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PENLANFURAN, A NEW FURANOID SESQUITERPENE FROM THE MARINE SPONGE DYSIDEA FRAGILIS (MONT) OF BRITTANY A STRIKING DIFFERENCE WITH THE SAME HAWAIIAN SPECIES

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Summary Penlanfuran (2), a furanoid sesquiterpene with a novel skeleton for sponge products, has been afforded by the marine sponge Dysidea fragilis (Mont) of Brittany, the same Hawaiian species gave different sesquiterpenoids

Marine sponges of the genus Dysidea have been unusually interesting sources of new terpenoids[1] In particular, D fragilis, collected at Hawaii, gave bridged bicyclic sesquiterpenoids[2]

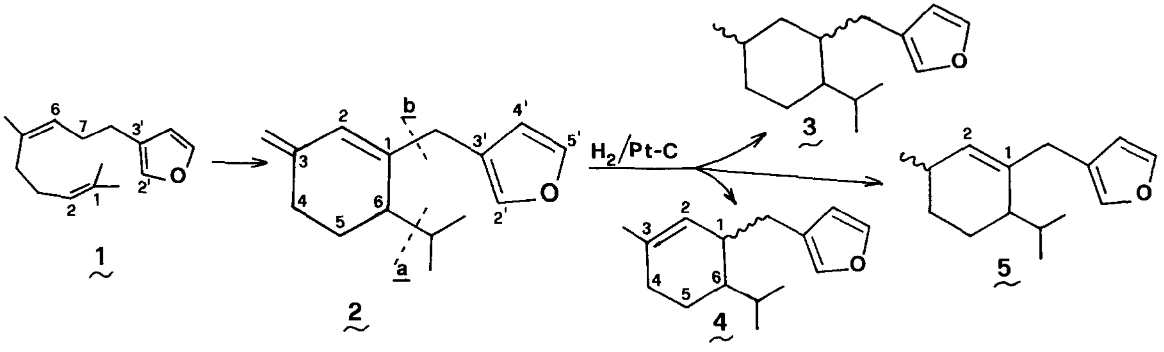
We now report that the same species of Brittany is devoid of the above products, giving instead penlanfuran (2)[3] with an unprecedented skeleton among sponge products The fresh sponge was ethanol extracted and the aqueous residue from ethanol evaporation was ether extracted The residue from ether evaporation, 20 g, was column chromatographed on Merck Kieselgel 60, gradient elution pet ether-ethyl ether Ehrlich reactive fractions were column chromatographed on 10% $AgNO_3$ - Kieselgel with n-hexane to give oily 2, 1 4 g (0 3% on dry animal w), $[\alpha]_D^{20}$ ($CHCl_3$, c 2 4) - 68 0°

UV λ_{max}^{MeOH} nm (ε = 12,000) IR ν_{max}^{neat} 3063, 1624, 1025, 875, and 785 cm^{-1} EIMS (VG ZAB2F) m/z (%) 216(23) $[M^+$ 216 1571 ± 0 002, calcd for $C_{15}H_{20}O^+$ 216 1514 $]$, 173 (53) $M-C_3H_7$ (ʃʃ a) $[$173 0973 ± 0 005, calcd for $C_{12}H_{13}O^+$ 173 0966 $]$, 135 (40) $M-C_5H_5O$ (ʃʃ b) $[$135 1197 ± 0 005, calcd for $C_{10}H_{15}{}^+$ 135 1174 $]$, 91 (64) $135-C_3H_8$ $[$91 0559 ± 0 005, calcd for $C_7H_7{}^+$ 91 0547 $]$, and 81 (100) $M-C_{10}H_{15}$ (ʃʃ b) $[$81 0350 ± 0 002, calcd for $C_5H_5O^+$ 81 0340 $]$ ^{13}C NMR off resonance) δ_{TMS} ($CDCl_3$) 143 7 (s,C(1) or C(3)), 143 4 (s,C(3) or C(1)), 142 8 (ddd, C(5')), 139 7 (dd, C(2')), 127 9 (d,C(2)), 122 9 (s,C(3')), 111 5 (dd,C(4')), 109 2 (t,$=CH_2$), 42 5 (d,C(6)), 31 4 (t, CH_2 or C(4)), 28 8 (t,C(4) or CH_2), 28 7 (d, CH), 23 2 (t,C(5)), 21 4,q, and 18 0 ppm, q, (CH_3) These data are either consistent with structure 2 or the isomers with the isopropyl group at C(4) or C(5) The 200 MHz ^1H NMR spectrum $[\delta_{TMS}$ ($CDCl_3$) 7 35 (dd, $J_{2',4'}$ = 1 7, $J_{2',5'}$= 1 6, H(2'), 7 23 (m, H(5')), 6 25 (m, H(4')), 6 03 (br s, H(2)), 4 71 s and 4 69 s ($=CH_2$), 3 26 and 3 16 (AB, J = 15 7, CH_2), 2 30 (m, $C(4)H_2$), 2 05 (m, C(6)H and CH), 1 64 (m, $C(5)H_2$), 0 96 (d, J=6 7, CH_3), and 0 80 ppm (d, J=6 7 Hz, CH_3)$]$ helped to clarify the point In fact, (a) irradiation at δ 3 20 revealed the furan couplings δ 7 23 (dd, $J_{5',4'}$=0 9,$J_{5',2'}$=1 6) and 6 25 (dd,

