Supplementary Information for

A multi-spectroscopic investigation into the diagenesis of avian polyene pigments: simulated maturation, chemical pathways and palaeontological implications

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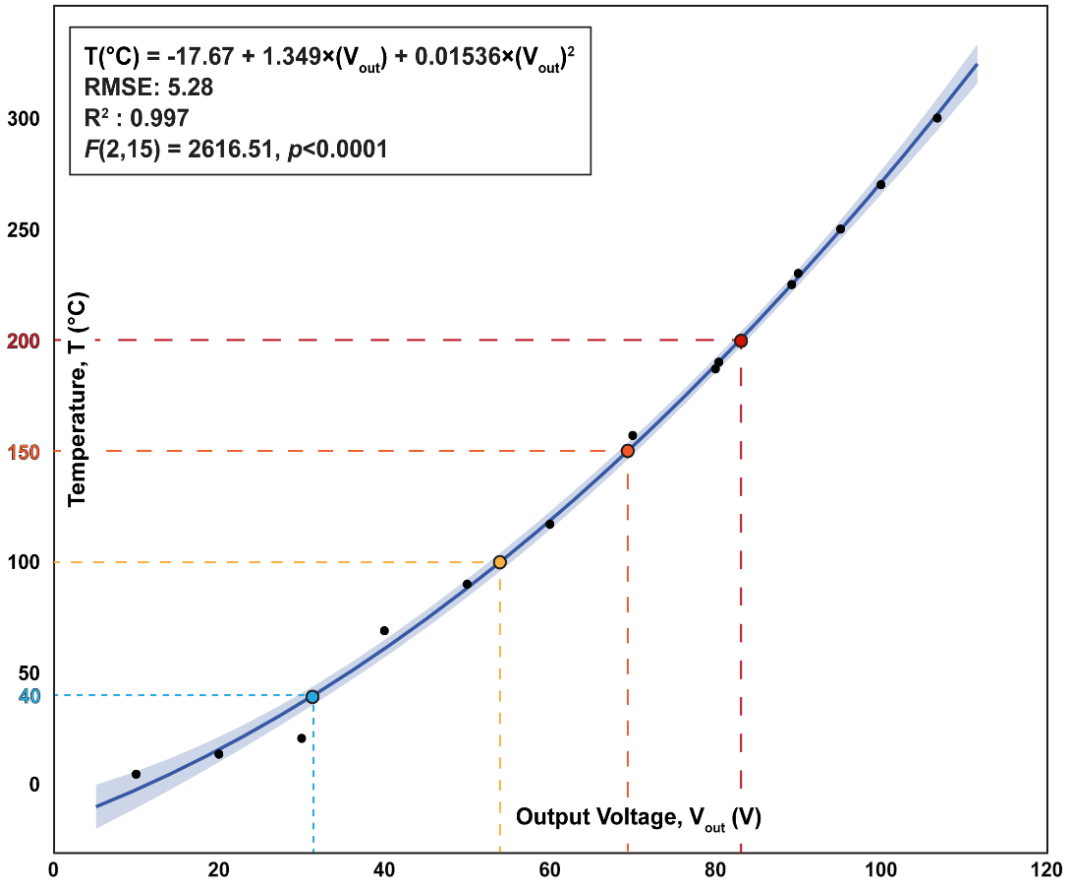

Fig S1 *Calibration of output voltage (V_{out}) vs. temperature (T) in a pressurised dry run without samples. The output voltages required to achieve the experimental temperatures (40°C, 100°C, 150°C and 200°C) on the maturation setup are calculated by fitting the datapoints to a quadratic equation and extrapolating the values on the V_{out} axis. Confidence intervals shown in grey and prediction intervals shown in blue.*

Table S1 *Output voltage calibrated ($V_{out,}$ in volts) against temperature (T, in °C). Extrapolated values indicated in red.*

No.	V_{out} (in V)	T (in °C)
1	10.0	4.4
2	20.0	13.4
3	30.0	20.5
4	31.4	40.0
5	40.0	69.0
6	50.0	90.0
7	54.0	100.0
8	60.0	117.0
9	69.4	150.0
10	70.0	157.0
11	80.0	187.0
12	80.4	190.0
13	83.0	200.0
14	89.2	225.0
15	90.0	230.0
16	95.1	250.0
17	100.0	270.0
18	106.8	300.0

