Electronic Supplementary Material (ESI) for Analytical Methods.
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Extraction, isolation and characterization of compounds

Compounds **1-10** were obtained using 5 lichens namely *Parmotrema grayana*, *Parmotrema cooperi*, *Heterodermia obscurata*, *Roccella montagnei* and *Cladonia sp.* Manually cleaned, air-dried and crushed lichens were sequentially extracted with CH_2Cl_2, followed by MeOH. In the case of *R. montagnei*, the extraction was carried out in acetone. The crude extracts were fractionated via column chromatography to isolate pure compounds. Melting points and spectral data of isolated compounds were identical with authentic samples or reported data.

Orsellenic acid (1)

The MeOH extract of *Parmotrema grayana* when chromatographed via silica gel MPLC firstly through eluent 80% hexane: CH_2Cl_2 to CH_2Cl_2: MeOH and re-chromatographed via eluent: hexane: ethyl acetate) and further chromatographed using gravity column chromatography (eluent: hexane: ethyl acetate) furnished orsellinic acid (**1**). ^{1}H NMR (300 MHz, DMSO): δ_H 2.39 (3H, s, 8-Me), 6.10 (1H, d, H-5, J = 2.4), 6.16 (1H, d, H-3, J = 2.4), 10-11 (1H, bs OH); ^{13}C NMR (75 MHz, DMSO): δ_C 104.9 (C-1), 161.5 (C-2), 100.3 (C-3), 164.2 (C-4), 110.7 (C-5), 142.6 (C-6), 172.9 (C-7), 23.4 (C-8).

Methylorsellinate (2)

The MeOH extract of *P. grayana* when subjected to MPLC (eluent: 80% hexane: CH_2Cl_2 to CH_2Cl_2: MeOH) resulted in crystals of methyl orsellinate (**2**) which were recrystallised using 50% CH_2Cl_2: hexane followed by 90% CH_2Cl_2: hexane to obtain colourless crystals of (**2**). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 2.48 (3H, s, 8-Me), 3.92 (3H, s, -COOMe), 6.24 (1H, d, H-5, J = 2.5), 6.28 (1H, d, H-3, J = 2.5), 11.56 (1H, bs OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 105.6 (C-1), 160.2 (C-2), 101.2 (C-3), 165.1 (C-4), 111.3 (C-5), 143.8 (C-6), 171.9 (C-7), 24.3 (C-8), 51.9 (C-7-OMe).

Methyl-β-orcinolcarboxylate (3)

The CH_2Cl_2 extract of *Heterodermia obscurata* when subjected to MPLC (eluent: hexane to CH_2Cl_2 to MeOH), and resubjected to gravity column chromatography (eluent: hexane: CH_2Cl_2

to 5% MeOH: CH_2Cl_2), yielded methyl-*β*-orcinol carboxylate (**3**) upon recrystalisation. ^{1}H NMR ($CDCl_3$): δ_H 2.10 (3H, s, 9-Me), 2.45 (3H, s, 8-Me), 3.91 (3H, s, COOMe), 6.19 (1H, s, H-5), 12.00 (1H, bs, 2-OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 105.2 (C-1), 163.0 (C-2), 108.5 (C-3), 158.0 (C-4), 110.5 (C-5), 140.0 (C-6), 172.4 (C-7), 24.1 (C-8), 7.7 (C-9), 51.8 (COOMe).

Ethylhaematomate (4)

The hexane extract of *Paromtrema cooperi* yielded ethylhaematomate when subjected to repeated silica gel column chromatography with increasing polarities (n-hexane: CH_2Cl_2, 9:1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.41 (3H, t, J10, 11 = 8.0 Hz), 2.52 (3H, s), 4.40 (2H, q, J11, 10 = 8.0 Hz), 6.27 (1H, s), 10.32 (1H, s), 12.38 (1H, s), 12.95 (1H, s). ^{13}C NMR (CDCl3, 100 MHz) δ 104.0 (C-1), 168.3 (C-2), 108.5 (C-3), 166.5 (C-4), 112.0 (C-5), 152.4 (C-6), 171.6 (C-7, ester C=O), 193.0 (C-8, aldehydic C=O), 25.2 (C-9), 61.8 (C-10), 14.1 (C-11).

