Structures of Rhodonocardins Produced by a *Nocardia* sp.

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Water-soluble wine-colored pigments, rhodonocardins A and B (RN-A and -B), were isolated along with antibiotic sakyomicins from the culture broth of *Nocardia* sp. Mild acidic hydrolysis of RN-A gave (+)-rhodinosose and RN-B. The CMR data suggested RN-A and -B to be glycosides of the same aglycone as that of sakyomicin A, except for the presence of a hydroxy group on C(5). The structures of RN-A and -B were determined as **Ia** and **Ib**, respectively, both of which contain a 1- α -2-deoxy-2-mercaptoglucosyl moiety on C(5).

Bright wine-red colored and water-soluble pigments, rhodonocardins A and B (abbreviated to RN-A and -B), were isolated along with antibiotic sakyomicins¹⁾ from a culture broth of *Nocardia* sp. No. 53. Neither RN-A nor -B showed antibiotic activity to any microorganisms tested. The structures of RN-A and -B were elucidated by comparing their spectroscopic data and products of chemical degradation with those of sakyomicin A,

which had been established to have the structure of **II** by single-crystal X-ray analysis.¹⁾

Mild acidic hydrolysis of RN-A gave (+)-rhodinosose and RN-B in a good yield. Comparing the ¹³C-NMR spectral data of *O*-acetyl-RN-A and -B with those of *O*-triacetyl-sakyomicin A as shown in Table I, it was suggested that rhodonocardins were glycosides of the same aglycone of sakyomicin A (**II**), except for the presence of a hydroxyl group on

Ia: R = (+)-Rhodinosyl
R' = 1- α -D-Glucosyl
R'' = 1- α -2-Deoxy-2-mercaptoglucosyl
Ib: R = H
R' = 1- α -D-Glucosyl
R'' = 1- α -2-Deoxy-2-mercaptoglucosyl

II: R = (+)-Rhodinosyl
Sakyomicin A

FIG. 1. Structures of RN-A, RN-B and Sakyomicin A.

TABLE I. CHEMICAL SHIFTS (ppm from TMS) IN THE ^{13}C -NMR SPECTRUM (in CDCl_3) OF THE *O*-ACETATES OF RHODONOCARDINS AND SAKYOMICIN A

Assignment*	Decaacetate of RN-A	Nonaacetate of RN-B	Triacetate of sakyomicin A
1	196.39 s**	199.67 s	197.10 s
2	81.03 d	80.62 d	81.14 d
3	74.65 s	74.88 s	74.94 s
3-Me	22.93 q	23.23 q	22.52 q
4	45.11 t	45.52 t	43.29 t
4a	79.10 s	77.75 s	76.76 s
5	159.24 s	158.78 s	145.85 d
6	107.94 d	108.35 d	117.42 d
6a	137.01 s	137.89 s	137.60 s
7	181.77 s	181.48 s	182.18 s
7a	122.68 s	122.80 s	122.68 s
8	149.77 s	149.77 s	149.59 s
9	129.88 d	129.88 d	129.93 d
10	135.67 d	135.61 d	135.90 d
11	125.78 d	125.31 d	125.84 d
11a	133.50 s	133.62 s	135.43 s
12	181.18 s	181.18 s	181.18 s
12a	132.39 s	131.92 s	133.39 s
12b	81.32 s	77.75 s	80.73 s
(R)	16.32 q	—	16.21 q
(R)	22.52 t	—	22.52 t
(R)	23.69 t	—	23.75 t
(R)	65.99 d	—	65.76 d
(R)	68.68 d	—	69.03 d
(R)	94.54 d	—	94.37 d
(G)	48.56 d	47.56 d	—
(G)	61.84 t $\times 2$	61.90 t $\times 2$	—
(G)	68.33 d	68.39 d	—
(G)	68.68 d $\times 2$	68.68 d	—
(G)	—	68.86 d	—
(G)	69.56 d	69.38 d	—
(G)	69.91 d $\times 2$	69.97 d $\times 2$	—
(G)	70.91 d	71.43 d	—
(G)	91.97 d	92.55 d	—
(G)	93.60 d	94.48 d	—
(Ac-Me)	20.65 q $\times 6$	20.59 q $\times 8$	20.89 q $\times 2$
(Ac-Me)	20.89 q $\times 3$	—	—
(Ac-Me)	21.18 q	21.12 q	21.00 q
(Ac-CO)	169.07	169.25	169.13
	~ 170.89 s $\times 10$	~ 170.77 s $\times 9$	~ 170.65 s $\times 3$

* (R) carbon in the rhodinosyl moiety; (G) carbon in the glucosyl moiety; (Ac-Me) carbon of the acetyl methyl; (Ac-CO) carbon of the acetyl carbonyl; numerical number: carbon in the aglycone skeleton (*cf.* Fig. 1).

