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A 2-OXO-3-PYRROLINE DIMER FROM *MERCURIALIS LEIOCARPA*

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Key Word Index—*Mercurialis leiocarpa*; Euphorbiaceae; 2-oxo-3-pyrroline derivative.

Abstract—A neutral component has been isolated from *Mercurialis leiocarpa* and its structure determined by X-ray analysis as 3,3'-bis-(1,1'-dimethyl-2,2'-dioxo-4,4'-dimethoxy-5,5'-dihydroxy-5,5'-dimethoxycarbonyl-3-pyrroline).

Mercurialis leiocarpa Sieb. et Zucc. [1], was used as an indigo dye in Japan between the 8th and 12th centuries. A neutral component has been isolated in crystalline form, and the structure determined by a single crystal diffraction analysis. The neutral component (**1**) (mp 266–268°, $[\alpha]_D^{20} = 0$), was isolated in 0.03% yield as colourless needles from the methanolic extract of the fresh herb of *Mercurialis leiocarpa*.

The molecular formula $C_{16}H_{20}N_2O_{10}$ was determined on the basis of the mass spectrum (m/z 400.1131) and elemental analysis. The IR spectrum showed the presence of a hydroxyl group (3475 and 3300 cm^{-1}), carbonyls (1760, 1745, 1700 and 1685 cm^{-1}) and an enol double bond (1645 cm^{-1}). The UV absorption spectrum gave no characteristic maxima. The ^1H ($CDCl_3$) and ^{13}C (DMSO-d_6) NMR spectra were rather simple, which suggested **1** to be a dimer of a $C_8H_{10}NO_5$ unit. In addition to the carbonyl absorptions in the IR spectrum, the appearance of the skeletal carbons as singlets in the ^{13}C NMR spectrum made the structural assignment difficult.

The correct structure was established by a single crystal X-ray diffraction study as 3,3'-bis-(1,1'-dimethyl-2,2'-dioxo-4,4'-dimethoxy-5,5'-dihydroxy-5,5'-dimethoxycarbonyl-3-pyrroline). The reddish colour of **1** in sodium methoxide–benzene and its decoloration on exposure to air were very similar to those of crysohermidine, isolated from *Mercurialis perennis* L. [2]. This seems to suggest the possibility of the transformation of **1** to crysohermidine.

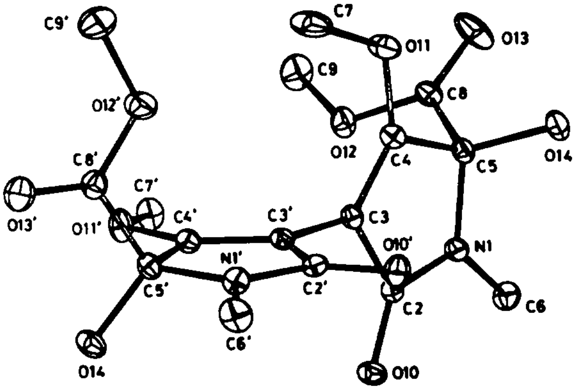

Fig. 1. Computer generated perspective drawing of **1**.

EXPERIMENTAL

Plant material. Mercurialis leiocarpa was collected in Mt. Makio, Osaka prefecture, Japan during the middle of October 1980 and identified by Dr. Ko Seto, Osaka Museum of Natural History (OSA). A voucher specimen has been deposited at the herbarium of OSA.

Extraction of M. leiocarpa *to isolate* **1**. Fresh whole plants (above-ground) (1 kg) were chopped and stored in MeOH (5 l.) at room temp. for 1 month. The methanolic filtrate was condensed under red. pres. to the residue, which was extracted with *n*-hexane to remove chlorophyll and dissolved into H_2O (200 ml). The aq. soln was extracted with EtOAc (200 ml × 5). The combined extracts were dried, and evaporated to dryness to give crystals (0.3 g: 0.03% yield), which were recrystallized from MeOH (30 ml), mp 266–268° (uncorr.) as colourless needles. $[M]^+$ at m/z 400.1131 (calc. for $C_{16}H_{20}N_2O_{10}$: 400.1132). (Found C, 47.93; H, 4.99; N, 6.97, $C_{16}H_{20}N_2O_{10}$ requires; C, 47.93; H, 4.97; N, 6.97%.) IR ν_{max}^{nujol} cm^{-1}: 3475, 3300, 1760, 1795, 1700, 1685, 1640, 1380, 1370, 1260, 1205, 1155, 1050, 940, 835. ^{1}H NMR ($CDCl_3$/TMS): δ1.61 (2H, *s*, OH), 2.83 (6H, *s*, OMe), 3.82 (6H, *s*, NMe), 3.92 (6H, *s*, OMe). ^{13}C NMR (DMSO-d_6/TMS): δ23.95 (*q*, OMe), 53.15 (*q*, NMe), 58.70 (*q*, OMe), 86.78 (*s*), 97.11 (*s*), 167.78 (*s*), 168.56 (*s*), 169.63 (*s*).

Crystal data. $C_{16}H_{20}N_2O_{10}$, $M_r = 400.1$, triclinic, space group PI, $a = 11.766$ (4), $b = 11.060$ (6), $c = 7.467$ (2) Å, $\alpha = 93.37$ (3), $\beta = 105.53$ (3), $= 97.43$ (3), $z = 2$, $D_m = 1.43$ g cm^{-3}, $D_c = 1.44$ g cm^{-3}, μ(MoKα) = 1.31 cm^{-1}, λ(MoKα) = 0.7107 Å, U = 924.0 (6) Å^3, crystal size 0.18 × 0.36 × 0.68 mm^3. The intensity data ($z \geqslant 50°$) were collected at room temperature on a Philips PW 1100 diffractometer. The ω-scan mode was employed. The scan range was $(1.0 + 0.3 \tan\theta)$, and the scan speed, 0.05 sec^{-1}. Background was counted for 7 sec at each side of the scan range. A total of 2172 reflections $[F_0^2 \geqslant 3\sigma(F_0^2)]$ were considered as observed. The intensity were corrected for Lorentz-polarization effects, but not for absorption. The structure was solved by use of MULTAN [3]. The refinement was performed by the block-diagonal least-squares method. The function minimized was $\Sigma w(F_0 - |F_c|)^2$, where $w = 1/(\sigma^2 F_0 + 0.005 F_0^2)$ was used. The value is 0.042. In the final cycles of the refinement, hydrogen atoms were included. All the parameter shifts of non-hydrogen atoms were less than their standard deviations. The maximum peak in the final difference Fourier map was 0.3 eÅ^{-3}. The atomic scattering factors were taken from the reference [4]. Computation were performed on a FACOM M18011-AD computer. The programs in the UNICS were used.

Final atom coordinates, a list of temperature factors, hydrogen atom positions, and final structure factors have been deposited at the Cambridge Crystallographic Data Centre.

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