Fig S2 *Comparison of Raman spectra (3200-200 cm^{-1}) of white (control), orange-pink (carotenoid), yellow (canary xanthophyll A/B), yellow (psittacofulvin), orange (psittacofulvin), red (psittacofulvin) and green (psittacofulvin) feathers across different temperature treatments.* Raman bands of interest were characterised using assignments by Lin-Vien, Colthup, Fateley and Grasselli (*1*), Socrates (*2*) and Kish (*3*).

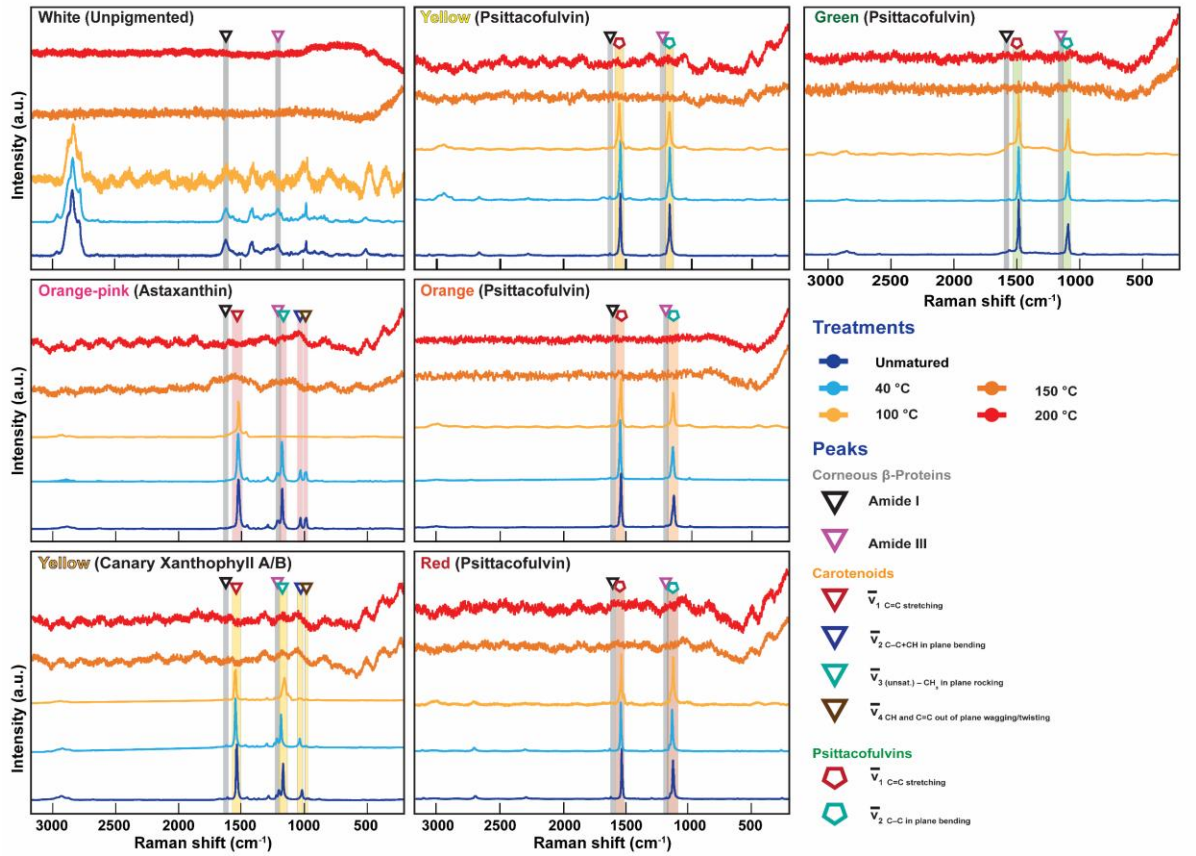

Table S3 *Assignment of characteristic bands to Raman spectra of feathers. Relative band intensities are denoted as follows: vs (very strong); s (strong);m (medium); w (weak);vw (very weak) and vwb (very weak -broad). Diagnostic bands for carotenoids and psittacofulvins are denoted by coloured cells. Raman bands of interest were characterised using assignments by Lin-Vien, Colthup, Fateley and Grasselli (1), Socrates (2) and Kish (3).*

