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Tetrahedron Letters 46 (2005) 931–932
Tetrahedron Letters

Stenotarsol, a new terpenoid from *Stenotarsus subtilis* (Coleoptera: Endomychidae)

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Received 15 November 2004; revised 13 December 2004; accepted 13 December 2004

Abstract—Stenotarsol (**1**), a new terpenoid alcohol, has been isolated from the beetle *Stenotarsus subtilis* (Endomychidae). Its structure has been determined on the basis of its spectral properties. Compound **1** represents a new type of terpene skeleton and is the first secondary metabolite reported so far from this family of beetles.

Mycophagy is fairly common within the Coleoptera. It has been estimated that as many as 25 beetle families directly feed on fungi.[1] The Endomychidae, commonly referred to as the Handsome Fungus Beetles, are important members of the mycophagous beetle fauna with 1300 described species in 120 genera worldwide.[2] These beetles are related to the ladybirds and look like them in appearance. Furthermore, both insects release hemolymph when molested. This well-described process, known as 'reflex bleeding', serves as an efficient protection against predators.[3] Such a defence mechanism is well documented in the Coccinellidae[4,5] and is known to be associated with the presence of alkaloids in the hemolymph. On the contrary, nothing is known about the defensive chemistry of the Endomychidae.

In this paper, we wish to report the isolation and structure determination of stenotarsol, a new terpenoid from *Stenotarsus subtilis*, an aggregating endomychid beetle collected in Panama.

The methanol extract of about 250 specimens of *S. subtilis* was partitioned between the two phases of the mixture ethyl acetate–hexane–isopropanol–water 2:1.5:1:3. The resulting organic phase was chromatographed successively on a silica gel and on an alumina column to afford 1.3 mg of a new UV absorbing sesquiterpenic alcohol ($[\alpha]_D^{20}$ 81.5 (*c* 0.13, $CHCl_3$); UV (MeOH): λ_{max} 224 nm (ε 27,360), 307 nm (ε 2440); IR: 3440, 1759, 1682, 1651, 771 cm^{-1}) for which the name stenotarsol was coined. Mass spectrometric investigations revealed its molecular formula to be $C_{15}H_{16}O_4$ (HR-EIMS: molecular ion at *m/z* 260.1068; calcd for

Table 1. NMR data of **1** (600 and 150.85 MHz, $CDCl_3$, δ, *J* in Hz)

Position	δ_C[a]	δ_H	HMBC (H to C)[b]
1	199.0	—	—
2	47.0	AB, δ_A 2.78, δ_B 2.50 (15.9)	C-1, C-3, C-4, C-10, C-11, C-12
3	38.0	—	—
4	35.7	AB, δ_A 3.12, δ_B 2.76 (17.4)	C-2, C-3, C-5, C-6, C-10
5	140.0	—	—
6	148.0	—	—
7	131.0	7.90, s	C-6, C-8, C-13, C-14
8	146.0	—	—
9	125.0	—	—
10	128.0	—	—
11	23.0	1.07, s	C-2, C-3, C-4, C-12
12	71.0	3.56, br s	C-2, C-4, C-11
13	20.0	2.44, s	C-5, C-6, C-7
14	171.0	—	—
15	72.0	AB, δ_A 5.62, δ_B 5.57 (17.4)	C-8, C-9, C-14

[a] Assignments by HMBC and HMQC.
[b] Optimized for $^nJ_{CH}$ = 5 and 10 Hz.

Keywords: Insect; Secondary metabolite; Structure determination.
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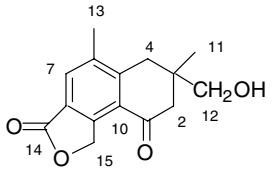
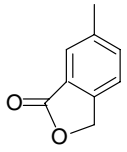
0040-4039/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2004.12.052

$C_{15}H_{16}O_4$ 260.1049). Moreover, a characteristic ion at *m/z* 229.0852 (calcd for $C_{14}H_{13}O_3$ 229.0865) showed the loss of a CH_2OH radical from the molecular ion.

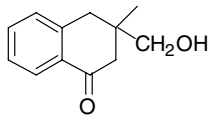
The structure of stenotarsol (**1**) was established by a detailed 1D and 2D NMR study (^1H–^1H COSY, HMQC, HMBC). The ^1H and ^{13}C NMR signals of **1** are reported in Table 1. They indicated the presence of two quaternary methyl groups, three isolated methylene groups, an isolated hydroxymethylene function, a penta substituted benzene ring, and two carbonyl groups assignable to an aromatic ketone and to a conjugated γ-lactone, respectively.



1



2



3

The connectivity of **1** could be elucidated by HMBC correlations. Most noteworthy were the correlations between CH_3-13 and C-5, C-6, and C-7, between CH-7 and C-6, C-8, and C-14, between CH_2-15 and C-14 and C-9, between CH_2-2 and C-10, C-1, and C-3, and between CH_2-4 and C-6, C-10, C-3, and C-5. Moreover, CH_3-11 and CH_2-12 showed striking HMBC correlations with C-2 and C-4. All these data led to the complete assignments reported in Table 1. These assignments are in good agreement with those reported for model compounds such as **2**[6] and **3**.[7]

There is no precedent in the literature of a natural compound possessing the carbon skeleton of stenotarsol. Nevertheless, based on the number of carbon atoms and the presence of several methyl or transformed methyl groups, it is tempting to assume that **1** is of terpene origin. Of course, such an assumption has to be confirmed. Stenotarsol is also the first secondary metabolite isolated from an endomychid beetle and no alkaloid could be found in the extract of the beetle. These facts suggest that this group of Coleoptera possess an original chemical defence system, distinct from that of the Coccinellidae to which they are taxonomically related.

Acknowledgements

Entomed S. A. is gratefully acknowledged for its financial support. We thank Dr. M. Luhmer and R. d'Orazio for the NMR spectra and M. Pamart for the mass spectra.

References and notes

1. Lawrence, J. F. Mycophagy in the Coleoptera: Feeding Strategies and Morphological Adaptations. In *Insect–Fungus Interactions*; Wilding, N., Collins, N. M., Hammond, P. M., Webber, J. F., Eds.; Academic: London, 1989; pp 1–23.
2. Skelley, P. E.; Leschen, R. A. B. Endomychidae. In *American Beetles*; Arnett, R. H., Jr., Thomas, M. C., Skelley, P. E., Frank, J. H., Eds.; Polyphaga: Scarabaeoidea through Curculionidae, Vol. 2; CRC: LLC, Boca Raton, pp 366–370.
3. Hollande, A. Ch. *Arch. Anat. Microsc. Morphol. Exp.* **1926**, *22*, 374–411.
4. Daloze, D.; Braekman, J. C.; Pasteels, J. M. *Chemoecology* **1994 & 1995**, *5/6*, 173–183.
5. Glisan King, A.; Meinwald, J. *Chem. Rev.* **1996**, 1105–1122.
6. Davies, H. M. L.; Matasi, J. J.; Ahmed, G. *J. Org. Chem.* **1996**, *61*, 2305–2313.
7. Ogawa, Y.; Matsusaki, H.; Hanaoka, K.; Ohkata, K.; Hanafusa, T. *J. Org. Chem.* **1978**, *43*, 849–855.