CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
[15] Selected data for the dimer: HR-MS (EI) calcd for $C_{24}H_{27}IS_2$: 506.0599; found: 506.0603; ^{13}C NMR ($CDCl_3$): $\delta = 95.8$ (CI).
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Polycephalin B and C: Unusual Tetramic Acids from Plasmodia of the Slime Mold *Physarum polycephalum* (Myxomycetes)**

Alexander Nowak and Bert Steffan*

Light plays an important role during the life cycle of the myxomycete *Physarum polycephalum*.[1] Young plasmodia, which are of a remarkable yellow color, live inside decaying trees and move away from the light, while older plasmodia, which have stopped growing, move towards the light and sporulate. Photoreceptors in the UV-A or blue light range which contain maxima at 350 nm (UV-A) and 460 nm (blue light) in their action spectra are responsible[1b] for these phenomena.

Despite intensive efforts the nature of the photoreceptor concerning this "blue-light phenomenon" is as yet unknown. Different types of pigments such as pteridines,[2] phenols,[3] peptides, flavines, flavones, nitrogen-containing polyenes,[4] or phytochromes[5] were assumed to be involved in the signal cascade. Since not only the yellow plasmodia of wild-type *P. polycephalum* but also the white mutants are photosensitive, it was considered that the chromophore of the blue-light receptor may be a flavin or a pteridine and that the orange-yellow pigments occuring in the wild type have no function for the signal transduction.

We were able to prove that the yellow wild type as well as the white mutant LU 897 × LU 898[6] contain a very similar but only quantitatively different set of pigments of the polyene type absorbing in the range under consideration.[7] Taking into account that the UV maximum of a chromophore can be bathochromically shifted up to 80 nm by integration into a protein, as described for the photoreceptor of the halophilic purple bacterium *Ectothiorhodospira halophila*,[8] the yellow polyenes in *Physarum* plasmodia can be thought of as acting as antenna pigments within a protein or protein complex of this organism.

High-performance liquid chromatography (HPLC) of a myxomycete culture exposed to diffuse light after growing for five days under exclusion of light shows remarkable differences in the intensities of certain peaks in comparison to a myxomycete culture growing under exclusion of light only (Figure 1).[9] Apparently light stimulates the formation of two metabolites, which cause a striking increase in the intensities of peak 1 ($t_{ret} = 34.47$ min) and peak 2 ($t_{ret} = 32.74$ min). Here we report on the isolation and structure elucidation of these metabolites, which we have named polycephalin C (**1**) and B (**2**).

Because the compounds are very sensitive to light, all steps from incubation and extraction to chromatography were carried out under exclusion of light and at low temperature (4 °C). Plasmodia cultivated under axenic conditions[10] were first thoroughly extracted with a mixture of acetone, meth-

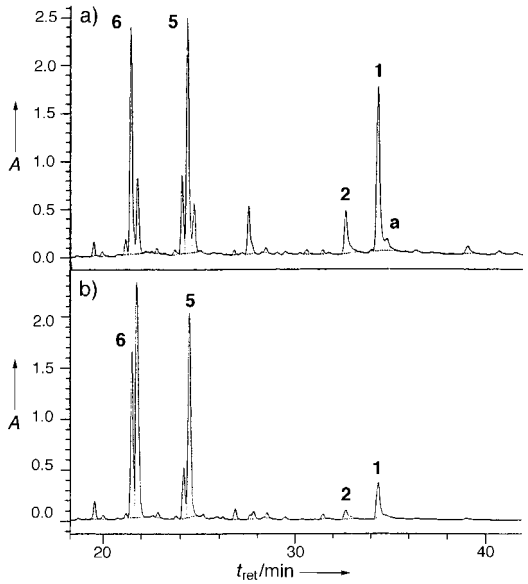

Figure 1. HPLD chromatograms for the chloroform extract of *P. polycephalum* cultures: a) growth for five days in the dark followed by two days under illumination; b) growth for seven days in the dark (control). Conditions for HPLC: column: Nucleosil 100–5 C_{18} (250 × 4 mm), mobile phase A: water/acetonitrile (9/1), 0.1% TFA, mobile phase B: acetonitrile, 0.1% TFA, linear gradient from A to B in 45 min, flow rate: 1.0 mL min^{-1}, photodiode array detection in the range of $\lambda = 200–800$ nm. A = absorbance, t_{ret} = retention time, TFA = trifluoroacetic acid.

