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A NEW XANTHONE FROM *LOROSTEMON* SPECIES*

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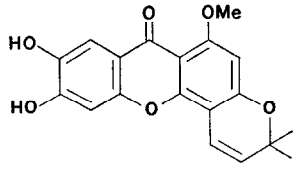
Key Word Index—*Lorostemon coelhoi*; *Lorostemon negrensis*; Guttiferae; 6,7-dihydroxy-1-methoxypyrano-(2′,3′:3,4)xanthone; lorostemin.

The trunk wood of two Amazonian Guttiferae species, *Lorostemon coelhoi* Paula and *L. negrensis* Froes,[2] yielded yellow crystals of a new compound, lorostemin. Preliminary scrutiny of MS and PMR spectra of the compound disclosed the formula $C_{13}H_3O_2(OH)_2$-OMe($CH{=}CHCMe_2O$) which is compatible with a xanthone structure. Two of the undefined protons must be *para* related and both *ortho* to hydroxyls. Their PMR singlets appear at a substantially lower field in the spectrum of the diacetate than in the spectrum of the dimethyl ether ($\Delta_{H\text{-}8}$ 0·40 ppm, $\Delta_{H\text{-}5}$ 0·48 ppm). The third singlet of the aromatic PMR region, which is not shifted upon acetylation, occurs at relatively high field (τ 3·43), and corresponds thus to a proton at C-2 or C-4 of a 1,3-dioxygenated ring.[3] Only the former alternative can be correct, since treatment of di-*O*-methyllorostemin with cold conc. H_2SO_4 leads to a 1-hydroxyxanthone ($AlCl_3$-shift of UV maxima) which gives a negative Gibbs test.[4] The angular pyrano-structure I which thus emerges for lorostemin is consistent with the wavelength of the principal UV maximum (275 nm). Linear pyranoxanthones show the corresponding band at 295 nm.[5]



(I)

Even diffuse daylight transforms lorostemin gradually into a sparingly soluble derivative. Both compounds are soluble in aqueous borax and show similar mass spectral fragmentation patterns. The PMR spectra of the acetates are identical with respect to the aromatic regions. The signals due to the side chain protons, however, are strikingly different, revealing the replacement of the olefinic protons of lorostemin by protons at saturated carbons in the derivative. Light induced double bond addition must thus be held responsible for its formation.

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EXPERIMENTAL

Isolation of lorostemin. The ground wood (7·5 kg) of *Lorostemon coelhoi* was extracted with benzene. The concentrated benzene solution gave a crystalline mass (80 g) which was separated by filtration from an oil (5 g). The crystals plus some ahering oil were recrystallized repeatedly from hot acetone, yielding in the first crops the photodimer. The mother liquors were evaporated. The residue was freed from oil by washings with light petrol. and recrystallized from hot MeOH giving lorostemin (I). The presence of lorostemin in the wood of *Lorostemon negrensis* was demonstrated by preparative TLC.

Lorostemin (I). Yellow crystals, m.p. 258–259° (Me_2CO) (Found: C, 67·15; H, 4·80. $C_{19}H_{16}O_6$ requires: C, 67·05; H, 4·75%). λ_{max}^{EtOH} (nm): 275, 338 (ε 42 000, 19 000); no $AlCl_3$/HCl shift; $\lambda_{max}^{EtOH+AlCl_3}$ (nm): 270, 350 (ε 34 500, 17 000); $\lambda_{max}^{EtOH+NaOAc+H_3BO_3}$ (nm): 270, 347 (ε 37 000, 19 400); $\lambda_{max}^{EtOH+NaOAc}$ (nm): 263, 370 (ε 38 500, 29 600); $\lambda_{max}^{EtOH+NaOH}$ (nm): 268, 372 (ε 39 000, 25 000). Gibbs test:[4] negative. ν_{max}^{KBr} (cm^{-1}): 3500, 1645, 1610, 1585, 1470, 1370, 1290, 1220, 1190, 1130, 1085, 960, 860, 840, 780, 740, 730. PMR [$(CD_3)_2CO$, τ]: 2·06 (*s*, H-8), 2·33 (*s*, H-5), 3·35 (*s*, H-2), 3·17 (*d*, *J* 10·3 Hz, H-4′), 4·10 (*d*, *J* 10·3, H-5′), 6·00 (*s*, $OC\underline{H}_3$), 8·41 (*s*, two $C\underline{H}_3$).