Colour	Pigment	Raman bands across different temperature treatments					Band assignments
		Unmat.	**40°C**	**100°C**	**150°C**	**200°C**	
White	–	3062 w	3063 w	–	–	–	
		2960 s shoulder	2960 s shoulder	2960 s shoulder	–	–	–CH_2 and –CH_3 stretching
		2933 vs	2934 vs	2930 m	–	–	
		2881 s	2873 s	2873 m	–	–	
		–	2770 w	–	–	–	
		2726 w	2725 w	–	–	–	
		1666 s	1667 s	–	–	–	Amide I
		1617 w shoulder	1614 w shoulder	–	–	–	
		1446 s	1448 s	1451 w b	–	–	–CH_2 and –CH_3 bending
		1414 w shoulder	1414 w shoulder	–	–	–	
		1318 vw	1317 vw	–	–	–	
		1235 m	1237 s	–	–	–	Amide III
		–	1208 w	–	–	–	

		–	1156 vw	–	–	–	
		1128 vw	1128 vw	–	–	–	
		1029 vw b	1031vw	–	–	–	
		1003 m	1003 m	1003 m	–	–	$\bar{\nu}$ (Unsat.)–CH3 in plane rocking
		934 vw	934 vw	–	–	–	
		–	885 vw	–	–	–	
		867 vwb	–	–	–	–	
		–	853 vw	–	–	–	
		–	829 vw	–	–	–	
		–	757 vw b	–	–	–	
		509 w	507 w b	–	–	–	S–S bridges
Orange–Pink	Astaxanthin	3062 w b	3064 w b	–	–	–	
		2980 w shoulder	2976 w shoulder	2961 m shoulder	–	–	–CH_2 and –CH_3 stretching
		2932–2934 w	2932–2934 m	2930 m	–	–	
		2875–2880 w shoulder	2874–2878 w shoulder	2873 m	–	–	
		2875–2880 w shoulder	2662–2673 w b	–	–	–	
		2659–2671 w	2662–2673 w b	–	–	–	
		–	2523 vw	–	–	–	
		2514 vw	–	–	–	–	
		2473 vw	2475 vw	–	–	–	
		2308–2311 vw	2308–2311 vw shoulder	–	–	–	
		2161–2163 vw	2159–2164 vw	–	–	–	
		2117 vw	2114 vw b	–	–	–	
		1666 w	–	–	–	–	Amide I
		1594 vw	1594 vw	–	–	–	–
		1577 vw	1575 vw	–	–	–	–
		1511–1517 vs	1514–1518 vs	1517 vw b	–	–	$\bar{\nu}_3$ C=C stretching modes of the polyene chain
		1445 m	1445 m	1450 wb	–	–	?N–heterocycles
		1392 w	1392 w	–	–	–	–
		1355 w	1355 w	–	–	–	–
		1300 w b	1300 w b	–	–	–	–
		–	1292 vw	–	–	–	
		1269–1270 m	1275 m	–	–	–	Amide III
		1198 s shoulder	1192–1196 s shoulder	–	–	–	
		1157 vs	1157 vs	–	–	–	$\bar{\nu}_2$ C–C + CH in plane bending
		1006 s	1006 s	–	–	–	$\bar{\nu}_3$ (Unsat.)–CH_3 in plane rocking
		961 m	957–967 m doublet	–	–	–	$\bar{\nu}_4$ CH and C=C out–of–plane wagging and twisting.
		885 vw	885 vw	–	–	–	
		825 vw	825 vw	–	–	–	

