十一、Fatty acid or ester 類化合物

Fatty acid or ester 類化合物廣佈於植物體內,在石斛中分到 5 個 此類化合物: alkyl acetate (16)、linoleic acid (13)、methyl and ethyl linolenates (3)和 octacosanyl hexadecanoate (2);在臺灣金線連中,正 己烷的抽出物經 GC, GC/MS 檢測,結果如 Figure 4,主要以此類化 合物為主,在分離過程中,則有分離到化合物 linoleic acid (13)。

Alkyl acetate (16) 化學結構的決定

本化合物為白色油狀物, EIMS (Chart 226)顯示裂片有 *m/z* 336 [M-60]⁺, 364 [M-60]⁺, 392 [M-60]⁺和 420 [M-60]⁺, 其它為直鏈烷基的標準裂片。



Chart 226 EIMS (70 eV) spectrum of alkyl acetate (16)

氫譜(Chart 227)顯示 0.68 (6H, t, J=6.4 Hz)為長鏈末端甲基之吸 收訊號, 1.23 (br s)為長鏈 methylene 的吸收訊號, 2.02 (3H, s)為 acetyl proton 的吸收訊號, 4.03 (2H, t, J=7.6 Hz)為酯類(ester group) 旁 COOCH₂ 質子的吸收訊號。

碳譜(Chart 228)顯示 14.1 為長鏈末端甲基碳的吸收訊號, 21.0-32.0 為長鏈 methylenes 的吸收訊號, 64.7 為酯類(ester group) 旁 $COOCH_2$ 的吸收訊號, 而 171.2 為 acetyl carbon (C=O)的吸收訊 號。

綜合上述資料,確認此化合物為 alkyl acetate 的混合物,包含 tetracosyl、hexacosyl、octacosyl 和 triaconyl acetate。



Linoleic acid (13) 化學結構的決定

本化合物為淡黃色油狀物,經由 EIMS 光譜(Chart 229)顯示分子量為 280。

IR 光譜(Chart 230)顯示在 3010 cm⁻¹為 C=C-H 的吸收 1712 為 carboxyl group (COOH)的吸收, 2919 和 2856 為飽和碳氫(CH)的吸收, 1473、1445 和 1424 為雙鍵的吸收。

氫譜(Chart 232)顯示 0.88 (3H, *m*)為末端甲基之吸收訊號, 1.25 (14H, *br s*)為 7 個 methylenes (CH₂)的吸收訊號, 1.64 (2H, *m*)、 2.05 (4H, *m*)、2.35 (2H, *t*, *J*=7.5 Hz)和 2.77 (2H, *t*, *J*=5.7 Hz)分別為 H-3、H-8、H-14、H-2 和 H-11 的吸收訊號, 而 5.35 (4H, *m*)為 olefinic protons (H-9、H-10、H-12 和 H-13)的吸收訊號。

碳譜(Chart 233)顯示 14.1 為末端甲基(C-18)的吸收訊號, 22.7-33.7 為 12 個 methylenes (CH₂)的吸收訊號, 127.9 128.1 130.0 和 130.2 為 olefinic carbons 的吸收訊號, 而 180.3 為 carboxyl carbon 的吸收訊號。

綜合上述資料與文獻值⁽¹⁹⁶⁾比對,確認此化合物之結構為 9,12 (z,z)-octadecadienoic acid,分子式為 C₁₈H₃₂O₂,又名為 linoleic acid。 其結構如下:



Chart 229 EIMS (70 eV) spectrum of linoleic acid (13)



Chart 230 IR spectrum of linoleic acid (13)



Chart 231 UV spectrum of linoleic acid (13)



Methyl and ethyl linolenates (3) 化學結構的決定

本化合物為淡黃色油狀物,經由 EIMS 顯示[M]⁺為 292 和 306。

IR 光譜(Chart 234)顯示在 2926 和 2863 cm⁻¹為飽和碳氫的吸收, 1710 cm⁻¹為 carbonyl group (C=O)的吸收,而 1256 cm⁻¹為醚基(C-O-C) 的吸收。

氫譜(Chart 235)顯示 0.95 (*t*, *J*=7.5 Hz)為末端甲基之吸收訊號, 1.23 (*t*, *J*=7.2 Hz)和 4.10 (*q*, *J*=7.1 Hz)為 ethoxyl proton 的吸收訊號, 1.28 (*br s*)、1.60 (*m*)、2.02 (*m*)、2.26 (*t*, *J*=7.2, 7.6 Hz)和 2.28 (*t*, *J*=7.3, 7.7 Hz)為 methylenes (CH₂)的吸收訊號, 3.64 (*s*)為 methoxyl proton 的吸收訊號, 5.33 (*m*)為 olefinic protons 的吸收訊號。

碳譜(Chart 236) 和 DEPT(Chart 237)顯示 14.3 為 methyl (CH₃) 的吸收訊號, 20.5-30.0 為 methylenes (CH₂)的吸收訊號, 34.1 為 OCH2 的吸收訊號, 51.4 為 methoxyl (OCH₃)的吸收訊號, 127.1、 127.7、 128.3、 128.3、 130.3 和 132.0 為 olefinic carbons 的吸收訊號, 而 174.3 為 carboxyl carbon 的吸收訊號。

綜合上述資料與文獻⁽¹⁹⁷⁾比對,確認此化合物為 methyl linolenate 和 ethyl linolenate 的混合,分子式為 $C_{19}H_{32}O_2$ 和 $C_{20}H_{34}O_2$ 。其結構如下:



 $R=CH_3$ methyl linolenate $R=C_2H_5$ ethyl linolenate



IR spectrum of methyl and ethyl linolenate (3) Chart 234









Chart 237 DEPT135 spectrum of methyl and ethyl linolenate (3)

Octacosanyl hexadecanoate (2) 化學結構的決定

本化合物為白色油狀物,經由 EIMS 光譜(Chart 238)顯示分子 量為 648。

IR 光譜(Chart 239)顯示在 2920 和 2851 cm⁻¹為飽和碳氫的吸收, 1736 為酯類 carbonyl (C=O)的吸收,其它還有 1474、1187 和 716 等 吸收。