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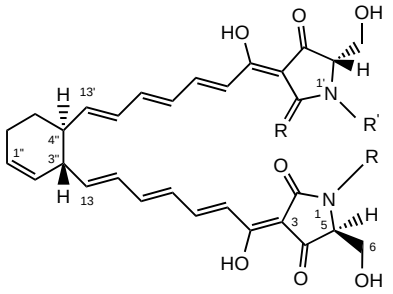
anol, ethyl acetate, and chloroform (3/2/1/1). After the removal of lipophilic components by partitioning between *n*-hexane and methanol/water (9/1), the aqueous phase was concentrated, dissolved again in water, and extracted with chloroform. The organic phase was concentrated and separated by chromatography on Sephadex LH-20 with methanol as eluent. Further purification by partition between ethyl acetate and citrate/HCl buffer (100 mM, pH 3.0) or an aqueous solution of EDTA (50 mM, pH 4.75) provided polycephalin C (**1**) and B (**2**) as amorphous orange-red powders. Starting from 220 g of biomass 7.2 mg (0.003 %) of **1** and 11.8 mg (0.005 %) of **2** were obtained in pure form.

According to the high-resolution ESI mass spectrum, **1** has the molecular formula $C_{32}H_{36}N_2O_8$. The UV spectrum (methanol) shows absorption maxima at $\lambda = 253$ and 390 nm. Addition of dilute hydrochloric acid leads to a slight bathochromic shift of the long-wave absorption band (to $\lambda =$ 394 nm), which is displaced hypsochromically to $\lambda = 395$ nm after addition of a dilute solution of sodium hydroxide. This behavior is typical for tetramic acids.[11] The IR spectrum of **1** contains inter alia bands at $\tilde{\nu} = 1686$ (lactam), 1635, 1598 (polyene), and 2854 cm^{-1} (*N*-methyl).

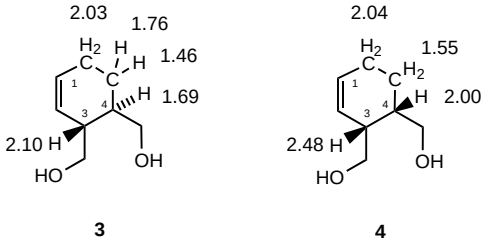
The ^1H NMR spectrum of **1** displays two overlapping groups of signals for triene moieties between $\delta = 7.51$ and 5.93, and signals for an AB_2 system at $\delta = 3.95$ ($2CH_2$) and 3.73 (2CH) for the two hydroxyethylidene groups. The aliphatic protons of the cyclohexene ring ($\delta = 1.56 - 2.80$) couple with those of both triene moieties. The ^{13}C NMR spectrum contains the signals for 14 olefinic CH, 4 aliphatic CH, 4 aliphatic CH_2, and 2 *N*-methyl groups as well as 8 quaternary carbon atoms. The HMBC and HMQC correlations connect each of the two hydroxyethylidene groups ($\delta = 59.29$, 69.35) with an *N*-methyltetramic acid ($\delta = 26.96$, 101.43, 173.31, 175.10, 194.34) that is linked with one of the triene chains, which are in turn leading vicinally into the cyclohexene ring. The above data indicate structure **1** for polycephalin C.[12]



1 R = R′ = CH_3
2 R = CH_3, R′ = H

The configuration at C-5 of the tetramic acid was established after hydration of **1** with hydrogen on Pd/C. The circular dichroism (CD) spectrum of the hydrated compound[13] shows a parallel lapse to that of decahydrophysarorubinic acid as well as that of the synthetically prepared 3-acetyl-5-hydroxymethyl-*N*-methyltetramic acid with 5*S* configuration.[7] Therefore, **1** should have *S* configuration at both C-5 and C-5′.

