

THE ULTRAVIOLET AND INFRARED SPECTRA OF SOME LICHEN DEPSIDES AND DEPSIDONES

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Received October 5, 1966

ABSTRACT

The ultraviolet and infrared spectral data for a number of lichen depsides, depsidones and their fission products have been recorded. The U.V. spectra of the orcinol depsides, orcinol depsidones and β -orcinol depsidones are characteristic while those of the β -orcinol depsides less useful for diagnostic purposes. The I.R. spectra are more useful and the carbonyl region is significant for this purpose.

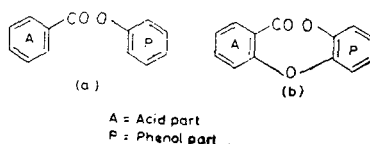
INTRODUCTION

With many lichens the quantities available are small and micro and ultra micro methods have to be adopted to analyse their components. Thalline reactions,^{1,2} microchemical and microcrystallographical studies, paper chromatography³ and T.L.C.⁴ have been successfully employed for identifying the various lichen acids available in small quantities and have proved to be of great help for taxonomic work.

Spectroscopic methods by their very nature are suitable for studying small amounts of compounds with considerable precision. In order to explore the possibility of using them for the identification of lichen substances a number of pure depsides and depsidones and their degradation products have been studied. The compounds were obtained in the course of the survey of Indian lichens carried out in our laboratories.

U.V. ABSORPTION SPECTRA OF DEPSIDES, DEPSIDONES AND THEIR DEGRADATION PRODUCTS

Of the characteristic lichen substances, the depsides and depsidones form a major group and are respectively represented by the general skeletal formulae (a) and (b).



No systematic study has been made of them though incidentally in connection with the elucidation of structure some data have been given. Phenyl benzoate (*a*), the simplest depside, has a U.V. max. at 232 m μ (log ϵ : 4.21); a *para* methoxyl in the A-portion produces a bathochromic shift of about 25 m μ .⁵ Calculation of the absorption maxima in this group of compounds, with different substitution patterns, becomes erroneous when carbonyl groups of different types are attached to both the aromatic nuclei.⁶ The data for the depsidones are however meagre, although Neelakantan *et al.*⁷ have discussed the U.V. spectra of chlorodepsidones in the study of vicanicin.

The U.V. data recorded in the present work are given in Tables I, II, IV and V and those relating to orcinol depsidones collected from literature are given in Table III. It may be mentioned that the U.V. is somewhat sensitive to the presence of impurities, the position of maxima and minima getting affected. For purposes of identification therefore preliminary purification is essential. The homogeneity of the sample can be conveniently determined by paper chromatography and T.L.C.

TABLE I
U.V. absorption maxima of some orcinol depsides

Compound	Maxima (m μ) (log ϵ)	Inflexion (m μ)
1. Lecanoric acid (I)	269 (4.24); 300 (4.01)	—
2. Evernic acid (II)	267 (4.29); 300 (4.06)	..
3. 3-Formyl lecanoric acid (III) (synthetic)	245 (4.4); 335 (3.79)	280
4. Diploschistesic acid (IV) (synthetic)	281 (4.30)	235
5. Sekikaic acid (V)	259 (4.24); 301 (3.93)	..
6. Gyrophoric acid (VI) ..	270 (4.48); 304 (4.31)	..

Hale⁸ based on limited data has drawn some conclusions regarding the relation between the U.V. absorption and chemical structure. The present more extensive study supports most of his conclusions. The orcinol depsides have characteristic bimodal spectra with absorption maxima at about 270 and 307 m μ . This is also shown by degradation products having simple

TABLE II

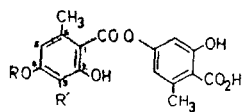
U.V. absorption maxima of some β -orcinol depsides

Compound	Maxima (m μ) (log ϵ)	Inflexion (m μ)
1. Thamnic acid (VII) ..	288 (3.67)	243
2. Dimethyl thamnolate (VIII) (synthetic)	265 (4.17)	292
3. Dimethyl hypothamnolate (IX) (synthetic)	262 (4.25)	310; 335
4. Atranorin (X)	252 (4.37)	290
5. Atranorin trimethylether (XI) ..	330 (3.49)	267
6. Barbatic acid (XII)	275 (4.40); 308 (3.95)	...
7. Methyl barbatate (XIII) ..	273 (4.77); 305 (4.35)	...

