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SYNTHESIS BY BENZILIC ACID REARRANGEMENT OF THE 2-OXO-3-PYRROLINE DIMERIC ALKALOID OF *MERCURIALIS LEIOCARPA*

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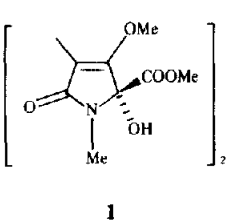
Key Word Index—*Mercurialis leiocarpa*; Euphorbiaceae; benzilic acid rearrengement; 2-oxo-3-pyrroline dimer.

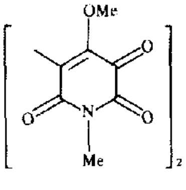
Abstract—The 2-oxo-3-pyrroline dimer, 3,3′-bis(1,1′-dimethyl-2,2′-dioxo-4,4′-dimethoxy-5,5′-dihydroxy-5,5′-dimethoxycarbonyl-3-pyrroline), present in *Mercurialis leiocarpa* has been synthesized.

INTRODUCTION

The structural elucidation of the 2-oxo-3-pyrroline dimer (**1**) derived from *Mercurialis leiocarpa* has been reported to be 3,3′-bis(1,1′-dimethyl-2,2′-dioxo-4,4′-dimethoxy-5,5′-dihydroxy-5,5′-dimethoxycarbonyl-3-pyrroline) [1] and is structurally similar to the 2,5,6-trioxo-3-pyridine dimer, 3,3′-bis(1,1′-dimethyl-2,2′,5,5′,6,6′-hexaoxo-4,4′-dimethoxy-3-pyridine) (**2**) from *Mercurialis perennis* [2]. We have now shown that **1** can be obtained from **2** by means of the benzilic acid type rearrangement.



1



2

The dimer (**2**) was prepared by the procedure described, [3] a two step-synthesis from 3-amino-4-methoxy-1-methylpyridine-2,6(1*H*, 3*H*)-*dione*. Treatment of (**2**) with an equimolar amount of sodium methoxide in methanol at room temperature gave (**1**) in 10% yield, which was identical in all respects on direct comparison with a sample of natural 2-oxo-3-pyrroline dimer (**1**) [1].

EXPERIMENTAL

The 2,5,6-*trioxo-3-pyridine dimer* (**2**) was synthesized in two steps from 3-amino-4-methoxy-1-methylpyridine-2,6(1*H*, 3*H*)-dione according to ref. [3]. Total yield 14%. Then **2** was identified by derivatization to its 5,5′,6,6′-tetraacetate [mp 174–176°; lit. [3], 174–175°].

The 2-*oxo-3-pyrroline dimer* (**1**) was synthesized as follows: to a solution of the 2,5,6-trioxo-3-pyridine (**2**) (198 mg, 0.59 mmol) in MeOH (10 ml) was injected a methanolic solution of NaOMe (2.4 ml of 0.5 mol solution, 1.2 mmol) at room temp. in N_2. The mixture was stirred overnight. An aqueous saturated solution of NH_4Cl (2 ml) was added until the mixture became neutral. It was extracted with EtOAc (10 ml × 6). The combined extracts were evapd to the residue (crude yield, 70 mg), purified by prep. TLC, using Kieselgel-60 F_{254}-Merck and EtOAc (devloper). Silica gel on the zone between R_f value 0.3 and 0.5 was cut off, and washed with MeOH. The collected washings were taken to dryness, which crystallized and this was recrystallized from EtOAc to give 22 mg. (10% yield) of the 2-oxo-3-pyrroline dimer (**1**), which was identical with an authentic sample of (**1**) in mp 265–268°, TLC (R_f value, 0.42; Kieselgel-60 F_{254}-Merck, EtOAc), and also in its ^1H NMR and IR spectra.

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