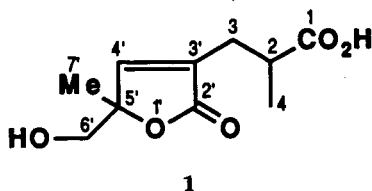


2-METHYL-3-(2-OXO-[5H]-5-HYDROXYMETHYL-5-METHYL-FURAN-3-YL)-PROPANOIC ACID, A NEW NECIC ACID LACTONE FROM *CROTALARIA VERRUCOSA*¹

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Plants of the genus *Crotalaria* are known to contain a large number of pyrrolizidine alkaloids (1-3). Seeds of *Crotalaria verrucosa* L., a member of the Leguminosae, have been reported to contain two otonecine esters trivially named as crotaverrine and acetyl-crotaverrine (4). The present investigation involves the isolation and characterization of a new racemic lactone acid **1** from the C₆H₆ extract of fresh leaves of the plant. This substance was structurally identified as 2-methyl-3-(2-oxo-[5H]-5-hydroxymethyl-5-methylfuran-3-yl)-propanoic acid with the aid of ¹H-nmr, ¹³C-nmr, ms, ir, and heteronuclear-decoupling data.



1

Compound **1**, mp 93°, was obtained as a colorless, crystalline solid by cc of the C₆H₆ extract over Si gel. The ¹³C-nmr spectrum for **1** showed the presence of 10 carbon atoms in the molecule. The absorptions in the ¹³C-nmr spectrum have been assigned unambiguously by SFORD spectra involving selective proton decoupling (5). Selective irradiation of the C-4' proton reduced the 146.341 doublet to a singlet, and similar irradiation of the C-4 methyl signal reduced the 14.276 quartet to a singlet in the off resonance decoupled spectra. Similarly, irradiation of the C-7' methyl signal re-

duced the 23.945 quartet to a singlet, and when the decoupler frequency was set to the resonance of the C-2 single proton signal, the 38.956 doublet appeared as a singlet; irradiation at the C-3 proton signal made the 26.359 triplet collapse to a singlet. Similar proton selective irradiation of the methylene signal of the C-6' protons collapsed the 70.407 triplet to a singlet. These data were rationalized in terms of structure **1** which was further supported by ¹H-nmr data of the acetate in which a 2-proton singlet at δ 4.8 shifted to 5.2 without appreciably affecting the other signals in the spectrum.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—A JEOL FX-100 spectrometer equipped with a ¹H/¹³C dual 5 mm probe was used to obtain the 99.6 MHz proton and 25.05 MHz carbon spectra at room temperature. The ¹³C-nmr spectrum has been analyzed with the aid of completely decoupled off-resonance coupled spectra and selective proton irradiation experiments. Ir spectra were recorded on a Pye-Unicam SP2000 ir spectrophotometer. Mp's are uncorrected.

PLANT MATERIAL.—The fresh leaves of *C. verrucosa* were collected from the experimental garden of the Regional Research Laboratory (CSIR), Jammu, India. A voucher specimen (No. 9916) of the plant is deposited in R. R. L. Jammu Herbarium.

EXTRACTION AND ISOLATION.—Fresh leaves were soaked in thiophene-free C₆H₆ at room temperature (37°) for 12 h, and the solvent was filtered. Concentration of the extract at 40° under diminished pressure yielded a crude residue. This residue was charged over a column of Si gel and eluted with mixtures of C₆H₆ and EtOAc in increasing polarity ratios. Elution with a 9:1 mixture of C₆H₆ and EtOAc yielded fractions that were observed to be homogeneous on tlc. The fractions were pooled and the residue on crystallization from C₆H₆ yielded **1**: mp 93°; ir ν max

¹RRL contribution No. 1901.

cm^{-1} 1745 (α,β -unsaturated- γ -lactone C=O), a broad hump extending from 3000 to 3600 (-OH of -COOH); ^1H nmr (CDCl_3) δ 0.90 (d, 3H, $J=6$ Hz, H-4), 1.53 (s, 3H, H-7'), 2.23 (m, 2H, H-3), 2.64 (m, 1H, H-2), 4.8 (s, 2H, H-6'), 6.3 (s, 1H, H-1), 7.2 (s, 1H, H-4'); ^{13}C nmr (CDCl_3) δ 14.276 (q, C-4), 23.945 (q, C-7'), 26.359 (t, C-3), 38.956 (d, C-2), 70.407 (t, C-6'), 77.015 (s, C-5'), 132.687 (s, C-3'), 146.341 (d, C-4'), 174.861 (s, C-1), 179.742 (s, C-2'); eims $[\text{M} + 1]^+$ at 215.0903 suggested $\text{C}_{10}\text{H}_{15}\text{O}_5$, calcd 215.0904.

ACETYLATION OF **1**.—Pure **1** (10 mg) was dissolved in pyridine (0.5 ml) and treated with a slight excess of Ac_2O . The reaction mixture was allowed to stand at room temperature overnight and, after usual processing, yielded a viscous mass which was purified by repeated cc over Si gel. The compound was pure (as determined on tlc); however, it could not be induced to crystallize: ^1H nmr (CDCl_3) δ 0.93 (d, 3H, $J=6$ Hz, H-4), 1.52 (s, 3H, H-7'), 2.07 (s, 3H, -OAc), 2.22

(m, 2H, H-3), 2.62 (m, 1H, H-2), 5.2 (s, 2H, H-6'), 6.3 (s, 1H, H-1), 7.15 (s, 1H, H-4').

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