		528 vw	528 vw	–	–	–	
		507 vw	506 vw	–	–	–	S–S bridges
		432 vw	432 vw	–	–	–	
Pale Yellow	Canary xanthophyll A/B	3063 w b	3051–3060 wm b	3060 vw b	–	–	–CH_2 and –CH_3 stretching
		2980 w shoulder	2970 w shoulder	2970 w shoulder	–	–	
		2934 w	2932–2936 m	2932–2936 m	–	–	
		2881 w shoulder	2876 w shoulder	2876 w shoulder	–	–	
		2683 vw	2679–2683 vw	–	–	–	
		2535 vw	–	–	–	–	
		2314 vw	2314 vw	–	–	–	
		1668 w b	–	1664 vw b	–	–	Amide I
		1603 w	1603 w	1603 w	–	–	
		1583 vw	1583 vs	–	–	–	
		–	–	1548 s	–	–	
		–	–	1538 vs	–	–	
		1528 vs	1528 vs	–	–	–	$\bar{\nu}_1$ C=C stretching modes of the polyene chain
		–	–	1503 s	–	–	
		1446 w	1446 w	1446 v wb	–	–	?N–heterocycles
		1390 w	1390 w	–	–	–	
		1354 w	–	–	–	–	
		–	–	1295 vw	–	–	
		1273 m	1273 m	–	–	–	Amide III
		1212 m	1212 m	–	–	–	
		1191 s	1190 s	–	–	–	
		1158 vs	1158 vs	–	–	–	$\bar{\nu}_2$ C–C + CH in plane bending
		–	–	1151 s shoulder	–	–	
		–	–	1139–1140 vs	–	–	
		–	–	1115 s shoulder	–	–	
		1006 s	1006 s	1006 vw	–	–	$\bar{\nu}_3$ (Unsat.)–CH3 in plane rocking
		966–951 w doublet	967–951 w doublet	–	–	–	$\bar{\nu}_4$ CH and C=C out–of–plane wagging and twisting
		870 vw	869 vw	–	–	–	
		515 vw b	520 vw b	–	–	–	S–S bridges
Yellow	Psittacofulvin	3066 vw	3074–3062 vw b		–	–	
		2980 w shoulder	2970 w shoulder	2970 vw shoulder	–	–	–CH_2 and –CH_3 stretching
		2937 w	2934–2936 m	2934–2936 w	–	–	

		2876 w shoulder	2875–2880 w shoulder	–	–	–	
		2674 vw	2670 vw b	–	–	–	
		2272 vw	2276 vw b	–	–	–	
		1675 vw b	1668–1670 vw–m b	–	–	–	Amide I
		1616 w b	1614–1620 vw b	1614–1620 vw b	–	–	
			1564 s	–	–	–	
		–	1548 vs	1548 w–s shoulder	–	–	
		1539 vs	1539 s–vs	1538 w–vs	–	–	$\bar{\nu}_1$ C=C stretching modes of the polyene chain
		–	1502 s	1502 w	–	–	
		–	1449 vw–w	–	–	–	
		1296 vw	1295 vw–w	1295 w	–	–	Amide III
		1196 w shoulder	1196 w shoulder	–	–	–	
		–	1175 vw	–	–	–	
		–	1152 vs	1149 m shoulder	–	–	
		–	1140 vs	–	–	–	
		1139 vs	1138 vs	1137 vs	–	–	$\bar{\nu}_2$ C–C
		–	1135 vs	–	–	–	
		–	1115 vw–vs	1120 m shoulder	–	–	
		1017 w	1015 vw	1015 vw	–	–	
		–	1003 m	1003 vw	–	–	
		–	–	–	–	–	
		559 vw b	–	–	–	–	
		293 w	–	–	–	–	
Orange	Psittacofulvin	3050 vw	3050 vw	–	–	–	
		–	2970 w shoulder	2970 w shoulder	–	–	–CH_2 and –CH_3 stretching
		–	2934 m	2932–2936 m	–	–	
		–	2874 w shoulder	2876 w shoulder	–	–	
		2651 m	2654 m	–	–	–	
		2264 w	2261–2268 w–m	–	–	–	
		–	1654–1660 w b	–	–	–	Amide I
		1611 w	1611 w	1615 w	–	–	
		–	1563 vw shoulder	1563 m shoulder	–	–	
		–	1538 vs	1536–1538 vs	–	–	