To confirm the structure of **1** and determine the relative stereochemistry at positions 3″ and 4″, the isomeric diols **3** and **4** were synthesized as model compounds. According to the method of Corey et al.,[14] 2,4-pentadienol and methyl acrylate were coupled by a Diels–Alder reaction, and the resulting species was reduced with $LiAlH_4$ to yield **3** and **4** (Figure 2).



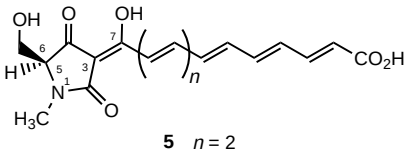
3 **4**

Figure 2. Structures and selected ^1H NMR data of *trans*- and *cis*-3,4-dihydroxymethylcyclohexene (**3** and **4**, respectively).

The coupling constant of the protons H-3 and H-4 is 5.3 Hz for the *cis* form **4**. The coupling constant of the *trans* compound **3** is 8.5 Hz, which is in accordance with the value found in **1** for the corresponding protons of the cyclohexene ring ($J = 8.8$ Hz). The protons at C-5 and C-6 of the *cis* isomer **4** appear as a coupled system of equivalent nuclei. In comparison, while the protons at position C-6 of the *trans* isomer **3** are isochronous, the protons of the methylene group at C-5 are not and appear at different shifts ($\delta = 1.46$ and 1.76). This is in exact agreement with the data obtained for **1**.

According to NMR spectroscopy and LC/APCI mass spectrometry (*m*/*z* 562, $C_{31}H_{34}N_2O_8$; APCI indicates chemical ionization at atmospheric pressure), peak 2 in the chromatogram in Figure 1) (polycephalin B) corresponds to an N-demethylated polycephalin C. The HMBC and HMQC correlations relate a hydroxyethylidene group ($\delta = 59.12$, 69.29) to an *N*-methyltetramic acid ($\delta = 26.95$, 101.44, 173.48, 174.81, 193.97). As in **1** the protons of the serine residue split into a doublet ($\delta = 3.96$, CH_2CH) and a triplet ($\delta = 3.76$, CH_2CH). The second hydroxyethylidene group ($\delta = 62.11$, 64.46) is connected to a tetramic acid without a substituent at N ($\delta =$ 101.44, 173.48, 174.81, 195.80). In this case the protons at position 6′ are not isochronous, and their signals split into a doublet of doublets. Thus, there are three signals at $\delta = 3.92$, 3.84, and 3.79 in the ^1H NMR spectrum of the serine residue. Which of the two tetramic acid moieties is N-methylated has not yet been determined. Considering these data polycephalin B is assigned structure **2**.[15]

Peak 5 in the chromatogram in Figure 1 corresponds to physarorubinic acid A (**5**), which we had isolated earlier.[7] Spectroscopic data reveal that peak 6 corresponds to a polyenetetramic acid which contains one less double bond.



5 *n* = 2
6 *n* = 1

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This compound, named physarorubinic acid B, has structure **6**.[16] Thus, two further polyene compounds which are responsible for the yellow color of the wild-type plasmodia of *Physarum polycephalum* have been isolated besides physarochrom A.[17]

Polycephalin C (**1**) is very sensitive to light and changes under specific illumination conditions to another compound corresponding to peak a (Figure 1). The structure elucidation of the compound corresponding to peak a will be reported in detail elsewhere together with the biosynthesis of **1**, which may contain the precursors **5** and **6**.