氫譜(Chart 240)顯示 0.86 (6H, *t*, *J*=6.4 Hz)為 2 個末端甲基之吸 收訊號, 1.23 (*br s*)為長鏈 methylenes (CH₂)的吸收訊號, 2.27 (2H, *t*, *J*=7.5 Hz)為 carbonyl group 旁 C<u>H₂</u>COO 質子的吸收訊號, 4.03 (2H, *t*, *J*=6.6 Hz)為酯類 ester group 旁 COOC<u>H₂</u> 質子的吸收訊號。

碳譜(Chart 241)顯示 14.1 為末端甲基碳的吸收訊號, 22.7-64.4 為 methylenes (CH₂) 的吸收訊號,其中 34.4 為 carbonyl group 旁 <u>CH₂COO</u> 的吸收訊號, 64.4 為酯類 ester group 旁 COO<u>C</u>H₂ 的吸 收訊號,而 174.0 為 carboxyl carbon (C=O)的吸收訊號。顯示為長 鏈酯類化合物,利用皂化反應(5% KOH/乙醇溶液) 4 小時後,得到 M⁺ 256 與 410 的化合物為 hexadecanoic acid 與 *n*-octacosanol, 推定此 化合物為 16 個碳的酸與 18 個碳的醇所形成的酯類。

綜合上述資料與文獻值⁽¹⁹⁸⁾比對,確認此化合物之結構為 octacosanyl hexadecanoate,分子式為 C₄₄H₈₈O₂。其結構如下:

$$CH_{3}(CH_{2})_{13}CH_{2}$$
 $-C$ $-OCH_{2}(CH_{2})_{26}CH_{3}$



Chart 238 EIMS (70 eV) spectrum of octacosanyl hexadecanoate (2)



Chart 239 IR spectrum of octacosanyl hexadecanoate (2)



十二、Pyrimidine 類化合物

在連珠石斛中分離得到一個 pyrimidine 類之核酸化合物 uracil (34), 這是首次於石斛屬植物中發現。

Uracil (34) 化學結構的決定

本化合物為無色針狀,經由 EIMS (Chart 242)顯示分子量為 m/z 112。



Chart 242 EIMS (70 eV) spectrum of uracil (34)

IR 光譜(Chart 243)在 3105 和 3040 cm⁻¹為 NH 的吸收, 1716 和 1670為 carbonyl C=O 的吸收 UV 光譜(Chart 244)在 206 和 259 nm (log

: 3.58 和 3.58)有最大吸收波長。

氫譜(Chart 245)顯示有 1 對不飽和質子(olefinic protons)的吸收訊號, 5.60 和 7.38, 耦合常數 *J*=7.6 Hz, 為 H-5 和 H-6。

碳譜(Chart 246)顯示有 4 個碳存在, 101.7、143.6、153.6 和 167.4, 其中 101.7和143.6為不飽和雙鍵 C-5和 C-6, 153.6和167.4 為 carbonyl carbon (CO), C-2和 C-4 的吸收訊號。

綜合上述資料,並與文獻⁽¹⁹⁹⁾比對,確定此化合物結構為 uracil, 分子式為 C₄H₄N₂O₂。結構如下:





Chart 243 IR spectrum of uracil (34)



Chart 244 UV spectrum of uracil (34)



十三、Sugar 類化合物

Ethyl â-D-glucopyranoside (44) 化學結構的決定

本化合物為無色油狀物, positive FABMS (Chart 247)顯示 $[M+Na]^+ c m/z 231$, $[M+H]^+ c m/z 209$ 。

IR 光譜(Chart 248)在 3388 cm⁻¹ (broad)為 hydroxyls 的吸收, 1076 cm⁻¹ 為醚基(C-O-C)的吸收。

氫譜(Chart 249)顯示在 3.21-4.29 有吸收訊號,為類似糖(â-D-glucose)的吸收訊號, 4.29 (1H, *d*, *J*=7.66 Hz)為糖上 H-1 的吸收訊號, 3.21 (1H, *m*)為 H-2 的吸收訊號, 3.44 (2H, *m*)為 H-4 和 H-5 的吸收訊號, 3.65 (2H, *m*)和 3.93 (2H, *m*)為 H-6 和 H-7 的混合吸收訊號, S外在 1.25 (3H, *t*, *J*=7.10 Hz)為 1 甲基質子(H-8)的吸收訊號 COSY (Chart 250)顯示 H-1 和 H-2, H-5 和 H-6 以及 H-7 和 H-8 有相關。

碳譜(Chart 251)和 DEPT(Chart 252)及 HMQC(Chart 253)顯示有 8 個碳,包括1個CH₃(15.4),2個OCH₂(62.5和66.1)和5個CH(71.3、74.7、77.5、77.7和103.7)。再由 HMBC(Chart 254)可知 H-1和 H-8 均與 C-7 (66.2)有長距離的相關,這說明了 1 號位置有 1 個 ethoxyl group。此外 H-2 與 C-3, H-3和 H-5 與 C-4 也有相關。

綜合上述資料,並與文獻⁽²⁰⁰⁾比對,確定此化合物為 ethyl \hat{a} -D-glucopyranoside,分子式為 $C_8H_{16}O_6$ 。結構如下:





Chart 247 positive FABMS spectrum of ethyl -D-glucopyranoside (44)



Chart 248 IR spectrum of ethyl

-D-glucopyranoside (44)



Chart 250 COSY spectrum of ethyl -D-glucopyranoside (44)



Chart 252 DEPT spectrum of ethyl -D-glucopyranoside (44)



Chart 253 HMQC spectrum of ethyl -D-glucopyranoside (44)



Chart 254 HMBC spectrum of ethyl -D-glucopyranoside (44)

十四、其它

Diethylene glycol (20) 化學結構的決定

本化合物為白色固體,氫譜(Chart 255)顯示在 3.40 (*br d*, *J*=3.9 Hz)和 3.46 (*br d*, *J*=4.1 Hz)相互耦合,碳譜(Chart 256)顯示具有 2 支含 氧的吸收訊息 60.7 和 72.5,經 DEPT(Chart 257)實驗顯示,此為 methylene group,而由 HMQC(Chart 258)顯示,可知此化合物碳氫的 關係。進一步的由文獻⁽²⁰¹⁾證實,本化合物為 diethylene glycol,此為 石斛屬植物首次分離。結構如下:

HOCH₂CH₂OCH₂CH₂OH



glycol(20)



Chart 257 DEPT spectrum of diethylene glycol(20)



Chart 258 HMQC spectrum of diethylene glycol (20)

