the carbonyl group does not form a conjugated system. This behaviour is evident from the scattered points in Fig. 1. A similar relationship has been reported by Jones *et al.*<sup>10</sup> for acetoxy steroids where a carbonyl group enters into a conjugated system.

**$CH_2$  deformation vibrations.**—Evans *et al.*<sup>2</sup> have compared the infrared and Raman spectra of pyrrolizidine molecule and have provided an interpretation to the absorption peaks in terms of the  $CH_2$  bending, wagging, twisting and rocking vibrations. The frequencies of these vibrations are known<sup>9</sup> to be practically independent of the nature of the substituent. We have therefore provided an interpretation of the  $CH_2$  vibrations of platynecine, retronecine and their esters in terms of similar vibrations of pyrrolizidine molecule (Table IV). It follows from Table IV that  $CH_2$  wagging

TABLE III  
C—O and C=O stretch vibrations

Compound	$\nu_{\text{C=O}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{C-O}}$ ( $\text{cm}^{-1}$ )			
		(i)	(ii)	(iii)	(iv)
III	..	1017	1050	..	..
IV	1712, 1718	1010	1038	1176	1278 (1273)*
V	1740	1040	1085	1146	1243 (1237)
VI	1738	1050	1080	1128	1290 (1240)
VII	1740	1030	1085	1132	1300 (1237)
VIII	1718, 1722	1000	1080	1140	1267 (1270)
IX	1722, 1730	1030	1057	..	1260 (1258)
X	..	1010	1040	..	..
XI	1740	1050	1080	1128	1290 (1237)
XII	1733	1015	1090	1138	1242 (1240)
XIII	1712	1035	1100	1172	1285 (1283)
XIV	1720	1018	1018	1137	1270 (1270)
XV	1730, 1735	1002	1078	1138	1255 (1253)
XVI	1720	1000	1078	..	1270 (1270)
XVII	1722	1028	1070	..	1271 (1267)

\* Numbers given in the parentheses correspond to the calculated values using eq. (1).

