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STUDIES OF AUSTRALIAN SOFT CORALS. XIV[1]

THE STRUCTURE OF LEMNALACTONE AND 7-EPI-LEMNALACTONE, A REASSESSMENT.

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In 1975, Baker[2] reported the isolation of lemnalactone [(1) or (2)] from *Paralemnalia digitiformis* and indicated its relationship with lemnacarnol (3)[3]. More recently, Tursch has reported the isolation of 2-desoxylemnacarnol (4)[4] and correlated its absolute configuration at positions C4, C5, C6 and C11 with lemnalactone. Moreover this latter report[4] deduced structure (2) for lemnalactone on the basis of infra red dilution studies, and assigned this configuration at C7 to several compounds in their series. Although X-ray structures have been reported[3,5], all correlations between lemnalactone and these X-ray determined structures give no information of the configuration at C7.

Extraction of a specimen of the soft coral *Paralemnalia digitiformis*[6] afforded a mixture of isomeric sesquiterpene lactones, $C_{15}H_{22}O_2$, (1) and (2) in 1.5% yield. The isomers were separated by fractional crystallisation to give lemnalactone (1) (m.p. 105-106°C, $[\alpha]_D$ - 240°)[7], and its low melting epimer, 7-*epi*-lemnalactone (2) (m.p. < 30°C, $[\alpha]_D$ - 84°)[8,9]. The structural relationship between (1) and (2) was demonstrated by reductive cleavage of the lactones to the related diols (5)[4] and (6)[4] which were monoacetylated at the primary alcohol position to give (7) and (8). Each monoacetate (7) and (8) was oxidised to the same ketone (9)[4]. Oxidation of either diol (5) or (6) afforded 2-desoxylemnacarnol (4)[4] identical with the natural product[10]. The absolute configuration at C4, C5, C6, and C11 was thus identical in each of the compounds (1), (2), (3), and (4).

It was possible to measure the coupling constants ($J_{6,7}$) for the lactones (1) and (2) and for their related dihydroderivatives (1a)[11] and (2a)[12]: (1) and (1a) $J_{6,7}$ = 12 Hz ; (2) and (2a) $J_{6,7}$ = 6 Hz. In a series of related sesquiterpene lactones, it has been shown that a coupling constant near 10 Hz indicates *trans* ring fusion while a value near 5 Hz indicates *cis* fusion[13]. Having both epimers at C7, it was possible to say that lemnalactone (1) ($J_{6,7}$ = 12 Hz) was *trans* fused (and not *cis* as reported)[4] while 7-*epi*-lemnalactone (2) ($J_{6,7}$ = 6 Hz) was *cis* fused.

Shift reagent studies on the two monoacetylated diols (7)[14] and (8)[15] confirmed the *transoid* relationship of the 6,7-substituents in (7) [from (1)] and the *cisoid* relationship of the 6,7-substituents in (8) [from (2)].

We have thus unambiguously demonstrated that the structure of lemnalactone is (1), and that of the new sesquiterpene lactone, 7-*epi*-lemnalactone is (2)[16].

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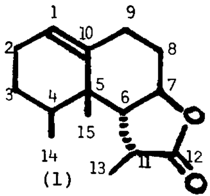
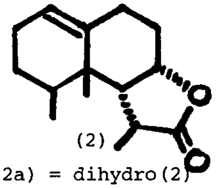


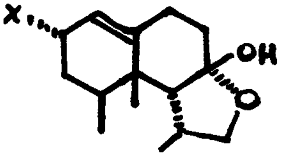
(1)

(1a) = dihydro(1)

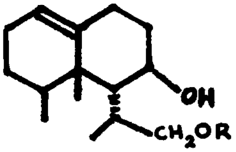


(2)

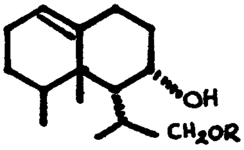
(2a) = dihydro(2)



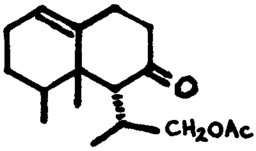
(3) X = OH, (4) X = H



(5) R = H, (7) R = Ac



(6) R = H, (8) R = Ac



(9)