Anoectolide A (42) 化學結構的決定

本化合物為無色油狀物,與化合物 3-hydroxybutanolide⁽⁹⁵⁾具有類 似的結構。氫譜(Chart 259)顯示具有9個氫質子,碳譜(Chart 260)與 DEPT 實驗(Chart 263)顯示有1個 methyl (18.5 和 18.5),2 個 methylenes (38.4 和 77.7),2 個 methines (68.3 和 72.4)和1個四級 碳(179.1),其中179.1 為 carbonyl 的吸收訊號,比化合物 3-hydroxybutanolide 多2個碳,經由 HMQC (Chart 264)和 COSY (Chart 261)光譜可推定為-OCH(CH₃)-的組含 HMBC (Chart 265)顯示 H-5 (3.54)除了跟鄰位甲基的碳有長距離的關連外,並且與自己相對的碳有 關連,因此推定此化合物為雙體的結構。

FABMS 顯示本化合物具有 3-hydroxybutanolide 的離子裂片 m/z 103 (C₄H₇O₃⁺),而且[M+H]⁺為 259,綜合上述(Table 44)推定本化合物 為 bi(3-*O*-ethoxybutanolide),分子式為 C₁₂H₁₈O₆,它是一個新的化合物,命名為 anoectolide A。其結構如下:



 Table 44. NMR spectral data of anoectolide A (42)

		$^{1}\mathrm{H}$	¹³ C	COSY	NOESY	HMBC		
1	С		179.1					
2	CH ₂	2.83(<i>dd</i> , 17.8, 5.8)	38.4	H-2, H-3	H-2, H-3	$C-1(J_2), C-3(J_2), C-4(J_3)$		
		2.36(<i>d</i> , 17.8)		H-2	H-2	$C-1(J_2), C-3(J_2), C-4(J_3)$		
3	СН	4.56(<i>m</i>)	68.3	H-2, H-4	H-2, H-4	C-1(J_3), C-4(J_2)		
4	CH ₂	4.43(<i>dd</i> , 10.0, 4.2)	77.7	H-4, H-3	H-3, H-4	$C-1(J_3), C-3(J_2)$		
		4.21(<i>d</i> , 10.0)		H-4	H-4	$C-1(J_3), C-2(J_3), C-3(J_2)$		
5	СН	3.54(<i>m</i>)	72.4	H-6, H-7	H-6, H-7	$C-3(J_3), C-5(J_2), C-6(J_2)$		
6	CH ₃	1.13(<i>d</i> , 6.1)	18.5	H-5	H-5	$C-5(J_2)$		



Chart 259 ¹H-NMR (CD₃OD+CDCl₃, 200 MHz) spectrum of anoectolide A (42)





Chart 261 COSY spectrum of anoectolide A (42)



Chart 262 NOESY spectrum of anoectolide A (42)



Chart 263 DEPT spectrum of anoectolide A (42)







Chart 265 HMBC spectrum of anoectolide A (42)

Anoectolide B (43) 化學結構的決定

本化合物為無色油狀物,與化合物 3-hydroxybutanolide⁽⁹⁵⁾具有類 似的結構。氫譜(Chart 266)顯示具有7個氫質子,碳譜(Chart 267)顯 示有6個碳原子,3個 methylenes(29.8,38.5和77.7),1個 methines (68.4)和2個四級碳(176.2和179.1),其中179.1為 butanolide 的 carbonyl 吸收訊號。本化合物比化合物 3-hydroxybutanolide 多2個 碳,包括1個 methylenes(29.8)和1個 carbonyl(176.2),初步推 定為-COCH₂-的組合。HMBC (Chart 269)顯示 methylenes(29.8)除了 跟鄰位 carbonyl(176.2)的碳有長距離的關連外,並且與自己相對的 碳有關連,因此推定此化合物為雙體的結構。

FABMS 顯示本化合物具有 3-hydroxybutanolide 的離子裂片 m/z 103 (C₄H₇O₃⁺),而且[M+H]⁺為 287,綜合上述(Table 45)推定本化合物 為 bi(3-*O*-acetoxybutanolide),分子式為 C₁₂H₁₄O₈,它是一個新的化合物,命名為 anoectolide B。其結構如下:



 Table 45. NMR spectral data of anoectolide B (43)

		$^{1}\mathrm{H}$	¹³ C	HMBC
1	С		179.1	
2	CH_2	2.81(<i>dd</i> , 17.8, 5.9)	38.5	$C-1(J_2)$
		2.35(<i>d</i> , 17.8)		$C-1(J_2), C-3(J_2), C-4(J_3)$
3	CH	4.55(<i>m</i>)	68.4	$C-1(J_3), C-4(J_2)$
4	CH ₂	4.41 <i>dd</i> , 10.0, 4.2)	77.7	C-3(<i>J</i> ₂)
		4.21(<i>d</i> , 10.0)		C-1(<i>J</i> ₃), C-2(<i>J</i> ₃), C-3(<i>J</i> ₂)
5	С		176.2	
6	CH	2.56(<i>s</i>)	29.8	$C-5(J_2), C-6(J_2)$



Chart 267 ¹C-NMR (CD₃OD+CDCl₃, 50 MHz) spectrum of anoectolide B (43)



Chart 268 HMQC spectrum of anoectolide B (43)



第二節 抗發炎及抗過敏之藥理活性

一、連珠石斛粗抽物之抗發炎及抗過敏試驗

1.嗜中性白血球去顆粒作用試驗

Table 46 顯示,連珠石斛正己烷粗抽物(DNH)、乙酸乙酯粗抽物 (DNE)和甲醇粗抽物(DNM),其濃度在 10 ì g/mL 下,對於 fMLP 引發 嗜中性白血球釋放 â-glucuronidase 和 lysozyme 的體外試驗,均有顯 著抑制作用(P<0.01),其中對嗜中性白血球釋放 â-glucuronidase 抑制 作用的 IC₅₀分別為 9.8、3.2 和 34.1 ì g/mL,對嗜中性白血球釋放 lysozyme 抑制作用的 IC₅₀分別為 14.8、2.6 和 43.7 ì g/mL。由此試驗 顯示,連珠石斛 3 種粗抽物的抗發炎活性,其大小依次為:連珠石斛 乙酸乙酯粗抽物(DNE)>連珠石斛正己烷粗抽物(DNH)>連珠石斛甲 醇粗抽物(DNM)。