** s, singlet; d, doublet; t, triplet; q, quartet.

C(5) (see Fig. 1). In the ^{13}C -NMR of *O*-decaacetyl RN-A (Table I), signals for three quaternary carbons [C(3), C(4a) and C(12b)] were observed at around 80 ppm (74.65, 79.10 and 81.32 ppm). A C–H long-range coupling

was observed between the signal at 79.10 ppm and the 6-H signal (6.75 ppm), and also between the signal at 74.65 ppm and the 3-CH₃ signal (1.32 ppm). Therefore the remaining signal at 81.32 ppm was assigned to C(12b).

TABLE II. CHEMICAL SHIFTS (ppm from TMS) IN THE ^1H -NMR SPECTRUM (in CDCl_3) OF *O*-NONAACETYL-RN-B

1.28	(3H, s)	3-Me
1.87	(2H, br. s)	C(4)-H
1.96	(9H, s) }	Ac-Me
1.97	(3H, s) }	
2.00	(3H, s) }	
2.04	(3H, s) }	
2.06	(3H, s) }	
2.20	(3H, s) }	
2.45	(3H, s) }	
3.11	(1H, br. s)	OH
3.67	(1H, dd, $J=11.0\text{ Hz}$, 3.6 Hz)	C(2')-H
3.95~4.08	(2H, m)	C(5',6')-H
4.10~4.16	(2H, m)	C(6'')-H
4.22	(1H, dd, $J=12.0\text{ Hz}$, 6.2 Hz)	C(6')-H
4.32	(1H, ddd, $J=10.0\text{ Hz}$, 4.0 Hz , 3.0 Hz)	C(5'')-H
4.57	(1H, br. s)	OH
5.00	(1H, dd, $J=9.6\text{ Hz}$, 3.9 Hz)	C(2'')-H
5.04	(1H, dd, $J=10.0\text{ Hz}$, 9.6 Hz)	C(4'')-H
5.10	(1H, dd, $J=10.0\text{ Hz}$, 9.6 Hz)	C(4')-H
5.25	(1H, d, $J=3.6\text{ Hz}$)	C(1')-H
5.27	(1H, d, $J=3.9\text{ Hz}$)	C(1'')-H
5.39	(1H, dd, $J=9.6\text{ Hz}$, 9.6 Hz)	C(3'')-H
5.40	(1H, dd, $J=11.0\text{ Hz}$, 9.6 Hz)	C(3')-H
5.48	(1H, s)	C(2)-H
6.67	(1H, s)	C(6)-H
7.33	(1H, dd, $J=8.0\text{ Hz}$, 1.0 Hz)	C(11)-H
7.70	(1H, dd, $J=8.0\text{ Hz}$, 8.0 Hz)	C(10)-H
7.99	(1H, dd, $J=8.0\text{ Hz}$, 1.0 Hz)	C(9)-H

The corresponding signal was shifted to 77.75 ppm in the ^{13}C -NMR of *O*-nonaacetyl RN-B (see Table I), indicating that the rhodinosyl moiety was attached to C(12b) in RN-A.²⁾

In the ^1H -NMR spectrum of *O*-nonaacetyl-RN-B (Table II), two anomeric proton signals (5.25 and 5.27 ppm) and their coupling constants (3.6 and 3.9 Hz) indicate that the RN-B molecule contained two α -glucosyl moieties. The fact that one of these anomeric proton signals at 5.25 ppm was coupled with the signal at 3.67 ppm, which was unusually shifted to a higher magnetic field, suggested the possibility for the presence of a thio group in the C-2' position. The ^{13}C -NMR spectrum of *O*-nonaacetyl-RN-B (see Table I) indicates the presence of a C(2') signal at 47.56 ppm in the glucose moiety. In a selective decoupling experiment with ^{13}C -NMR, irradiation of 3.67 ppm resulted in the change of the doublet signal at 47.56 ppm into a singlet. These NMR

data may suggest that RN-B contained a 2-deoxy-2-mercaptoglucose moiety in the molecule.

