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臺灣蘭科植物 - 石斛、連珠石斛與臺灣金線連之化學成分及藥理活性研究

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中文摘要

本研究針對蘭科石斛屬(*Dendrobium*)和開唇蘭(金線連)屬(*Anoectochilus*)植物之基原、化學成分及藥理活性等項考察，確認了石斛和金線連在植物學上的分類和地位，整理了相關的研究，作為從事石斛和金線連化學成分與藥理活性研究之參考。

延續本研究室對於臺灣蘭科植物的成分與藥理活性之探討，本論文共完成三種蘭科植物 - 石斛、連珠石斛和臺灣金線連的成分分析，及體外活性測試，茲分別敘述於後：

石斛(*Dendrobium moniliforme* SWARTZ)成分研究之結果為：由石斛莖部正己烷粗抽物分離得到十四個化合物，包含 heptacosane (1)，octacosanyl hexadecanoate (2)，methyl and ethyl linolenates (3)，4-methoxybenzaldehyde (4)，alkyl *trans*-ferulates (5)，pheophytin a (6)，alkyl 4-hydroxy-*cis*-cinnamates (7)，alkyl 4-hydroxy-*trans*-cinnamates (8)，stigmast-4-en-3-one (9)，phytosterols (10)，denbinobin (11)，vanillin (12)，linoleic acid (13)和 heptatriaconsanoic acid (14)；由石斛莖部乙酸乙酯粗抽物分離得到十一個化合物，包含 alkyl *trans*-ferulates (5)，alkyl 4'-hydroxy-*cis*-cinnamates (7)，alkyl 4-hydroxy-*trans*-cinnamates (8)，denbinobin (11)，aliphatic acids (14)，alkyl hexadecanoates (15)，alkyl acetates (16)，dengibsin (17)，moniliquinone (18)，moniliformol (19)和 diethyl glycol (20)；由石斛根部正己烷粗抽物分離得到六個化合物，包含 alkyl *trans*-ferulates (5)，phytosterols (10)，denbinobin (11)，aliphatic acids (14)，ergosterol (21)，ergosterol peroxide (22)。以上化合物之中，18 和 19 為新化合物，而 2，12，13，15，16，17 和 20 為石斛屬植物首次分離得到的化合物。

連珠石斛(*Dendrobium nakaharai* SCHLECHTER)成分研究結果：由連珠石斛正己烷粗抽物分離得到十七個化合物，包含 alkyl *trans*-ferulates (5), pheophytin a (6), stigmast-4-en-3-one (9), phytosterols (10), linoleic acid (13), aliphatic acids (14), ergosterol (21), *trans*- β -carotene (23), 2,3,4,7-tetramethoxyphenanthrene (24), nakaharain (25), aliphatic alcohols (26), nakaquinone (27), 2,5-dihydroxy-3,4-dimethoxyphenanthrene (28), confusarin (29), nudol (30), bulbophyllanthrin (31)和 nakaharaiquinone (32); 由連珠石斛乙酸乙酯粗抽物分離得到十個化合物，包含 alkyl *trans*-ferulates (5), alkyl 4'-hydroxy-*cis*-cinnamates (7), alkyl 4'-hydroxy-*trans*-cinnamates (8), protocatechuic acid (33), nakaharain (25), 2,5-dihydroxy-3,4-dimethoxyphenanthrene (28), uracil (34), nakaharoside A (35), nakaharoside B (36)和 vitexin (37)。以上化合物之中，25, 27, 32, 35 和 36 為新化合物，而 23, 24, 28, 31, 33, 34 和 37 為石斛屬植物首次分離得到的化合物。

臺灣金線連(*Anoectochilus formosanus* HAYATA)成分研究結果：由臺灣金線連正己烷粗抽物分離得到六個化合物，包含 pheophytin a (6), linoleic acid (13), *trans*- β -carotene (23), 2-methoxy-4-vinylphenol (38), 4-vinylphenol (39)和 lutein (40); 由臺灣金線連乙酸乙酯粗抽物分離得到五個化合物，包含 pheophytin a (6), phytosterols (10), uracil (34), pheophytin b (41)和 anoectolide A (42); 由臺灣金線連甲醇粗抽物分離得到四個化合物，包含 phytosterols (10), anoectolide A (42), anoectolide B (43)和 ethyl β -D-glucopyranoside (44)。以上化合物之中，42 和 43 為新化合物，而 6, 13, 23, 34, 38, 39, 40, 41 和 44 為開唇屬蘭植物首次分離得到的化合物。

在抗發炎及抗過敏試驗方面，連珠石斛和臺灣金線連的粗抽物對於 fMLP 引發嗜中性白血球釋放 β -glucuronidase 和 lysozyme 的體外試驗和 compound 48/80 引發肥大細胞釋放 β -glucuronidase 和 histamine 的體外試驗均有顯著的抑制作用。此外，對 11 個化合物進行抗發炎和抗過敏活性試驗：

1. 石斛分離純化的化合物：4 對嗜中性白血球釋放超氧自由基所造成的發炎，可能有抑制作用；11 有好的中樞和周邊抗發炎及抗過敏活性；12 對嗜中性白血球的抗發炎可能有活性。
2. 連珠石斛分離純化的化合物：新化合物 25 抗發炎及抗過敏活性不佳；28 對嗜中性白血球的抗發炎有不錯的活性；33, 34 和 37 對嗜中性白血球所引發的發炎可能有抑制效果。

3. 臺灣金線連分離純化的化合物：6, 13 和 23 可能具有對嗜中性白血球和周邊的抗發炎活性。

此外，其它化合物的抗發炎和抗過敏活性試驗仍在進行中。

Chemical and Pharmacological Studies of Taiwanese Orchids –
Dendrobium moniliforme SWARTZ, *Dendrobium nakaharai*
SCHLECHTER and *Anoectochilus formosanus* HAYATA

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Abstract

This study was first based on the investigations and literature survey of plant origin, phytochemistry and pharmacology of *Dendrobium* genus and *Anoectochilus* genus. We could understand the plant taxonomy and position of Shi-Hu and Kinsenren. This research provided some information for chemical and pharmacological studies of Shi-Hu and Kinsenren.