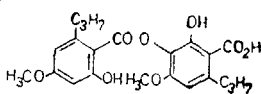
TABLE III

U.V. absorption maxima of some orcinol depsidones

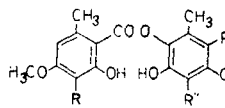
Compound	Maxima (m μ) (log ϵ)
1. Physodic acid (XIV) ⁸	256 (4.10); 300-310 (3.50, shoulder)
2. Norlobaridone (XV) ¹⁰ ..	270 (3.96)
3. Grayanic acid (XVI) ⁹	258 (4.10); 300-310 (3.5, shoulder)



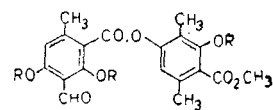
- (I) R = R' = H
 (II) R = CH₃, R' = H
 (III) R = H, R' = CHO
 (IV) R = H, R' = OH



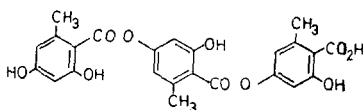
(V)



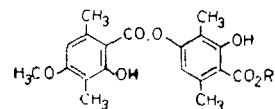
- (VII) R = R' = COOH; R² = CHO
 (VIIa) R = R' = COOH; R² = CH₃
 (VIII) R = R' = COOCH₃; R² = CHO
 (IX) R = R' = COOCH₃; R² = CH₃



- (X) R = H
 (XI) R = CH₃



(VI)



- (XII) R = H
 (XIII) R = CH₃

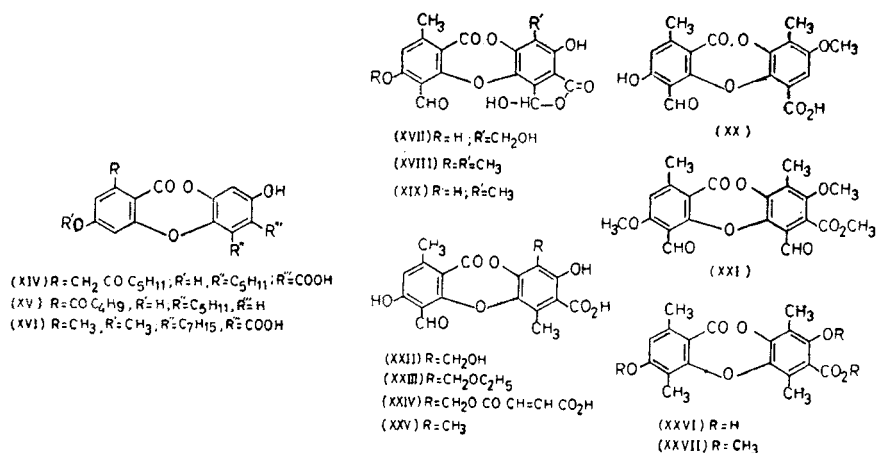


TABLE IV

U.V. absorption maxima of some β -ornicol depsidones

Compound	Maxima ($m\mu$) (log ϵ)	Inflexion ($m\mu$)
1. Salazinic acid (XVII)	... 236.5 (4.55); 313 (3.81)	260
2. Stictic acid (XVIII) 310 (3.92)	240; 268
3. Norstictic acid (XIX)	.. 239 (4.33); 320 (3.40)	270
4. Psoromic acid (XX) 239 (4.52); 325 (3.52)	270
5. Stictic acid methyl ether, methyl ester (XXI)	.. 223 (4.57); 314 (3.89)	270
6. Protocetraric acid (XXII)	.. 239 (4.40); 314 (3.56)	274
7. Cetraric acid (XXIII)	.. 237.5 (4.17); 305 (3.54)	269.5
8. Fumarprotocetraric acid (XXIV) 236 (4.61); 309 (3.91)	270
9. Virensic acid (XXV)	... 240 (4.47); 307 (3.67)	..
10. Hypoprotocetraric acid (XXVI) (from virensic acid) 225 (4.42); 280 (4.05)	..
11. Hypoprotocetraric acid methyl ether methyl ester (XXVII)	269 (3.92)	..