RN-B was refluxed in 2N HCl for 1.5 hr to give D-glucose and deglucosyl-RN-B. The ^{13}C -NMR data of the *O*-hexaacetyl derivative of the latter compound (Table III) suggest that it had a linear structure (IV), which would result from the rearrangement of the original angular structure (III) as shown in Fig. 2. The same rearrangement has been reported in cases of aquayamycin and others having the structure of hydrobenz[*a*]anthraquinone.^{3~5)} The fact that this rearrangement could take place only when RN-B was vigorously hydrolyzed shows that the glucosyl moiety was attached to C(4a) of the aglycone.

The high-resolution MS of the hexaacetate of deglucosyl-RN-B indicated the presence of a sulfur atom [m/z 758.1528; calcd. value 758.1514 for $\text{C}_{35}\text{H}_{34}\text{O}_{17}\text{S}$ ($\text{M}^+ - 60$)].

FIG. 2. Rearrangement of Deglucosyl-RN-B to the Linear Compound (IV).

TABLE III. CHEMICAL SHIFTS (ppm from TMS) IN THE ^{13}C -NMR SPECTRUM (in CDCl_3) OF THE HEXAACETATE OF DEGLUCOSYL-RN-B

Observed signals	Multiplicity	Assignment for linear structure IV	Possible angular	Chemical shifts for structure III*
76.70	s	1	12b	77.75
73.71	d	2	2	80.62
76.70	s	3	3	74.88
22.47	q	3-Me	3-Me	23.23
43.23	t	4	4	45.52
200.49	s	4a	1	199.67
78.98	s	5	4a	77.75
119.29	d	6	6	108.35**
131.10	s	6a	6a	137.89
192.24	s	7	7	181.48**
123.91	s	7a	7a	122.80
145.85	s	8	8	149.77
130.17	d	9	9	129.88
131.34	d	10	10	135.61
127.36	d	11	11	125.31
125.78	s	11a	11a	133.62
192.24	s	12	12	181.18**
129.12	s	12a	12a	131.92
141.23	s	12b	5	158.78**
91.44	d	1'		92.55
43.53	d	2'		47.56
68.68	d	3'		68.86
69.85	d	4'		69.38
70.79	d	5'		69.97
61.49	t	6'		61.90

* Based on the signals observed in the ^{13}C -NMR Spectrum of *O*-acetyl-RN-B (see Table I).

** Large discrepancy with the observed chemical shift.

Consequently, the molecular formulae of RN-A and -B were assigned to be $\text{C}_{37}\text{H}_{46}\text{O}_{20}\text{S}$ (SIMS: m/z 843, $\text{M}^+ + 1$) and $\text{C}_{31}\text{H}_{36}\text{O}_{18}\text{S}$

(SIMS: m/z 729, $\text{M}^+ + 1$), respectively.

In the ^1H -NMR of *O*-nonaacetyl-RN-B, a significant nuclear Overhauser effect was ob-

served between the signal of the C(2') proton at 3.67 ppm and the signal of the C(6) proton at 6.67 ppm, indicating that the 1'- α -2'-deoxy-2'-mercaptoglucosyl group was attached to C(5) of the aglycone. The possibility of the 5-deoxy-5-mercaptoglucosyl moiety instead of the 2-deoxy-2-mercaptoglucosyl was also excluded by the fact that the signal for C(1) of authentic pentaacetyl-5-deoxy-5-mercapto- α -glucose was observed at 73.13 ppm in the ^{13}C -NMR spectrum, while the signal for C(1') of *O*-nonaacetyl RN-B was found at either 92.55 or 94.48 ppm (see Table I).

From these experimental results, the structure **1a** can be assigned to RN-A and **1b** to RN-B.

