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Two New Pungent Principles isolated from the Pericarps of *Zanthoxylum ailanthoides*

The new pungent principles, γ-sanshoöl and hydroxy γ-sanshoöl, were isolated from the pericarps of *Zanthoxylum ailanthoides* Sieb. *et* Zucc. Their structures were determined as (2*E*,4*E*,8*Z*,10*E*,12*E*)-*N*-isobutyl-2,4,8,10,12-tetradecapentaenamide and (2*E*,4*E*,8*Z*,10*E*,-12*E*)-2′-hydroxy-*N*-isobutyl-2,4,8,10,12-tetradecapentaenamide by chemical and spectroscopic evidences.

Keywords——pungent principle; *Zanthoxylum ailanthoides*; Rutaceae; γ-sanshoöl; hydroxy γ-sanshoöl; unsaturated aliphatic acid amide; ^{13}C-NMR spectrum

We reported previously the isolation and structure determination of three unsaturated aliphatic acid amides from the roots of *Asiasarum heterotropoides* Maek. var. *mandshuricum* Maek. (Aristolochiaceae).[1] In the course of investigation on the pungent principle of the pericarps of *Zanthoxylum ailanthoides* Sieb. *et* Zucc. (Japanese name Karasusanshoh, Rutaceae), two new unsaturated aliphatic acid amides, named as γ-sanshoöl (**1**) and hydroxy γ-sanshoöl (**2**), were isolated. Now, we wish to describe the isolation and structure elucidation of **1** and **2**.

The dry-powdered pericarps of *Z. ailanthoides* were extracted with methanol. After removal of the chloroform soluble part from the methanol extract, the residue was further extracted with ethyl acetate and *n*-butyl alcohol. The chloroform fraction showed strong pungency, while the other fractions did not. The chloroform fraction was chromatographed on silica gel to give two compounds, **1** (yield 0.27%) and **2** (0.43%), by eluting with benzene–ethyl acetate (10: 1—1: 1). The pungency of **1** was stronger than that of **2**.

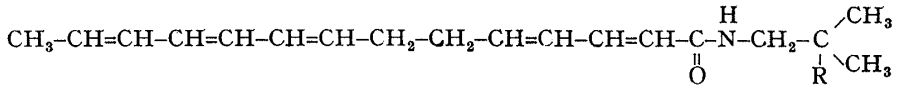
1 was obtained as unstable colorless needles (*n*-hexane), mp 88—89°, $C_{18}H_{27}NO$.[2] The proton nuclear magnetic resonance (^{1}H-NMR), infrared absorption (IR) and ultraviolet absorption (UV) spectra of **1** denoted the presence of α,β,γ,δ-unsaturated acid amide and isobutyl as functions.[3]; ^{1}H-NMR ($CDCl_3$) δ: 0.93 (6H, d, J=7 Hz, 3′-H), 1.78 (4H, m, 14- and 2′-H), 2.28 (4H, m, 6- and 7-H), 3.17 (2H, dd, J=7, 6 Hz, 1′-H), 5.30—5.54 (2H, m), 5.73 (1H, m), 5.76 (1H, d, J=15 Hz, 2-H), 6.00—6.30 (6H, m), and 7.18 (1H, dd, J=15, 10 Hz, 3-H). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3300 (NH), 1680, 1640, 1620 (CH=CH, C=O), and 990 (CH=CH). UV λ_{max}^{EtOH} nm (ε): 260 (4.8×10^4), 272 (5.7×10^4), and 280 (4.5×10^4). On hydrogenation with PtO_2 as a catalyst, **1** gave the decahydro-derivative (**3**), $C_{18}H_{37}NO$,[2] colorless needles (*n*-hexane), mp 64°. The acid hydrolysis of **3** (5% HCl in EtOH; refluxed for 12 hr) gave myristic acid, mp 55° (MeOH) and isobutylamine HCl, mp 171° (EtOAc). The mass spectrum of **1** showed the molecular ion peak (M^+, 18%) at *m/z* 273, the base peak at *m/z* 107 (C_8H_{11}), and a prominent peak at *m/z* 167 ($M^+ - C_8H_{10}$, 53%). From these results, the structure of **1** was established as *N*-isobutyl-2,4,8,10,12-tetradecapentaenamide.[1,4]

In order to confirm the geometry of **1**, the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra of α-sanshoöl (**4**)[5] and β-sanshoöl (**5**),[6] which were analogous to **1**, were recorded in $CDCl_3$ as well as that of **1**. The results are shown in Table I. The signal assignments of **1** were performed by comparing with carbon signals of (2*E*, 4*E*, 8*E*, 10*E*)-*N*-isobutyl-2,4,8,10-dodecatetraenamide (**6**),[1] **4** and **5**. And we attempted to carry out experiments using Eu(dpm)$_3$ in order to confirm its assignments; it is well known that lanthanide-induced shifts are observed in the NMR spectra of acid amides.[4,7] Four olefinic carbon signals of C-2, C-3, C-4 and C-5 in **1** shifted to downfield by addition of Eu(dpm)$_3$ and their chemical shifts were identical with those of C-2—C-5 in **6**. The C-7—C-14 carbon signals in **1** did not shift by addition of Eu(dpm)$_3$ and appeared at almost the same chemical shift of C-5—C-12 in **4**, in which the C-5 and the C-8 carbon signals shifted obviously to upfield due to the C-6 *cis* double bond shielding effect