TABLE V

U.V. absorption maxima of some degradation products of depsides and depsidones

Compound	Maxima (in $m\mu$) ($\log \epsilon$)
1. Orcinol ^{10a}	273.5 (3.24); 280 (3.22)
2. Atranol	282 (4.15)
3. Orsellinic acid	260 (4.10); 300 (3.60)
4. β -orcinol carboxylic acid	259 (3.96); 299 (3.48)
5. Haematommic acid	235 (4.37); 253 (4.23); 285 (4.17)
6. Methyl orsellinate	262 (4.19); 302 (3.77)
7. Methyl β -orcinol carboxylate.. .. .	266 (4.20); 298 (3.63)
8. Methyl haematommate	245 (4.14); 287 (3.76); 334 (4.05)
9. Everninic acid ^{10a}	251.5 (4.07); 293 (3.73)
10. Rhizonic acid	255 (3.98); 295 (3.46)
11. Methyl everninate ^{10a}	261 (4.32); 299 (4.00)
12. Methyl rhizonate	265 (4.27); 306 (3.65)
13. Methyl 5-hydroxy orsellinate	270 (3.92); 325 (3.06)
14. Methyl 5-hydroxy rhizonate	260 (3.97); 335 (3.61); 313 (inf.)
15. Methyl 3-hydroxy orsellinate	230 (4.14); 275 (4.01)

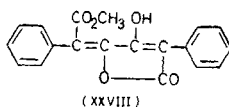
orsellinic acid units and could therefore be considered to be characteristic of them. Methylation of the hydroxyls and variation of the length of the alkyl side-chains have little effect. Introduction of a formyl or hydroxyl function in the 3 position of the A-portion [*cf.* (III) and (IV)] is however found to produce radical changes in the absorption bands. The U.V. spectra of the β -orcinol depsides, according to Hale, resemble those of β -orcinol depsidones but the absorption maxima are not so sharp. The present study shows that the spectra of the β -orcinol depsides are not very characteristic. The orcinol depsidones have poorly defined curves with the absorption maxima at 245–255 $m\mu$ and a slight peak or levelling at 310–320 $m\mu$ ^{9,10} useful for diagnostic purposes. β -Orcinol depsidones also have bimodal spectra with maxima

near 238 and 312 $m\mu$, the intensity of the shorter wavelength absorption band being much higher than that of the longer wavelength band.

INFRARED SPECTRA

This method has advantage over the U.V. in that the characteristic frequencies are not appreciably affected by small quantities of impurities. Little systematic work seems to have been done in the past and in this paper are recorded our observations on the commoner depsides and depsidones. The spectra were taken using KBr discs on a Perkin-Elmer Model-137 Infracord spectrophotometer. Even though the instrument has a limited range and resolution, it is more easily available and the spectra are sufficiently informative when we use the strong and sharp bands (*see* Table VI). In a typical experiment a small thallus of the lichen, *Alectoria virens* Tayl., was extracted with petroleum ether and then with ether and the spectra of the crude extracts were examined. Vulpinic acid (XXVIII) could be identified in the petroleum ether extract and virensic acid (XXV) in the ether extract by a direct comparison of the spectra with those of authentic samples. The crude extracts of *Cladonia amaurocraea* and *Cl. rangiferina* were similarly examined and the components atranorin and barbatic acid in the former and atranorin and fumarprotocetraric acid in the latter were clearly indicated. Thus the I.R. method seems to be good for the identification of depsides and depsidones available in only small quantities.

The absorption bands in the following regions seem to be of diagnostic value: (a) Hydroxyl and C-H stretching region (3500–2600), (b) carbonyl region (1780–1600), (c) aromatic region (1600–1500). The CH_3 -region (near 1400), and C-O-C region (near 1250) are less useful.