1. As Part XIII : *Aust.J.Chem.*, 31, 1817 (1978).
2. J.T. Baker, *Pure Appl.Chem.*, 48, 35 (1976).
3. B. Tursch, M. Colin, D. Daloze, D. Losman and R. Karlsson, *Bull.Soc.Chim.Belges*, 84, 81 (1975).
4. D. Daloze, J.C. Braekman, P. Georget and B. Tursch, *Bull.Soc.Chim.Belges*, 86, 47 (1977).
5. D. Losman, *Acta Cryst.*, B33, 1959 (1977).
6. We thank Dr. J. Verseveldt for identification of this specimen.
7. R.J. Wells, private communication. A sample of lemnalactone is gratefully acknowledged.
8. Satisfactory analytical data were obtained for all new compounds.
9. *7-epi-lemnalactone (2)* ^{1}H-nmr ($CDCl_3$): δ unshifted ($Eufod_3$ shifted): δ5.60 (5.60), m, H1; 4.70 (4.75), ddd, J = 3, 6.5, 10 Hz, H7; 2.36 (2.63), dq, J = 6.5, 12 Hz, H11; unknown (2.50), dd, J = 6.5, 12 Hz, H6; 1.37 (1.60), d, J = 6.5 Hz, 11-CH_3; 0.90 (1.0), d, J = 7 Hz, 4-CH_3; 1.05 (1.12), s, 5-CH_3.
10. We thank Drs. Braekman and Daloze for an authentic sample of 2-desoxylemnacarnol (4).
11. *Dihydrolemnalactone (1a)*, m.p. 64-65°C, $[\alpha]_D$ - 22°C (c, 0.55): ^{1}H-nmr ($CDCl_3$): δ4.20 (6.35), m, H7; 2.76 (7.0), dq, J = 6.5, 13 Hz, H11; 1.35 (4.80), d, J = 6 Hz, 11-CH_3; unknown (4.40), dd, J = 12, 13 Hz, H6; 0.93 (1.75), d, J = 6.6 Hz, 4-CH_3; 1.06 (2.0), s, 5-CH_3 (*cis* decalin).
12. *Dihydro-7-epi lemnalactone (2a)*: m.p. 84-85°, $[\alpha]_D$ + 38° (c, 0.4), ^{1}H-n.m.r. ($CHCl_3$): δ 4.90, m, H7; 2.63, dq, J = 6, 12 Hz, H11; 2.26, dd, J = 6, 12 Hz, H6; 1.33, d, J = 6 Hz, 11-CH_3; 0.8, d, J = 6.5 Hz, 4-CH_3; 0.81, s, 5-CH_3 (*trans* decalin).
13. J.T. Pinhey and S. Sternhell, *Aust.J.Chem.*, 18, 543 (1965).
14. *Monoacetate (7)*, $[\alpha]_D$ - 39° (c, 0.3), ^{1}H-n.m.r. ($CDCl_3$): δ5.39 (6.0), m, H-1; 4.30 (8.0) m, $W_{h/2}$ < 10 Hz, H7; 4.19 (5.54), dd, J = 3, 10 Hz ; 3.66 (5.06), dd, J = 10, 10 Hz, 12-CH_2 ; 2.25 (3.25), m, J = 3, 6, 10 Hz, H11; δ1.76 (4.15), dd, J = < 1, 3 Hz, H6; 1.09 (1.9), d, J = 6 Hz, 11-CH_3; 0.86 (1.45), d, J = 6.5 Hz, 4-CH_3; 1.40 (2.55), s, 5-CH_3; 2.05 (2.8), s, acetate.
15. *Monoacetate (8)*, m.p. 90-91°, $[\alpha]_D$ - 79°, (c, 0.3): ^{1}H-n.m.r. ($CDCl_3$): δ5.40 (5.87), m, H1; 4.31 (6.7), m, $W_{h/2}$ > 25 Hz, H7; 4.03 [(6.5), dd, J = 5, 11 Hz; (5.7), dd, J = 10, 11 Hz], d, J = 8 Hz, 12-CH_2; 2.53 (7.3), m, H11; 1.96 (4.56), dd, J = < 2, 4 Hz, H6; 1.19 (2.47), d, J = 7 Hz, 11-CH_3; 0.86 (1.23), d, J = 6 Hz, 4-CH_3; 1.01 (1.4), s, 5-CH_3; 2.06 (2.9), s, acetate.
16. The structure of (2a) has recently been confirmed by X-ray crystallography.

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