Atranorin (5)

The ubiquitous depside atranorin was isolated from CH_2Cl_2 extract of *Parmotrema grayana* when subjected to MPLC (eluent: hexane to 50% CH_2Cl_2: MeOH). Fractions eluting between 80% CH_2Cl_2: Hexane to 100% CH_2Cl_2 gave crystals which were re-crystalized using 80% CH_2Cl_2: hexane to obtain white needle-like crystals of atranorin (**5**) ^{1}H NMR (300 MHz, CDCl3): δH 2.09 (3H, s, Me-8’), 2.54 (3H, s, Me-9’), 2.68 (3H, s, Me-9), 3.98 (3H, s, -CO2Me), 6.39 (1H, s, H-5), 6.51 (1H, s, H-5’), 10.35 (1H, s, -CHO), 11.91 (1H, s, OH-2’), 12.48 (1H, s, OH-2), 12.53 (1H, s, OH-4); 13C NMR (75 MHz, CDCl3): δC 102.9 (C-1), 169.1 (C-2), 108.6 (C-3), 167.5 (C-4), 112.8 (C-5), 152.4 (C-6), 169.7 (C-7), 193.8 (C-8), 25.5 (C-9), 116.8 (C-1’), 162.9 (C-2’), 110.3 (C-3’), 152.0 (C-4’), 116.0 (C-5’),139.8 (C-6’), 52.3 (C-7’-OMe), 172.2 (C-7’), 23.9 (C-8’), 9.3 (C-9’).

Lecanoric acid (6)

The MeOH extract of *Parmotrema grayana* when chromatographed via silica gel MPLC firstly through eluent 80% hexane: CH_2Cl_2 to CH_2Cl_2: MeOH and re-chromatographed via eluent: hexane: ethyl acetate) and further chromatographed using gravity column chromatography (eluent: hexane: ethyl acetate) gave pale yellow crystals of lecanoric acid (**6**), which was re-

crystalized using 2% MeOH:CH_2Cl_2 as solvent. ^{1}H NMR (300 MHz, DMSO): δ_H 2.35 (3H, s, 8'-Me), 2.37 (3H, s, 8-Me), 6.22 (2H, s, 3, 5-H), 6.59 (1H, d, 5'-H, *J* = 2.1 Hz), 6.62 (1H, d, 3'-H, *J* = 2.1 Hz), 9.99 (1H, s, 2'-OH), 10.31 (1H, s, 2-OH); ^{13}C NMR (75 MHz, DMSO): δ_C 108.1 (C-1), 160.0 (C-2), 100.4 (C-3), 161.0 (C-4), 109.8 (C-5), 139.4 (C-6), 166.6 (C-7), 21.37 (C-8), 116.3 (C-1'), 158.8 (C-2'), 107.3 (C-3'), 152.1 (C-4'), 114.6 (C-5'), 140.2 (C-6'), 170.4 (C-7'), 21.4 (C-8').

Erythrin (7)

The crude acetone extract of *Roccella montagnei* was subjected to MPLC (eluent: 10% hexane: CH_2Cl_2 to CH_2Cl_2: MeOH). Fractions obtained around 5% MeOH: CH_2Cl_2 to about 12% MeOH: CH_2Cl_2 contained erythrin (**7**) as the major component. These fractions were combined and re-subjected again to MPLC using the solvent gradient CH_2Cl_2 to 50% CH_2Cl_2: MeOH to provide pure erythrin (**7**) in white crystalline form. ^{1}H NMR (300 MHz ,CD_3OD): δ_H 2.51 (3H, s, 8-Me), 4.34-4.42 (1H, dd, 1'-H, *J* = 11.7 Hz), 4.56-4.61 (1H, dd, 1'-H, *J* =11.5 Hz), 3.87-3.95 (1H, dt, 2'-H, *J* =13.5 Hz), 3.63-3.68 (2H, m, 3', 4'-H), 3.76-3.82 (1H, dd, 4'-H, *J* = 13.5 Hz), 6.15 (1H, d, 3-H, *J* = 2.1 Hz), 6.20 (1H, dd, 5-H, *J* = 2.1 Hz); ^{13}C NMR (75 MHz, CD_3OD): δ_C 106.1 (C-1), 166.0 (C-2), 101.7 (C-3), 163.7 (C-4), 112.4 (C-5), 144.9 (C-6), 172.9 (C-7), 24.5 (C-8), 68.0 (C-1'), 71.0 (C-2'), 73.7 (C-3'), 64.5 (C-4').

