

Synthesis of Sphingolipids Which Affect Physiological Function of Skin

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Synthesis of four diastereomeric cerebroside B_{1a} (1a) and B_{1b} (1b) has been achieved. The crucial step in the synthesis of cerebroside B_{1b} consists in a regio- and stereoselective formation of the *erythro*-sphingosine moiety by the reaction of dienal 4 with 2-nitroethanol followed by resolution with optically active α -hydroxypalmitic acids. Using the aglycone thus obtained, the first total synthesis of optically active cerebroside B_{1a} and B_{1b} was accomplished. The absolute configuration of 1b was determined to be (2S, 3R, 4E, 8Z, 2'R)-1-O-(β -D-glucopyranosyl)-N-(2'-hydroxyhexadecanoyl)-4,8-sphingadienine.

Our developed methods for preparation of *erythro*-sphingosine has been applied to the first total synthesis of symbioramide (2), a novel ceramide obtained from the cultured dinoflagellate *Symbiodinium sp.*, which is the first example of SR Ca²⁺-ATPase activator of marine origin and also exhibits antileukemic activity and simultaneously established the complete stereostructure of 2 to be (2S, 3R, 2'R, 3'E)-N-(2'-hydroxy-3'-octadecenoyl)-dihydro-sphingosine.

A new sphingosine derivative (3) isolated and characterized as an N-lauroyl derivative from *Anemonia sulcata* collected near Sousse, was also synthesized and the *L-erythro* configuration of 3 was firmly established.