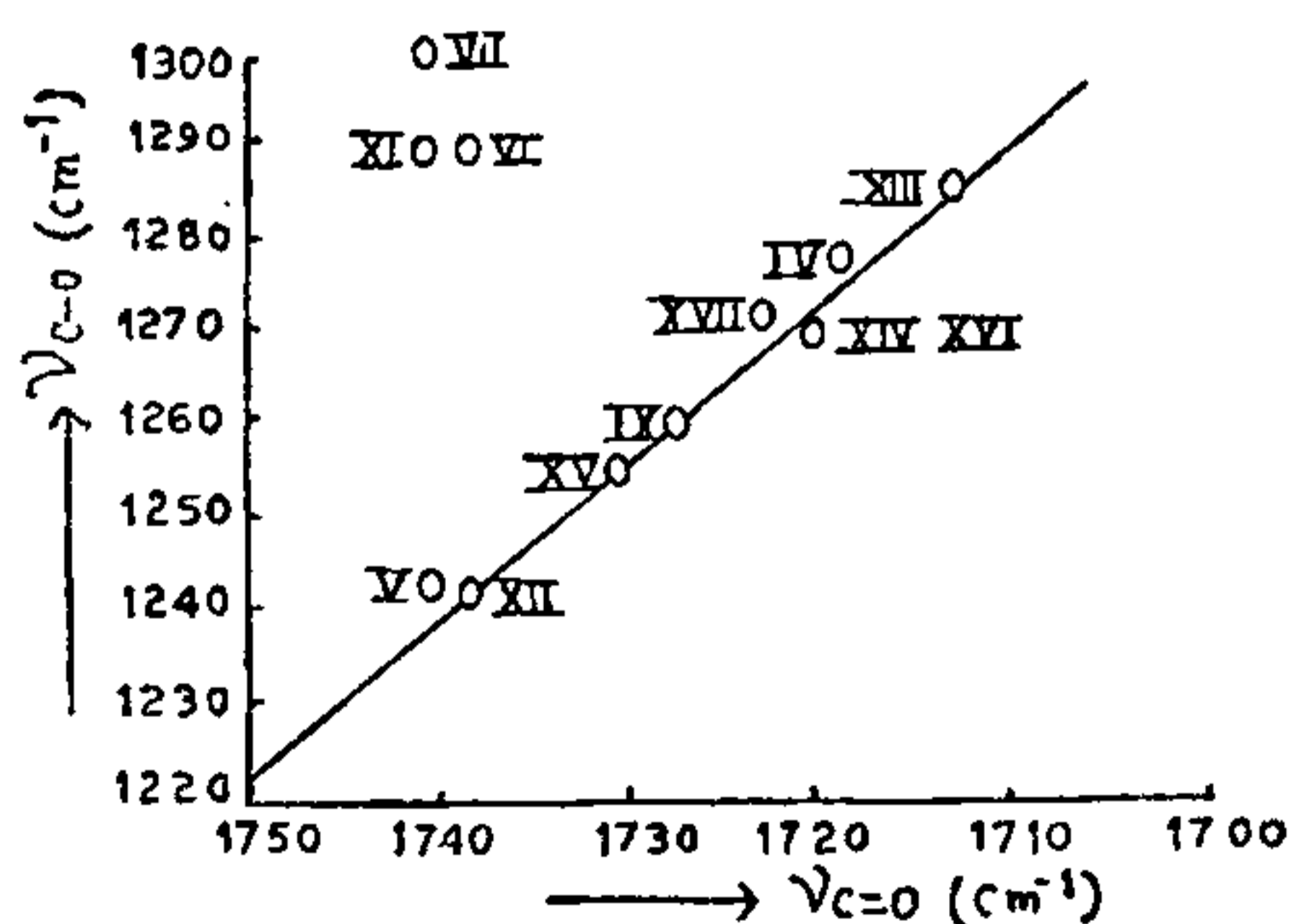


FIG. 1. C—O and C=O co-relationship.

vibrations appear in the ranges 970–990, 1102–1155, 1202–1250  $\text{cm}^{-1}$ , the twisting vibrations in the ranges 1150–1180, 1258–1299, 1337–1365  $\text{cm}^{-1}$  and the rocking vibrations in the ranges 785–852 and 1175–1208  $\text{cm}^{-1}$ . The absorption band at 1456  $\text{cm}^{-1}$  in pyrrolidine has been interpreted<sup>2</sup> as due to  $\text{CH}_2$  bending vibration. In pyrrolizidine this band appears

TABLE IV  
 $\text{CH}_2$  deformation vibrations

Compound	Wagging ( $\text{cm}^{-1}$ )	Twisting ( $\text{cm}^{-1}$ )	Rocking ( $\text{cm}^{-1}$ )
I	980, 1100, 1225	1171, 1284, 1299, 1337	806, 1195
II	1155	1175, 1290, 1352	845, 1208
III	985, 1225	1170, 1275, 1285, 1355	832, 1192, 1207
IV	990, 1210	1180, 1278, 1299, 1340	848, 1185
V	1108, 1225	1170, 1350	1180
VI	1122	1165, 1270	..
VII	1132	1150, 1275, 1282	835
VIII	1120, 1228	1160, 1265	852
IX	965, 1120, 1225	1275	810
X	990, 1102, 1202	1180, 1280, 1292, 1350	909, 1185
XI	970, 1120	1290	1175
XII	...	1160, 1365	1180
XIII	1125, 1210	1160, 1285, 1340	840, 1185 (Sh)
XIV	1225	1270, 1364	785, 1175 (W)
XV	1250	1270, 1290	1190 (W)
XVI	1000, 1240	1180, 1255	835 (W), 1180 (W)
XVII	1248	1168, 1258, 1297	847

at 1452  $\text{cm}^{-1}$ , while in cyclopentane and cyclohexane, it appears near 1465  $\text{cm}^{-1}$ . The lower frequency shift of this band in pyrrolidine and pyrrolizidine with respect to cyclic hydrocarbons could be attributed to the presence of nitrogen atom. In platynecine and retronecine each having two alcoholic groups, this band experiences a further lower frequency shift appearing at 1432 and 1430  $\text{cm}^{-1}$  respectively. However this band could not be separated out in the corresponding esters due to overlap by a nujol band.

