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3-METHOXY-4,6-DIHYDROXYMORPHINANDIEN-7-ONE, AN ALKALOID FROM *CROTON BONPLANDIANUM*

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Key Word Index—*Croton bonplandianum*; Euphorbiaceae; 3-methoxy-4,6-dihydroxymorphinandien-7-one; structural determination.

Abstract—A new alkaloid, 3-methoxy-4,6-dihydroxymorphinandien-7-one, and norsinoacutine have been isolated from extracts of *Croton bonplandianum.*

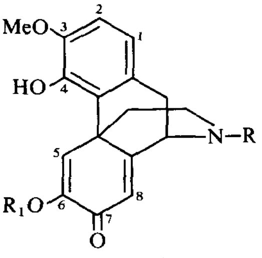
INTRODUCTION

Several alkaloids [1–18] have been isolated from species of the genus *Croton*, but no work has been reported on *Croton bonplandianum.* A systematic chemical examination of this plant was, therefore, undertaken and the alkaloidal constituents are reported in the present communication.

RESULTS AND DISCUSSION

The new alkaloid isolated is assigned the structure 3-methoxy-4,6-dihydroxymorphinandien-7-one (**1**) $C_{17}H_{17}NO_4$ on the basis of following evidence. The presence of nitrogen as a secondary amine was suggested by the appearance of a band at 3215 cm^{-1} in the IR spectrum [1]. The other IR bands at 3400 cm^{-1} show the presence of an OH group and the bands at 1665, 1634 and 1608 cm^{-1} indicate the presence of a dienone [1]. Furthermore the appearance of an UV absorption band at 238 nm confirms the presence of a cross conjugated system [2].

The compound (50 mg) when heated under reflux (2 hr) in MeOH with excess MeI in the presence of Na_2CO_3, yielded the *N*-*O*-trimethylmethiodide derivative (30 mg), $C_{21}H_{26}INO_4 . Me_2CO$, mp 163–5° ($Me_2CO$), which was found to be identical with *N*-*O*-dimethylnorsinoacutine methiodide [3], thereby suggesting that the new alkaloid differed from norsinoacutine $C_{18}H_{19}NO_4$ (**2**) only in the presence of a OH group in place of a OMe group. The same methiodide is also obtained from the *N*-methyl-4,6-dihydroxy-3-methoxymorphinandienone [19] which confirms the presence of two OH groups and one OMe group.



1 R = R$_1$ = H
2 R = H; R$_1$ = Me

The signals observed in the NMR spectrum at δ 6.56 (H, C-1), 6.83 (H, C-2), 7.63 (H, C-5), 6.15 (H, C-8) and 3.83 (3 H, OMe, C-3) are due to the presence of two aromatic protons, two olefinic protons and one OMe group, respectively [1]. The signal at δ 3.75, observed in norsinoacutine did not appear in the spectrum of **1**, showing the absence of a OMe group at C-4 [1].

The mass spectrum [4,20] of the compound showed a M^+ at *m*/*e* 299 and other prominent peaks at *m*/*e* 284 ($M^+ - Me$), 277 ($M^+ - CO$), 256 (284 − CO) and 164 which supported the proposed structure for the compound.

Another compound, mp 113°, $C_{18}H_{19}NO_4$(**2**) was obtained from the alkaloidal mixture on column chromatography, which was identified as nonsinoacutine [5].

EXPERIMENTAL

Extraction and isolation of alkaloids. The air dried and powdered plant (5 kg) was extracted with 2% HOAc soln. The extract (10 l.) was concd under red. pres. to 500 ml and basified with 25% NH_4OH soln. The basified extract was continuously shaken with $CHCl_3$ for 2 hr and the organic layer separated. The solvent was removed *in vacuo* to yield a mixture of alkaloids. The crude alkaloidal mixture showed two spots on TLC, was adsorbed on an Al_2O_3 column and eluted with $CHCl_3$–MeOH (19:1). The first eluate yielded an amorphous compound, which on crystallization from EtOAc at 0° yielded crystals of norsinoacutine [5] (310 mg), mp 113°. Successive elution with MeOH yielded another compound (145 mg), mp 143° (MeOH–EtOAc). Found: C, 65.19; H, 6.41; N, 3.59; $C_{17}H_{17}NO_4$. EtOAc requires C, 65.12, H, 6.46, N, 3.62%. UV λ_{max}^{MeOH} nm: 238; IR ν_{max}^{KBr} cm^{-1}: 3400, 3215, 1665, 1634, 1608; MS *m*/*e* (rel. int.): 299 (M^+), 284, 277, 266, 256: ^1H NMR ($CDCl_3$) δ 3.83 (3 H), 6.15 (1 H), 6.56 (1 H), 6.83 (1 H), 7.63 (1 H).

Preparation of methiodide derivative. **1** (50 mg) when heated under reflux (2 hr) in MeOH with excess MeI in the presence of Na_2CO_3 gave a product, which was adsorbed onto an Al_2O_3 column. Elution with Me_2CO–MeOH (8:1) yielded the methiodide derivative (39 mg) which crystallized from Me_2CO, mp 163–5°. Found C, 53.1; H, 5.9; $C_{21}H_{26}INO_4 . Me_2CO$ requires C, 53.2; H, 6.0%. It was identical with *N*-*O*-dimethylnorsinoacutine methiodide [3].

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