Phytochemistry, 1979, Vol. 18, pp. 702–704. ©Pergamon Press Ltd. Printed in England. 0031-9422/79/0401-0702 $02.00/0

SATIVANINE-A AND SATIVANINE-B, TWO NEW CYCLOPEPTIDE ALKALOIDS FROM THE BARK OF *ZIZYPHUS SATIVA**

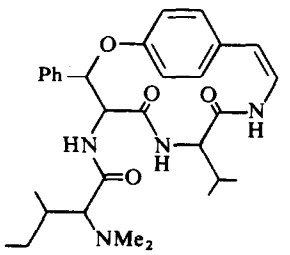
RUDOLF TSCHESCHE, ARIF H. SHAH and GERT ECKHARDT
Institut für Organische Chemie und Biochemie der Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, W. Germany

(*Received* 2 *August* 1978)

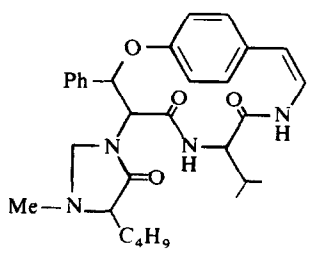
Key Word Index—*Zizyphus sativa*; Rhamnaceae; cyclopeptide alkaloids; sativanine-A and sativanine-B.

Abstract—From the bark of *Zizyphus sativa*, in addition to already described cyclopeptide alkaloids, two new compounds of this class, sativanine-A (**1**) and sativanine-B (**2**), were isolated. Both alkaloids contain 14-membered ring systems. **1** belongs to the integerrine type, while **2** is similar to nummularine-G, with an additional ring in the side chain.

In continuation of our work on cyclopeptide alkaloids from the Rhamnaceae we now report on the alkaloids of *Zizyphus sativa*. The major alkaloids obtained were the known substances frangulanine [2], nummularine-B [3] and mucronine-D [4]. However, repeated chromatography on silica gel gave very small amounts of the previously undescribed cyclopeptide alkaloids, sativanine-A and sativanine-B. Sativanine-A belongs to the integerrine type [5] whilst the structure of sativanine-B is related to nummularine-G [6], so providing the second example of the occurrence of this type of alkaloid in plants.



1 Sativanine-A



2 Sativanine-B

Sativanine-A (**1**)

The UV spectrum of **1** showed end absorption characteristic of a styrylamine chromophore in the 14-membered cyclopeptide alkaloids. The elementary composition of **1** was determined by high resolution MS as $C_{30}H_{40}N_4O_4$. The MS of **1** (Fig. 1) is very similar to that of integerrine [7], the main difference being that the molecular ion and all fragments which contain the amino acid bound to the nitrogen of the styrylamine function (**b, g, j, e, h, k, l**) are displaced by 14 mu to lower values. From this it can be concluded that **1** contains valine at that position. At *m/e* 72 the amino fragment $H_2\overset{+}{N}{=}CH{-}CH(CH_3)_2$ is observed.

It may be concluded that the terminal amino acid of **1** is *N,N*-dimethylisoleucine from the secondary fragmentation of fragment **a**, which shows the elimination of an ethyl radical giving *m/e* 85 with a strong metastable ion for that process at *m/e* 63.4 [8]. The elementary composition of all fragments was substantiated by high resolution mass measurements.

Sativanine-B (**2**)

The UV spectrum of **2** revealed the presence of a 14-membered ring cyclopeptide alkaloid system. By high resolution MS the elementary composition of **2** was determined as $C_{30}H_{38}N_4O_4$. The MS of **2** (Fig. 2) differs greatly from those of most 14-membered cyclopeptide alkaloids but resembles closely that of nummularine-G [6], indicating the presence of an additional ring in the side chain. The amino acid which is linked with the nitrogen of the styrylamine function must be valine, as the molecular ion and all the fragments containing this amino acid [**j, e, f, h**, $H_2\overset{+}{N}{=}CH{-}CH(CH_3)_2$, *m/e* 72] are shifted by 14 mu to lower mass compared to nummularine-G. The fragments **c, d** and $C_8H_{15}N_2O^+$ (*m/e* 155), however, are found at the same *m/e* values as in the MS of nummularine-G, which proves that the ring in the side chain is made up from a C_6 amino acid. Because of the very small amount of material it was not possible to confirm whether this amino acid was a derivative of leucine or isoleucine.