(a) *The hydroxyl and C-H stretching region* (3500–2600 cm^{-1}).—In spite of its complexity and poor resolution, this region may be useful for structure determination.¹¹ Usually the phenolic hydroxyl groups in depsides are involved in chelation barring a few exceptions. It will be possible to detect non-chelated ones by the presence of a sharp band near 3510 cm^{-1} ; *e.g.*, lecanoric acid (I) and gyrophoric acid (VI). Chelated hydroxyls present *ortho* to a carboxyl group give a rather broad band near 3030 cm^{-1} ; the intensity is variable. The hydroxyl of a carboxyl group shows a number of bands in the

TABLE VI

Infrared absorption maxima of some depsides and depsidones

(s = strong, m = medium, w = weak and sh = shoulder)

Name	Band frequencies in wave numbers cm^{-1}				
<i>Depsides:</i>					
1. Lecanoric acid (I)	3509 m	1718 sh	1600 s	1475 m	1309 m
	3425 m	1637 s	1575 s	1449 m	1282 m
	3030 m	1626 sh	1497 m	1425 sh	1266 sh
	2941 m	1399 m	1247 s
	2825 m	1370—	1203 s
	1351 w	1175 s
	—	—	1143 s
	1075 m
2. Gyrophoric acid (VI)	3509 m	1724 sh	1595 s	1481 m	1307 s
	3425 sh	1652 s	1570 s	1449 s	1266—
	3030 m	1639 s	1493 s	1429 sh	1235 w
	2941 m	1404 m	1198 s
	1370 m	1170 s
	1136 s
	1087 sh
3. Barbatic acid (XII)	3175 m	..	1600 s	1429 m	1282 sh
	3125 m	1681 sh	1563 m	1393 m	1259 s
	3058 m	1639 s	1493 m	1387 m	1242 sh
	2890 m	1613 s	1222 s
	1148 s
	1124 s
	1073 m
4. Sekikaic acid (V)	3030 sh	1724 sh	1567 m	1449 m	1316 m
	2933 m	1639 s	1497 m	1403 m	1285 s
	2857 sh	1613 s	..	1370 sh	1272 s
	1351 m	1250 s
	1333 m	1227 s
	1198 s
	1153 s
	1126 s
	1089 m

TABLE VI (Contd.)

Name	Band frequencies in wave numbers cm.^{-1}				
5. Diploschistesic acid (IV) (Synthetic)	3448 w	1701 sh	1600 s	1453 s	1299 m
	3077 m	1639 s	1567 sh	1429 s	1258 s
	3030 m	1629 sh	1497 m	1399 m	1202 s
	2959 m		1480 m	..	1164 s
	1136 s
	1075 w
6. 3-Formyl lecanoric acid (III) (Synthetic)	3135 sh	1642 s	1592 m	1439 m	1299 s
	3040 m	1634 s	1558 m	1404 m	1238 s
	2941 m	..	1471 sh	1370 m	1198 s
	1325 sh	1164 s
	1130 s
	1121 sh
7. Atranorin (X)	3175 w	1653 s	1563 m	1439 m	1292 s
	3030 sh	1639 s	1550 sh	1404 s	1258 s
	2915 m	1613 sh	1515 w	1370 m	1242 s
	1205 w
	1190 m
	1167 s
	1149 s
	1111 s
8. Atranorin trimethyl ether (XI)	2915 w	1724 s	1587 s	1460 m	1295 m
	..	1706 s	1550 sh	1439 m	1266 m
	..	1672 s	..	1422 m	1212 s
	1389 m	1189 m
	1139 s
	1107 s
	1076 s
9. Thamnic acid (VII)	3150 m	1736 s	1600 sh	1527 sh	1274 sh
	3030 sh	1667 s	1575 sh	1445 s	1258 s
	2924 m	1656 s	1550 sh	1406 s	1227 s
	..	1626 s	..	1385 s	1190 s
	1361 s	1174 s
	1120 m
..	1090 s	

TABLE VI (Contd.)

Name	Band frequencies in wave numbers cm^{-1}				
10. Dimethyl thamnolate (VIII) (Synthetic)	3125 sh	1736 s	1608 s	1460 sh	1330 s
	2924 m	1692 sh	1527 sh	1439 s	1285 s
	2874 m	1626 s	..	1425 s	1250 s
	2801 m	1389 s	1198 s
	1359 s	1170 s
	1124 sh
	1111 s
	1096 s
	1058 m

