Tetrahedron Letters,Vol.23,No.31,pp 3179-3180,1982
Printed in Great Britain 0040-4039/82/313179-02$03.00/0

ACETYLSANADAOL, A DITERPENE HAVING A NOVEL SKELETON, FROM THE BROWN ALGA, PACHYDICTYON CORIACEUM

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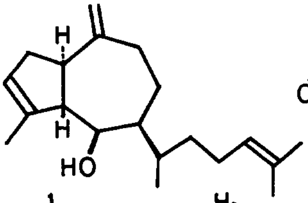
Abstract: Structures of new diterpenoids, sanadaol (4) and acetylsanadaol (5), isolated from Pachydictyon coriaceum, are determined, and sanadaol is produced by an acid-catalyzed ene reaction of dictyodial.

Brown algae of Dictyotaceae have been currently of interest because of their unique and biologically active constituents.[1] From Pachydictyon coriaceum, which was collected at the Gulf of California, two diterpenes, pachydictyol A (1)[2] and acetoxycrenulatin (2),[3] have been isolated. Here we wish to report the isolation of different type of diterpenes from the same species of alga, collected at the Izu-Shimoda beach. Chromatographic separation of the methanol extract (24.0 g) of P. coriaceum (sanadagusa in Japanese; collected in June, 1981)[4] afforded two new diterpenoids, sanadaol (4; 16 mg) and acetylsanadaol (5; 15 mg) together with the known diterpenes, dictyol E (240 mg),[5] and dictyolactone (500 mg).[6]

Sanadaol (4), $[\alpha]_D$ +74.8° (c 1.33, $CHCl_3$), IR($CHCl_3$) 3560 (OH), 2710, 1685, 1630 (C=C-CHO) cm^{-1}, showed the highest ion peak at m/e 302 corresponding to the molecular formula $C_{20}H_{30}O_2$ in the mass spectrum. The ^{13}C-NMR spectrum[7] also confirmed this molecular formula. The structure of sanadaol (4) was deduced from the ^1H-NMR spectrum (Table). Observation of long range couplings between H-2 and H-7 (J=1 Hz; W-type), and also H-2 and H-8a (J=1.5 Hz; homo-allylic) was helpful to elucidate the structure. The configuration of the hydroxy group at C-18 was determined by means of a lanthanide shift reagent; on addition of 0.39 molar equivalents of Eu $(fod)_3$, the signal due to the exomethylene protons (H-20) shifted to down-field much more



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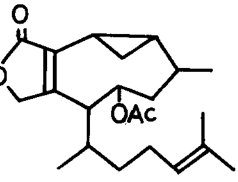

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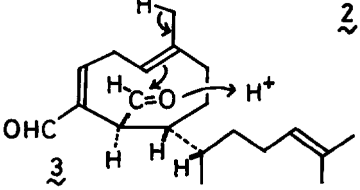

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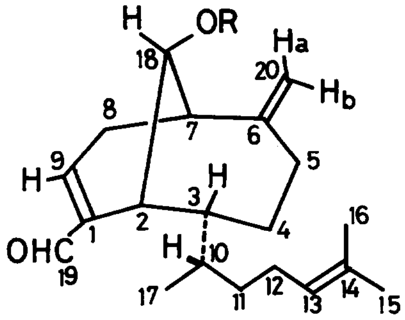

4; R=H 5; R=Ac

significantly (Δδ 1.58 for H-20a and 1.10 for H-20b) than those of H-9 (Δδ 0.73) and H-19 (Δδ 0.85). The structure 4 of sanadaol was unambiguously confirmed by the following chemical conversion. A solution of dictyodial in dichloromethane was allowed to stand with silica gel (Merck, Kieselgel 60, Art. 7734) at room temperature for 12 hr, affording sanadaol. An acid-catalyzed ene reaction might be involved in this transformation.

Acetylsanadaol (5),[8] $[\alpha]_D$ +42.5° (c 0.89, $CHCl_3$), IR($CHCl_3$) 1730, 1690, 1630 cm^{-1}, exhibited the ^{1}H-NMR spectrum essentially the same as that of sanadaol, except the presence of an acetyl signal and down-field chemical shift of H-18 in the former. Indeed, acetylation of 4 gave a product, the spectral data of which were identical with those of acetylsanadaol.

The bicyclo[4.3.1]decane skeleton of sanadaol (4) and acetylsanadaol (5) has never been found in natural products thus far. Formation of sanadaol from dictyodial (3) suggested that sanadaol could be an artifact which was produced during chromatographic separation. Moreover, sanadaol was not detected by thin layer chromatography in the crude methanol extract. However, acetylsanadaol is without doubt a natural product, since sanadaol could not be acetylated during the isolation process.

Table. ^{1}H-NMR spectrum (270 MHz) of sanadaol (4) ($CDCl_3$)

proton	chemical shift (δ)	proton	chemical shift (δ)
H- 2	3.19 (dddd,J=5.0,1.5,1,1 Hz)	H-12	2.0 (2H,m)
3	1.6 (obscured by Me signals)	13	5.16 (t,J=7.0 Hz)
4	1.3 (2H,m)	15	1.69 (s)
5	2.25 (2H.m)	16	1.62 (s)
7	2.88 (dddt,J=7.0,4.3,1,1 Hz)	17	0.77 (d,J=6.2 Hz)
8a	2.75 (dddd,J=21.0,7.0,3.5,1.5 Hz)	18	3.78 (ddd,J=9.0,5.0,4.3 Hz)
8b	2.56 (dd,J=21.0,3.5 Hz)	19	9.47 (d,J=1 Hz)
9	6.80 (td,J=3.5,1 Hz)	20	4.90 (2H,td,J=1,1 Hz)
10	1.6 (obscured by Me signals)		
11	1.0 (2H,m)	OH	2.10 (d,J=9.0 Hz)

Acknowledgements: The authors wish to thank Drs. W. Fenical and L. Minale for the NMR spectrum of dictyolactone. We are indebted to Drs. M. Chihara and Y. Yokohama for their kind suggestions.

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7. Carbon-13 NMR spectrum of sanadaol (4); δ($CDCl_3$) 193.1(d), 150.5(d), 146.4(s), 143.9(s), 130.8(s), 125.3(d), 116.5(t), 68.9(d), 46.0(d) 39.2(d), 37.7(d), 36.2(d), 35.9(t), 31.9(t), 29.9(t), 25.7(q), 25.4(t), 24.2(t), 17.7(2xq). Mass spectrum of 4; m/e 302(M^+), 284, 273, 269, 255, 241, 173, 145, 109, 82, 69.
8. Proton NMR spectrum of acetylsanadaol (5); δ($CDCl_3$,100 MHz) 0.72 (3H,d,J=6 Hz), 1.58, 1.66 (3H,brs), 2.03 (3H,s), 4.73 (2H,brs), 4.75 (1H,m), 5.1 (1H,brt,J=7 Hz), 6.76 (1H,t,J=3.5 Hz), 9.42 (1H,s). Mass spectrum of 5; m/e 344(M^+), 326, 284, 266, 173, 145, 109, 82, 69. Carbon-13 NMR spectrum of 5; δ($CDCl_3$) 192.6(d), 170.3(s), 150.3(d), 146.9(s), 143.2(s), 131.0(s), 125.1(d), 115.4(t), 72.4(d), 42.4(d), 39.5(d), 37.2(d), 36.0(d), 35.9(t), 32.7(t), 30.5(t), 25.7(q), 25.3(t), 24.6(t), 21.3(q), 17.7(q), 17.4(q).

(Received in Japan 26 March 1982)