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LAEVIGATIN, A SESQUITERPENOID FURAN FROM EUPATORIUM LAEVIGATUM LAM.

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Above ground parts of a flowering specimen of Eupatorium laevigatum Lam. (Compositae), trivial names cambarã or camarã [1], collected in the vicinity of Porto Alegre, in the Brazilian state of Rio Grande do Sul, afforded an essential oil from which an optically active sesquiterpenoid furan, named laevigatin, mp 65-66°C, $[\alpha]_D = +88^{\circ}$, crystallized out.

Molecular formula $C_{15}H_{16}O$ was indicated by high resolution mass spectrometry [M 212.1253 found, M 212.1201 calculated]. UV (λ_{max}^{EtOH} 276, 290sh, 302sh nm, ε6300, 5900, 2300) and IR (ν_{max}^{KBr} 1623, 1604, 1553, 1500, 1100, 809 cm^{-1}) spectra revealed its aromatic character as well as the absence of hydroxyl or carbonyl groups. The ^{1}HNMR spectrum (CCl_4) exhibited signals of two aromatic methyl groups (7.70 and 7.67τ), a methyl inserted in a secondary carbon atom (8.75τ,d,J7.0Hz), four aromatic (m, 2.60-3.10τ) and three benzylic protons (m,6.70-7.50τ). Inspection of the proton-decoupled and the single-frequency off-resonance decoupled ^{13}CNMR spectra revealed three methyl (10.74, 21.56 and 21.56δ) and one methylene (29.97δ) signals, one non-aromatic (34.57δ) and four aromatic (123.41, 126.43, 127.13 and 138.75δ) methine resonances and six quaternary aromatic carbon signals (118.03, 125.00, 128.00, 135.50, 136.00 and 153.00δ).

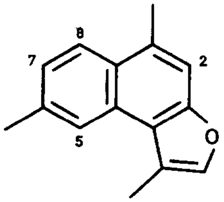
Dehydrogenation of laevigatin with DDQ-C_6H_6 at reflux temp. gave furanocadalene (1)[2,3,4], characterized by its mp 98-100°C, UV, IR, MS, ^{1}HNMR, ^{13}CNMR and direct comparison (mmp, tlc, IR) with a sample kindly supplied by Dr. H. Hikino, Pharmaceutical Institute, School of Medicine, Tohoku University, Sendai, Japan.

Oxidation of furanocadalene (1) with m-$ClC_6H_4CO_3H$-$CHCl_3$ afforded the lactone 2 (mp 187-188°C, ν_{max}^{KBr} 1795 cm^{-1}, M 226.1027 found, $C_{15}H_{14}O_2$ requires M 226.1060). The signal at 2.02τ in the ^{1}HNMR spectrum of furanocadalene (1) was assigned to the isolated peri proton at C_5[2,3] but it should actually be assigned to the α-hydrogen on the furan ring. This signal is clearly absent in the spectrum of the lactone 2 which, in

CDCl$_3$ solution, is mostly in the enol form 3 as is evidenced by the singlet (7.87τ) due to the methyl group on the heterocyclic ring. The aromatic protons are shown as a pair of o-related hydrogens (2.10τ,d, J9.0Hz and 2.82τ,dd, J9.0 and 1.8Hz) and two isolated hydrogens (3.15τ,bs) in the vicinity of aromatic methyl groups (7.40 and 7.90τ). The isolated peri-proton at C$_5$ is sterically forced out of the plane originating a signal at a higher field (3.15τ) than the peri-proton at C$_8$ (2.10τ).

On the basis of these data only structure 4 can be ascribed to laevigatin that, besides pyrocurzerenone (5), obtained from *Curcuma zedoaria* Roscoe (Zingiberaceae)[2,3], seems to be the only sesquiterpenoid of the cadinane type containing a furan ring.

A complete analysis of the remaining essential oil is on progress.



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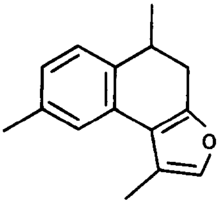

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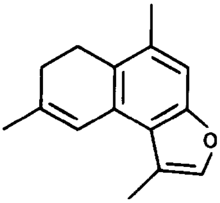

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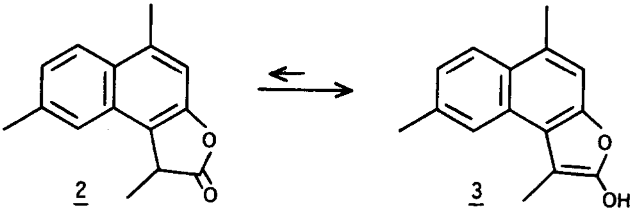

2 3

Footnote

^{13}CNMR spectra were determined for CDCl$_3$ solutions containing TMS as internal standard (δ = 0ppm) in a Varian CFT-20 instrument and the high resolution mass spectra were obtained in a Varian CH-5 spectrometer.

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References

1. Corrêa, M.P. (1926) Dicionário das Plantas Úteis do Brasil, Vol. 1, p. 411,Imprensa Nacional, Rio de Janeiro.
2. Hikino, H., Agatsuma, K., Konno, C. and Takemoto, T. (1968) Tetrahedron Letters 4417.
3. Hikino, H., Konno, C., Agatsuma, K., Takemoto, T., Horibe, I., Tori, K., Ueyama, M. and Takeda, K. (1975) J. Chem. Soc. Perkin I, 478.
4. Viswanatha, V. and Krishna Rao, G. S. (1974) J. Chem. Soc. Perkin I, 450.