p-glucuroindase and lysozyme in neurophils (<i>in vitro</i>)						
Drugs	(µg/mL)		Percent	Release		
		β-glucuronidase	(%inh)	lysozyme	(%inh)	
Control		25.4±1.0		58.9±0.8		
DNH	(3)	16.4±0.6**	35.5±1.2	42.2±2.5	16.1±1.6	
	(10)	12.5±0.6**	50.8 ± 1.5	33.1±5.8**	35.1±8.2	
	(30)	1.8±0.7**	92.9±2.8	3.0±1.2**	94.3±2.2	
IC ₅₀		9.8±0.1 μ	g/mL	14.8±1.1	µg/mL	
DNE	(3)	14.1±0.6**	44.5±1.2	27.3±1.1**	45.5±1.8	
	(10)	4.1±1.3**	84.2±5.2	7.7±1.8**	85.1±2.7	
	(30)	0.05±0.4**	99.9±1.7	-0.6±1.3**	101.6±2.8	
IC ₅₀		3.2±0.5 μ	g/mL	2.6±0.6 µg/mL		
DNM	(10)	18.4±2.4*	27.9±6.9	38.6±3.6*	23.6±2.3	
	(30)	10.3±0.9**	59.5±2.0	25.3±2.0**	49.9±0.8	
	(100)	3.6±1.4**	86.1±5.4	9.0±3.0**	82.8±5.0	
IC ₅₀		34.1±8.0 µ	ıg∕mL	43.7±3.1 μg/mL		
TFP	(10µM)	28.7±2.8	-10.9 ± 12.5	53.9±2.7	-7.5 ± 4.8	
	(20µM)	14.6±1.8**	43.3±8.2	26.3±5.2**	48.4 ± 4.5	
	(30µM)	9.9±1.5**	60.9±7.0	12.8±4.7**	74.9±8.6	
IC ₅₀		24.4±0.5	μΜ	22.8±0.:	5 μΜ	

Table 46. Effect of extracts of *D. nakaharai* on the release of B glucuronidase and lysozyme in neutrophils (*in vitro*)

Neutrophil suspensions were preincubated at 37 with 0.5% DMSO or test compounds for 3 min in the presence of cytochalasin B (5 μ g/ml). Forty-five minutes after the addition of formylmethionyl-leucyl-phenyl-alanine (fMLP) (1 μ M), the amount of β -glucuronidase and lysozyme in the supernatant were determined. Values are presented as mean \pm S. E., N=3, * *P*<0.05, ** *P*<0.01.DNH: *n*-Hexane extract of *D. nakaharai*, DNE: Ethyl acetate extract of *D. nakaharai*, DNM: Methanol extract of *D. nakaharai*; Trifluoperazine (TFP) (as positive control).

2.肥滿細胞去顆粒作用試驗

Table 47 顯示,連珠石斛正己烷粗抽物(DNH)對於 compound 48/80 引發肥滿細胞釋放 â-glucuronidase 和 histamine 的體外試驗,無抑制作用,而連珠石斛乙酸乙酯粗抽物(DNE)在 30 ì g/mL 濃度下,對於 compound 48/80 引發肥滿細胞釋放 â-glucuronidase 和 histamine 的體外試驗,有明顯抑制作用(P<0.01),但是連珠石斛甲醇粗抽物 (DNM)對於 compound 48/80 引發肥滿細胞釋放 â-glucuronidase 的體 外試驗,需在 100 ì g/mL 濃度下,才有明顯的抑制作用。

	0			()	
Drugs	(µg/mL)		Percent	Release	
		β-glucuronidase	(%inh)	histamine	(%inh)
Control		32.6±1.1		65.1±2.4	
DNH	(10)	30.4±1.7	6.8±2.3	56.9±3.8	12.7±2.6
	(30)	29.6±0.4	8.8±4.3	57.8±2.8	11.2±2.5
DNE	(10)	30.5±0.6	6.3±1.7	59.4±2.8	8.7±1.0
	(30)	23.1±1.9**	29.3±4.3	45.6±3.9**	30.1±3.2
	(100)	17.4±0.9**	46.6±3.6	31.8±1.2**	51.1±1.0
DNM	(30)	30.4±0.7	6.4±4.0	64.0±3.9	1.8 ± 2.2
	(100)	24.9±0.7**	23.3±1.6	57.5±3.1	11.8 ± 2.5
Mepacrine	(10µM)	21.7±0.7**	33.1±4.2	55.7±2.0	14.8±2.9
	(30µM)	9.7±3.0**	70.4 ± 6.1	25.3±2.4**	60.1±3.0
	(100µM)	0.8±0.5**	97.3±1.2	11.8±0.8**	82.0±1.4
IC ₅₀		24.3±2.2 μM		43.8±1.9 μM	

Table 47. Effect of extracts of *D.nakaharai* on the release of β-glucuronidase and histamine in mast cells (*in vitro*)

Mast cell suspensions were preincubated at 37 with 0.5% DMSO or test compounds for 3 min. Fifteen minutes after the addition of compound 48/80, the amount of β -glucuronidase and histamine in the supernatant were determined. Values are presented as mean ± S. E., N=3, * *P*<0.05, ** *P*<0.01; Mepacrine (as positive control).

二、DNE-I~DNE-VI 之抗發炎及抗過敏試驗

經由上述實驗結果,得知連珠石斛乙酸乙酯粗抽物(DNE)對抗發 炎及抗過敏活性有較佳的作用,進一步對連珠石斛乙酸乙酯粗抽物 (DNE)再做分離。DNE 再經 Sephadex LH-20 管柱層析分離,利用薄 層層析(TLC)比較合併為 6 個部分 DNE-I~DNE-VI (Scheme 15),再進 行抗發炎及抗過敏活性試驗。

1.嗜中性白血球去顆粒作用試驗

Table 48 顯示, DNE-I~DNE-VI 濃度在 10 ì g/mL 下,對於 fMLP 引發嗜中性白血球釋放 â-glucuronidase 和 lysozyme 的體外試驗,均 有顯著抑制作用(P<0.01),其中對嗜中性白血球釋放 â-glucuronidase 抑制作用的 IC₅₀分別為 10.1、4.0、1.9、1.4、9.2 和 40.0 ì g/mL,對 嗜中性白血球釋放 lysozyme 抑制作用的 IC₅₀分別為 12.7、2.8、1.5、 1.4、4.5 和 38.6 ì g/mL。由此試驗分別顯示其抗發炎活性。(對嗜中性 白血球釋放 â-glucu- ronidase 抑制作用的活性大小依次為: DNE-IV, DNE-III, DNE-II DNE-V, DNE-I > DNE-VI;對嗜中性白血球釋放 lysozyme 抑制作用的活性大小依次為: DNE-III, DNE-II, DNE-II, DNE-II, DNE-VI。)

