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The Structure of Squalene-Derived Polyether, 15(28)-Anhydrothysiferyl  
23-Acetate Isolated from the Marine Red Alga  
*Laurencia obtusa* (Hudson) Lamouroux

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紅藻マギレソゾ (*Laurencia obtusa*) から単離されたスクワレン由来の  
ポリエーテル、15(28)-anhydrothysiferyl 23-acetate の構造

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## ABSTRACT

Investigation on the constituents of the marine red alga *Laurencia obtusa* (Hudson) Lamouroux (“magiresozo” in Japanese) collected at Teuri Island off the coast of Haboro near Rumoi in Hokkaido enabled the isolation of a new squalene-derived polyether that was a minor component. Its structure was elucidated as 15(28)-anhydrothysiferyl 23-acetate on the basis of spectral evidence and chemical transformation.

## INTRODUCTION

Among the species of *Laurencia*, *L. obtusa* (“magiresozo” in Japanese) has drawn great attention in view of both diversity of metabolites and taxonomic confusion. In the course of our investigation on the constituents of *L. obtusa* collected at Teuri Island off the coast of Haboro in Hokkaido, we reported the various kinds of oxygenated squalene derivatives, 2, 3, 4, 5, 6, and 7<sup>1)</sup> (Fig. 1) which were very different from those isolated from the same species collected on the Atlantic Ocean or the Mediterranean Sea (Fig. 2)<sup>2)</sup>. Further investigation of the extract obtained from the title alga collected at Teuri Island led to the isolation of a new compound that was a minor component, classified to the oxygenated squalene. Combination of spectral analyses and chemical transformation to the known compound 2 enabled the researchers to assign its structure as 15(28)-anhydrothysiferyl-23-acetate (1). In this paper we would like to report the isolation and structural determination of this new compound.

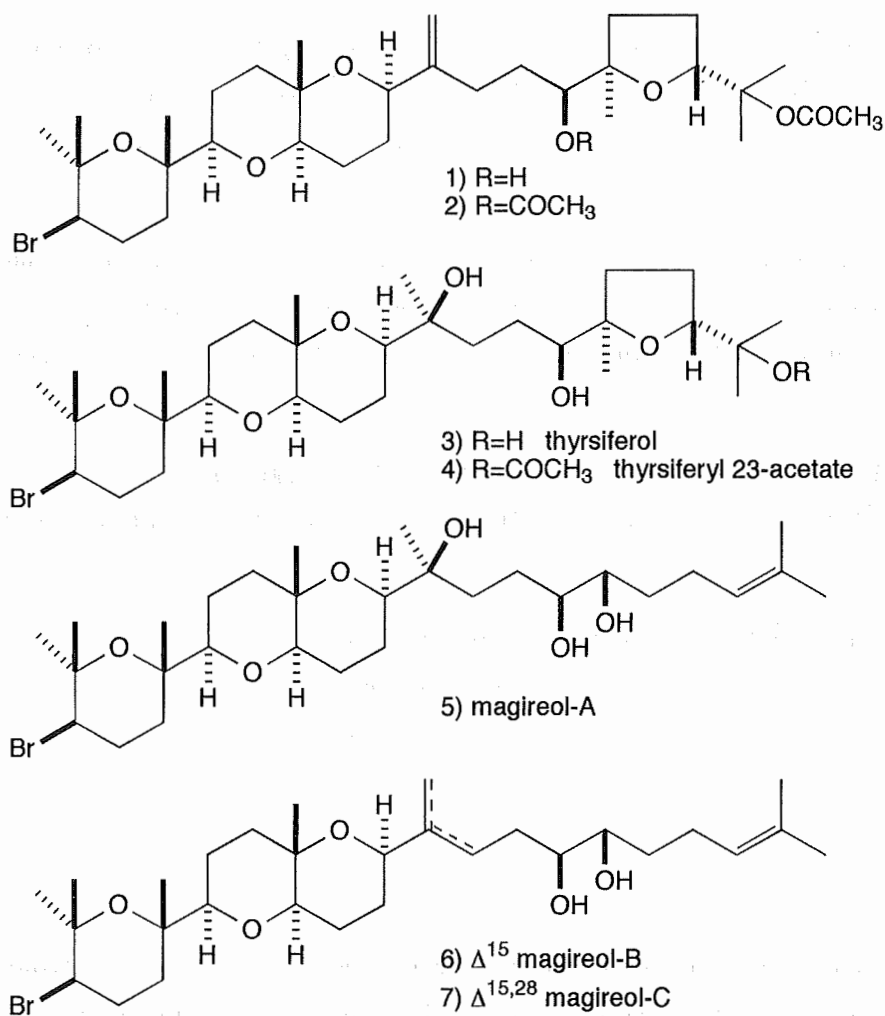


Fig. 1. Representative squalene-derived polyethers isolated from *Laurencia obtusa* collected at Teuri Island