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[12] **1**: TLC (silica gel 60 F_{254}, chloroform/methanol/water 60/40/9): R_f = 0.56; HPLC (for conditions see Figure 1): t_{ret} = 34.47 min; UV (c = 4.1427 μM, 3 mL of methanol): λ_{max} (lg ε) = 253 (4.15), 390 nm (4.74); UV (c = 3.94 μM, 3 mL of methanol + 50 μL of 3 M HCl): λ_{max} (lg ε) = 224 (4.22), 250 (4.20), 395 (4.93), 415 nm (sh, 4.92); UV (c = 3.7535 μM, 3 mL of methanol + 50 μL of 2 M NaOH): λ_{max} (lg ε) = 264 (4.29), 360 nm (4.70); CD (methanol): λ_{max} ($\Delta\varepsilon_{rel}$) = 213.5 (+1.42), 250.5 (−3.24), 271.5 (+0.57), 301 (+0.035), 363 (+5.73), 424 nm (−3.88); ^{1}H NMR ($CD_3OD/CDCl_3$ 1/1, 600.13 MHz): δ = 7.51 (dd, J = 15.5, 11.0 Hz, 2H; 9-H, 9′-H), 7.14 (d, J = 15.5 Hz, 2H; 8-H, 8′-H), 6.69 (dd, J = 15.4, 9.2 Hz, 1H; 11-H), 6.68 (dd, J = 15.4, 9.2 Hz, 1H; 11′-H), 6.42 (dd, J = 11.0, 15.4 Hz, 2H; 10-H, 10′-H), 6.27 (dd, J = 9.2, 15.1 Hz, 1H; 12′-H), 6.24 (dd, J = 9.2, 15.1 Hz, 1H; 12-H), 6.02 (dd, J = 15.1, 8.0 Hz, 1H; 13′-H), 5.93 (dd, J = 15.1, 7.9 Hz, 1H; 13-H), 5.83 (ddd, J = 10.1, 2.6, 3.4 Hz, 1H; 1″-H), 5.54 (ddd, J = 10.1, 2.5, 1.9 Hz, 1H; 2″-H), 3.95 (d, J = 3.3 Hz, 4H; 6-H_2, 6′-H_2), 3.73 (t, J = 3.3 Hz, 2H; 5-H, 5′-H), 3.05 (s, 6H; 2NCH_3), 2.80 (dm, J = 8.8 Hz, 1H; 3″-H), 2.25 (dddm, J = 8.0, 8.8, 2.8 Hz, 1H; 4″-H), 2.12 (br m, 2H; 6″-H_2), 1.84 (m, 1H; 5″-H_a), 1.56 (m, 1H; 5″-H_b); ^{13}C NMR ($CD_3OD/CDCl_3$ 1/1, 150.9 MHz): δ = 194.34 (s; C-4, C-4′), 175.10 (s; C-2, C-2′), 173.31 (s; C-7, C-7′), 145.50 (d; C-9, C-9′), 145.40 (d; C-13′), 144.54 (d; C-13), 144.24 (d; C-11′), 143.92 (d; C-11), 131.30 (d; C-12), 130.53 (d; C-12′), 130.22 (d; C-10, C-10′), 128.60 (d; C-1″, 128.03 (d; C-2″), 120.96 (d; C-8, C-8′), 101.43 (s; C-3, C-3′), 69.35 (d; C-5, C-5′), 59.29 (t; C-6, C-6′), 45.29 (d; C-3″), 43.88 (d; C-4″), 27.64 (t; C-5″), 26.96 (q; 2NCH_3), 24.41 (t; C-6″); IR (KBr): $\tilde{\nu}$ = 3418 (m), 3022 (w), 2925 (w), 2854 (w), 1686 (m), 1635 (s), 1598 (s), 1553 (s), 1480 (m), 1445 (m), 1407 (m), 1363 (w), 1287 (w), 1254 (w), 1132 (w), 1007 (m), 915 (w), 895 (w), 612 cm^{-1} (w); $[\alpha]_D$ = −73.2 (c = 0.0041 in methanol); ESI-MS: m/z: 577 $[M+H]^+$, 599 $[M+Na]^+$, 615 $[M-H+Ca]^+$, 1175 $[2M+Na]^+$; HR-MS (EI) calcd for $C_{32}H_{37}N_2O_8$ $[M+H]^+$: 577.25945, found: 577.25995.