2.肥滿細胞去顆粒作用試驗

Table 49 顯示, DNE-I~DNE-VI 在 30 ì g/mL 濃度下,對於 compound 48/80 引發肥滿細胞釋放 â-glucuronidase 和 histamine 的體 外試驗,均有明顯抑制作用(*P*<0.01),其中 DNE-I~DNE-V 對肥滿細 胞釋放 â-glucuronidase 抑制作用的 IC₅₀分別為 46.3、33.0、34.1、34.7 和 36.5 ì g/mL,而 DNE-II~DNE-V 對肥滿細胞釋放 histamine 抑制作 用的 IC₅₀分別為 35.9、34.3、31.7 和 36.1 ì g/mL。由此試驗分別顯示 其抗過敏活性。(對肥滿細胞釋放 â-glucuronidase 和 histamine 抑制作 用的活性大小依次為:DNE-II,DNE-III,DNE-IV,DNE-V>DNE-I,DNE-VI。)

Drugs	(µg/mL)	Percent		Release		
		β-glucuronidase	(%inh)	lysozyme	(%inh)	
Control		28.5±1.1		42.8±2.8		
DNE-I	(3)	18.7±1.0**	33.8±6.0	29.5±0.6**	30.4±5.0	
	(10)	12.8±0.6**	54.6±3.6	23.3±3.5**	44.7±9.7	
	(30)	5.9±1.0**	79.1±3.8	7.1±1.9**	83.2±4.7	
IC ₅₀		10.1±2.6 μ	g/mL	12.7±3.3	12.7±3.3 µg/mL	
DNE-II	(1)	20.5±1.7**	27.7±6.6	28.1±1.8**	33.8±6.2	
	(3)	14.9±0.6**	47.3±3.9	22.1±5.0**	47.5±12.9	
	(10)	4.0±0.3**	85.7±1.7	6.4±2.6**	84.6±6.3	
IC ₅₀		4.0±0.5 με	r∕mL	2.8±1.5 µ	ıg/mL	
DNE-III	(0.3)	21.9±0.4**	22.5±2.9	34.3±3.0**	19.2±8.6	
	(1)	17.9±0.7**	36.9±3.7	25.0±4.8**	41.1±11.8	
	(3)	9.0±1.5**	68.3±5.3	10.1±2.4**	76.8±4.9	
IC_{50}	50 1.9±0.2 μg/n		y/mL	1.5±0.3 µ	3μg/mL	
DNE-IV	(0.3)	17.9±1.5**	36.5±6.5	28.1±3.2**	33.9±8.5	
	(1)	15.5±1.2**	45.0±5.7	24.1±4.4**	42.8±11.6	
	(3)	7.9±2.0**	71.6±7.9	9.4±5.0**	77.1±11.9	
IC ₅₀		1.4±0.5 με	y/mL	1.4±0.6 μg/mL		
DNE-V	(1)	21.4±1.48**	24.3±6.7	30.1±3.0**	28.8±9.2	
	(3)	19.7±0.3**	30.6±3.0	23.8±4.0**	44.2±9.4	
	(10)	13.4±0.9**	52.3 ± 5.0	5.7±5.2**	86.1±12.4	
IC_{50}		9.2±1.3 μg	y/mL	4.5±1.7 μg/mL		
DNE-VI	(10)	20.9±1.3**	26.1±6.0	33.9±2.2**	20.3±6.1	
	(30)	17.7±1.0**	37.8±4.6	22.8±4.0**	46.0±10.3	
	(100)	-0.5±2.6**	101.6±6.0	-0.9±1.9**	101.9±3.0	
IC_{50}		40.0±3.0 μ	g/mL	38.6±6.0 μg/mL		
TFP	(3µM)	23.5±0.8	16.8±2.2	38.7±5.3	8.9±1.9	
	(10µM)	15.1±1.6**	44.9±8.6	29.7±6.8	28.0±6.1	
	(30µM)	3.2±0.7**	88.6±2.7	1.3±2.2**	96.9±4.1	
IC ₅₀		14.2±0.7	μM	16.0±0.9 μM		

Table 48. Effect of the ethyl acetate extract of *D. nakaharai* on the release of β -glucuronidase and lysozyme in neutrophils (*in vitro*)

Neutrophil suspensions were preincubated at 37 with 0.5% DMSO or test compounds for 3 min in the presence of cytochalasin B (5 μ g/mL). Forty-five minutes after the addition of formylmethionyl-leucyl-phenyl-alanine (fMLP) (1 μ M), the amount of β -glucuronidase and lysozyme in the supernatant were determined. Values are presented as mean \pm S. E., N=3, * *P*<0.05, ** *P*<0.01; Trifluoperazine (TFP) (as positive control).

Drugs	(µg/mL)		Percent	Release	
		β-glucuronidase	(%inh)	histamine	(%inh)
Control		55.8±0.3		72.9±2.0	
DNE-I	(10)	41.3±1.1**	26.1±1.6	71.1±0.3	2.3±2.9
	(30)	29.9±2.2**	46.5±3.8	61.8±1.1**	15.2 ± 2.7
	(100)	12.4±1.5**	77.8±2.9	44.9±4.5**	38.4±6.3
IC ₅₀		46.3±2.5	µg/mL		
DNE-II	(10)	43.3±0.4**	22.4±1.2	60.7±1.1**	16.7±1.5
	(30)	16.2±1.1**	71.0±2.0	25.1±1.1**	65.6±1.5
	(100)	4.0±0.4**	92.8±0.7	0.9±0.6**	98.6±0.9
IC ₅₀		33.0±0.3	µg/mL	35.9±0.8	µg/mL
DNE-III	(10)	41.5±1.8**	25.6±2.9	60.9±2.5**	16.5 ± 2.4
	(30)	20.5±1.7**	63.2±3.2	21.0±1.9**	71.2±1.9
	(100)	6.3±0.6**	88.6±1.0	0.2±0.4**	99.7±0.5
IC ₅₀		34.1±2.3	µg/mL	34.3±1.2	µg/mL
DNE-IV	(10)	42.3±0.5**	24.2±0.6	59.1±2.0**	18.8±2.7
	(30)	17.5±1.1**	68.7±1.9	14.8±2.2**	79.8±2.6
	(100)	7.9±0.3**	85.7±0.6	0.1±0.5**	99.8±0.7
IC ₅₀		34.7±0.7	7 μg/mL 31.7±1.4 μg/mL		µg/mL
DNE-V	(10)	43.4±3.8**	18.7±6.4	62.9±1.9*	13.5±4.5
	(30)	17.2±3.5**	69.2±6.2	16.3±5.7**	77.2±8.1
	(100)	5.9±1.0**	89.4±2.0	2.6±0.9**	96.3±1.3
IC ₅₀		36.5±4.6	µg/mL	36.1±2.4	µg/mL
DNE-VI	(30)	45.1±1.4**	19.2±2.7	61.1±4.4**	16.4±3.7
	(100)	36.1±2.3**	35.3±3.9	53.5±2.6**	26.4±5.4
Mepacrine	(10µM)	35.2±1.7**	36.7±2.4	52.5±3.4**	29.3±3.9
	(30µM)	28.2±0.9**	48.9±2.2	40.5±2.4**	45.5±2.9
	(100µM)	5.6±0.4**	89.7±0.9	10.8±1.3**	85.5±1.7
IC ₅₀		32.5±1.	7 μΜ	40.8±4.3	3 μΜ

