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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°, $\text{C}_{18}\text{H}_{27}\text{NO}$.²⁾ The proton nuclear magnetic resonance (^1H -NMR), infrared absorption (IR) and ultraviolet absorption (UV) spectra of 1 denoted the presence of $\alpha,\beta,\gamma,\delta$ -unsaturated acid amide and isobutyl as functions.³⁾ ^1H -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 $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} : 3300 (NH), 1680, 1640, 1620 ($\text{CH}=\text{CH}$, $\text{C}=\text{O}$), and 990 ($\text{CH}=\text{CH}$). UV $\lambda_{\text{max}}^{\text{EtOH}}$ 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), $\text{C}_{18}\text{H}_{37}\text{NO}$,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 ($\text{M}^+ - \text{C}_8\text{H}_{10}$, 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 $\text{Eu}(\text{dpm})_3$ 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 $\text{Eu}(\text{dpm})_3$ 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 $\text{Eu}(\text{dpm})_3$ 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 $\Delta_{\text{Eu}} = \delta_1 - \delta_{\text{complex}}$, where complex = 4 : 1 Eu(dpm)₃; $-\Delta_{\text{Eu}}$ signify downfield shifts.

c—f) The assignments may be reversed.

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, $\text{C}_{18}\text{H}_{27}\text{NO}_2$, 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 ^1H -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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