CHEMISTRY LETTERS, pp. 1517-1518, 1982.

NEW DITERPENOIDS FROM PACHYDICTYON CORIACEUM

Midori ISHITSUKA, Takenori KUSUMI, Jiro TANAKA⁺, and Hiroshi KAKISAWA^{*} Department of Chemistry (⁺Biology), The University of Tsukuba, Sakura-mura, Ibaraki 305

From <u>Pachydictyon</u> <u>coriaceum</u>, new diterpenoids, acetyldictyolal (7), acetals (5a) and (5b), and acetyldictyol C ($\underline{9}$), were isolated.

We have reported¹⁾ the isolation of novel diterpenes, sanadaol (<u>1</u>) and acetylsanadaol (<u>2</u>) from <u>Pachydictyon coriaceum</u> (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 A²⁾ and acetoxycrenulatin.³⁾ Chemotaxonomical interest prompted us to investigate the minor components of this alga, and we further isolated new diterpenoids, acetyldictyolal (<u>7</u>), acetals (<u>5a</u>) and (<u>5b</u>), and acetyldictyol C (<u>9</u>), together with the known diterpenes, dictyolactone⁴⁾ (<u>3</u>; 2.0 % of the methanol extract), dictyol E⁵⁾ (1.1 %), dictyodial⁴⁾ (<u>6</u>; 1.2 %), and 18-hydroxy-2,7-dolabelladiene⁶⁾ (<u>8</u>; 0.5 %). The last diterpene (<u>8</u>) 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 ¹H-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 (<u>6</u>), the configurations at C-2 and C-3 were deduced as illustrated in the structure <u>7</u>. The structure was unambiguously determined by the chemical conversion; hydrolysis (K₂CO₃/MeOH) of <u>7</u> gave the hemiacetal (<u>4</u>) as an epimeric mixture, which was oxidized with manganese dioxide, affording dictyolactone (<u>3</u>). Acetyldictyolal (<u>7</u>) 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 lH-singlets due to acetal protons (H-18 and 19) in its ¹H-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 (<u>6</u>), together with sanadaol (<u>1</u>).¹⁾ These acetals can be artifacts, which were formed from dictyodial (<u>6</u>) and methanol.

Acetyldictyol C $(\underline{9}; 0.1 \ \$), {}^{8}$ oil, $[\alpha]_{D}$ -7.2° (c 0.6, CHCl₃), unexpectedly resisted acetylation (Ac₂O/Pyr at room temperature), although a secondary hydroxy group was obviously present (¹H-NMR; δ 3.85). Acetylation at higher temperature (100°C/48 hr) gave diacetate (<u>10</u>).⁸) This inertness of the hydroxy group of <u>9</u> was reminiscent of the sterically hindered C-6 hydroxy group of dictyol C (<u>11</u>).⁵) Indeed, hydrolysis of 9 (KOH/MeOH/3 h) at 65°C yielded 11, which was identified by comparison



of its ¹H- and ¹³C-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.

The authors thank Professor Mitsuo Chihara of this university for helpful discussion.

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- 8) Acetyldictyolal (7); λ_{max} (EtOH) 230 nm; ¹H-NMR(100 MHz) δ (CDCl₃) 0.86(3H,d,J=7 Hz), 1.57, 1.66, $\begin{array}{c} \hline 1.77 & , \ 1.97 & (3\mathrm{H},\mathrm{s}) & , \ 2.76 & (1\mathrm{H},\mathrm{brt},\mathrm{J=8} \ \mathrm{Hz}) & , \ 4.5 & (2\mathrm{H},\mathrm{m}) & , \ 5.1 & (1\mathrm{H},\mathrm{brt},\mathrm{J=7} \ \mathrm{Hz}) & , \ 5.36 & (1\mathrm{H},\mathrm{brd},\mathrm{J=10} \ \mathrm{Hz}) & , \\ \hline 6.80 & (1\mathrm{H} & ,\mathrm{dd},\mathrm{J=8,4} \ \mathrm{Hz}) & , \ 9.40 & (1\mathrm{H},\mathrm{brs}) & ; \ \begin{array}{c} 1^3\mathrm{C-NMR} & \delta & (\mathrm{CDCl}_3) & 16.8 & (\mathrm{q}) & , \ 17.3 & (\mathrm{q}) & , \ 17.7 & (\mathrm{q}) & , \ 21.1 & (\mathrm{q}) & , \ 25.7 & (\mathrm{q}) & , \end{array}$ $\begin{array}{c} 26.2(\texttt{t}) &, 28.5(\texttt{t}), 29.1(\texttt{t}), 32.1(\texttt{d}), 38.0(\texttt{t}), 41.4(\texttt{t}), 42.3(\texttt{d}), 46.9(\texttt{d}), 63.1(\texttt{t}), 122.1(\texttt{d}), \\ 124.9(\texttt{d}) &, 130.9(\texttt{s}), 138.3(\texttt{s}), 150.1(\texttt{s}), 156.9(\texttt{d}), 170.8(\texttt{s}), 195.9(\texttt{d}): \texttt{Acetal} & (\texttt{5a}); \ ^{1}\text{H-NMR}(100 \\ \text{MHz}) & \delta(\texttt{CDC1}_3) & 0.88(\texttt{3H},\texttt{d},\texttt{J=6} \ \text{Hz}), 1.58, 1.68, 1.73 \ (\texttt{each} \ \texttt{3H},\texttt{brs}), 3.26(\texttt{3H},\texttt{s}), 3.33(\texttt{3H},\texttt{s}), 5.01(\texttt{1H}, \texttt{s}) \\ \end{array}$ 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); ¹³C-NMR δ(CDCl₃) 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); ¹H-NMR(100 MHz) δ (CDCl₃) 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); ¹H-NMR(100 MHz) δ(CDCl₃) 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); ¹³C-NMR $\delta (\text{CDC1}_3) \ 16.3(\text{q}) \ , \ 17.5(\text{q}) \ , \ 17.7(\text{q}) \ , \ 19.7(\text{t}) \ , \ 22.5(\text{q}) \ , \ 25.6(\text{t}) \ , \ 25.7(\text{q}) \ , \ 26.2(\text{q}) \ , \ 33.0(\text{t}) \ , \ 34.5(\text{s}) \ , \ \ 34.5(\text{s}) \ , \ \ 34.5(\text{s}) \ , \ \$ (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): <u>Diacetate</u> (10) 1 H-NMR(60 MHz) δ (CDCl₃) 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).

(Received July 9, 1982)