Table 49. Effect of the ethyl acetate extract of *D. nakaharai* on the release of β -glucuronidase and histamine in mast cells (*in vitro*)

Mast cell suspensions were preincubated at 37 with 0.5% DMSO or test compounds for 3 min. Fifteen minutes after the addition of compound 48/80, the amount of β -glucuronidase and histamine in the supernatant were determined. Values are presented as mean \pm S. E., N=3, * *P*<0.05, ** *P*<0.01; Mepacrine (as positive control).

三、臺灣金線連粗抽物之抗發炎及抗過敏試驗

1.嗜中性白血球去顆粒作用試驗

Table 50 顯示,臺灣金線連正己烷粗抽物(Af-H)和乙酸乙酯粗抽物(Af-E),其濃度在 10 i g/mL 之下,對於 fMLP 引發嗜中性白血球釋放â-glucuronidase 和 lysozyme 的體外試驗,均有顯著抑制作用(P<0.01),其中臺灣金線連正己烷粗抽物(Af-H)對嗜中性白血球釋放â-glucuroni- dase 抑制作用的 IC₅₀為 5.3 i g/mL,對嗜中性白血球釋放lysozyme 抑制作用的 IC₅₀分別為 5.7 i g/mL;臺灣金線連乙酸乙酯粗抽物(Af-E)對嗜中性白血球釋放â-glucuronidase 抑制作用的 IC₅₀為 13.4 i g/mL;而臺灣金線連甲醇粗抽物(Af-M)要在 30 i g/mL 濃度下,對fMLP 引發嗜中性白血球釋放â-glucuronidase 和 lysozyme 的體外試驗,才有抑制作用。由此試驗顯示,臺灣金線連可能具有抗發炎活性,以正己烷粗抽物(Af-H)最好,其次乙酸乙酯粗抽物(Af-E),而甲醇粗抽物(Af-M)較差。

Drugs	(µg/mL)		Percent	Release	
		β-glucuronidase	(%inh)	lysozyme	(%inh)
Control		32.9±0.5		57.1±1.1	
Af-H	(1)	24.5±0.7**	25.7±1.4	47.2±2.5	17.3±3.0
	(3)	21.1±0.8**	36.1±2.5	42.6±3.5*	25.5±5.3
	(10)	7.5±0.9**	77.2±2.5	9.2±2.4**	84.0±4.0
IC ₅₀		5.3±0.3 µg/mL		5.7±0.5 μg/mL	
Af-E	(3)	21.2±1.5**	35.7±3.7	39.1±4.2*	31.7±6.2
	(10)	16.5±0.7**	49.7±3.1	33.9±1.6**	40.6±1.7
	(30)	10.7±0.6**	67.7±1.5	28.8±2.5**	49.5±3.5
IC ₅₀		13.4±0.4 µ	ıg∕mL		
Af-M	(10)	25.0±1.0**	24.1±2.4	45.3±2.6	20.7±3.4
	(30)	19.5±1.0**	40.9±3.0	40.9±2.6*	28.4±2.0
TFP	(10µM)	36.4±2.8	-10.9 ± 12.5	61.2±2.7	-7.5±4.8
	(20µM)	18.5±1.8**	43.3±8.2	29.9±5.2**	48.4±4.5
	(30µM)	12.5±1.5**	60.9±7.0	14.6±4.7**	74.9±8.6
IC ₅₀		24.4±0.5	μM	22.8±0.	5 μΜ

Table 50. Effect of extracts of *A. formosanus* on the release of β -glucuronidase and lysozyme in neutrophils (*in vitro*)

Neutrophil suspensions were preincubated at 37 with 0.5% DMSO or test compounds for 3 min in the presence of cytochalasin B (5 μ g/mL). Forty-five minutes after the addition of formylmethionyl-leucyl-phenyl-alanine (fMLP) (1 μ M), the amount of β -glucuronidase and lysozyme in the supernatant were determined. Values are presented as mean \pm S. E., N=3, * *P*<0.05, ** *P*<0.01.Af-H: *n*-Hexane extract of *A. formosanus*, Af-E: Ethyl acetate extract of *A. formosanus*, Af-M: Methanol extract of *A. formosanus*; Trifluoperazine (TFP) (as positive control).
2.肥滿細胞去顆粒作用試驗

Table 51 顯示,臺灣金線連三種粗抽物對於 compound 48/80 引發 肥滿細胞釋放 â-glucuronidase 和 histamine 的體外試驗,抑制作用不 佳。

Drugs	(µg/mL)		Percent	Release	
		β-glucuronidase	(%inh)	histamine	(%inh)
Control		37.0±2.6		53.4±2.8	
Af-H	(30)	26.8±0.6**	27.4±1.4	45.9±1.2	14.0±3.5
Af-E	(30)	27.0±1.2**	26.7±5.1	43.5±0.9	18.5±0.8
	(100)	26.2±0.6**	29.2±1.3	38.1±0.1**	28.6±1.4
Af-M	(30)	31.4±0.4	14.8±3.8	49.8±2.4	6.6±6.2
	(100)	33.0±2.0	11.0±2.5	51.7±2.7	3.1±6.3
Mepacrine	(10µM)	24.6±0.7**	33.1±4.2	45.7±2.0	14.8±2.9
	(20µM)	11.0±3.0**	70.4±6.1	20.7±2.4**	60.1±3.0
	(30µM)	0.9±0.5**	97.3±1.2	9.7±0.8**	82.0±1.4
IC ₅₀		24.3±2.2	μΜ	43.8±1.9	μΜ

Table 51. Effect of extracts of *A. formosanus* on the Release of β -glucuronidase and histamine in mast cells (*in vitro*)

Mast cell suspensions were preincubated at 37 with 0.5% DMSO or test compounds for 3 min. Fifteen minutes after the addition of compound 48/80, the amount β -glucuronidase and histamine in the supernatant were determined. Values are presented as mean \pm S. E., N=3, * *P*<0.05, ** *P*<0.01; Mepacrine (as positive control).