EXPERIMENTAL

Plant material was collected from the Hazara district of Pakistan. Mps were determined on a Kofler microscope stage. MS analyses were performed at 70 eV with evapn of the samples in the ion source at *ca* 200°. TLC, unless otherwise specified, was carried out on Si gel Merck 60 F_{254}. Extraction of the

* Part XXXI in the series "Alkaloids from Rhamnaceae." For Part XXX see ref. [1].

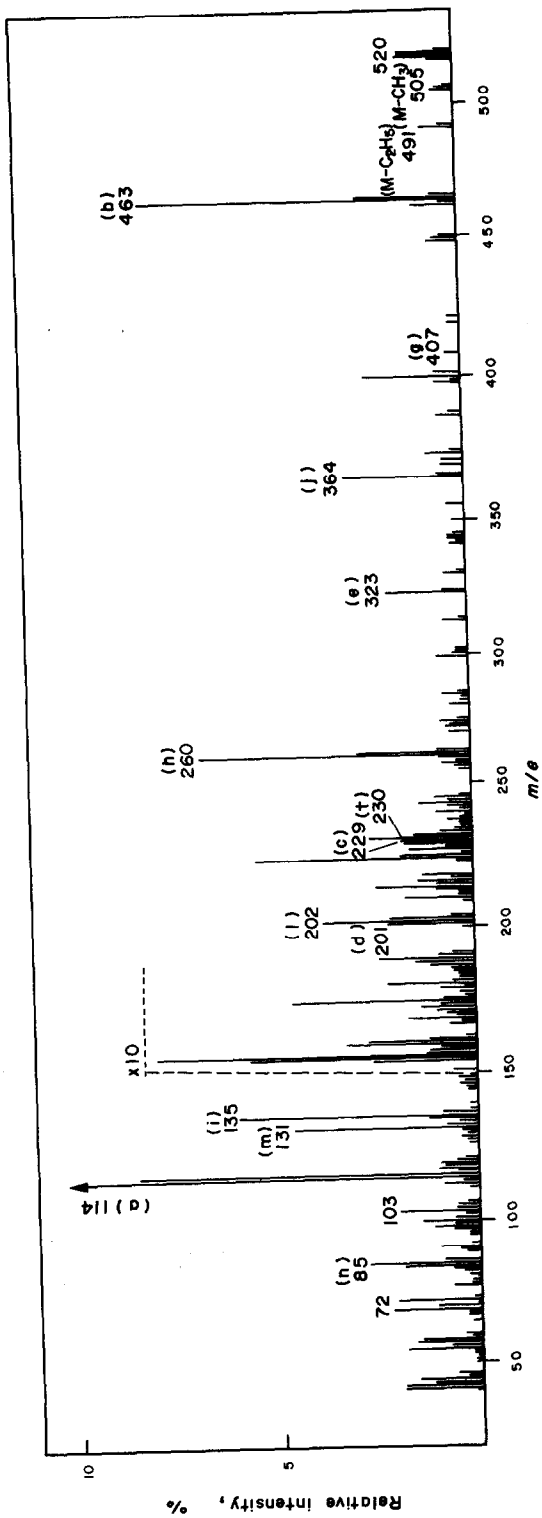


Fig. 1. Mass spectrum of sativanine-A (1) at 70 eV.