		–	1531 vs	–	–	–	
		1527 vs	1528 vs	–	–	–	$\bar{\nu}_1$ C=C stretching modes of the polyene chain
		–	–	1503 m–s	–	–	
		–	1450 vw b	1450 w b	–	–	
		1298 vw	1296 vw	1296 vw	–	–	Amide III
		–	1150 s shoulder	1150 s shoulder	–	–	
		1134 vs	1134–1135 vs	1134–1137 vs	–	–	$\bar{\nu}_2$ C–C
		–	–	1115 s shoulder	–	–	
		–	–	1015 vw	–	–	
		–	1003 vw	–	–	–	
		–	294 vw	–	–	–	
Red	Psittacofulvin	3046 w	3049–3054 w	3054 w	–	–	
		–	–	2935 w b	–	–	–CH_2 and –CH_3 stretching
		–	–	2874 vw b	–	–	
		2648 m	2652–2657 m	2652–2657 m	–	–	
		2260 w	2263 w	2268 w	–	–	
		1647 vw b	1650 vw b	1650 vw b	–	–	
		1611 w	1611 w	1611 w	–	–	Amide I
		1527 vs	1527–1528 vs	1527–1528 vs	–	–	$\bar{\nu}_1$ C=C stretching modes of the polyene chain
		–	1519 s shoulder	1519 w shoulder	–	–	
		–	–	1504 m	–	–	
		1298 vw	1185 vw	1295 vw	–	–	Amide III
		1185 vw	1152 m shoulder	1185 vw	–	–	
		1152 m shoulder	1150 m shoulder	1150 m shoulder	–	–	
		1133 vs	1133 vs	1133 vs	–	–	$\bar{\nu}_2$ C–C
		–	1120 m shoulder	–	–	–	
		–	–	1030 vw b	–	–	
		–	–	1003 vw	–	–	
		634 vw	634 vw	–	–	–	
		294 w	294 vw	294 vw	–	–	
Green	Psittacofulvin	3067 w b	3074 w b	3070 w b	–	–	
		2980 w shoulder	2980 vw shoulder	–	–	–	CH_2 and –CH_3 stretching
		2932 m	2932–2938 w	2932–2938 w	–	–	
		2872 w shoulder	2872–2877 vw shoulder	2872–2877 vw shoulder	–	–	
		–	2670–2672 w	2668 w	–	–	
		2272 vw	–	–	–	–	
		1667 vw	–	–	–	–	

	1615 vw	1615 vw	1610 m	–	–	Amide I
	–	–	1550 w shoulder	–	–	
	1539 vs	1537–1539 vs	1538 vs	–	–	$\bar{\nu}_1$ C=C stretching modes of the polyene chain
		1503 vs	1503 w	–	–	
	1447 vw b					
	1297 vw	1295 vw m	1295 w	–	–	Amide III
	1198 vw	1195 vw	1195 vw	–	–	
	–	–	1150 w shoulder	–	–	
	1139 vs	1135–1139 vs	1136–1138 vs	–	–	$\bar{\nu}_2$ C–C
	–	1115 vs	1115 m	–	–	
	1018 vw	1018 vw	1018 vw	–	–	
	1003 vw	1003 vw	1003 vw	–	–	
	559 vw b	–	–	–	–	

Fig S3 *Comparison of FT–IR–ATR spectra of white (control), orange-pink (carotenoid), yellow (canary xanthophyll A/B), yellow (psittacofulvin), orange (psittacofulvin), red (psittacofulvin), and green (psittacofulvin) feathers across different thermal treatments.*

