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SATIVANINE-G, A CYCLOPEPTIDE ALKALOID FROM *ZIZYPHUS SATIVA*

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Key Word Index—*Zizyphus sativa*; Rhamnaceae; peptide alkaloid; sativanine-G.

Abstract—In addition to the already described peptide alkaloids from the bark of *Zizyphus sativa*, a new compound of this class, sativanine-G, has been isolated and its structure elucidated. This alkaloid contains a 13-membered ring system and belongs to the nummularine-C class.

INTRODUCTION

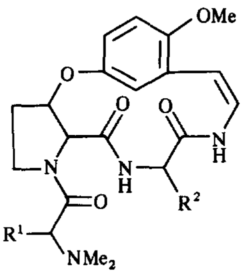
In continuation of our work on cyclopeptide alkaloids from the family Rhamnaceae we now report a new alkaloid from *Zizyphus sativa*. The alkaloids frangulanine [1], nummularine-B [2], mucronine-D [3], sativanines-A, -B [4], -C [5], -D, -E and -F [6] have earlier been reported from this plant. We have now isolated a new alkaloid, sativanine-G, by repeated chromatography and prep. TLC of the alkaloid fraction isolated from the stem bark.

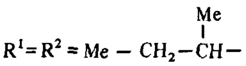
RESULTS AND DISCUSSION

Sativanine-G, mp 92°, $C_{28}H_{42}N_4O_5$ ($[M]^+$ m/z 514.3168) was recognised to be a 13-membered cyclopeptide alkaloid from its UV spectrum [3]. The IR spectrum exhibited bands for –NH, *sec.* amide, –OMe, –NMe, $>C{=}C<$ and aryl ether. On acid hydrolysis it gave *N*,*N*-dimethylisoleucine and isoleucine. Mass spectral peaks of sativanine-G correspond with those of nummularine-C [2] with the only exception that the base peak of the former is 34 mu lower than that of the latter. These data reveal that sativanine-G possesses the structure **1** which differs from nummularine-C (**2**) by having *N*,*N*-dimethylisoleucine instead of *N*,*N*-dimethylphenylalanine as the end amino acid and isoleucine instead of leucine as the amino acid residue bound to the styrylamine moiety. Sativanine-G is a new addition to the growing list of 13-membered cyclopeptide alkaloids which belong to the nummularine-C type.

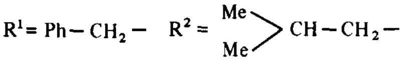
EXPERIMENTAL

Mps are uncorr IR and UV were determined in KBr and MeOH, respectively. MS analysis was performed at 70 eV with



1 

$R^1 = R^2 = Me-CH_2-\overset{Me}{\overset{|}{C}H}-$

2 

$R^1 = Ph-CH_2-\quad R^2 = {Me \atop Me}\!>\!CH-CH_2-$

evapn of the sample in the ion source at *ca* 200°. TLC was done on silica gel Merck $60F_{254}$

Extraction and isolation. Bark of *Z. sativa* Gaertn [7, 8] was collected in Hazara District, Pakistan. Extraction of plant material (10 kg) was carried out in the usual manner [9] and semi-solid crude alkaloids (6.6 g.) were obtained. The alkaloid mixture was fractionated on a silica gel M (900 g, Geb. Herrmann/Köln) column, eluting with increasingly polar CH_2Cl_2–MeOH mixtures into 20 fractions. The chromatographic separation was followed by UV monitoring and collected fractions were analysed by TLC proving in every case to be a mixture of two or three main components The fractions were separated into individual components by prep TLC and repeated CC Sativanine-G (6 mg) was obtained from fraction 16 by repeated prep. TLC on silica gel using cyclohexane–EtOAc–MeOH (10.5:1) and cyclohexane–EtOAc–Me_2CO–MeOH (30:5·10:1) as solvent systems

Sativanine-G. $C_{28}H_{42}N_4O_5$ ($[M]^+$ 514.3168, calc. for: 514.3181). UV λ_{max} nm: 320 and 258, IR ν_{max} cm^{-1}: 3380 (–NH), 1670, 1635 (*sec* amide), 2835 (–OMe), 2780 (–NMe), 1610 ($>C=C<$), 1230 and 1040 (aryl ether); MS: *m/z* 514 $[M]^+$, 457, 401, 400, 374, 304, 259, 233, 216, 209, 165, 114 (base peak), 96, 86 Sativanine-G (3 mg) was hydrolysed with 6 N HCl (10 hr) in a sealed tube. The hydrolysate was evapd to dryness and examined by PC (*n*-BuOH–HOAc–H_2O, 4:1:5). *N,N*-Dimethylisoleucine and isoleucine were identified by comparison with authentic compounds.

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CANTHIN-6-ONE, UNDULATONE AND TWO QUASSINOIDS FROM *HANNOA KLAINEANA* ROOTS

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Key Word Index—*Hannoa klaineana*; Simaroubaceae; canthin alkaloid, canthin-6-one; coumarin, scopoletin; quassinoids; undulatone; 15-desacetylundulatone; 6α-tigloyloxyglaucarubol

Abstract—Canthin-6-one, scopoletin, undulatone and two new quassinoids, 15-desacetylundulatone and 6α-tigloyloxyglaucarubol were isolated from *Hannoa klaineana* roots; quassinoids were obtained in high yields from this plant material.

INTRODUCTION

The isolation and identification of seven alkaloids from three different samples of *Hannoa klaineana* Pierre et Engler roots have been reported [1]. Further investigations performed on one sample of the same plant material have led to the isolation and the identification of an eighth alkaloid, canthin-6-one (**1**), a coumarin, scopoletin (**2**) and three quassinoids: undulatone (**3**) firstly isolated from *Hannoa undulata* [2] and two new related compounds, 15-des-acetylundulatone (**4**) previously obtained by chemical hydrolysis of undulatone [2], and 6α-tigloyloxyglaucarubol (**5**).

RESULTS AND DISCUSSION

A methanolic extract of *H. klaineana* roots was fractionated by column chromatography and the fractions further purified either by reverse phase column chromatography (quassinoids) or by preparative TLC (scopoletin, canthin-6-one). This method was found to be more effective for the isolation of polar quassinoids which are not quantitatively extracted by liquid–liquid partition between aqueous methanol and chloroform.

Canthin-6-one (**1**), scopoletin (**2**) and undulatone (**3**) were identified by UV, IR, ^1H NMR, MS and by direct TLC comparison with authentic samples. Canthin-6-one had already been isolated from numerous species of Simaroubaceae [3, 4]. As in the case of compound **3**, the UV absorption of **4** at 225 nm was attributed to the presence of α,β-unsaturated ester and α,β-unsaturated ketone functions. The IR spectrum of **4** showed absorptions at 1730, 1700 and 1670 cm^{-1} indicative of δ-lactone, α,β-unsaturated ester and α,β-unsaturated ketone functions; these data confirmed the interpretation of the UV spectrum and indicated the possible absence from **4** of the acetate function of **3**. The mass spectrum showed a molecular ion at *m/z* 492 and a fragment at *m/z* 392 $[M-100]^+$; moreover ions at *m/z* 83 (C_5H_7O) and 55 (C_4H_7)