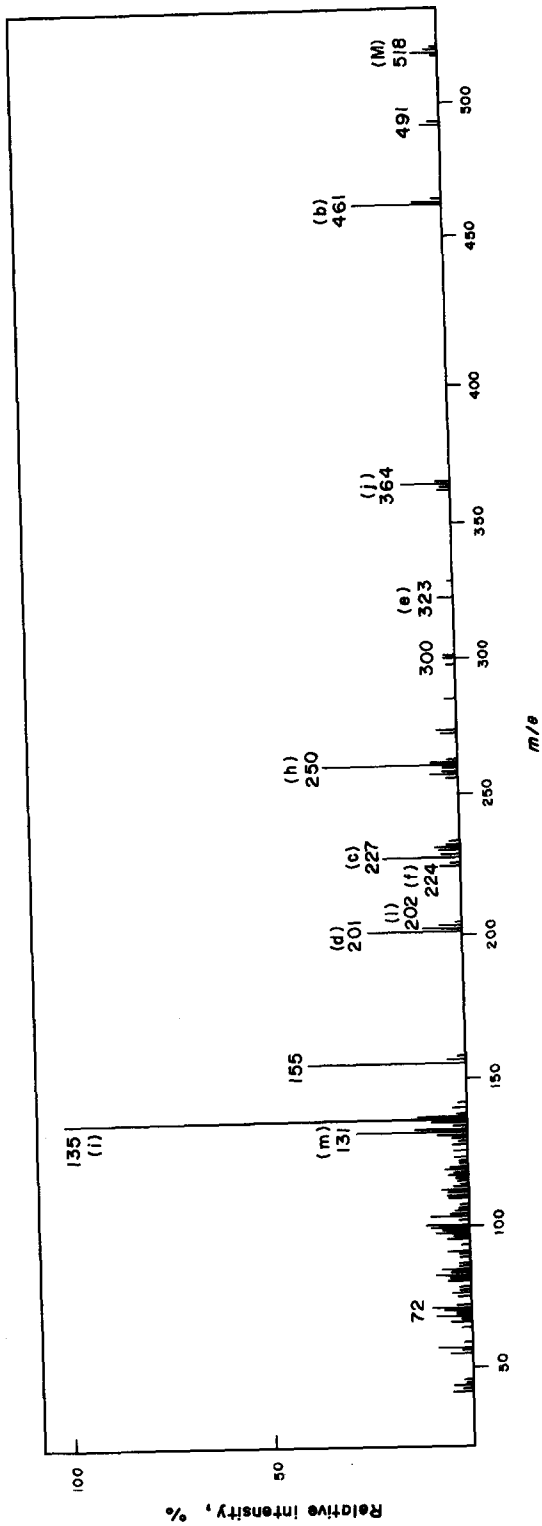


Fig. 2. Mass spectrum of sativanine-B (2) at 70 eV.

powdered bark (5 kg) was carried out in the usual manner [9] and the crude alkaloids (5.440 g) were fractionated on a 500 g Si gel (Gebr. Herrmann/Köln) column, eluting with increasingly polar CH_2Cl_2/MeOH mixtures, into 9 fractions. The chromatographic separation was followed by LKB Uvicord, and the collected fractions were analysed by TLC, proving in every case to be mixtures of two or three main components, which were purified using PLC or column chromatography.

Frangulanine (102 mg), nummularine-B (69 mg) and mucronine-D (5 mg) were obtained and identified by spectroscopic methods and by chromatographic comparison with the authentic samples in several solvent systems.

Sativanine-A. 0.48 mg were obtained from fraction IV by repeated chromatography on Si gel using cyclohexane–Me_2CO–MeOH (35:15:1) and cyclohexane–EtOAc–MeOH (30:15:4) as solvent systems: mp 80° (uncorr.); UV (MeOH) strong end absorption and shoulders at 250 and 280 nm. Mol. wt. (MS) 520.3055; calcd. for $C_{30}H_{40}N_4O_4$, 520.3050.