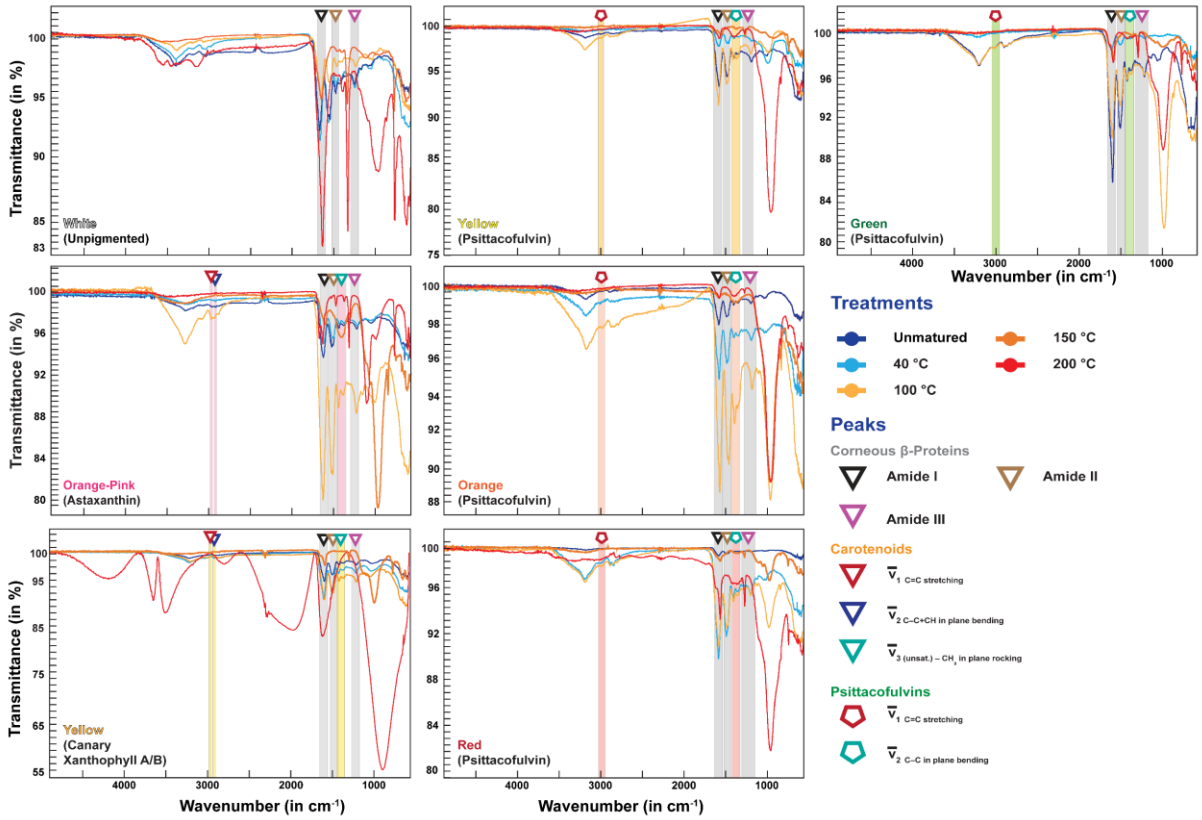

Table S4 *Assignment of characteristic bands to μ-ATR/FTIR spectra of feathers. Relative band intensities are denoted as follows: vs (very strong); s (strong);m (medium); w (weak);vw (very weak) and vwb (very weak -broad). FTIR bands of interest were located and identified as per manuals by Lin-Vien, Colthup, Fateley and Grasselli (1) and Socrates (2).*

Colour	Pigment	FT–IR bands across different temperature treatments					Band assignments
		Unmat.	**40°C**	**100°C**	**150°C**	**200°C**	
White	–	–	–	3268–3272 m	3421m	3393 m	
		3266m	3266 m		–	3045 m	
		2957 w	2957 w	2961 w	–	–	$\bar{\nu}(CH_3)$ stretching
		2929 w	2925 w		–	–	$\bar{\nu}(CH_2)$ stretching
		–	–	2876 w	–	–	
		1627 s	1627–1631 s	1627 s	–	–	$\bar{\nu}$(C=O) Amide I
		–	–		1607 s	1603 s	
		1532 s	1532 s	1527–1532 s	–	–	δ(N–H) + $\bar{\nu}$(C–N) Amide II
		1447 m	1447–1453 m	1449 m		–	δ(C–H) bending
		–	–		1424 w	–	
		1403 w	1400 w	1410 w		–	δ(C–H) bending
		–	–	–	1382 w		
		–	–	–	–	1371 m	
		–	–	–	–	1314 s	
		1235 m	1235 m	1234 m	1235 m	–	$\bar{\nu}$(C–N), δ(N–H) Amide III
		1159 w	1159 w	1159 w		–	
		–	–		1102 w	–	

