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NEW DITERPENOIDS FROM PACHYDICTYON CORIACEUM

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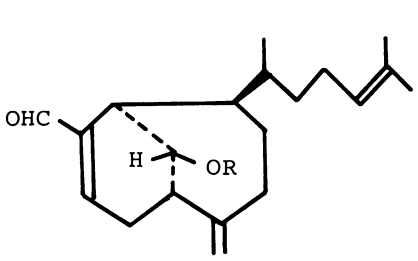
From Pachydictyon coriaceum, new diterpenoids, acetyldictyolal (7), acetals (5a) and (5b), and acetyldictyol C (9), were isolated.

We have reported[1] the isolation of novel diterpenes, sanadaol (1) and acetylsanadaol (2) from Pachydictyon coriaceum (sanadagusa), which was collected at the Izu-Shimoda beach. The same species of alga growing at the Gulf of California has been reported to produce different types of diterpenes, pachydictyol A[2] and acetoxycrenulatin.[3] Chemotaxonomical interest prompted us to investigate the minor components of this alga, and we further isolated new diterpenoids, acetyldictyolal (7), acetals (5a) and (5b), and acetyldictyol C (9), together with the known diterpenes, dictyolactone[4] (3; 2.0 % of the methanol extract), dictyol E[5] (1.1 %), dictyodial[4] (6; 1.2 %), and 18-hydroxy-2,7-dolabelladiene[6] (8; 0.5 %). The last diterpene (8) has been found in a mollusk, Dolabella californica.

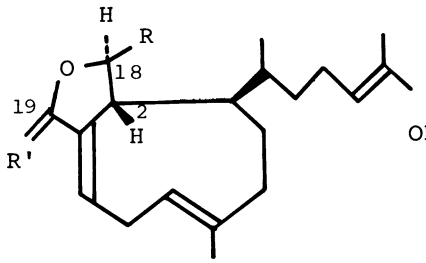
Acetyldictyolal (7; 0.1 %) exhibited IR bands due to an α,β-unsaturated aldehyde (2720 and 1685 cm^{-1}) and an ester (1735 cm^{-1}) groups. The structure 7 was deduced for acetyldictyolal from the spectral data.[8] In the ^{1}H-NMR spectrum, the proton at C-2 appeared as a broad triplet (δ 2.76, J=8 Hz). Decoupling works revealed that this proton was also coupled with the aldehyde proton (J=1.0 Hz), but not with the vicinal proton at C-3. On the analogy of the corresponding protons of dictyodial (6), the configurations at C-2 and C-3 were deduced as illustrated in the structure 7. The structure was unambiguously determined by the chemical conversion; hydrolysis (K_2CO_3/MeOH) of 7 gave the hemiacetal (4) as an epimeric mixture, which was oxidized with manganese dioxide, affording dictyolactone (3). Acetyldictyolal (7) was also isolated from Dictyota dichotoma.[7]

Acetals (5a; 0.2 %, and 5b; 0.2 %)[8] were separable by column chromatography. Each of them showed two methoxy signals, besides two 1H-singlets due to acetal protons (H-18 and 19) in its ^{1}H-NMR spectrum. The configuration at C-18 of each isomer was deduced by the null coupling constant between H-2 and 18, although the configuration at C-19 was unclarified. When the acetals were allowed to stand with silica gel, they changed into dictyodial (6), together with sanadaol (1).[1] These acetals can be artifacts, which were formed from dictyodial (6) and methanol.

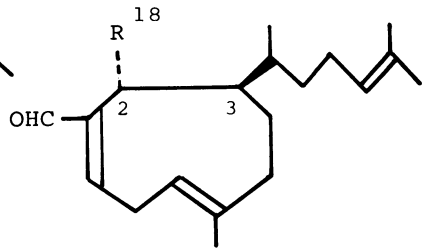
Acetyldictyol C (9; 0.1 %),[8] oil, $[\alpha]_D$ -7.2° (c 0.6, $CHCl_3$), unexpectedly resisted acetylation (Ac_2O/Pyr at room temperature), although a secondary hydroxy group was obviously present (^{1}H-NMR; δ 3.85). Acetylation at higher temperature (100°C/48 hr) gave diacetate (10).[8] This inertness of the hydroxy group of 9 was reminiscent of the sterically hindered C-6 hydroxy group of dictyol C (11).[5] Indeed, hydrolysis of 9 (KOH/MeOH/3 h) at 65°C yielded 11, which was identified by comparison