Di-O-methyllorostemin was obtained with CH_2N_2 in Et_2O and washings of the reaction product with 3% aq. NaOH, as light yellow crystals, m.p. > 280°. ν_{max}^{KBr} (cm^{-1}): 1638, 1600, 1560, 1500, 1460, 1448, 1428, 1381, 1370, 1270, 1245, 1223, 1205, 1175, 1158, 1116, 1110, 1090, 1015, 985, 890, 870, 830, 820, 785, 770, 725, 690. PMR ($CDCl_3$, τ): 2·38 (*s*, H-8), 3·20 (*s*, H-5), 3·43 (*s*, H-2), 3·28 (*d*, *J* 10·0 Hz, H-4′), 4·32 (*d*, *J* 10·0 Hz, H-5′), 6·05 (*s*, three $OC\underline{H}_3$), 8·53 [*s*, $C(C\underline{H}_3)_2$].

Di-O-acetyllorostemin was obtained as crystals, m.p. 195–196° (light petrol.–C_6H_6). ν_{max}^{KBr} (cm^{-1}): 1765, 1658, 1625, 1603, 1562, 1490, 1465, 1445, 1376, 1280, 1180–1210, 1157, 1124, 1105, 1020, 933, 890, 840, 780. PMR ($CDCl_3$, τ): 1·98 (*s*, H-8), 2·72 (*s*, H-5), 3·43 (*s*, H-2), 3·20 (*s*, *J* 10·0 Hz, H-4′), 4·32 (*s*, *J* 10·0 Hz, H-5′), 6·11 (*s*, $OC\underline{H}_3$), 7·70 (*s*, two $COC\underline{H}_3$), 8·53 [*s*, $C(C\underline{H}_3)_2$]. MS. M 424 (100%), *m/e* (%) 409 (97), 382 (20), 368 (88), 340 (24), 339 (15), 325 (71), 324 (18), 312 (5), 311 (15), 310 (15), 297 (10), 296 (12), 295 (15), 282 (5), 281 (9), 153 (5), 115 (6). *De-O-methyllorostemin* was obtained by treatment of I with conc. H_2SO_4 at room temp. (5 min.), addition of the mixture to crushed ice and filtration. Intensely greenish-yellow crystals, m.p. 182–184°. Gibbs test:[4] negative.

Lorostemin photodimer. Red crystals, m.p. 272–274° (Me_2CO) (Found: C, 67·21; H, 4·81. $C_{38}H_{32}O_{12}$ requires: C, 67·05; H, 4·75%). ν_{max}^{KBr} (cm^{-1}): 3500, 1645, 1590, 1560, 1530, 1465, 1455, 1376, 1322, 1290, 1265, 1250, 1200, 1170, 1120, 1005, 1090, 970, 850, 845, 840, 782, 740, 735, 700. MS: *m/e* (%) 340 (44), 339 (16), 325 (100), 312 (4), 311 (16), 310 (9), 297 (6), 296 (9), 295 (9), 282 (5), 281 (5), 162·5 (8), 153 (7), 115 (7). The *acetate* was obtained as white crystals, m.p. 188–190° (light petrol.–C_6H_6). PMR ($CDCl_3$, τ): 1·87 (*s*, H-8), 2·65 (*s*, H-5), 3·36 (*s*, H-2), 5·35 (*d*, *J* 6·0 Hz, H-4′), 5·85 (*s*, $OC\underline{H}_3$), 7·28 (*d*, *J* 6·0 Hz, H-5′), 7·60 (*s*, $COC\underline{H}_3$), 8·45 (*s*, low intensity peak due to $CC\underline{H}_3$ of a secondary product), 8·68 (*idem.*), 8·77 (*s*, two $CC\underline{H}_3$), 9·12 (*s*, two $CC\underline{H}_3$).

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THALICMININE FROM *OCOTEA PUBERULA*

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Key Word Index—*Ocotea puberula*; Lauraceae; thalicimine.

Plant. Ocotea pubercula (Nees et Mart) Nees from Provincia de Misiones (Argentina).