		1074 vw	1074 m	1073 m	–	–	$\bar{\nu}$(Si–O) stretching from clay matrix
		–	–	–	992 vw	–	
		–	–	–	–	965 s b	
		–	–	–	946 vw	–	
		–	–	932 w	–	–	
		–	–	–	778 s	779 s	
Orange-pink	Astaxanthin	–	–	–	–	3332–3431 m	
		3265 m	3272 m	3270–3279 m	3269 m	–	
		–	2961 w	2961 w	–	–	$\bar{\nu}$(CH_3) stretching
		2918 w	–	–	–	–	$\bar{\nu}$(CH_2) stretching
		1634 s	1634 s	1634 s	1623–1633 s	1640–1686 s	$\bar{\nu}$(C=O) Amide I
		1532 s	1532 s	–	–	–	δ(N–H), $\bar{\nu}$(C–N) Amide II
		–	–	1516 s	–	–	
		1449 m	1449 m	1447 m		–	δ(C–H) bending
		–	–	–	1417–1430 m	–	
		1393 m	1393–1396 m	1389 m	–	1393 m	
		–	–	–	–	1326–1331 s	
		1237 m	1237–1240 m	1233 m	–		$\bar{\nu}$(C–N), δ(N–H) Amide III
		–	1159 w	1159 w	–		
		–	–	–	–	1122–1132 s	
		1074 vw	1074–1081 m	–	–	–	$\bar{\nu}$(Si–O) stretching from clay matrix
		–	–	1037 m	–	–	
		–	–	–	994–976 vs	996–1010m	
		–	–	–	–	–	
		–	–	–	873 m	–	
		–	–	–	–	779–789 s	
		–	–	–	730–755 w	–	
		–	–	–	–	607–614 s	
Pale Yellow	Canary Xanthophyll A/B	–	–	–	3732 m	–	
		–	–	–	3586 m	–	
		–	–	–	–	3453 m	
		3268 m	3268 m	3273 m	–	–	
		2961 w	2961 w	2964 w	–	–	$\bar{\nu}$(CH_3) stretching
		2922 w	–	2929 w	–	–	$\bar{\nu}$(CH_2) stretching
		–	–	–	2346 w	2348 m	
		–	–	–	1662 s	–	
		1628 vs	1627 s	1627–1630 s	–	1614–1619 s	$\bar{\nu}$(C=O), Amide I
		1532 s	1516–1532 s	1532 s	–	–	δ(N–H), $\bar{\nu}$(C–N) Amide II
		1453 m	1449 m	1446 m	–	–	δ(C–H) bending
		1403 w	1407 w	1403 w	–	–	
					–	1315 m	
		1237 m	1237 m	1233 m	–	–	$\bar{\nu}$(C–N), δ(N–H), Amide III
		–	1159 m	–	–	–	
		–	–	1113 m	–	–	
		–	–	–	–	1099 w	
		1063 m	1049–1060 m	–	–	–	$\bar{\nu}$(Si–O) stretching from clay matrix
		–	–	–	–	1006 s	
		–	–	–	914 vs		
		–	–	876 w	–	872 w	