EXPERIMENTAL

Spectral analyses. All the melting points (mp) were measured with a Shimadzu or Yanagimoto melting point apparatus, and were uncorrected. Infrared (IR) spectra were recorded on a Shimadzu IR-400 spectrophotometer. Ultraviolet (UV) spectra were taken on a Shimadzu UV-240 spectrophotometer. Optical rotation data were taken on JASCO DIP-SL and JASCO ORD Model J-5 spectropolarimeters. ^1H - and ^{13}C -NMR spectra were taken on a Hitachi R-22 (90 MHz), JEOL JNM-PS 100 (100 MHz), Bruker WH-270 (270 MHz), JEOL JNM-FX 100 (25.0 MHz) or JEOL JNM-GX 400 (400 MHz). Chemical shifts are given in ppm from tetramethylsilane (TMS) as an internal standard. Coupling constants are given in Hz (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet). Mass spectra (MS) were recorded on a Hitachi M-52 or M-80B (in-beam EI and CI) mass spectrometer operating at an ionization energy of 70 eV. Molecular secondary ion mass spectra (SIMS) were also taken on a Hitachi M-80B mass spectrometer.

Preparative high-performance liquid chromatography (HPLC) was carried out on a stainless column [8 mm ϕ $\times$ 300 mm; Nucleosil C₁₈ (10 μm)] using an Altex Model 110A pump and JASCO UVIDEC 100-II UV detector (290 nm).

Isolation of rhodonocardin A (RN-A) and rhodonocardin B (RN-B).⁶⁾ RN-A and RN-B showed the same *R_f* value [*R_f* = 0.30, *n*-BuOH-AcOH-H₂O (4:1:1)]. RN-A and RN-B were separated by preparative HPLC [solvent, MeOH-H₂O (20:80); flow rate, 4.0 ml/min]. (*V_R* value of RN-A = 78.0 ml; *V_R* value of RN-B = 52.0 ml)

RN-A: mp 214~215°C, $[\alpha]_{\text{D}}^{20} + 29^\circ$ (*c* = 0.1, MeOH); UV (MeOH) λ : 298 (ϵ 10,000), 436 shoulder (ϵ 6000) and 504 (ϵ 6700) nm; IR (KBr) ν : 3350 br., 1730 and 1625 cm^{-1} ; ^1H -NMR 100 MHz (CD₃COOD) δ : 0.59 (3H, d,

J = 6 Hz), 1.27 (3H, s), 1.8~2.4 (6H, overlapped with solvent signal), 3.3~4.4 (14H, m), 4.47 (1H, s), 5.24 (1H, br. s), 5.32 (1H, br. s), 5.42 (1H, br. s), 6.77 (1H, s), 7.0~7.8 (3H, m). ^1H -NMR 90 MHz (CD₃OD) δ : 0.55 (3H, d, *J* = 7 Hz), 1.20 (3H, s), 4.22 (1H, s), 5.13 (1H, d, *J* = 3 Hz), 5.28 (1H, br. s), 5.36 (1H, d, *J* = 3 Hz). The other signals were broad and not well defined. MS: *m/z* 843 (MH⁺) (SIMS), C₃₇H₄₆O₂₀S.

RN-B: mp 223°C, $[\alpha]_{\text{D}}^{20} + 29^\circ$ (*c* = 0.1, MeOH); UV (MeOH) λ : 293 (ϵ 13,000), 438 shoulder (ϵ 8000) and 491 (ϵ 9600) nm; IR (KBr) ν : 3350 br, 1730 and 1625 cm^{-1} . ^1H -NMR 100 MHz (CD₃COOD) δ : 1.27 (3H, s), 1.8~2.4 (2H, overlapped with solvent signal), 3.6~4.2 (12H, m), 4.62 (1H, s), 5.26 (1H, d, *J* = 3 Hz), 5.48 (1H, br. s), 6.76 (1H, s), 7.29 (1H, d, *J* = 10 Hz), 7.57 (1H, d, *J* = 8 Hz), 7.68 (1H, m). ^1H -NMR 90 MHz (CD₃OD) δ : 1.20 (3H, s), 4.31 (1H, s), 5.13 (1H, d, *J* = 3 Hz), 5.36 (1H, d, *J* = 3 Hz). The other signals were broad and not well defined. MS: *m/z* 729 (MH⁺) (SIMS), C₃₁H₃₆O₁₈S.