[13] Hydrogenated polycephalin C: UV (methanol): λ_{max} = 240 (sh), 272, 280 nm (sh); CD (methanol): λ_{max} ($\Delta\varepsilon_{rel}$) = 203 (−4.99), 221, (+2.33), 239.5 (−1.04), 265.5 (+1.14), 290.5 (−2.68).

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[15] **2**: TLC (silica gel 60 F_{254}, chloroform/methanol/water 60/40/9): R_f = 0.47; HPLC (for conditions see Figure 1): t_{ret} = 32.74 min; UV (c = 4.235 μM, 3 mL of methanol): λ_{max} (lg ε) = 247 (414), 386 (4.74), 406 nm (sh, 4.69); UV (c = 4.035 μM, 3 mL of methanol + 50 μL of 3 M HCl): λ_{max} = 220, 254, 388 nm; CD (methanol) λ_{max} ($\Delta\varepsilon_{rel}$) = 206 (+1.73), 250 (−1.54), 271 (+0.58), 297 (+0.25), 361 (+4.76), 415.5 (−4.51); ^{1}H NMR ($CD_3OD/CDCl_3$ 1/1, 600.13 MHz): δ = 7.54 (dd, J = 14.9, 11.4 Hz, 2H; 9-H, 9′-H), 7.17 (d, J = 14.9 Hz, 2H; 8-H, 8′-H), 6.73 (dd, J = 14.7, 10.6 Hz, 1H; 11′-H), 6.71 (dd, J = 14.7, 10.5 Hz, 1H; 11-H), 6.44 (dd, J = 11.4, 14.7 Hz, 2H; 10-H, 10′-H), 6.28 (dd, J = 10.6, 15.2 Hz, 1H; 12′-H), 6.26 (dd, J = 10.5, 15.1 Hz, 1H; 12-H), 6.04 (dd, J = 15.2, 8.2 Hz, 1H; 13′-H), 5.94 (dd, J = 15.1, 8.2 Hz, 1H; 13-H), 5.84 (ddd, J = 10.1, 6.3, 3.8 Hz, 1H; 1″-H), 5.54 (dd, J = 10.1, 2.2 Hz, 1H; 2″-H), 3.96 (d, J = 2.9 Hz, 2H; 6-H_2), 3.92 (dd, J = 3.2, 5.3 Hz, 1H; 5′-H), 3.84 (dd, J = 3.2, 11.6 Hz, 1H; 6′-H_a), 3.79 (dd, 5.3, 11.6 Hz, 1H; 6′-H_b), 3.76 (t, J = 2.9 Hz, 1H; 5-H), 3.06 (s, 6H; 2 NCH_3), 2.81 (m, 1H; 3″-H), 2.26 (dm, J = 8.2 Hz, 1H; 4″-H), 2.13 (br m, 2H; 6″-H_2), 1.85 (m, 1H; 5″-H_a), 1.57 (m, 1H; 5″-H_b); ^{13}C NMR ($CD_3OD/CDCl_3$ 1/1, 150.9 MHz): δ = 195.80 (s; C-4′), 193.97 (s; C-4), 174.81 (s; C-2, C-2′), 173.48 (s; C-7, C-7′), 145.68 (d; C-9, C-9′), 144.67 (d; C-13′), 144.62 (d; C-13), 144.11 (d; C-11, C-11′), 130.64 (d; C-10, C-10′), 130.44 (d; C-12), 130.25 (d; C-12′), 128.75 (d; C-1″), 128.06 (d; C-2″), 120.92 (d; C-8, C-8′), 101.44 (s; C-3, C-3′), 69.29 (d; C-5), 64.46 (d; C-5′), 62.11 (t; C-6′), 59.12 (t; C-6), 45.29 (d; C-3″), 43.91 (d; C-4″), 27.72 (t; C-5″), 26.95 (q; 2 NCH_3), 24.61 (t; C-6″); IR (KBr): $\tilde{\nu}$ = 3402 (s), 2924 (s), 2854 (m), 1686 (m), 1654 (s), 1636 (s), 1599 (s), 1554 (m), 1466 (w), 1438 (w), 1407 (w), 1288 (w), 1260 (w), 1008 (w), 915 (w), 896 (w), 611 cm^{-1} (w); LC-APCI-MS (negative mode): m/z: 562 $[M]^-$, 561 $[M-H]^-$, 544 $[M-H_2O]^-$, 543 $[M-H-H_2O]^-$; LC-APCI-MS (positive mode): m/z: 563 $[M+H]^+$, 545 ($[M+H-H_2O]^+$.

