Table 1. Sphingosine composition of human blood plasma sphingomyelins. In the shorthand designations used d stands for dihydroxy; the number before the colon indicates carbon chain length and the number after the colon number of double bonds. See text for further details.

Aldehyde identified	Parent base	Relative amounts Natural bases	Hydrogenated bases
Tetradecanal	d16:0	1	11
Tetradecenal	d16:1	10	0
Pentadecanal	d17:0	0.3	5
Pentadecenal	d17:1	5	0
Hexadecanal	d18:0	1.5	80
Hexadecenal	d18:1	65	0
Hexadecadienal	d18:2	15	0
Unidentified	Unidentified	2	4

configuration of carbon atom 2 is analogous to sphingosine [7] and probably D.

The purified DNP-derivatives of total natural and hydrogenated bases were oxidized with lead tetraacetate and the aldehydes produced quantitatively analyzed by gas chromatography on Reoplex 400 columns (Fig. 1 and Table 1). The lower sphingosine homologues have been identified before.[3,6] The unidentified peaks may be monoenic, branched chain [8] dihydroxy bases.

Based on the above reported findings the dienic long chain base may be given the following structure: D-*erythro*-1,3-dihydroxy-2-amino-4, 14(*cis*, *trans*)-octadecadiene. In analogy with sphingosine the *trans* double bond is probably in the 4 position. The unusual location of the extra double bond close to the methyl end of the long chain base may have a special biological meaning.

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Bacterial Carotenoids

XXVI.* C_{50}-Carotenoids. 2. Bacterioruberin

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The principal carotenoid of several halophilic bacteria, α-bacterioruberin, was assigned the structure *1* on the basis of earlier work in this laboratory.[1-3] However, 1,1'-dihydroxy-3,4,3',4'-tetradehydro-1,2,1',2'-tetrahydrolycopene (*1*, $C_{40}H_{56}O_2$) has recently been synthesized by Schneider and Weedon and a direct comparison with natural α-bacterioruberin revealed that the two compounds are not identical.[4,5] The structure of bacterioruberin (the prefix α should be reserved for carotenoids containing an α-cyclogeranylidene ring and will be omitted) is now being re-investigated using improved methods including NMR and mass spectrometry.

The molecular formula $C_{50}H_{76}O_4$ has been established by high resolution mass spectrometry. The previously reported physical data for bacterioruberin have been confirmed, as has the absence of primary, secondary and allylic hydroxyl groups and functional groups susceptible to hydride reduction: the infrared data preclude functional groups other than tertiary hydroxyl groups. Experiments involving silylation [6] and dehydration (with phosphorus oxychloride [7]) demonstrated the presence of four tertiary hydroxyl groups. The silylation reaction was shown to comprise four consecutive steps by isolation of three

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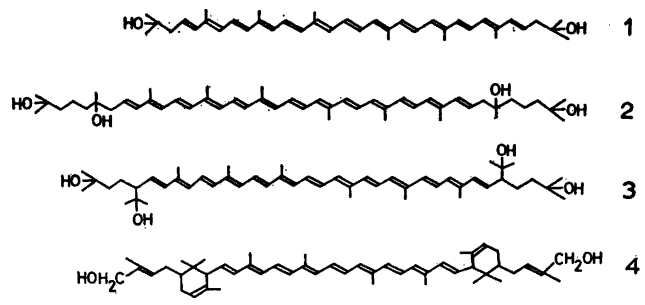

intermediates, which gave the expected products on further silylation or alkaline hydrolysis. All four silyl ethers gave bacterioruberin on complete hydrolysis. The dehydration reaction was similarly shown to involve four consecutive reactions, the extent of dehydration being verified by silylation. No change in the visible light absorption spectrum occurred during dehydration. Partition ratios [8] and R_F-values [9] for bacterioruberin and its silylation and dehydration products are given in Table 1. The presence of four hydroxy groups in bacterioruberin is also supported by integration of the NMR-spectrum of bacterioruberin per-trimethylsilyl ether (signals at *ca.* τ 9.8—10 and τ 8.02—8.06 in ratio 2:1).