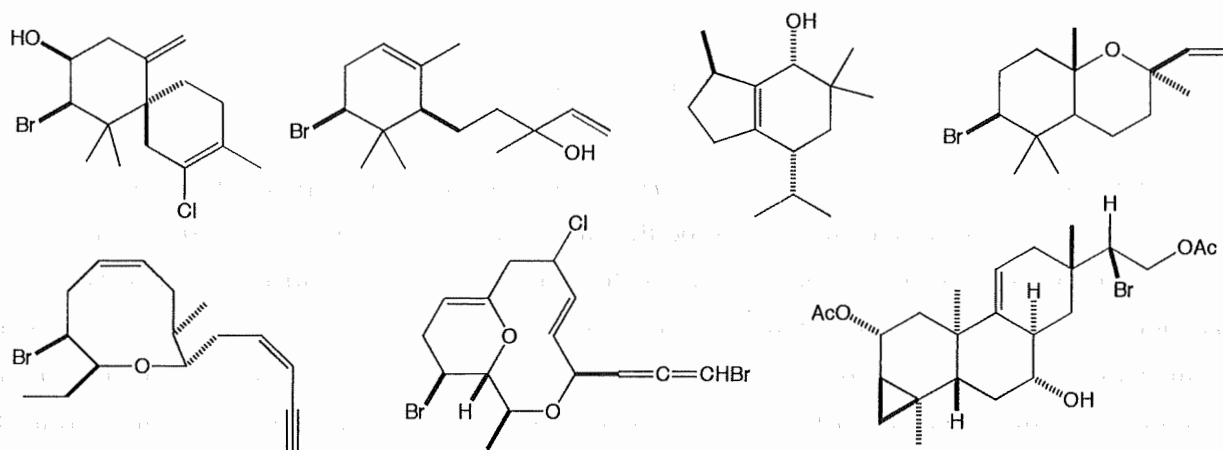


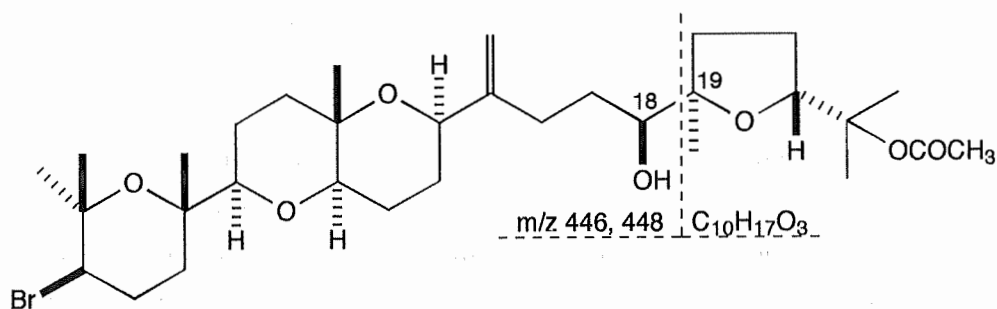
Fig. 2. Representative metabolites isolated from *L. obtusa* collected on the Atlantic Ocean or Mediterranean Sea.

## RESULTS AND DISCUSSION

**Isolation procedure:** The neutral extract (2.0 g) obtained from the fresh alga by the ordinary method using methanol was subjected to separation by silica-gel column chromatography. After removal of non-polar components by benzene elution, ethyl acetate was eluted to afford a greenish viscous oil. Checking by TLC showed the presence of complex components. The ethyl acetate fraction was further separated by open column chromatography on reverse phase (C-18) support with a step gradient in a total of four runs. For each run, 15% and 5% water, 5% dichloromethane in methanol and dichloromethane were used as eluents, in that order. The fraction eluted with a mixed solvent of methanol and water (85 : 15) was further purified on Megpack Sil C-18 HPLC column using 10% water in methanol to yield the pure new compound 1 as a glassy solid (0.2 % yield on the basis of the neutral oil) in addition to the known compounds, thysiferol (2) and thysiferol 23-acetate (3).

