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A NEW CLASS OF INDOLE ALKALOID 'ELEGANSAMINE' CONSTRUCTED FROM A MONOTERPENOID INDOLE ALKALOID AND AN IRIDOID

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Summary Elegansamine (1) isolated from *Gelsemium elegans* (Thailand) was proved to be a new type of alkaloid composed by the carbon-carbon linkage of a monoterpenoid indole alkaloid and a monoterpene unit having the iridoid skeleton.

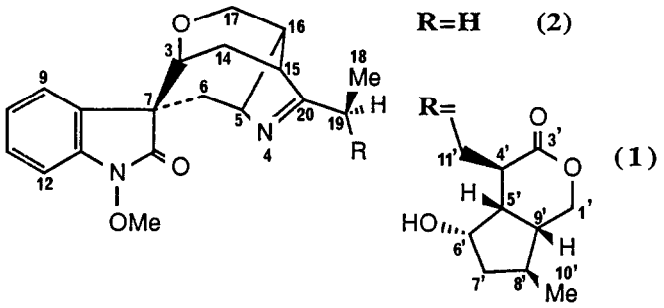
As part of our continuing research on the chemistry of *Gelsemium* alkaloids,[1)-3)] the investigation of the alkaloid constituents of the branches of *Gelsemium elegans* resulted in the isolation of a new alkaloid, named elegansamine. We disclose herein the structure of this minor alkaloid having hitherto unencountered type of constitution.

From the methanol extracts of the branches collected in Thailand, elegansamine (**1**) was obtained as colorless prisms, mp.172-173.°C (MeOH), together with nine known bases, i.e. gelsemine, gelsevirine, koumine, gelsenicine (**2**), 14-hydroxygelsenicine, humantenine, 19-(Z)-akuammidine, and koumidine. Elegansamine (**1**) showed the UV spectrum characteristic to N(a)-methoxy oxindole nucleus. High resolution mass spectrum showed the M^+ 508.2572, corresponding to the formula $C_{29}H_{36}N_2O_6$ (Calcd. 508.2571), and gave the base peak m/z 326, corresponding to the molecular weight of gelsenicine (**2**)($C_{19}H_{22}N_2O_3$), indicating that elegansamine (**1**) was constructed from gelsenicine (**2**) or its isomer and a monoterpene unit containing three oxygen atom.

In the ^{1}H-NMR spectrum ($CDCl_3$), in addition to some readily assignable signals due to gelsenicine moiety such as four aromatic protons (δ7.50 C_9-H, δ7.26 C_{11}-H, δ7.07 C_{10}-H, δ6.89 C_{12}-H), N-OMe (δ3.95 3H,s), C_3-H (δ3.70 1H, dd, J=4.9 and 2.2Hz), C_{15}-H (δ2.91 1H, t-like, J=9Hz), and C_{16}-H (δ2.54 1H, m.), characteristic signals of a doublet on C_{18} protons (δ1.47 3H, J=7.3Hz) and a multiplet due to C_{19} proton (δ2.66) were observed in place of the ethyl group in gelsenicine (**2**), suggesting that monoterpene unit might be connected at C_{19} position. From the ^{13}C-NMR spectrum of (**1**) (see Table), the composing indole alkaloid part and the monoterpene unit were respectively demonstrated to be gelsenicine and an iridoid skeleton, which possessed a lactone function, a C-Me group, and a secondary hydroxy group.

At this stage X-ray structural analysis was carried out. The crystal of elegansamine (**1**) had the following crystal data: monoclinic, $P2_1$, a=10.701(3), b=7.940(2), c=17.039(4)Å, Z=2, Cell volume=1415Å^3, Dc=1.26 gcm^{-3}. A total of 3115 unique independent intensities were measured within the range of $3 \leqq 2\theta \leqq 120°, 150°$ on a four-circle diffractometer (Rigaku

AFC-5) using CuKα radiation (λ=1.54Å). The structure was solved by the direct method using MULTAN 80 and refined anisotropically (isotropically for H) by the least-squares method to an R value of 0.0496, using the 2834 reflections for which F(0)>3σ(Fo). The ORTEP drawing is shown in Fig. The CD spectrum of (1) closely resembles that of gelsenicine (2)[5] and therefore gelsenicine part and the iridoid residue in (1) have the same absolute configuration as the conventional indole alkaloids and iridoid monoterpenes, respectively.



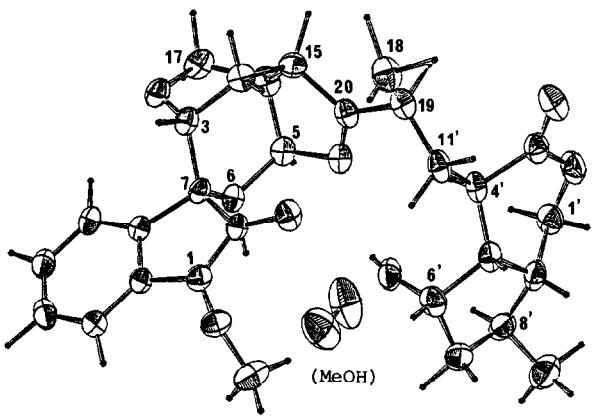


Fig. ORTEP Drawing of (1)

Table. ^{13}C-NMR[4]

No.	(2)	(1)
2	172.1(s)	171.5(s)
3	74.9(d)*	75.0(d)
5	72.5(d)*	72.5(d)
6	37.7(t)	37.4(t)
7	55.8(s)	56.1(s)
8	132.3(s)	131.9(s)
9	124.6(d)	124.7(d)
10	123.3(d)	123.4(d)
11	128.0(d)	128.1(d)
12	106.5(d)	106.6(d)
13	138.0(s)	138.0(s)
14	25.6(t)	27.7(t)
15	39.8(d)**	40.1(d)
16	42.5(d)**	42.5(d)
17	62.1(t)	61.9(t)
18	10.0(q)	19.3(q)*
19	25.6(t)	37.7(d)**
20	184.1(s)	186.2(s)
-OMe	63.3(q)	63.2(q)
1'	---	70.4(t)
3'	---	177.9(s)
4'	---	48.7(d)
5'	---	37.7(d)**
6'	---	71.2(d)
7'	---	43.7(t)
8'	---	35.1(d)**
9'	---	45.1(d)
10'	---	18.7(q)*
11'	---	33.1(t)

References and Notes

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4) Chemical shift in ppm downfield from TMS. Solvent;$CDCl_3$. Signals bearing the same superscript may be interchangeable within vertical column.

5) CD spectral data: (1)(c=0.95x10^{-2}, MeOH, 23°C) $[\theta]_{312}0$, $[\theta]_{260}$-18200, $[\theta]_{245.5}0$, $[\theta]_{234}$+18200, $[\theta]_{222}0$, $[\theta]_{209}$-59000.
(2)(c=1.0x10^{-2}, MeOH, 23°C) $[\theta]_{314}0$, $[\theta]_{262}$-24200, $[\theta]_{248.5}0$, $[\theta]_{234}$+39300, $[\theta]_{221}0$, $[\theta]_{211}$-73300.

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