Sativanine-B. 0.42 mg were obtained from fraction V using C_6H_6–Me_2CO–MeOH (25:30:4) and C_6H_6–EtOAc–MeOH (25:15:4) as solvent systems; mp: amorphous; UV (MeOH) strong end absorption with shoulder at 280 nm. Mol. wt. (MS) 518.2888; calcd. for $C_{30}H_{38}N_4O_4$, 518.2893.

Acknowledgements—We thank M. H. Shah and Dr. Aslam Khan, A. R. I. Tarnah, Peshawar, Pakistan, for the plant material and the Deutsche Forschungsgemeinschaft for financial support. A.H.S. thanks the Heinrich Hertz Stiftung for a scholarship.

REFERENCES

1. Tschesche, R. and Hillebrand, D. (1977) *Phytochemistry* **16**, 1718.
2. Tschesche, R., Last, H. and Fehlhaber, H.-W. (1967) *Chem. Ber.* **100**, 3937.
3. Tschesche, R., Miana, G. A. and Eckhardt, G. (1974) *Chem. Ber.* **107**, 3180.
4. Tschesche, R., David, S. T., Uhlendorf, J. and Fehlhaber, H.-W. (1972) *Chem. Ber.* **105**, 3106.
5. Tschesche, R. and Kaußmann, E. U. (1975) *The Alkaloids* (Manske, R. H. F., ed.) Bd. XV, p. 165. Academic Press, New York.
6. Tschesche, R., Elgamal, M. and Eckhardt, G. (1977) *Chem. Ber.* **110**, 2649.
7. Tschesche, R., Rheingans, J., Fehlhaber, H.-W. and Legler, G. (1967) *Chem. Ber.* **100**, 3924.
8. Fehlhaber, H.-W. (1968) *Z. Analyt. Chem.* **235**, 91.
9. Tschesche, R., Welters, R. and Fehlhaber, H.-W. (1967) *Chem. Ber.* **100**, 323.

Phytochemistry, 1979, Vol. 18, pp. 704–705. Pergamon Press. Printed in England.

ALKALOIDS FROM PODS OF *ERYTHRINA ARBORESCENS*

K. P. TIWARI and M. MASOOD
Department of Chemistry, University of Allahabad, Allahabad 211002, India

(*Revised received* 22 *September* 1978)

Key Word Index—*Erythrina arborescens*; Leguminosae; erysodine; orientaline; hypaphorine; a new quaternary alkaloid—erysodinophorine.

INTRODUCTION

Erythrina arborescens is distributed throughout the upper gangetic plains, Assam and Manipur, extending west towards Nepal [1, 2]. The seed of this plant has been reported to contain erysodine, erysovine, erysopine, hypaphorine, erythrascine, orientaline and erysophorine [2, 3]. The present investigation was carried out in order to determine the chemical constituents of the pod walls of *E. arborescens*.

RESULTS AND DISCUSSION

The EtOH extract of the pod walls of *E. arborescens* yielded erysodine, orientaline, hypaphorine (mmp, co-chromatography and spectral studies) and a new alkaloid provisionally named as erysodinophorine. Hydrolysis of erysodinophorine with EtOH–HCl afforded two alkaloids erysodine and hypaphorine. The molecular formula, $C_{32}H_{38}N_3O_5$, of erysodinophorine was established from elemental analysis, the integrals of the proton signals (37H in D_2O) and from the molecular formulae of the products of the hydrolysis of erysodinophorine. Like erysophorine, erysodinophorine also did not respond to the Ehrlich test for α and β unsubstituted indoles, whereas the acid hydrolysed product, on the other hand, gave a positive test. The negative response was presumably due to the attachment of the bulky ester function which blocks the free α position of the indole ring in erysodinophorine [3]. The UV spectrum of erysodinophorine is very similar to that of erysophorine indicating its marked structural similarity [3]. The compound showed major bands in the IR at 3400 (broad, —OH and >NH), 1754 (phenolic ester group), 1620 (indole ring), 1590, 1496, 1258, 1082 (spiroamine ring). The absence of a peak at 1442 cm^{-1} in the IR suggests