11. Dimethyl hypothamnolate (IX) (Synthetic)	3509 w	1724 sh	1600 s	1429 s	1325 m
	3226 m	1684 s	1582 sh	1370 s	1295 s
	2874 m	1634 s	1550 m	1361 sh	1266 s
	1202 s
	1167 s
	1117 s
	1105 m
	1064 m
<i>Depsidones:</i>					
12. Virensic acid (XXV)	3021 m	1724 s	1570 w	1422 m	1305 w
	2941 m	1639 s	1543 m	1389 m	1266 s
	..	1613 s	1475 w	1370 m	1242 m
	1348 m	1198 m
	1149 s
	1121 m
	1075 w
13. Hyposalazinolide dimethyl ether	2899—	1754 s	1600 m	1408 m	1307 m
	2817 w	1724 s	1550 m	1370 w	1274 m
	..	1667 w	1475 m	1333 m	1250 w
	1205 w
	1190 w
	1176 w
	1130 s
	1099 w
..	1087 m	

TABLE VI (Contd.)

Name	Band frequencies in wave numbers cm. ⁻¹				
14. Protocetraric acid (XXII)	3571 w	1739 s	1613 s	1466 m	1342 m
	3058 m	1686 s	1575 sh	1439 sh	1302 m
	2941 m	1639 s	1563 m	1404 m	1266 s
	2857 m	1379 m	1250 s
	1359 m	1227 m
	1183 m
	1143 m
	1111 s
	1085 m
15. Cetraric acid (XXIII)	3175 sh	1754 s	1613 sh	1449 s	1316 m
	3030 m	1704 m	1575 m	1408 m	1269 s
	2959 m	1661 s	1538 sh	1383 m	1266 s
	1366 sh	1247 sh
	1351 sh	1195 s
	1153 s
	1124 m
	1111 m
	1089 s
..	1070 s	
16. Stictic acid (XVIII)	3378 m	1748 s	1610 m	1449 m	1325 m
	3125 w	1718 s	1540 m	1418 s	1290 s
	2841 w	1692 s	1491 sh	1379 m	1250 s
	2717 w	1366 m	1220 s
	1183 sh
	1160 sh
	1143 s
	1093 m
	1074 m
17. Norstictic acid (XIX)	3425 m	1754 s	1613 sh	1527 m	1282 s
	3053 w	1724 sh	1563 m	1481 sh	1242 m
	2924 w	1695 s	1543 m	1445 m	1190 m
	..	1639 s	..	1429 m	1156 s
	1379 m	1136 sh
	1342 m	1087 m
	1058 m

TABLE VI (Contd.)

Name	Band frequencies in wave numbers cm^{-1}				
18. Salazinic acid (XVII)	3311 m	1779 s	1563 m	1449 s	1299 s
	2941 w	1748 s	1538 sh	1439 s	1258 s
	2899 w	1661 s	1493 m	1374 m	1217 m
	..	1639 sh	1198 m
	1163 s
	1149 s
	1136 s
	1075 s
19. Psoromic acid (XX)	3571 w	1745 s	1626 m	1493 s	1285 s
	3279 s	1695 sh	1587 s	1453 s	1258 s
	3175 s	1653 s	1563 s	1425 s	1235 sh
	3030 sh	1385 s	1208 s
	1355 m	1179 m
	1166 s
	1130 s
	1058 m

region 3000–2500 cm^{-1} ; they are often weak and overlap with C–H bands near 2940 cm^{-1} . In the case of salazinic acid (XVII), stictic acid (XVIII) and nor-stictic acid (XIX), a strong and sharp band occurs between 3425 and 3333 cm^{-1} possibly due to the presence of the OH group in the lactol and the low frequency may be due to hydrogen bond formation with the oxygen of diphenyl ether linkage. In the case of pyrogallol derivatives like diploschistesic acid (IV), further bands may be due to other types of hydrogen bridges.

(b) *The carbonyl region (1780–1600 cm^{-1}).*—Different types of carbonyl groups occur in depsides and depsidones and the identification of most of them is possible with the help of infrared spectra. But sometimes anomalous absorption bands appear leading to wrong conclusions.¹²

(i) *The depsidone carbonyl.*—Normally the range is 1750–1720 cm^{-1} . The band moves towards higher frequencies in compounds with free *para*-hydroxyl group and to a lesser extent with *para*-methoxyl. Absorption is found in this region also in those depsides which are completely methylated, but not in the case of hydroxy depsides. With this limitation this band will serve for the identification of a depsidone, Thamnic acid (VII) and hypo-

thamnolic acid are the two hydroxy depsides of more complex type, which show a carbonyl frequency near $1740\text{--}1724\text{ cm.}^{-1}$. The high frequency may be due to the fact that the only hydroxyl group in A-portion of these depsides is not available for chelation with the depside carbonyl as it already forms a hydrogen bond with the carboxyl carbonyl. This explanation seems to be valid since in the closely related case of sekekaic acid (V) where this feature is absent, the depside $\text{C}=\text{O}$ frequency is normal.