		–	–	1151 s shoulder	–	779 s	
						3371 m	
		3269 m	3272 m	3276 m			
		–	–	–	3326 m		
		–	2961 w	2961 w	–		$\bar{\nu}(CH_3)$ stretching
		1630 s	1627 s	1629 s	–	1616–1630 m	$\bar{\nu}$(C=O), Amide I
		–	–	–	1614 s	–	
		1513 s	1516–1627 s	1531 s	–	–	δ(N–H), $\bar{\nu}$(C–N) Amide II
		1446 w	1446–1449 m	1449 m	–	1446 m	δ (C–H) bending
		–	–	–	1424 m	–	
		–	1396 w	1393 w		–	
Yellow	Psittacofulvin	–	–		1314 s	1315–1318 m	
		1230	1230 w	1226–1237 m	–	–	$\bar{\nu}$(C–N), δ (N–H), Amide III
		–	–	–	1103 s	–	
		–	–	–	–	1092 w	
		1043 m	1036 s	1046 m	–	–	$\bar{\nu}$(Si–O) stretching from clay matrix
		–	–	–	–	1000–1007 s	
		–	–	–	992 w	–	
		–	–	–	918 w	–	
		–	–	872 w	876 w	876 w	
		–	–			780 m	
		–	–	–	–	3418 m	
		–	–	–	3343 m	–	
		3258 m	3276 m	3264–3272 m	–	–	
		–	–	2961 w	–	–	$\bar{\nu}(CH_3)$ stretching
		1630 s	1630 s	1628 s	–	–	$\bar{\nu}$(C=O), Amide I
					1615 s	1619 m	
		1534 s	1531 s	1515 s	–	–	δ(N–H), $\bar{\nu}$(C–N) Amide II
		1449 m	1446–1449 m	1449 m	–	–	δ(C–H) bending
					1428 m		
		1393 m	1389–1396 w	1393–1410 w	–	–	
Orange	Psittacofulvin	–	–	–	–	1343 m	
		–	–	–	1313 s	1318 m	
		1233 m	1226–1233 m	1233 m	–	–	$\bar{\nu}$(C–N), δ(N–H), Amide III
		–	1138–1159 w	–	–	–	
		–	–	–	1099 m	1099 w	
		1042 m	1035 s	–	–	–	$\bar{\nu}$(Si–O) stretching from clay matrix
		–	–	1006 s	–	1001 s	
		–	–	–	993 m		
		–	–	–	872 w	872 m	
		–	–	–	779 s	780 m	
		–	–	–	638 s	–	
		–	–	–	613 s	–	
					3428 m		
		3273 m	3273 m	3273 m	3269 m	–	
		–	2957 w	2964 w	–	–	$\bar{\nu}(CH_3)$ stretching
Red	Psittacofulvin	2925	2922 w	–	–	–	$\bar{\nu}(CH_2)$ stretching
		–	–	–	2338 m	–	
		1634 s	1631–1643 s	1627–1633 s	–	–	$\bar{\nu}$ (C=O), Amide I

		–	–	–	1612 s	1616 s	
		1538 s	1534–1538 s		–	–	δ(N–H), $\bar{\nu}$(C–N) Amide II
		–	–	1516 s	–	–	
		1453 m	1449–1453 m	1449 m	–	–	δ(C–H) bending
		–	–	–	–	1436 m	
		–	–	–	1403–1421 w	–	
		1400 w	1385–1410 w	1396 w	1400 w	–	
		–	–	–	1315–1318 w	1316 m	
		1237 m	1237 m	1233–1237m	–	–	$\bar{\nu}$(C–N), δ(N–H) Amide III
		–	1159 w	–	–	–	
		1070 w	1015–1070 m	1013 s	1085 m	–	$\bar{\nu}$(Si–O) stretching from clay matrix
		–	–	–	993–1004 vs	979–1001 s	
		–	872 m		876 m	873 m	
		–			777–780 m	780 m	
Green	Psittacofulvin	–	–	–	–	3417 m	
		3273 m	3283 m	3279 m	3293 m	–	
		2957 w	–	2964 w	–	–	$\bar{\nu}$(CH_3) stretching
		2918 w	–		–	–	$\bar{\nu}$(CH_2) stretching
			2338 m		–	–	
		1631 s	1637 s	1627–1631 s	1611–1633 s	–	$\bar{\nu}$(C=O), Amide I
		–	–	–	–	1620–1640 s	
		1538 s	1531 s	1532 s	–		δ(N–H), $\bar{\nu}$(C–N) Amide II
		1450 m	1453 m	1453 m	–	1445 m	δ(C–H) bending
		1407 w	1407 w	1393 w	1421 m	–	
		–	–	–	1311–1318 m–s	1317 m	
		1235 m	1237 w	1233 w	–	–	$\bar{\nu}$(C–N), δ(N–H) Amide III
		1070 w	–	–	–	–	$\bar{\nu}$(Si–O) stretching from clay matrix
		–	–		1007–1013 s	1006–1011 s	
		–	–	992 s	–	–	
		–	–	872 w	876 m	872 m	
		–	–	–	777–780 m	781 m	

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