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2,3-DIMETHYL-4-METHOXYBUTENOLIDES FROM RED ALGAE, COELOSEIRA PACIFICA AND AHNFELTIA PARADOXA

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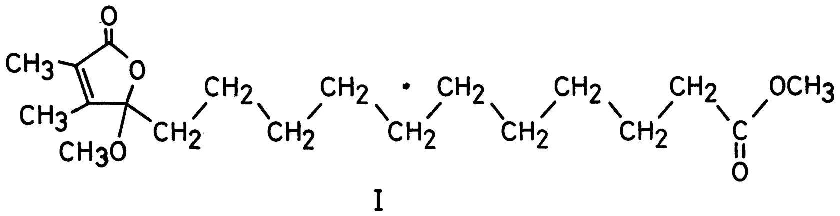
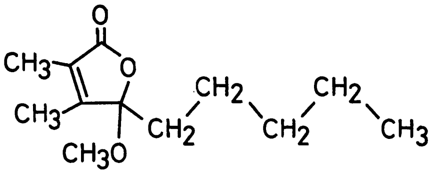
Three new butenolide derivatives were isolated from the red algae, C. pacifica and A. paradoxa. The structures of these compounds were determined from their spectral properties, one of which was confirmed by synthesis.

In the course of our chemical studies on marine algae of the Japanese coast,[1)] we have found three substances from the red algae, Coeloseira pacifica Dawson and Ahnfeltia paradoxa Okamura. This letter deals with the isolation and structural determination of these unprecedented lactones.

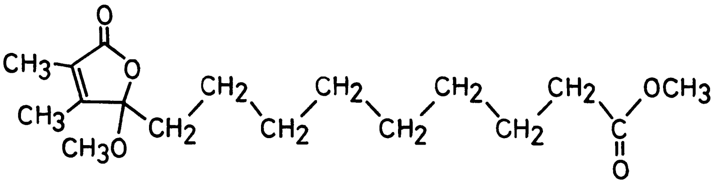
Silica gel chromatography of the hexane soluble portion of the methanol extract of fresh C. pacifica (Isomatsu in Japanese), collected at Chōshi, Chiba, in May 1979, followed by preparative TLC and HPLC gave colorless crystals (compound I), mp 54-55 °C. A molecular formula of $C_{19}H_{32}O_5$ was established for I by accurate MS measurement of the M^+-CH_3O peak (found 309.2083, calcd 309.2066) in conjunction with the analysis of proton decoupled and off resonance ^{13}C-NMR spectra. The IR (CCl_4) absorption at 1738 cm^{-1}, ^1H-NMR (CCl_4) singlet(3H) at δ 3.61 and ^{13}C-NMR ($CDCl_3$) signals at δ 174.2(s), 51.4(q) revealed the presence of $COOCH_3$ group. Attachment of this ester group to $[-(CH_2)_{10}-]$ was deduced from the ^1H-NMR signals at δ 2.22 (2H, t), 1.9-1.5(2H, m), 1.5-1.2(16H, br. s), and ^{13}C-NMR signals at δ 35.5(t), 34.0(t), 29.3(br. t; 4C), 29.1(br. t; 2C), 24.9(t), 22.6(t). The IR absorptions at 1768, 1690 cm^{-1}, a UV maximum at 211 nm (ε 9,400) and ^{13}C-NMR signals at δ 171.6(s), 155.8(s), 127.2(s) indicated the presence of a butenolide moiety. The characteristic signals at δ 110.0(s), 50.0(q) in ^{13}C-NMR and 3H-singlet at δ 3.05 in ^1H-NMR detected a methoxy group bonded to the γ-carbon atom of the butenolide. That the two methyl groups are bonded to α- and β-carbon atoms of the butenolide was deduced from a 6H-sharp singlet at δ 1.82 in ^1H-NMR, which was splitted to two broad singlets at δ 1.59 and 1.33 in C_6D_6, and two quartets at δ 10.7 and 8.4 in ^{13}C-NMR. These spectral properties revealed the structure I for the new compound. The MS spectrum, m/e 309 (M^+-CH_3O), 281, 277($M^+-CH_3OH-CH_3O$), 276, 267, 235, 141[base peak, $M^+-(CH_2)_{10}COOCH_3$], 137, 125 and 113, supported the structure.