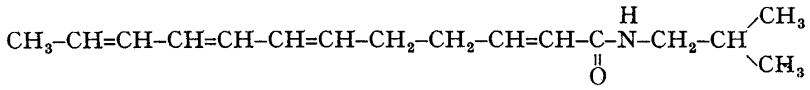
TABLE I. ^{13}C-NMR Chemical Shifts[a] of **1**, **2**, **4**, **5**, and **6**

Carbon	**1**		**2**	**6**[1]	Carbon	**4**	**5**
C-1	166.6	(——)[b]	167.8	166.6	C-1	166.2	166.1
C-2	122.5	(−7.5)	122.2	122.5	C-2	124.4	124.4
C-3	141.0	(−7.8)	141.5	141.0	C-3	143.4	143.5
C-4	129.0	(−0.6)	128.9	128.9			
C-5	141.7	(−1.1)	142.2	141.7			
C-6	33.0	(——)	33.0	32.9	C-4	32.1	31.9
C-7	27.1	(——)	27.2	31.9	C-5	26.6	31.5
C-8	129.6[c]	(——)	129.7[d]	127.6	C-6	129.7	129.4
C-9	130.1[c]	(——)	129.9[d]	131.3[e]	C-7	129.7	131.6[f]
C-10	125.5	(——)	125.4	131.6[e]	C-8	125.4	131.7[f]
C-11	133.5	(——)	133.5	130.0	C-9	133.6	132.3
C-12	132.0	(——)	132.0	18.0	C-10	131.9	131.9[f]
C-13	130.1	(——)	130.0		C-11	130.2	130.3
C-14	18.3	(——)	18.2		C-12	18.3	18.3
C-1′	47.0	(−6.1)	50.7	47.1	C-1′	47.0	47.0
C-2′	28.7	(−2.5)	71.0	28.7	C-2′	28.6	28.7
C-3′	20.1	(−1.6)	27.2	20.2	C-3′	20.2	20.2

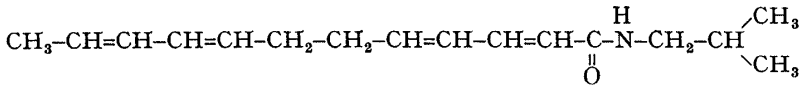
a) ^{13}C-NMR spectra were taken with a Varian NV-16 spectrometer (15.1 MHz) in $CDCl_3$ with TMS as an internal reference and are expressed in terms of ppm.
b) Values in parentheses indicate $\Delta_{Eu}=\delta_1-\delta_{complex}$, where complex=4 : 1 Eu(dpm)$_3$; $-\Delta_{Eu}$ signify downfield shifts.
c—*f*) The assignments may be reversed.



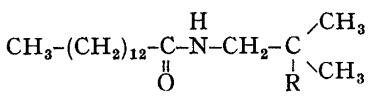
1: R=H 2*E*,4*E*,8*Z*,10*E*,12*E*
2: R=OH 2*E*,4*E*,8*Z*,10*E*,12*E*



4 2*E*,6*Z*,8*E*,10*E*
5 2*E*,6*E*,8*E*,10*E*



6 2*E*,4*E*,8*E*,10*E*



3: R=H
7: R=OH

Chart 1

in comparison with the all-*trans* isomer (**5**). Consequently, the geometry of **1** was concluded to be 2*E*, 4*E*, 8*Z*, 10*E*, 12*E*.

The molecular formula of **2**, $C_{18}H_{27}NO_2$, unstable colorless needles ($CHCl_3$), mp 122—123° was confirmed by high resolution mass spectrometry (M^+: *m/z* 289.1995, Calcd: *m/z* 289.2040). The spectral data of **2** were similar to those of **1**, but in the ^{1}H-NMR spectrum of **2** was shown a singlet methyl signal at δ 1.24 instead of doublet methyl signals at δ 0.93 in that of **1** and in the IR spectrum of **2** was observed the absorption band due to a hydroxyl function at 3400 cm^{-1}. Hydrogenation of **2** with PtO_2 in EtOH afforded, in almost quantitative yield, the

decahydro-derivative (**7**), *m/z* 299 (M^+), colorless needles (*n*-hexane), mp 65°. **7** in pyridine at 0° was treated with $SOCl_2$ and then hydrogenated with PtO_2 as a catalyst to give a product, which was identified as **3**. The above data indicated that **2** was a hydroxyl derivative of **1**. In the ^{13}C-NMR spectrum of **2** (Table I), the C-2′ carbon signal was shifted to downfield at δ 71.0 in comparison with that of **1** and was singlet in the off-resonance ^{13}C-NMR spectrum. The C-2—C-14 carbon signals in **2** appeared at almost the same chemical shifts of the C-2—C-14 in **1**. These evidences confirmed the structure of **2** to be (2*E*, 4*E*, 8*Z*, 10*E*, 12*E*)-2′-hydroxy-*N*-isobutyl-2,4,8,10,12-tetradecapentaenamide.

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References and Notes

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Tokyo Metropolitan Research Laboratory of Public Health, Hyakunincho 3-24-1, Shinjuku-ku, Tokyo, 160, Japan

Ichiro Yasuda

Tokyo College of Pharmacy, Horinouchi 1432-1, Hachioji, Tokyo, 192-03, Japan

Koichi Takeya
Hideji Itokawa*

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