[16] **6**: TLC (silica gel 60 F_{254}, chloroform/methanol/water 60/40/9): R_f = 0.25; HPLC (for conditions see Figure 1): t_{ret} = 20.9 min; UV (methanol): λ_{max} (lg ε) = 247 (3.67), 286 (3.67), 393 (4.37), 409 nm (sh); UV (c = 17.3 μM, 1.5 mL of methanol + 25 μL of 3 M HCl): λ_{max} (lg ε) = 287 (3.67), 396 (4.43), 413 (4.46), 438 nm (sh); UV (c = 17.3 μM, 1.5 mL of methanol + 25 μL of 2 M NaOH): λ_{max} (lg ε) = 248 (3.80), 371 nm (4.35); CD (methanol): λ_{max} ($\Delta\varepsilon_{rel}$) = 207.0 (−2.06), 223.0 (+1.12), 260.0 nm (−0.63); ^{1}H NMR ($CD_3OD/CDCl_3$ 1/1, 600.15 MHz): δ = 7.54 (dd, J = 14.8, 12.0 Hz, 1H; 9-H), 7.36 (dd, J = 15.1, 11.5 Hz, 1H; 14-H), 7.31 (br, 1H; 8-H), 6.81 (dd, J = 13.6, 11.4 Hz, 1H; 11-H), 6.74 (dd, J = 13.9, 11.4 Hz, 1H; 12-H), 6.69 (dd, J = 13.6. 12.0 Hz, 1H; 10-H), 6.61 (dd, J = 13.9, 11.5 Hz, 1H; 13-H), 6.00 (d, J = 15.1 Hz, 1H; 15-H), 3.96 (br s, 2H; 6-H_2), 3.77 (br s, 1H; 5-H), 3.07 (s, 3H; NCH_3); ^{13}C-NMR ($CD_3OD/CDCl_3$ 1/1, 150.9 MHz): δ = 194 (br, C-4), 174.07 (C-2), 172.64 (C-7), 169.63 (C-16), 144.66 (C-9), 143.91 (C-14), 141.74 (C-11), 139.90 (C-12), 135.46 (C-10), 135.11 (C-13), 124.28 (C-15), 123.80 (C-8), 102.43 (C-3), 69.07 (C-5), 59.22 (C-6), 27.01 (NCH_3); IR (KBr):$\tilde{\nu}$ = 3418 (s), 2924 (s), 2853 (m), 1686 (s), 1618 (s), 1588 (s), 1549 (m), 1465 (m), 1406 (m), 1305 (m), 1260 (m), 1126 (m), 1081 (w), 1010 (m), 917 (w), 884 (w), 806 (w), 611 cm^{-1} (w); $[\alpha]_D$ = −146.8 (c = 0.019 in methanol); APCI-MS (positive mode): m/z: 320 $[M+H]^+$; HR-APCI-MS calcd for $C_{16}H_{18}NO_6$ $[M+H]^+$: 320.1134, found: 320.1148.

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