Sekikaic acid (8)

The MeOH extract of *Heterodermia obscurata* when subjected to MPLC firstly as hexane: CH_2Cl_2 to CH_2Cl_2: MeOH as eluent and subjected to another MPLC (eluent:20% hexane: CH_2Cl_2 to 20% MeOH: CH_2Cl_2) and gravity column chromatography (eluent:5% hexane: CH_2Cl_2 to 10% MeOH: CH_2Cl_2), afforded the sekikaic acid (**8**). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 0.92-1.02 (6H, two overlapping t, 3",3'"-Me), 1.62-1.78 (4H, m, 2", 2'"-CH_2), 2.94-3.02 (4H, m, 1", 1'"-CH_2), 3.82 (3H, s, 4-OCH_3), 3.89 (3H, s, 4'-OCH_3), 6.38 (2H, d, 3, 5-H, *J* = 2.4 Hz), 6.44 (1H, s, 5'-H), 11.10 (1H, s, 2-OH), 11.51 (1H, s, 2'-OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 104.4 (C-1), 165.1 (C-2), 98.8 (C-3), 164.1 (C-4), 110.7 (C-5), 148.7 (C-6), 168.5 (C-7), 55.3 (4-OCH_3), 104.9 (C-1'), 156.5 (C-2'), 124.7 (C-3'), 155.9 (C-4'), 55.9 (4'-OCH_3), 106.2 (C-5'), 146.9 (C-6'), 174.9 (C-7'), 38.7 (C-1"), 25.0 (C-2"), 14.3 (C- 3"), 38.9 (C-1'"), 24.8 (C-2'"), 14.3 (C-3'").

Lobaric acid (9)

The MeOH extract of a *Cladonia sp*. when subjected to MPLC (eluent: hexane: CH_2Cl_2 to CH_2Cl_2: MeOH) and rechromatographed using (eluent: 25% hexane: CH_2Cl_2 to 30% MeOH: CH_2Cl_2), afforded the depsidone lobaric acid (**9**), which was further purified by recrystallisation (97% CH_2Cl_2: MeOH) to obtain white crystals of (**9**). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 0.85-0.90 (6H, two overlapping t, 5",5'"-Me), 1.30-1.39 (6H, m, 4", 3'", 4'"-CH_2), 1.50-1.60 (4H, m, 3", 2'"-CH_2), 2.77 (2H, t, 1'"-CH_2, J = 14.4 Hz), 2.87 (2H, t, 2"-CH_2, J = 14.4 Hz), 3.90 (3H, s, OCH_3), 6.69 (1H, s, 3'-H), 6.97 (1H, d, 3-H, J = 2.4 Hz), 7.09 (1H, d, 5- H, J = 2.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 110.8 (C-1), 162.4 (C-2), 106.0 (C-3), 163.8 (C-4), 111.4 (C-5), 148.3 (C-6), 161.7 (C-7), 56.5 (-OCH_3), 120.2 (C-1'), 152.5 (C-2'), 105.6 (C-3'), 144.1 (C-4'), 140.1 (C-5'), 133.8 (C-6'), 167.9 (C-7'), 202.0 (C-1"), 41.0 (C-2"), 25.4 (C- 3"), 21.4 (C- 4"), 13.8 (C- 5"), 27.3 (C-1"'), 30.3 (C-2"'), 31.3 (C-3"'), 21.9 (C-5"'), 13.8 (C-5"').