Norloboridone (XV), the orcinol depsidone from the lichen *Parmelia conspersa* on the other hand did not show the usual depsidone carbonyl absorption but gave a frequency near 1680 cm.^{-1} ; this was explained¹⁰ as due to extensive inter-molecular hydrogen bonding also indicated by the hydroxyl band at 3300 cm.^{-1} .

(ii) *Depside carbonyl*.—If depside carbonyl (A ring) is chelated with an *ortho* hydroxyl group its stretching frequency is near 1650 cm.^{-1} . This is also affected by a hydroxyl substituent at the *para* position. When the chelation is removed as in methylated or acetylated depsides, the frequency goes up to 1740 cm.^{-1} as in simple phenyl benzoate. The study of 6-methyl salicylic acid and its esters¹³ has earlier shown that in them owing to steric hindrance the chelation between the carbonyl and the hydroxyl is weaker than in simple salicylic acid esters. In the case of a few such compounds, the non-chelated aromatic ester vibration (non-bonded) is also visible and may be of diagnostic value. In lecanoric acid (I) and gyrophoric acid (VI) for example, such band (weak) is visible near 1724 cm.^{-1} . It is normally difficult to distinguish between the depside and the chelated ester carbonyls in the P-part but may be possible with higher resolution.

(iii) *Carboxyl carbonyl*.—The chelated carboxyl group of the P-part shows a strong band near $1650\text{--}1630\text{ cm.}^{-1}$ and this together with a number of weak absorption bands in the region $3000\text{--}2500\text{ cm.}^{-1}$ may be taken as clear indication of its presence and it can be distinguished from the chelated depside carbonyl.

(iv) *Aldehyde carbonyl*.—Both chelated as well as non-chelated aldehyde groups are met with. In the case of the former, methylation of the compound brings about a shift in the carbonyl absorption towards higher frequencies; disappearance of the band after catalytic hydrogenation is characteristic of aldehyde group. For example, the chelated aldehyde carbonyl absorption appears near $1650\text{--}1640\text{ cm.}^{-1}$ [atranorin (X), salazinic acid (XVII) and norstictic acid (XIX)]; the frequency is raised after methylation to

1680–1665 cm^{-1} , e.g., atranorin methyl ether (XI) and stictic acid (XVIII). A weak absorption band around 2720 cm^{-1} is ascribed to the C–H stretching of the aldehyde group.

(v) *Lactol carbonyl*.—The lactol CO has been studied earlier by Grove and Willis¹⁴ and it has strong absorption near 1750 cm^{-1} . We have now examined stictic, norstictic and salazinic acids and they all show this strong absorption.

(c) *The aromatic region (1600–1500 cm^{-1})*.—In all the cases examined two strong bands appear one near 1600 cm^{-1} , and another near 1585 cm^{-1} . A third one near 1550 cm^{-1} is found in the depsidones and some depsides. The first is due to the benzene ring and is fairly strong. The second varies slightly in position and is attributable to benzoyl group (Rasmussen *et al.*¹⁵). The origin of the third band at 1550 cm^{-1} is not clear but it is associated with penta-substituted benzene rings.

(d) *CH₃ region (near 1400 cm^{-1})*.—Methyl groups are present in all the depsides and depsidones and one or two bands appear near 1429 cm^{-1} and 1379 cm^{-1} ; it is not possible to differentiate the C-methyl groups of orcinol and β -orcinol derivatives.

(e) *C–O–C region (near 1250 cm^{-1})*.—With all methoxy compounds and depsidones bands are present near 1460, 1340, 1250, 1180, 1125 and 1028 cm^{-1} due to the C–O–C group (*cf.* Briggs *et al.*¹⁶). Since weak bands are always present in this region even with non-methoxylated depsides, there is lack of definiteness and this region is only of limited use.

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