**OH— deformation vibrations.**—The absorption bands in the range 1240–1265  $\text{cm}^{-1}$  (Table I) have

TABLE V  
Ring deformation vibrations

Compound	$\delta_{ccc}$ ( $\text{cm}^{-1}$ )	Ring modes ( $\text{cm}^{-1}$ )			
		(i)	(ii)	(iii)	(iv)
I	..	612	806, 902	980	1080, 1109
II	..	..	890, 906	..	1078, 1098
III	750	550, 602	880, 882, 895	962	1088, 1112
IV	..	615	872	965	1085, 1120
V	730	620	..	..	1085, 1108
VI	750	630	..	..	1075
VII	755	..	885	965	..
VIII	..	622	..	975	1077
IX	745	530, 622	..	965	1098
X	748	545, 600	868, 912	967	1080, 1102
XI	755	630	..	970	1075, 1120
XII	..	610	890	..	1100
XIII	..	618	870, 915	988	1085, 1097
XIV	760	625	850	..	..
XV	745	..	875	960	1078, 1130
XVI	760	570, 610	870	965	1075, 1120
XVII	740	565, 610	840	960	1070, 1103

been assigned to the OH-deformation vibrations. An OH- out of plane deformation band of medium intensity is observed at about  $635\text{ cm}^{-1}$  in mono-substituted compounds. In platynecine and retronecine each having two OH groups, two such bands are observed in this region.

**Ring deformation modes.**—These are found to appear in the spectra of platynecine, retronecine and their esters, in the ranges  $740\text{--}760$ ,  $800\text{--}915$ ,  $960\text{--}980$  and  $1075\text{--}1130\text{ cm}^{-1}$  (Table V). The band of medium intensity in the  $740\text{--}760\text{ cm}^{-1}$  range

could be assigned to CCC deformation vibration between the two rings. In compounds containing a mono-substituted benzene ring, this band could not be separated from a similar band due to aromatic CH out of plane deformation vibration. The intensity of this band increases with the presence of an electron donating group at 7 and 9 positions. It is thus found that the intensity of this band is minimum in a di-substituted ester (XV), more in mono-substituted ester (XVI) and maximum in retronecine (X) where both the 7 and 9 positions are occupied by hydroxyl groups.

The  $902\text{ cm}^{-1}$  band in pyrrolizidine has been interpreted<sup>2</sup> as due to the ring breathing. Pyrrolizidine, platynecine and retronecine, each having two five membered rings, show two absorption bands appearing at  $890, 906$ ;  $880, 895$  and  $868, 892\text{ cm}^{-1}$  respectively. They are however not identifiable in all the corresponding pyrrolizidine esters. A band in the  $960\text{--}980\text{ cm}^{-1}$  range is found to be characteristic of all the platynecine and retronecine derivatives. In most of the cases it appears at about  $965\text{ cm}^{-1}$ . Another band near  $610\text{ cm}^{-1}$  also appears nearly at a constant position in all the esters. This band could also be attributed to the ring deformation mode.

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1. Culvenor, C. C. J., *J. Pharm. Sci.*, 1968, 57, 1112.
2. Evans, J. C. and Wahr, J. C., *J. Chem. Phys.*, 1959, 31, 655.
3. Culvenor, C. C. J. and Bon, R. Dal, *Aust. J. Chem.*, 1959, 12, 1256.
4. — and Smith, L. W., *Ibid.*, 1959, 12, 255.
5. Leisegang, E. C. and Schuler, B. O. G., *J.S. Afr. Chem. Inst.*, 1957, 10, 1.
6. Puri, S. C., Sawhney, R. S. and Atal, C. K., *Indian J. Pharm.*, 1972, 34, 123.
7. Wright Jr. W. B., *J. Org. Chem.*, 1959, 24, 1362.
8. Colthup, N. B., Daly, L. H. and Wiberly, S. E., *Introduction to Infrared and Raman Spectroscopy*, Acad. Press, New York, 1964.
9. Bellamy, L. J., *Infrared Spectra of Complex Molecules*, Methuen and Co., Ltd., London, 1958.
10. Jones, R. N. and Herling, F., *J. Am. Chem. Soc.*, 1956, 78, 1152.