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A NEW HALOGENATED C_{15} NON-TERPENOID COMPOUND FROM THE MARINE RED ALGA, *LAURENCIA OBTUSA*

KIRMIZI DENİZ YOSUNU *LAURENCİA OBTUSA*'DAN YENİ BİR HALOJENLİ C_{15} NON-TERPENOİD MADDE

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Kırmızı deniz yosunu Laurencia obtusa Türk kıyılarında oldukça fazla dağılmış ve toplanan bölgeye ve zamana bağlı olarak değişen çok zengin halojenli sekonder metabolitlerin kaynağıdır. Bu çalışmada Laurencia obtusa'dan yeni bir C_{15} terpenoid olmayan asetilenik madde izole edildi ve yapısı spektroskopik metodlarla aydınlatıldı.

Anahtar Kelimeler: *Laurencia obtusa; Kırmızı deniz yosunu; Deniz kaynaklı doğa madde*

Introduction

The red marine alga *Laurencia obtusa* is widely distributed in Turkish waters and a rich source of halogenated secondary metabolites, which vary depending on the collecting region and season(1-3). In the present work we have isolated a new C_{15} nonterpenoid acetylenic compound from *Laurencia obtusa* and its structure was deduced by spectroscopic methods.

Materials and Method

General procedure

Melting point was determined on a melting point microscope (Reichert) and was uncorrected. Optical rotation was measured with a warning polarimeter. The IR spectrum was obtained on a Perkin-Elmer 1600 FT-IR instrument as a film on a NaCl disk. Mass spectra were taken on AEI MS 30 and Kratos MS 50 (reagent gas for CI-MS: NH3). The ^1H and ^{13}C NMR spectra were recorded on 360 and 90.5 MHz appartus respectively in $CDCl_3$, using TMS as internal standard. The following silica gels were used: silica gel GF_{254} (Merck) for analytical (0.25 mm) and preparative (0.5 mm) TLC.

Extraction and Isolation

Laurancia obtusa was collected in April 1992 at Didim near Aydın, air-dried, and ground with a blender. Dried alga (460 g) was macerated with $CHCl_3$/MeOH (2:1, v/v) to afford 25 g extract. The extract was chromatographed on a silica gel column (35-70 mesh; 4.6x45 cm) with petrol (50-75°C) and increasing amounts of Et_2O (v/v). The residue (1.6 g) from the combined fractions 103-120 (Et_2O) was further chromatographed on silica gel column (70-230 mesh; 1.5x25 cm) with $CHCl_3$, then subjected to prep. TLC with petrol/ether(1:1) and was chromatographed on a silica gel column (70/230 mesh; 1.5x15 cm) with ether to give pure compound **1** (96mg).

Compound 1

Colorless solid, m.p. 58-60°C. $[\alpha]_D^{25}$ = +36.67° (c 0.54, MeOH); IR ν_{max} (NaCl) 3287, 3025, 2919, 2849, 2361, 2095, 1735, 1459, 1374, 1240, 1053, 952, 850 cm^{-1}; ^1H and ^{13}C NMR (Table); MS m/z (rel. int.) Cl 355, 357 (100:99.3) $[M^{+1}]$, 295, 297 (39.7:38.2) $[M\text{-}CH_3CO_2H]^+$, 289, 291 (15:1:14.7) $[M\text{-}C_5H_5]$+, 233(12.8) $[M\text{-}C_3H_6Br]^+$, 215 (73.9) $[M\text{-}Br\text{-}CH_3CO_2H]^+$, 174(11.7)$[M\text{-}CH_3CO_2H\text{-}C_3H_6Br]^+$, 107(43.4), 93(17.3).