$J_{4',5'}$=0.9, $J_{4',2'}$=1 7), (b) irradiation at δ4 70 resulted in a simplification of the δ2 30 m, (c) irradiation at 2 05 showed the diastereotopic methyls as two singlets, (d) irradiation at δ1 64 changed the δ2 30 m into an AB system with J=15 6 Hz, which rules out the C(5) position for the isopropyl group, (e) irradiation at =CH_2 caused a +13% NOE of the C(2)H resonance, (f) irradiation at the δ0 80 CH_3 caused both a +10% NOE of the C(4')H resonance and a +23% NOE of the C(2')H resonance, which unambiguously proves that the isopropyl group is at C(6) rather than at C(4)

The structural assignment is further supported by the results of catalytic hydrogenation of **2** in ethanol over 5%Pt-C This led to a mixture which could be separated on a 10% $AgNO_3$-Kieselgel 60 column, eluant pet ether, until **3** was eluted, and then with increasing amounts of ethyl ether, whereby **5** was eluted before **4**. HPLC on a RP18 column, eluant MeOH-H_2O 9 1, showed that **3**,[4] **5**[5] and **4**[6] are mixtures of respectively four (ratio 1 4 8 4), two (ratio 5 7), and two diastereomers (ratio 20 1)

Penlanfuran **2** has a rare skeleton which, formally, has already been encountered with the non-furanoid plant product humbertiol[7] Biogenesis from a so far unknown 6-cis-farnesol derivative,[8] such as **1**, is conceivable, though other routes are also possible



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References and Notes

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2) Schulte, G ,Scheuer, P J ,McConnell, O J Helv Chim Acta, 1980, 63, 2159
3) The sponge was collected in August 1982 in Brittany, near the Chateau de Taureau, out of the Pointe de Pen-Lan, from which the name of the product is derived
4) m/z 220 (M^+), ^1H NMR δ_{TMS} ($CDCl_3$) 7 34 (m, H(2')), 7 18 (m, H(5')), 6 24 (m, H(4')), 2 7-1 1 (12H, series of m), 1 0-0 7 (9H, series of d)
5) m/z 218 (M^+), ^1H NMR δ_{TMS} ($CDCl_3$) 7 34(m, H(2')), 7 21(m, H(5')), 6 24(m, H(4')), 5 44(m,H(2)), 3 07 (br s, exo-CH_2), 2 5-1 1 (7H, series of m), 0 98-0 70 (9H, series of d)
6) m/z 218 (M^+), ^1H NMR (200 MHz) δ_{TMS} ($CDCl_3$) 7 35 (m, H(2')), 7 20 (m, H(5')), 6 28 (m, H(4')), 5 38 (m, H(2)), 2 6-1 1 (9H, series of m), 1 62 (br s, C(3)CH_3) 0 97 (d, J=5 9 Hz, $CH(CH_3)_2$ On irradiation at δ1 62, the δ5 38m became a d, J = 4 4 Hz
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