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GLANDULIFEROL, A NEW HALOGENATED SESQUITERPENOID FROM LAURENCIA GLANDULIFERA KÜTZING*

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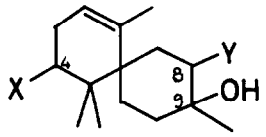
Recently several number of halogenated spiro-fused sesquiterpenoids have been isolated from the red algae Laurencia species (Rhodomelaceae): spirolaurenone from L. glandulifera (1a), johnstonol from L. johnstonii (1b) and L. okamurai (1c), prepacifenol from L. filiformis (1d) and L. pacifica (1d)(1e), pacifenol from L. tasmanica (1d)(1e) and caespitol from L. caespitosa (1f). In a previous paper (2), we described the structure of three chamigrene-type bromosesquiterpenoids from L. glandulifera. Further investigations of the neutral oil from L. glandulifera have led to the isolation of a new halogenated sesquiterpene alcohol containing bromine and chlorine, designated as glanduliferol, in ca. 0.01% yield of the dried plant. We wish to propose formula I for glanduliferol on the basis of its chemical and spectroscopic evidence.



I : X=Br, Y=Cl

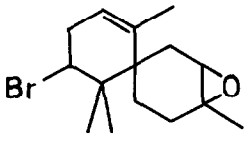
II : X=Cl, Y=Br

Glanduliferol (I), colorless gum, $(\alpha)_D$ -21.7° (c 1.66, $CHCl_3$), was analysed for $C_{15}H_{24}OBrCl$ (M^+ 336, 334); $\nu_{max}^{CHCl_3}$ 3580, 1655, 1400, 1390, 1342, 1130, 1105, 1070, 1045, 990, 980, 928 and 832 cm^{-1}; τ (CCl_4, 100 MHz) 9.04, 8.78, 8.70 (each 3H, s), 8.0 (3H, br. s), 7.83 (2H, d, J=9.5 Hz), ca. 7.5 (2H, m), 5.53 (1H, dd, J=10 and 7.0 Hz), 5.33 (1H, t, J=9.5 Hz) and 4.8 (1H, m).

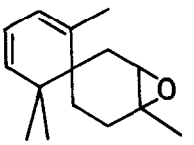
Double resonance experiments in the NMR spectrum of I (3) indicate the

presence of ■-CMe=CH-CH_2-CHBr(or Cl)-■ and ■-CH_2-CHCl(or Br)-■ groupings in I.

NMR spectrum and non-acetylated hydroxyl group with acetic anhydride-pyridine indicated the presence of a tertiary OH group in I. By the treatment with 1N KOH-EtOH (reflux 1 hr), I afforded a conjugated cyclohexadiene, which was identical with a dehydrobromination product (IV) derived from 4-bromo-α-chamigren-8,9-epoxide (III) (2). The structure of glanduliferol could, therefore, be represented as I or II.



III



IV

On the other hand, treatment of I with 5% KOH-MeOH (reflux 5 min) gave a dehydrochlorination product, which was identified as 4-bromo-α-chamigren-8,9-epoxide (III) (2) by the mixed m.p. and by a comparison of the IR and NMR spectra and optical rotation with those of an authentic specimen.

From these chemical reactions and the spectral data (4), glanduliferol is represented by formula I (4-bromo-8-chloro-9-hydroxy-α-chamigrene).

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✳ Part XXV of "Constituents of Marine Plants." Part XXIV, M. Suzuki, E. Kurosawa and T. Irie, Tetrahedron Letters, 821 (1974).

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(2) Part XXIV of this series.

(3) Full details of NMDR studies will be discussed in a full paper.

(4) Formula I for glanduliferol was also supported by the mass spectrum of I, which indicate similar fragmentations to those of 4-bromo-α-chamigren-8,9-epoxide (III) (2) and will be discussed in detail in a full paper.