四、化合物之抗發炎及抗過敏試驗

由石斛、連珠石斛與臺灣金線連分離得到的化合物,進行抗發炎 及抗過敏活性試驗,其結果顯示於 Table 52 至 Table 60.

1. Denbinobin (11)抗發炎及抗過敏試驗

Denbinobin (11)在 1 ì M 濃度下,對於 LPS 於刺激巨噬細胞株 RAW 264.7 釋放 TNF-á 和 PGE₂ 之抑制試驗,有顯著的抑制作用 (P<0.01),其抑制率分別為 62 和 43 %,但是在相同的條件下,對刺 激細胞釋放 NO 之抑制試驗,並無影響。而對於 LPS 及 IFN-ã 刺激小 神經膠總細胞株 N9 釋放 TNF-á 和 Nitrite 的作用,其抑制率分別為 70 和 44 %。此外,在 30 ì M 濃度下,對於 compound 48/80 引發肥滿 細胞釋放 â-glucuroni- dase 和 histamine 的體外試驗,亦有明顯抑制作 用(P<0.01),其抑制率分別為 40 和 39 %。 2. Vanillin (38)抗發炎及抗過敏試驗

Vanillin (**38**)在 30 ì M 濃度下,對於 fMLP 和 PMA 引發嗜中性白 血球釋放超氧自由基(superoxide anion)的抑制試驗,具有抑制作用, 其抑制率分別為 38 和 52 %,其中對 PMA 引發嗜中性白血球釋放超 氧自由基抑制效果較佳, IC_{50} 為 24.4 ì M。

3. p-Anisaldehyde (4)抗發炎及抗過敏試驗

p-Anisaldehyde (4)在 10-30 ì M 濃度下,對於 fMLP 引發嗜中性白血球釋放超氧自由基的抑制試驗,有弱的抑制作用。

4. Nakaharain (25)抗發炎及抗過敏試驗

實驗顯示 nakaharain (25)無好的抗發炎和抗過敏活性。

5. 2,5-Dihydroxy-3,4-dimethoxyphenanthrene (28)抗發炎及抗 過敏試驗

2,5-Dihydroxy-3,4-dimethoxyphenanthrene (28)在 30 ì M 濃度下, 對於 fMLP 引發嗜中性白血球釋放 â-glucuronidase 和 lysozyme 的體 外試驗,均具有抑制作用,其中對於嗜中性白血球釋放 â-glucuronidase 的 IC₅₀ 為 20.5 ì M。對於 compound 48/80 引發肥滿細胞釋放 â-glucuronidase 和 histamine 的體外試驗,有弱的抑制作用。對於 fMLP 引發嗜中性白血球釋放超氧自由基的抑制試驗,其 IC₅₀為 20.7 ì M。 另外對於 LPS 於刺激巨噬細胞株 RAW 264.7 釋放 NO 之抑制試驗, 則較弱。此外在較低濃度 10 ì M 時,對於 PMA 引發嗜中性白血球釋 放超氧自由基的抑制試驗,有 38%的抑制作用。而對於 LPS 及 IFN-ã 刺激小神經膠總細胞株 N9 釋放 TNF-á 之抑制試驗,則較弱。綜合上 述試驗得知,28 對嗜中性白血球有抑制效果。

6. Vitexin (37)抗發炎及抗過敏試驗

Vitexin (**37**)在 30 ì M 濃度下,對於 fMLP 引發嗜中性白血球釋放 â-glucuronidase 和 lysozyme 的體外試驗,均具有抑制作用,其抑制率 分別為 42 和 38 %。此外在低濃度 1 ì M 下,對於 fMLP 引發嗜中性 白血球釋放超氧自由基的抑制試驗,具顯著的抑制作用,其抑制率為 33 %。綜合上述試驗得知,**37** 對嗜中性白血球所引發的發炎可能有 抑制效果。 7. Protocatechuic acid (33)抗發炎及抗過敏試驗

Protocatechuic acid (**33**)在 30 ì M 濃度下,對於 fMLP 引發嗜中性 白血球釋放 â-glucuronidase 和 lysozyme 的體外試驗,均具有抑制作 用,其抑制率分別為 33 和 36 %。此外在 10 ì M 濃度下,對於 fMLP 引發嗜中性白血球釋放超氧自由基的抑制試驗,具顯著的抑制作用, 其抑制率為 44 %。綜合上述試驗得知,**33** 對嗜中性白血球所引發的 發炎可能有抑制效果。

8. Uracil (34)抗發炎及抗過敏試驗

Uracil (34)在 30 ì M 濃度下,對於 fMLP 引發嗜中性白血球釋放 â-glucuronidase 和 lysozyme 的體外試驗,均具有抑制作用,其抑制率 分別為 35 和 32 %。而對於 fMLP 引發嗜中性白血球釋放超氧自由基 的抑制試驗,在較低濃度 3 ì M 下,即具顯著的抑制作用,其 IC₅₀為 21.3 ì M。綜合上述試驗得知,34 對嗜中性白血球所引發的發炎可能 有抑制效果。

9. trans-â-Carotene (23)抗發炎及抗過敏試驗

trans-â-Carotene (**23**)在 30 ì M 濃度下,對於 fMLP 引發嗜中性白血球釋放 â-glucuronidase 和 lysozyme 的體外試驗,具有抑制作用, 其抑制率分別為 25 和 38 %。