In the course of our studies on the constituents and pharmacological activity of Taiwanese Orchidaceae plants, this study carried out the chemical analysis and *in vitro* bioactivity tests of three species of Orchidaceae plants - *Dendrobium moniliforme* SWARTZ, *Dendrobium nakaharai* SCHLECHTER and *Anoectochilus formosanus* HAYATA.

Studies on the constituents of *D. moniliforme* resulted in the isolation of fourteen compounds from *n*-hexane extract of stems, including heptacosane (1), octacosanyl hexadecanoate (2), methyl and ethyl linolenates (3), 4-methoxybenzaldehyde (4), alkyl *trans*-ferulates (5), pheophytin a (6), alkyl 4'-hydroxy-*cis*-cinnamates (7), alkyl 4'-hydroxy-*trans*-cinnamates (8), stigmast-4-en-3-one (9), phytosterols (10), denbinobin (11), vanillin (12), linoleic acid (13) and heptatriaconsanoic acid (14). Eleven compounds were isolated from ethyl acetate extract of the stems, including alkyl *trans*-ferulates (5), alkyl 4'-hydroxy-*cis*-cinnamates (7), alkyl 4'-hydroxy-*trans*-cinnamates (8), denbinobin (11), aliphatic acids (14), alkyl hexadecanoates (15), alkyl acetates (16), dengibsin (17), moniliquinone (18), moniliformol (19) and diethyl glycol (20). Six compounds were isolated from *n*-hexane extract of the roots, including alkyl *trans*-ferulates (5), phytosterols (10),

denbinobin (**11**), aliphatic acids (**14**), ergosterol (**21**) and ergosterol peroxide (**22**). Among these, **18** and **19** were new compounds, and **2**, **12**, **13**, **15**, **16**, **17** and **20** were the first report of *Dendrobium* genus.

Studies on the constituents of whole plants of *D. nakaharai*, seventeen compounds were isolated from *n*-hexane extract, including alkyl *trans*-ferulates (**5**), pheophytin a (**6**), stigmast-4-en-3-one (**9**), phytosterols (**10**), linoleic acid (**13**), aliphatic acids (**14**), ergosterol (**21**), *trans*- β -carotene (**23**), 2,3,4,7-tetramethoxyphenanthrene (**24**), nakaharain (**25**), aliphatic alcohols (**26**), nakaquinone (**27**), 2,5-dihydroxy-3,4-dimethoxyphenanthrene (**28**), confusarin (**29**), nudol (**30**), bulbophyllanthrin (**31**) and nakaharaiquinone (**32**). Ten compounds were isolated from ethyl acetate extract, including alkyl *trans*-ferulates (**5**), alkyl 4'-hydroxy-*cis*-cinnamates (**7**), alkyl 4'-hydroxy-*trans*-cinnamates (**8**), protocatechuic acid (**33**), nakaharain (**25**), 2,5-dihydroxy-3,4-dimethoxyphenanthrene (**28**), uracil (**34**), nakaharoside A (**35**), nakaharoside B (**36**) and vitexin (**37**). Among these, **25**, **27**, **32**, **35** and **36** were new compounds, and **23**, **24**, **28**, **31**, **33**, **34** and **37** were the first report of *Dendrobium* genus.

Studies on the constituents of whole plants of *A. formosanus*, six compounds were isolated from *n*-hexane extract, including pheophytin a (**6**), linoleic acid (**13**), *trans*- β -carotene (**23**), 2-methoxy-4-vinylphenol (**38**), 4-vinylphenol (**39**) and lutein (**40**). Five compounds were isolated from ethyl acetate extract, including pheophytin a (**6**), phytosterols (**10**), uracil (**34**), pheophytin b (**41**) and anoectolide A (**42**). Four compounds were isolated from methanol extract, including phytosterols (**10**), anoectolide A (**42**), anoectolide B (**43**) and ethyl β -D-glucopyranoside (**44**). Among these, **42** and **43** were new compounds, and **6**, **13**, **23**, **34**, **38**, **39**, **40**, **41** and **44** were first report of *A. formosanus*.

In the anti-inflammatory and anti-allergic assays, the crude extracts of *D. nakaharai* and *A. formosanus* significantly inhibited the release of β -glucuronidase and lysozyme on neutrophil degranulation induced by fMLP *in vitro* and inhibited the release of β -glucuronidase and histamine on mast cells induced by compound 48/80 *in vitro*. In addition, the anti-inflammatory and anti-allergic activities of eleven compounds were investigated.

1. The isolated compounds from *D. nakaharai* showed that a new compound, **25** had not benefit in anti-inflammation and

anti-allergy. **28** had better anti-inflammation against neutrophil. **33, 34** and **37** may have inhibition of the inflammatory against neutrophil.

2. The isolated compounds from *D. moniliforme* showed that **4** may have effect of anti-inflammatory against the neutrophil superoxide formation. **11** may have benefit in controlling central and peripheral inflammation as well as allergy against mast cell. **12** had inhibition against neutrophil.
3. The isolated compounds from *A. formosanus* showed that **6, 13** and **23** may have benefit in controlling neutrophil and peripheral inflammation

However, other compounds are still under test.