I

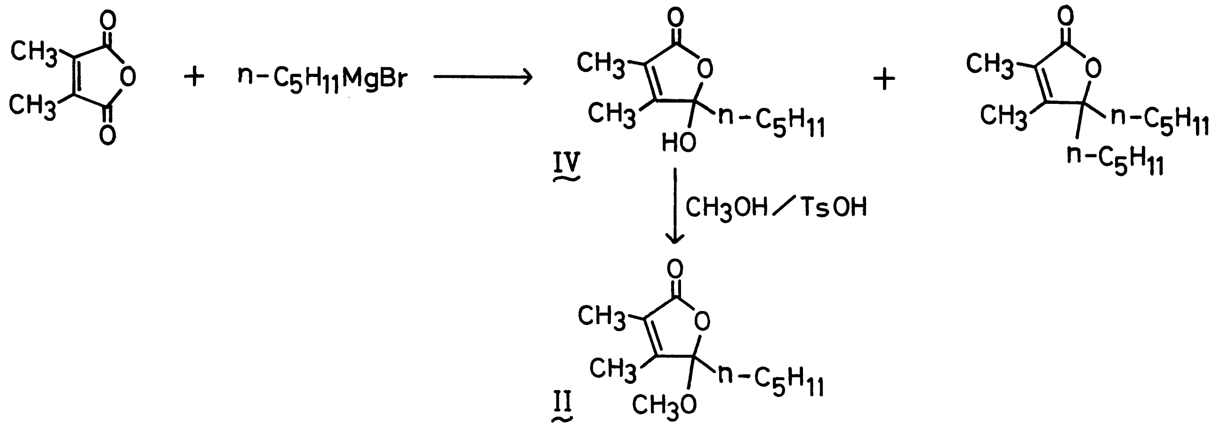


II



III

Along with the constituents of C. pacifica, we investigated the constituents of A. paradoxa (Harigane in Japanese), collected at Chōshi, Chiba, in May 1979, and found that this red alga contains two new substances, compound II, oil, $C_{12}H_{20}O_3$, m/e found 181.1204, calcd for M^+-CH_3O 181.1228, and compound III, $C_{17}H_{28}O_5$, together with compound I. Compound II showed the very similar spectral features[2)] to those of compound I except that the aliphatic ester moiety of compound I was replaced by n-amyl group in compound II. The supposed structure II was confirmed by the synthesis from dimethylmaleic anhydride and n-amyl magnesium bromide followed by methanolysis. The natural compound II was coincident with the synthetic compound in all respects.[3)]



Although compound III was detected in very minute amount, the structure III was deduced from the analysis of the MS spectrum; m/e 281(M^+-CH_3O), 253, 249(M^+-CH_3OH-CH_3O), 248, 239, 207, 141[base peak, M^+-$(CH_2)_8COOCH_3$], 137, 125 and 113.

The butenolide II was further found to be contained in other red algae, Porphyra yezoensis Ueda (Susabinori) and Hypnea japonica Tanaka (Kagiibaranori).

The authers wish to express their thanks to Professor Yasuji Yamada of Tokyo Pharmaceutical College for measurements of accurate MS spectra, and to Professor Mitsuo Chihara of this University for collection and identification of the algae.

Reference and Notes

1) Previous paper; M. Ishitsuka, T. Kusumi, Y. Nomura, T. Konno, and H. Kakisawa, Chem. Lett., 1979, 1269.
2) UV (MeOH) 211 nm (ε 9,600); MS m/e 181, 153, 141(base), 125, 113; IR (film) 1765, 1690 cm^{-1}; ^1H-NMR (CCl_4) δ 3.04(3H, s), 1.82(6H, s), 2.0-1.5(2H, m), 1.5-1.2 (6H, br.s), 0.93(3H, t); ^{13}C-NMR ($CDCl_3$) δ 171.7(s), 156.0(s), 127.3(s), 110.1(s), 50.1(q), 35.5(t), 31.6(t), 22.4(t, 2C), 13.9(q), 10.8(q), 8.4(q).
3) Compounds I and II showed $[\alpha]_D$=0, and these compounds were possible to be present in algae as lactol forms such as IV and the methyl group was incorporated in the course of isolation process.

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