**Structure of the new compound 1 :** The compound 1, glassy solid,  $[\alpha]_D + 9.3^\circ$  ( $\text{CHCl}_3$ ,  $c=1.18$ ) was analyzed for  $\text{C}_{32}\text{H}_{53}\text{O}_7\text{Br}$  by HR-MS (FI-MS, obsd  $m/z$ , 629.3083, calcd for  $\text{C}_{32}\text{H}_{54}\text{O}_7^{81}\text{Br}$ ,  $m/z$ , 629.3092) and showed strong absorption at  $950\text{--}1200\text{ cm}^{-1}$  in its IR spectrum, suggesting the presence of ether linkages in the molecule. Its DEPT spectrum showed the presence of eight methyls ( $\delta$  19.5, 20.1, 22.1 x 2, 22.5, 23.6, 23.7, and 31.0), eleven methylenes ( $\delta$  21.7, 23.0, 26.3, 26.8, 28.3, 29.5, 29.9, 31.2, 37.1, 38.7, and 109.8), six methines ( $\delta$  59.1, 72.5, 76.1, 78.7, 86.1, and 86.7), and seven quaternary carbons ( $\delta$  72.9, 74.4, 75.0, 82.5, 86.4, 151.4, and 170.4). The presence of hydroxyl and an acetoxy group(s) is evident in its spectral data [ $\nu_{\text{max}}$  3400, 1730, and  $1210\text{ cm}^{-1}$ ;  $\delta$  1.99 (3H, s),  $\delta$  170.4]. Since all six methine signals [ $\delta$  3.09 (dd,  $J=10.7, 2.4\text{ Hz}$ ), 3.42 (dd,  $J=11.2, 5.4$ ), 3.51 (br t,  $J=7.3$ ), 3.89 (dd,  $J=12.2, 3.9$ ), 4.01 (dd,  $J=9.3, 5.6$ ), 4.28 (br t,  $J=4.9$ )] were shifted in the low field region of the  $^1\text{H}$  NMR spectrum coupled with the isolation of various kinds of squalene-derived polyethers from this *L. obtusa*, it was deduced that 1 is a kind of squalene-derived polyether. On detailed comparison of the spectral properties of 1 with 3, 4, 5, 6, and 7, it was suggested that the structure of 1 is similar to that of thysiferol 23-acetate (3), except for the presence of an *exo*-methylene group [ $\delta$  4.88 and 5.04 (1H each, br s),  $\delta$  109.8 and 151.4], instead of one of eight methyl groups in 3. Whereas thysiferol 23-acetate (3) has eight oxygen atoms and nine methyl groups in the molecule, the compound 1 displayed the presence of seven oxygen atoms in its HR-MS and eight tertiary methyl groups [ $\delta$  1.14, 1.20, 1.23, 1.27, 1.40, 1.44, 1.48, and 1.99 (3H each, s),] and one *exo*-methylene group [ $\delta$  4.88 and 5.04 (1H each, br s),  $\delta$  109.8 and 151.4] in its  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, suggesting that 1 is derived via dehydration of a 1-hydroxyethylidene group in 3. Absence of a signal due to a vinyl methyl group in 1 in its  $^1\text{H}$  NMR spectrum indicates the *exo*-methylene group to be located at C-15(28). The arrangement of the acetoxy group on C-23 in 1 was elucidated on the basis of the absence of a signal due to a proton on carbon bearing an acetoxy group in the  $^1\text{H}$  NMR spectrum and the presence of fragment ions at  $m/z$  486, 488 ( $\text{M}^+ - \text{C}_{10}\text{H}_{17}\text{O}_3$ ) in the MS spectrum as the fragments resulting from cleavage between the C-18 and C-19 bond, shown as follows.

Consequently, Formula 1 could be proposed for this compound. Confirmation of the structure



of 1 was carried out as follows. The compound 1 was treated with acetic anhydride and pyridine at room temperature for 16 h and the product was purified by silica-gel chromatography to yield a pure corresponding acetate which was found to be identical to 2 in all respects including optical rotation,  $[\alpha]_D + 9.83$  (CHCl<sub>3</sub>, c = 0.30). Therefore, the structure of compound 1 including absolute configuration is represented by Formula 1.

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