Usnic acid (10)

The CH_2Cl_2 extract of *Parmotrema grayana* when subjected to MPLC (eluent: hexane to 70% CH_2Cl_2: MeOH) and subjected to gravity column chromatography (eluent: hexane: CH_2Cl_2: 5% MeOH: CH_2Cl_2) yielded usnic acid (**10**) as yellow prisms. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.76 (3H, s, Me-13), 2.11 (3H, s, Me-16), 2.66 (3H, s, Me-15), 2.67 (3H, s, Me-18), 5.97 (1H, s, H-4), 11.01 (1H, s, OH-10), 13.30 (1H, s, OH-8), 18.81 (1H, s, OH-3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 198.1 (C-1), 179.4 (C-2), 155.2 (C-3), 98.3 (C-4), 101.5 (C-5), 98.4 (C-6), 109.3 (C-7), 157.5 (C-8), 103.9 (C-9), 163.9 (C-10), 105.2 (C-11), 59.1 (C-12), 27.8 (C-13), 200.3 (C-14), 32.1 (C-15), 7.5 (C-16), 201.7 (C-17), 31.2 (C-18).

Table Caption

Table S1: product ions of deprotonated secondary at optimum collision energy

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Name of compound	$[M-H]^-$	Exact mass	Observed mass	Error
Orsellinic acid	$C_7H_7O_2$	123.0446	123.0445	-0.8497
	C_5H_5O	81.034	81.0342	1.9764
	C_6H_7	79.0547	79.0545	-3.4821
Methylorsellinate	$C_8H_5O_3$	149.0237	149.0238	-1.1348
	C_7H_5O	105.034	105.0323	-16.5648
Methyl –β-orcinolcarboxylate	$C_9H_7O_3$	163.0395	163.0366	-17.9051
	C_8H_7O	119.0496	119.0513	13.5242
Ethylhaematomate	$C_9H_7O_5$	195.0306	195.0293	6.417
	$C_9H_5O_4$	177.0187	177.0195	4.0461
	$C8H_7O_4$	167.0344	167.0347	1.5934
	$C_8H_7O_3$	151.0395	151.0391	-0.0215
	$C_7H_7O_2$	123.0446	123.0445	-0.8497
	C_7H_5O	105.034	105.0343	2.4769
Atranorin	$C_{10}H_{11}O_4$	195.0657	195.0661	1.8762
	$C_9H_5O_4$	177.187	177.0177	-6.1223
	$C_9H_7O_3$	163.0395	163.0395	-0.1177
Lecanoric acid	$C_8H_7O_4$	167.0344	167.0343	-08012
	$C_8H_5O_3$	149.0238	149.0233	-3.819
	$C_7H_7O_2$	123.0809	123.0800	-8.0441
Erythrin	$C_{12}H_{15}O_7$	271.0817	271.0818	0.0808
	$C_8H_7O_4$	167.0344	167.0349	2.7907
	$C_8H_5O_3$	149.0238	149.0238	-0.4638
Sekikaic acid	$C_{11}H_{13}O_4$	209.0828	209.0813	6.772
	$C_{11}H_{13}O_5$	225.0761	225.0762	-0.8829
	$C_{10}H_{13}O_2$	165.0915	165.0933	10.5709
	$C_9H_{10}O_2$	150.068	150.0703	14.7951
	$C_{10}H_{13}O_3$	181.0864	181.0882	9.5564
	$C_7H_6O_2$	122.0367	122.0393	18.1948
Lobaric acid	$C_{24}H_{27}O_6$	411.1807	411.1793	-3.5602
	$C_{23}H_{27}O_4$	367.1909	367.1917	2.0843
	$C_{18}H_{16}O_4$	296.1048	296.1072	7.9052
	$C_{22}H_{24}O_4$	352.1674	352.1715	11.473
	$C_{17}H_{13}O_4$	281.0813	281.0835	7.5277
	$C_{13}H_{13}O_4$	233.0813	233.0811	-1.2188
Usnic acid	$C_{17}H_{12}O_7$	328.0583	328.0589	1.8199
	$C_{17}H_{13}O_6$	313.0712	313.0712	-0.0426
	$C_{13}H_{11}O_4$	231.0657	231.0644	-5.7732
	$C_{14}H_{11}O_5$	259.0606	259.0656	19.1123