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FUROCAESPITANE AND RELATED C_{12} METABOLITES FROM LAURENCIA CAESPITOSA

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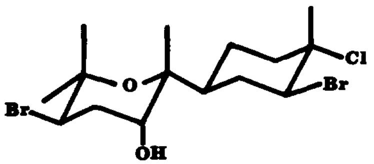
Summary: The work includes the isolation of two new degraded C_{12} terpenoids whose precise structures, as well as the absolute configuration of their chiral centres, are determined by X-ray diffraction analyses.

We have published[1] the structure of the very unstable C_{12} terpenoid furocaespitane (2), a compound isolated among others from the red alga Laurencia caespitosa, caespitol (1) being the major sesquiterpene of the extract.[2] The structure 2 was proposed for furocaespitane on the basis of mainly spectroscopic studies and the exceptional and unique nature of the same has given rise to alternative proposals of "more inmediate biogenesis".[3] In this communication structure 2 is confirmed in an inequivocal manner for the compound and the absolute configuration of its chiral centres is included, new data being provided at the same time that justify the possible biogenetic interrelationship with C_{15} caespitol (1) and emphasise its being considered a degraded bisabolane. The work includes the isolation and structural determination of two new C_{12} terpenoids, compounds 4[4] and 5[5] whose precise structures, as well as the absolute configuration of their chiral centres are determined by single X-ray diffraction analyses. Both compounds, 4 and 5, are minor components of the extracts of this seaweed, the former being isolated after previous esterification with diazomethane of the most polar fractions of the chromatography of the



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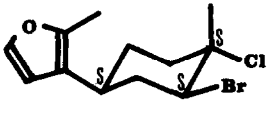

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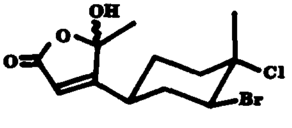

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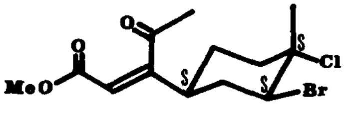

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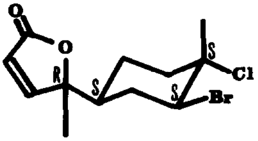


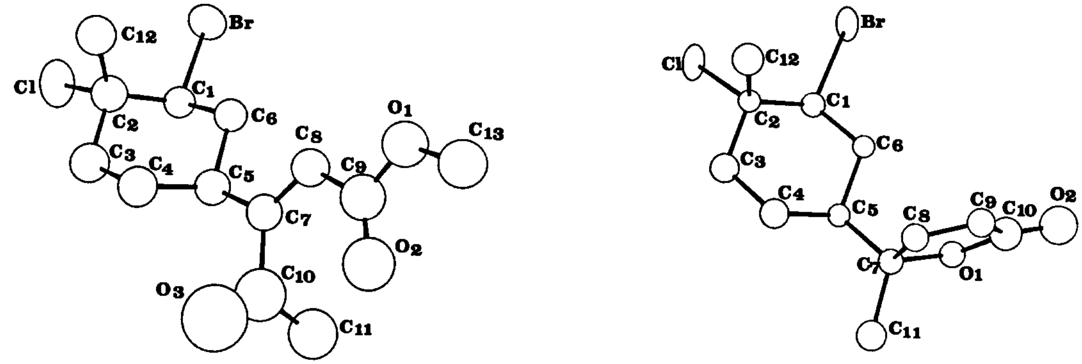
5

extracts.

Crystals of (4)[6] ($C_{13}H_{18}BrClO_3$), M = 337.64, are orthorhombic, space group $P2_12_12_1$, a = 5.933(12), b = 12.400(20), c = 20.369(56) Å, V = 1498 Å^3, D_c = 1.49 g cm^{-3}, Z = 4. The structure was solved by direct methods, R = 0.057 for 979 reflections with $I>3\sigma(I)$. The averaged Bijvoet differences are 1.87 for the right enantiomer (left stereodiagram, Figure 1) vs 4.51 for the wrong one. Crystals of (5)[6] ($C_{12}H_{16}BrClO_2$), M = 307.61, are monoclinic, space group $P2_1$, a = 6.976(5), b = 10.197(5), c = 9.637(5) Å, β = 107.1(1)°, V = 655 Å^3, D_c = 1.56 gcm^{-3}, Z = 2, R = 0.071 for 1038 reflections with $I>3\sigma(I)$. The averaged Bijvoet differences are 2.55 for the right enantiomer (right stereodiagram, Figure 1) vs 3.81 for the wrong one.

The interrelationship 2 - 4 is achieved by oxidation with m-chloroperbenzoic acid of furocaespitane (2), followed by methylation of the resulting lactol 3 with diazomethane to give the keto-ester 4

FIGURE 1. Stereodiagrams including absolute configurations of compounds 4 and 5.



Acknowledgements. This work was supported by grants from the Spanish CAICYT to J.D.M and M.L.R.

REFERENCES AND NOTES

1. A.G. González, J. Darias, and J.D. Martín, Tetrahedron Lett., 3625-3626 (1973).
2. A.G. González, J. Darias, J.D. Martín, and C. Pérez, Tetrahedron Lett., 1249-1250 (1974).
3. T. Money, in "Specialist Periodical Report, Terpenoids and Steroids", 1975, 5, p. 48.
4. Compound (4), m.p. 52-53°C; $[\alpha]_D$ = +37 (c, 0.14 $CHCl_3$). IR ($CHCl_3$) 1700, 1635, 1440, 1385, 1250, 1170, and 1020. ^1H-NMR ($CDCl_3$, δ-scale) 1.69, 2.36, 3.72 (s, 3H each), 4.44 (dd, J = 11 and 4 Hz, 1 H), 5.70 (s, 1 H). ^{13}C-NMR ($CDCl_3$) 24.04 (q), 29.94 (t), 30.78 (t), 37.37 (t), 42.32 (t), 42.64 (d), 52.10 (q), 61.05 (d), 70.35 (s), 116.09 (d), 162.20 (s), 165.64 (s). High resolution mass spectrum $C_{13}H_{18}{}^{81}Br^{35}ClO_3$, observed 338.0110, Δ = -0.3; $C_{13}H_{15}{}^{81}Br^{37}ClO_2$, 320.9896, Δ = -0.2; $C_{12}H_{13}O_2$, 189.0906, Δ = +1.0.
5. Compound (5), m.p. 122-123°C; $[\alpha]_D$ = +16.0 (c, 0.23 $CHCl_3$). IR (KBr) 3100, 3000, 1755, 1620, 1380, 1140, 990, 950, and 820 cm^{-1}. ^1H-NMR ($CDCl_3$, δ-scale) 1.45 (s, 3 H), 1.67 (s, 3 H), 4.29 (dd, J = 12 and 4.5 Hz, 1 H), 6.06 (d, J = 5.5 Hz, 1 H), 7.35 (d, J = 5.5 Hz, 1 H). ^{13}C-NMR ($CDCl_3$) 22.12 (q), 24.00 (q), 24.49 (t), 36.17 (t), 42.19 (t), 45.43 (d), 61.73 (d), 70.72 (s), 89.40 (s), 121.50 (d), 158.87 (s). Mass spectrum, $C_{12}H_{16}BrClO_2$, M^+ at m/z 310, 308, 306 (0.1, 0.4, 0.2); further peaks found at m/z 267 (12), 265 (39), 263 (44), 183 (23), 147 (16), 98(100)
6. Complete crystallographic data are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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