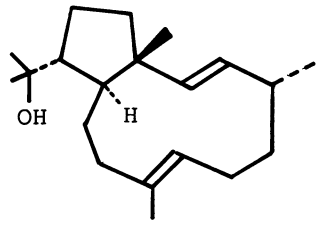
1; R = H
2; R = Ac



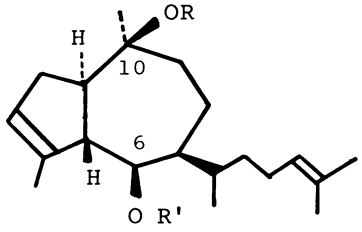
3; R = H, R' = O
4; R = H, R' = H, OH
5a,b; R = OMe, R' = H, OMe



6; R = CHO
7; R = CH_2OAc



8



9; R = Ac, R' = H
10; R = R' = Ac
11; R = R' = H

of its ^{1}H- and ^{13}C-NMR spectra with those reported for dictyol C.[5)]

It is of interest that P. coriaceum produces diterpenoids having various kinds of skeletons, which have never been found in terrestrial plants.

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8) Acetyldictyolal (7); λ_{max}(EtOH) 230 nm; ^{1}H-NMR(100 MHz) δ($CDCl_3$) 0.86(3H,d,J=7 Hz), 1.57, 1.66, 1.77 , 1.97 (3H,s), 2.76(1H,brt,J=8 Hz), 4.5(2H,m), 5.1(1H,brt,J=7 Hz), 5.36(1H,brd,J=10 Hz), 6.80(1H ,dd,J=8,4 Hz), 9.40(1H,brs); ^{13}C-NMR δ($CDCl_3$) 16.8(q), 17.3(q), 17.7(q), 21.1(q), 25.7(q), 26.2(t) , 28.5(t), 29.1(t), 32.1(d), 38.0(t), 41.4(t), 42.3(d), 46.9(d), 63.1(t), 122.1(d), 124.9(d) , 130.9(s), 138.3(s), 150.1(s), 156.9(d), 170.8(s), 195.9(d): Acetal (5a); ^{1}H-NMR(100 MHz) δ($CDCl_3$) 0.88(3H,d,J=6 Hz), 1.58, 1.68, 1.73 (each 3H,brs), 3.26(3H,s), 3.33(3H,s), 5.01(1H, s), 5.10(1H,s), 5.15(1H,brt,J=7 Hz), 5.5(1H,brdd,J=10,4 Hz), 5.80(1H,brd,J=7 Hz); ^{13}C-NMR δ($CDCl_3$) 17.1(2xq), 17.6(q), 25.7(q), 25.9(t), 28.2(t), 30.4(t), 31.5(d), 38.4(t), 40.6(t), 46.9(d), 51.6 (d), 54.5(q), 54.7(q), 107.3(2xd), 125.0(d), 125.4(d), 126.2(d), 130.8(s), 135.0(s), 146.2(s): Acetal (5b); ^{1}H-NMR(100 MHz) δ($CDCl_3$) 0.93(3H,d,J=6 Hz), 1.61, 1,69, 1.72(each 3H,brs), 3.32(3H, s), 3.47(3H,s), 5.10(1H,s), 5.1(1H,brt,J=7 Hz), 5.27(1H,brs), 5.40(1H,dd,J=10,4 Hz), 5.88(1H,brd, J=7 Hz): Acetyldictyol C (9); ^{1}H-NMR(100 MHz) δ($CDCl_3$) 0.96(3H,d,J=6 Hz), 1.49(3H,s), 1.58, 1.66, 1.82(each 3H,brs), 1.97(3H,s), 3.85(1H,brd,J=8 Hz), 5.07(1H,brt,J=7 Hz), 5.23(1H,brs); ^{13}C-NMR δ ($CDCl_3$) 16.3(q), 17.5(q), 17.7(q), 19.7(t), 22.5(q), 25.6(t), 25.7(q), 26.2(q), 33.0(t), 34.5 (d), 34.9(t), 40.5(t), 49.7(d), 51.7(d), 52.2(d), 74.6(d), 84.4(s), 123.1(d), 124.7(d), 131.5(s), 142.4(s), 170.4(s): Diacetate (10) ^{1}H-NMR(60 MHz) δ($CDCl_3$) 0.83(3H,d,J=6 Hz), 1.53, 1.56, 1.60, 1.68, 2.03, 2.06(each 3H,s), 5.1-5.3(3H,m).

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