The methyl signals of the NMR-spectrum are in accordance with a chromophore

Table 1. Adsorptive properties and partition ratios of various *trans* derivatives of bacterioruberin.

Compound	R_F-value Schleicher & Schüll No. 287 paper					Partition ratio	
	20 % [a]	10 %	5 %	2 %	1 %	Petroleum ether/95 % methanol	Petroleum ether/85 % methanol
Bacterioruberin	0.43						3:97 [b]
mono-TMS ether	0.71	0.29	0.07			16:84	60:40
di-TMS ether		0.44	0.16	0.10		68:32	
tri-TMS ether		0.91	0.66	0.24		100:0	
tetra-TMS ether				0.96		100:0	
Mono-anhydro-bacterioruberin	0.70	0.22				3:97	29:71
mono-TMS ether		0.46	0.12				
di-TMS ether		0.90	0.61				
tri-TMS ether					0.90		
Bis-anhydro-bacterioruberin		0.45	0.19	0.05		34:66	85:15
mono-TMS ether			0.65	0.23			
di-TMS ether			0.99	0.99			
Tris-anhydro-bacterioruberin		0.83	0.50	0.23		84:16	
mono-TMS ether			0.96	0.70			
Tetra-anhydro-bacterioruberin			0.92	0.70			

[a] Acetone in petroleum ether
[b] 29:71 in petroleum ether/70 % methanol
TMS = trimethylsilyl

identical with that of *1* (signals at τ 8.02 and 8.06 in ratio 2:1 and absence of end-of-chain methyl signal at τ 8.19). In particular two structures are being considered, a decapreno-carotenoid with linearly extended isoprenoid chain (*2*) and structure *3*, the carbon skeleton of which is analogous with that of the structure recently assigned to *dehydrogenans*—P439 (*4*).[10,11]

In the mass spectrum significant peaks due to the loss of up to two fragments of 58 mass units (acetone) from the molecular ion and from other major fragments are better accommodated by structure *3*. The NMR-spectra so far obtained do not permit a differentiation between *2* and *3*.

Further work on the structure of bacteriorubberin including syntheses of model substances is in progress and further details will be published.

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N-Isothiocyanatoamines

VI. The Reactivity of *N*-Isothiocyanatodiisopropylamine towards Hydrogen Sulfide, Thio- and Selenoamides

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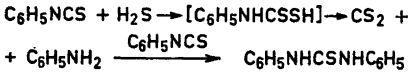
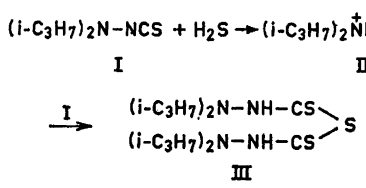
Phenyl isothiocyanate is known to react with hydrogen sulfide at room temperature to form carbon disulfide and 1,3-diphenylthiourea.[1] The reaction probably takes place *via* phenyldithiocarbamic acid. This in turn undergoes spontaneous decomposition into carbon disulfide and aniline, which is converted to the thiourea by excess phenyl isothiocyanate.



In a related reaction,[2] phenyl isothiocyanate under forcing conditions eliminates hydrogen sulfide from thiourea to form, in addition to the above products, cyanamide. During our work on *N*-isothiocyanatoamines,[3-7] we examined the reaction between N-isothiocyanatodiisopropylamine (I) and hydrogen sulfide, expected to give the stable *N*,*N*-diisopropyldithiocarbazic acid (II).[7,8] However, the product obtained was identified as bis-(*N*,*N*-diisopropylthiocarbazoyl)sulfide (III). The following mechanism is proposed.



A sample of II was prepared[7] from diisopropylhydrazine and carbon disulfide.