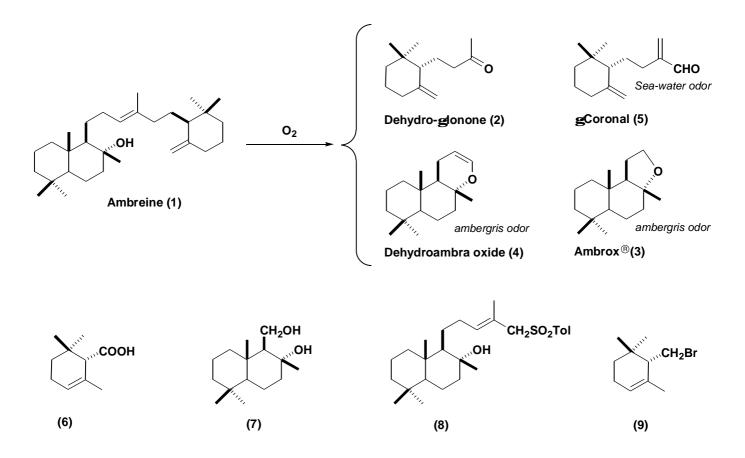
Synthesis of Ambergris-fragrances and (+)-Ambreine

Takayuki Oritani

Division of Biosciene, Graduate School of Agricultural Science, Tohoku University, Sendai 981-8555, Japan. Fax: 8122-717-8783, E-mail: oritani@biochem.tohoku.ac.jp

Ambergris, a precious animal perfume obtained as an intestinal concret ion in the sperm whale, is composed principally of non-volatile material: 30-40% of epicoprosterol and 25-45% of ambrein (1) – a tricyclic triterpene alcohol. Autoxidative decomposition of ambreine (1) resulted in volatile odoriferous constituents as follows: C_{11} - γ -cyclohomogeranial, C_{13} -dihydro- γ -ionone (2), C_{14} - γ -coronal (5), C_{16} -ambrox (3) and C_{17} -dehydroambra oxide (4).

First, the absolute stereochemistry of dihydro- γ -ionone (2) was confirmed by synthesis of (+)-(S)-2 from (-)-(S)- α -cyclogeranic acid (6). Cyclization of farnesyl acetate with chlorosulfonic acid gave (±)-drimane-8,11-diol 11-acetate, which was resolved by lipase catalyzed hydrolysis to give (+)-drimane-8,11-diol (7). A series of one carbon elongation reactions of (+)-7 gave (-)-ambrox (3). Wittig reaction of (+)-ambreinolal, prepared from (+)-7, with 1-methoxycarbonylethylidenetriphenylphosphorane, followed by DIBAL reduction, chlorination and then the reaction with sodium tolylsulfinate, gave the allylic sulfone (8). Enantiomerically pure (+)-ambreine (1) was synthesized by the coupling of the C₂₀-bicyclic building block (8) and (+)- γ -cyclogeranyl bromide (9). (+)- γ -Coronal (5) was synthesized by the coupling of (+)-9 with ethyl 3-tributylstannyl-2-methylenepropanoate by Baldwin's method, followed by DIBAL reduction and MnO₂ oxidation.



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