Acid hydrolysis of RN-A (formation of RN-B and (+)-rhodnose). A solution of RN-A (100 mg) in 2N hydrochloric acid (6 ml) was stirred at room temperature for 1 hr. The reaction solution was concentrated under reduced pressure below 40°C, and then separated by preparative HPLC [Nucleosil C₁₈ (10 μm ; MeOH-H₂O (20:80)] to give RN-B (69 mg).

The identification of the sugar was commenced by stirring a solution of RN-A (98 mg) in 2N hydrochloric acid (6 ml) at room temperature for 1 hr. Dimethyl sulfoxide (6 ml), 2N hydrochloric acid (2 ml) and 2,4-dinitrophenylhydrazine (210 mg) were added to the reaction solution, which was then allowed to stand at room temperature for 24 hr, before being extracted with benzene. The benzene extract was dried over anhydrous Na₂SO₄ and filtered. The filtrate was then separated by preparative TLC [Kieselgel PF₂₅₄; benzene-AcOEt (1:3)] to afford the 2,4-dinitrophenylhydrazone of (+)-rhodnose (24 mg). Optical rotation $[\alpha]_{\text{D}}^{20} + 15.5^\circ$ (*c* = 1.6, pyridine) and the spectral data were identical with those of the 2,4-DNP derivative of authentic (+)-rhodnose¹⁾ (2,3,6-trideoxy-D-threo-aldohehexose).

Acetylation of RN-A. RN-A (319 mg) was dissolved in pyridine (30 ml) and acetic anhydride (3 ml), and allowed to stand overnight. The ether extract of the reaction solution was washed with 3N HCl and sat. NaCl solution, dried over anhydrous Na₂SO₄, and filtered. The filtrate was concentrated under a reduced pressure and then separated by preparative TLC [Kieselgel PF₂₅₄; benzene-AcOEt (1:2)] to afford the decaacetate of RN-A (114 mg), mp 159~160°C. UV (MeOH) λ : 291 (ϵ 11,000), 311 shoulder (ϵ 9100) and 480 (ϵ 5600) nm. IR (KBr) ν : 3480 br, 1750, 1665 and 1595 cm^{-1} . ^1H -NMR 400 MHz (CDCl₃) δ : 0.53 (3H, d, *J* = 6.8 Hz), 1.32 (3H, s), 1.7~1.9 (4H, m), 1.98 (6H, s), 2.01 (3H, s), 2.03 (3H, s), 2.04 (3H, s), 2.08 (3H, s), 2.11 (3H, s), 2.13 (3H, s), 2.26 (3H, s), 2.51 (3H, s),

3.29 (1H, br. s, OH), 3.59 (1H, m), 3.72 (1H, dd, $J=11.5$ Hz, 3.4 Hz), 4.06~4.20 (4H, m), 4.29 (1H, dd, $J=12.6$ Hz, 6.2 Hz), 4.41 (1H, br. d), 4.58 (1H, br. s), 5.06 (1H, dd, $J=10.2$ Hz, 3.9 Hz), 5.12 (1H, dd, $J=10.2$ Hz, 9.3 Hz), 5.19 (1H, dd, $J=9.5$ Hz, 9.5 Hz), 5.31 (1H, d, $J=3.7$ Hz), 5.34 (1H, d, $J=3.7$ Hz), 5.46 (1H, d, $J=1.5$ Hz), 5.48~5.51 (2H, m), 5.50 (1H, s), 6.75 (1H, s), 7.39 (1H, dd, $J=7.9$ Hz, 1.2 Hz), 7.77 (1H, dd, $J=7.9$ Hz, 7.9 Hz), 8.10 (1H, dd, $J=7.9$ Hz, 1.2 Hz). ^{13}C -NMR: see Table II.

Acetylation of RN-B. A solution of RN-A (400 mg) in 2N hydrochloric acid (10 ml) was allowed to stand overnight. The reaction solution was treated according to the same procedure as that for RN-A to afford the nonacetate of RN-B (56 mg), mp 158~159°C; UV (MeOH) λ : 289 (ϵ 12,000), 310 shoulder (ϵ 8900) and 470 (ϵ 5700) nm. IR (CHCl₃) ν : 3400 br., 1750, 1665 and 1590 cm⁻¹. ^1H - and ^{13}C -NMR: see Tables I and II, respectively.

