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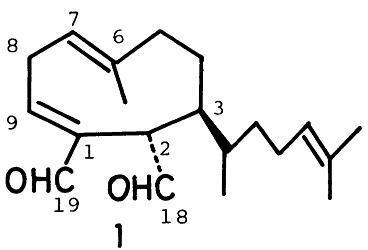
TRANSANNULAR CYCLIZATION OF DICTYODIAL ON SILICA GEL

Midori ISHITSUKA, Takenori KUSUMI, and Hiroshi KAKISAWA*
Department of Chemistry, The University of Tsukuba, Sakura, Ibaraki 305

Transannular cyclization of dictyodial (1), catalyzed with silica gel, produces an oxetane (4) besides sanadaol (2) and isosanadaol (5).

Currently new diterpenes sanadaol (2) and acetylsanadaol (3) have been isolated from the brown alga, *Pachydictyon coriaceum*.1) Their structures have been firmly determined by chemical conversion of dictyodial (1),2) the structure of which has been established by x-ray analysis, into sanadaol (2). The conversion of 1 was carried out under exteremely mild reaction conditions. Thus, when 1 (230 mg) was allowed to stand with silica gel (10 g; Merck, Kieselgel 60 F_{254}, Art. 7734) in dichloromethane (10 ml) at room temperature for 12 h, there was obtained sanadaol (2; 74 mg, 33%), together with two unknown products, A (30 mg, 13%) and B(28 mg, 12%). This paper describes the structure elucidation of these products, one of which has a unique oxetane structure.

Compound A has the same molecular composition ($C_{20}H_{30}O_2$) as that of sanadaol (2). Of the two aldehydic proton signals at δ 10.13 (d, J=3 Hz) and 9.28 (s) in the ^{1}H-NMR spectrum of dictyodial (1), the signal corresponding to the former doublet is absent in the ^{1}H-NMR spectrum of compound A. The unconjugated aldehyde group at C-18 and the olefin group at C-6 must be involved in the reaction, because the



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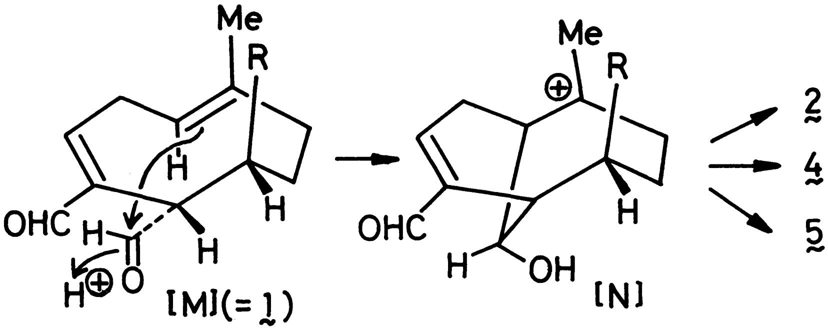
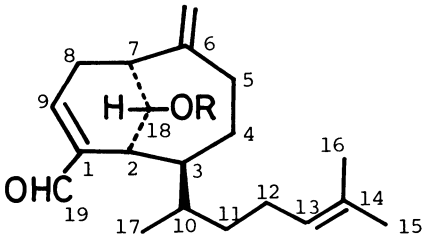
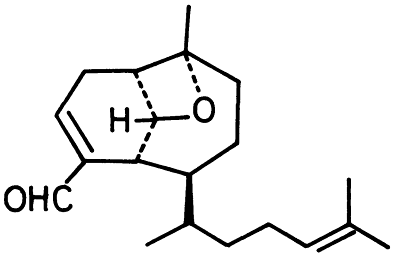




2; R=H 3; R=Ac



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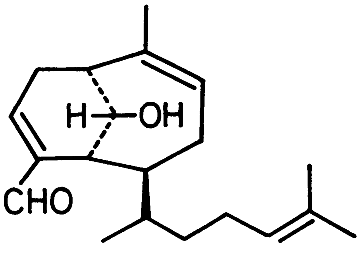

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signals due to the olefinic proton at C-7 and the olefinic methyl at C-6 are not present in the ^{1}H-NMR spectrum of compound A. The ^{1}H-NMR spectrum considerably resembles that of sanadaol (2), except for a sharp singlet at δ 1.36 due to a tertiary methyl group instead of the exo-methylene signals in 2. On the basis of these data, the structure 4$^{3)}$ was deduced for compound A. The downfield chemical shifts of the signals assignable to H-18 (δ 4.40) and C-6 (δ 90.9) in the NMR spectra of the compound A are compatible with the oxetane structure in 4. It should be emphasized that an oxetane was formed under very mild conditions, in the absence of light or strong acids.