Results and Discussion

The IR spectrum of compound **1** showed the presence of acetylene (3287, 2095 cm^{-1}) and ester carbonyl (1735 cm^{-1}) groups. Although, compound **1**

failed to show a molecular ion in EI-MS, CI-MS showed $[M+1]^+$ peaks at m/z 355, 357 with the intensities of 100:99.3 indicating the presence of one bromine atom. The molecular formula of $C_{17}H_{23}BrO_3$ was deduced from CI-MS spectrum, suggesting six degress of unsaturation and ^{13}C NMR-DEPT spectrum [2xCH_3, 4xCH_2, BrCH, 3x OCH, 2x CH=CH, -C≡CH, CO]. The mass, ^1H NMR and spin decoupling experiments indicated the presence of a *cis* conjugated terminal enyne group [(m/z 289, 291 $[M-C_5H_5]^+$; δ 3.13 (1H, d, J=2.1 Hz), 5.56 (1H, dd, J=10.8, 2.1 Hz) and 6.01 (1H, ddd, J=10.8, 7.6, 7.6Hz)]. This was in agreement with the *cis*-configuration of the double bond in the enyne side chain of other related metabolites such as Z-dihydrorhodophytin **2**(4), *cis*-pinnatifidenyne **3** (5). The mass spectrum also indicated a significant peak, $[M-C_3H_6Br]^+$, corresponding to fragmentation of CHBr-CH_2-CH_3 side chain. The NMR data (Table) also showed two additional vinly protons which was placed at C_9 and C_{10} and the presence of an acetoxyl group attached to C_7. Detailed ^1H NMR spin decoupling experiments of **1** combined with ^1H-^1H and ^1H-^{13}C COSY spectra led to of all protons for the straight carbon skeleton shown in fig 1.

Table. ^{13}C and ^1H NMR spetral data of compound 1

Carbon No.	δC[a]	δH[b](J, Hz)
1	82.38	3.13 d, 2.1
2	80.08	
3	110.89	5.56 dd, 10.8, 2.1
4	140.34	6.01 ddd, 10.8, 7.6, 7.6
5	34.28	2.51-2.69 m
6	72.70	4.09-4.15 m
7	74.99	4.91 ddd, 7.5, 1.5, 1.1
8	29.25	2.51-2.69 m 2.35 ddd, 14.2, 7.4, 2.7
9	127.10	5.76 dd, 10.4, 7.7
10	130.17	5.87 dd, 10.4, 7.7
11	30.49	2.51-2.69 m
12	79.59	3.99 ddd, 10.5, 7.6, 2.9
13	59.79	4.09-4.15 m
14	30.05	1.82 ddq, 15.1, 7.8, 7.8 2.20 dddd, 15.1, 7.2, 2.9
15	12.06	1.10 t, 7.2
16	170.74	
OAc	21.29	2.14 s

Assignments made by ^1H-^1H and ^1H-^{13}C COSY. Recorded in CDC_{13} at [a]90.5 MHz and [b]360 MHz.

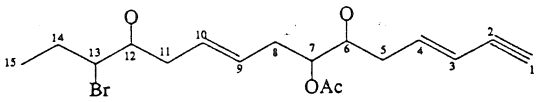
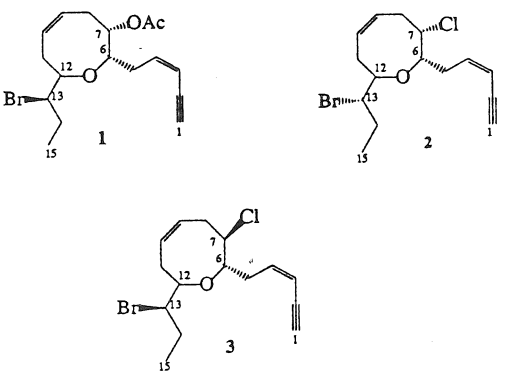


Fig. 1



The complete structure of **1** was established from comparison of its NMR spectra with the previously described acetylenes: Z-dihydrorhodophytin **2**(4), *cis*-pinnatifidenyne **3**(5) and other similar natural compounds (1,2, 6,7, 11,12). The ^1H NMR coupling constant between H_6 and H_7 (J=1.1, 1.5) suggests that both H_6 and H_7 are equatorial (4).

Furthermore, the relative stereochemistry of the bromine atom at C_{13} was deduced to be β from comparison coupling constant of H_{13} H_{12} and H_{14} with those of previously published data (5, 12). Based on all these data, structure of compound **1** was proposed to be that of formula 1.

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