Acetylation of sakyomicin A.¹⁾ Under the same conditions as those for RN-A, acetylation of sakyomicin A (50 mg) gave the triacetate of sakyomicin A (36 mg), mp 205~206°C; UV (MeOH) λ : 254 (ϵ 9100), 305 shoulder (ϵ 3100) and 357 (ϵ 2500) nm. IR (KBr) ν : 3480 br., 1770, 1735 and 1660 cm⁻¹. ^1H -NMR 100 MHz (CDCl₃) δ : 0.54 (3H, d, $J=6$ Hz), 1.31 (3H, s), 1.87 (2H, m), 1.98 (3H, s), 2.24 (3H, s), 2.44 (3H, s), 1.7~2.4 (4H, m), 3.21 (1H, br. s, OH), 3.72 (1H, m), 4.65 (1H, br. s), 5.42 (1H, d), 5.44 (1H, s), 6.37 (1H, d, $J=9$ Hz), 6.84 (1H, d, $J=9$ Hz), 7.40 (1H, br. d, $J=7$ Hz), 7.76 (1H, dd, $J=7$ Hz, 7 Hz), 8.10 (1H, br. d, $J=7$ Hz). MS (CI-MS, NH₃ gas): m/z 630 [(M+NH₄)⁺].

Acid hydrolysis of RN-B and subsequent acetylation (formation of the hexaacetate of deglucosyl-RN-B and ethyl tetra-*O*-acetyl-D-glucopyranoside). A solution of RN-B (200 mg) in 2N hydrochloric acid (5 ml) was refluxed for 1.5 hr. The reaction mixture was concentrated after adding ethanol and benzene under reduced pressure, and then separated by column chromatography [Kieselgel PF₂₅₄, *n*-BuOH-AcOH-H₂O (4:1:1)] into two fractions containing crude deglucosyl RN-B and the sugar compounds, respectively.

The deglucosyl RN-B fraction was acetylated by adding pyridine and acetic anhydride to give the hexaacetate of deglucosyl-RN-B (59 mg), which was further purified by preparative TLC [Kieselgel PF₂₅₄, benzene-AcOEt (1:1)] to afford crystalline deglucosyl RN-B hexaacetate, mp 134~135°C (12 mg).

The fraction containing the sugar compounds was acetylated by the same treatment to give the acetylated

product (50 mg), which was purified by repeated preparative TLC on a Kieselgel PF₂₅₄ plate developed with benzene-AcOEt (5:1) to give two compounds, their *R_f*-values being 0.54 and 0.46, respectively, with a 6 mg yield of each. These samples were identical with the α - and β -derivatives of ethyl tetra-*O*-acetyl-D-glucopyranoside, respectively, regarding their optical rotation and NMR spectral data.

Hexaacetate of deglucosyl-RN-B: mp 134~135°C. UV (MeOH) λ : 243 (ϵ 16,500), 284 shoulder (ϵ 18,500), 292 (ϵ 21,000), 319 shoulder (ϵ 8900), 332 shoulder (ϵ 7700) and 404 (ϵ 4500) nm. IR (KBr) ν : 3450 br., 1750, 1695 and 1670 cm⁻¹. ^1H -NMR 400 MHz (CDCl₃) δ : 1.16 (3H, br. s), 2.01 (3H, s), 2.06 (3H, s), 2.10 (3H, s), 2.23 (3H, s), 2.35 (3H, s), 2.36 (3H, s), 2.01~2.36 (2H, superimposed on MeO signals), 2.88 (1H, dd, $J=10.6$ Hz, 2.1 Hz), 3.83 (1H, m), 4.09~4.28 (3H, m), 4.19 (1H, br. s), 5.06 (1H, dd, $J=9.6$ Hz, 9.6 Hz), 5.31 (1H, dd, $J=10.6$ Hz, 9.6 Hz), 5.41 (1H, d, $J=2.1$ Hz), 5.75 (1H, br. s), 6.47 (1H, s), 7.22 (1H, br. d, $J=8.0$ Hz), 7.41 (1H, dd, $J=8.0$ Hz, 8.0 Hz), 7.90 (1H, br. d, $J=8.0$ Hz). MS m/z : 818 (M⁺) (in-beam EI). High-resolution MS: m/z 758.1528; calcd. for C₃₅H₃₄O₁₇S, 758.1514 (M⁺ - 60).

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