Compound B ($C_{20}H_{30}O_2$) is also an isomer of sanadaol (2). In fact, the ^{1}H-NMR spectrum of this compound is extremely similar with that of 2. The only significant difference between their spectra is the appearence of an olefinic methyl signal (δ 1.76) in the spectrum of B instead of the exo-methylene signal in that of 2. This spectral property, and also other spectral data$^{4)}$ allowed us to deduce the structure 5 for compound B, which was designated as isosanadaol.

The relative configuration of the hydroxyl group at C-18 was determined as depicted in structure 5 by use of a lanthanide shift reagent in ^{1}H-NMR works; on addition of 0.13 molar equivalent of $Eu(fod)_3$ the signal due to 5-H shifts to downfield more significantly ($\Delta\delta$ 0.95) than the signal due to 9-H ($\Delta\delta$ 0.39).

The reaction may proceed *via* the conformer M to the cation N, which is the common intermediate leading to 2, 4, and 5. Noteworthy is the fact that all the products have an R* (relative) configuration at C-18. No epimer at C-18 has been isolated so far.

References

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2) J. Finer, J. Clardy, W. H. Fenical, L. Minale, R. Riccio, J. Battaile, M. Kirkup, and R. E. Moore, J. Org. Chem., 44, 2044 (1979).

3) 4; UV λ_{max}(MeOH) 232(ε16200)nm: IR(CCl_4) 1685, 1630, 1150, 960 cm^{-1}: ^{1}H-NMR δ ($CDCl_3$) 0.61(3H,d,J=6 Hz,H-17), 1.36(3H,s,H-20), 1.59, 1.66(each 3H,bs,H-16,15), 2.47(2H,dd,J=7,4 Hz,H-8), 2.6(1H,m,H-3), 3.22(1H,dt,J=8,7 Hz,H-7), 3.58(1H,dd,J=7, 3.5 Hz,H-2), 4.40(1H,dd,J=8,7 Hz,H-18), 5.07(1H,bt,J=7 Hz,H-13), 6.90(1H,t,J=4 Hz, H-9), 9.47(1H,s,H-19): ^{13}C-NMR δ($CDCl_3$) 193.1(d), 151.9(d), 142.4(s), 130.9(s), 125.0(d), 90.9(s), 75.1(d), 40.6(d), 40.3(d), 37.7(d), 36.8(t), 35.7(t), 35.1(d), 30.7(q), 26.0(t), 25.7(q), 24.5(t), 21.3(t), 17.7(q), 16.1(q).

4) 5; UV λ_{max}(MeOH) 229(ε 19800)nm: IR(CCl_4) 3600-3100(br), 1690, 1635, 1155, 1065, 1045 cm^{-1}: ^{1}H-NMR δ($CDCl_3$) 0.64(3H,d,J=6 Hz,H-17), 1.60, 1.66, 1.76(each 3H,bs, H-16,15,20), 2.65(2H,bs,H-8), 3.32(1H,bd,J=5 Hz,H-2), 3.80(1H,bt,J=5 Hz,H-18), 5.10(1H,bt,J=7 Hz,H-13), 5.57(1H,m,H-5), 6.88(1H,t,J=3 Hz,H-9), 9.43(1H,s,H-19): ^{13}C-NMR δ($CDCl_3$) 193.0(d), 152.6(d), 142.3(s), 139.1(s), 131.0(s), 125.9(d), 125.0 (d), 69.5(d), 42.5(d), 40.9(d), 36.9(d), 36.6(t), 35.8(d), 33.3(t), 28.3(q), 25.7 (q), 25.6(t), 24.9(t), 17.7(q), 17.2(q).

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