10. Linoleic acid 抗發炎及抗過敏試驗

Linoleic acid (13) 對於 fMLP 引發嗜中性白血球釋放 â-glucuronidase 和 lysozyme 的體外試驗,均具顯著抑制作用,IC₅₀分 別為 18.4 和 19.8 ì M。

11. Pheophytin a (6)抗發炎及抗過敏試驗

Pheophytin a (6)在低濃度 10 ì M 下,對於 fMLP 引發嗜中性白血 球釋放 â-glucuronidase 和 lysozyme 的體外試驗,均具有抑制作用, 其抑制率分別為 25 和 40 %,但是較高濃度 30 ì M 下,其抑制作用減 弱為 16 和 32 %。此外在 30 ì M 濃度下,對於 LPS 於刺激巨噬細胞 株 RAW 264.7 釋放 TNF-á 之抑制試驗,具有 26 % 抑制作用。這說明 6 可能具有弱的抗發炎活性。

Compounds	(μM)		Percent	Release	
*	\	β-glucuronidase	(%inh)	lysozyme	(%inh)
Control		26.4±0.8		33.1±0.9	
11	(10)	34.6±2.8	-30.8±7.4	40.9±5.8	-22.7±14.9
	(30)	31.4±1.8	-18.7±3.7	36.4±4.8	-9.3±11.8
TFP	(3)	29.2±2.8	-10.9±12.5	35.5±2.7	-7.5±4.8
	(10)	14.8±1.8**	43.3±8.2	17.3±5.2**	48.4±4.5
	(30)	10.0±1.5**	60.9±7.0	8.5±4.7**	74.9±8.6
IC ₅₀		24.4±0.5 μľ	Μ	22.8±0.5	μΜ
Control		32.5±0.4		48.2±3.0	
4	(10)	27.9±0.8	14.1±1.5	44.1±3.1	8.2±5.1
	(30)	27.8±0.4	14.6±0.2	44.4±2.3	7.8±1.0
12	(10)	28.4±0.9	12.7±2.1	45.2±2.9	6.1±0.1
	(30)	27.5±0.9	15.4±1.6	45.2±2.7	5.9±2.3
25	(10)	28.4±0.6	12.7±0.7	43.8±2.5	9.1±1.0
	(30)	27.5±1.2	15.4±2.9	40.6±2.5	15.6±0.3
28	(3)	28.5±0.5	12.2±2.2	51.0±2.5	-6.0±1.6
	(10)	23.8±0.8**	26.5±3.7	45.0±0.9	5.9±4.9
	(30)	9.7±0.1**	70.2±0.8	26.5±0.7**	44.8±1.9
IC_{50}		20.5±0.7 μl	M		
33	(10)	25.4±1.3*	21.9±3.0	36.5±0.7	23.6±5.4
	(30)	21.8±0.4**	32.9±2.3	30.3±1.3**	36.4±6.3
34	(10)	25.6±0.5*	21.1±1.2	39.7±1.5	16.7±7.8
	(30)	21.3±1.6**	34.5±4.2	32.4±2.6**	31.8±9.0
37	(10)	22.5±0.9**	30.8±2.0	35.1±2.6*	27.1±2.6
	(30)	18.9±0.3**	41.7±1.2	29.6±0.9**	38.2±2.1
TFP	(3)	37.8±1.3	-14.6±12.7	56.7±4.0	-17.6±11.5
	(10)	24.9±1.3**	21.3±11.4	39.4±1.9	17.5±3.1
	(30)	3.7±0.4**	87.8±3.4	1.1±1.6**	97.3±4.9
IC ₅₀		18.9±2.1 μl	М	18.3±0.9	μM
Control		22.0±0.4		40.0±1.7	
6	(10)	16.6±0.2*	24.5±2.2	24.2±3.4**	39.8±6.9
	(30)	18.5±0.7	15.9±2.6	27.3±4.3**	32.4±7.9
13	(3)	16.5±0.6*	25.2±1.4	37.6±1.0	5.7±3.8
	(10)	13.9±0.8**	37.1±2.3	31.5±1.4*	20.7±5.3
	(30)	4.3±0.7**	80.8±2.9	7.3±4.0**	81.0±10.3
IC_{50}		18.4±2.7 μľ	M	19.8±2.3	μM
23	(10)	20.4±0.5	7.4±1.0	34.1±2.4	14.7±5.4
	(30)	16.4±0.1**	25.3±1.6	25.1±3.9**	37.7±8.1
TFP	(3)	25.1±2.5	-14.5±7.2	40.4±1.8	-1.3±1.5
	(10)	13.9±3.6**	36.8±6.2	34.9±2.6	12.7±1.2
	(20)	5.8±2.1**	73.6±3.6	10.4±3.2**	74.3±5.1
IC ₅₀		14.4±0.8 μľ	M	15.5±0.6	μM

Table 52. Effect of compounds on the release of β -glucuronidase and lysozyme in neutrophils (*in vitro*)

Neutrophil suspensions were preincubated at 37 with 0.5% DMSO or test compounds for 3 min in the presence of cytochalasin B (5 µg/mL). Forty-five minutes after the addition of formylmethionyl-leucyl-phenyl-alanine (fMLP) (1 µM), the amount of β -glucuronidase and lysozyme in the supernatant were determined. Values are presented as mean ± S.E., N=3,* *P*<0.05, ** *P*<0.01; Trifluoperazine (TFP) (as positive control).

Compounds	(µM)	· · · · · · · · · · · · · · · · · · ·	Percent	Release	
		β -glucuronidase	(%inh)	histamine	(%inh)
Control		29.5±1.1		47.6±1.3	
11	(10)	19.5±2.3**	33.4±5.4	33.1±2.1**	30.5±2.6
	(30)	17.6±0.9**	40.2±2.1	29.1±0.5**	38.8±1.4
mepacrine	(10)	19.5±0.7**	33.1±4.2	40.7±2.0	14.8±2.9
	(30)	8.7±3.0**	70.4±6.1	18.4±2.4**	60.1±3.0
	(100)	0.7±0.5**	97.3±1.2	8.6±0.8**	82.0±1.4
IC ₅₀		24.3±2.2 µ	ιM	43.8±1.9	μM
Control		43.2±1.6		56.6±2.0	
4	(10)	39.1±4.1	9.9±6.2	48.5±4.8	14.6±6.6
	(30)	38.8±0.5	10.2 ± 2.4	48.5±2.1	14.5 ± 1.4
12	(10)	42.6±0.5	1.2 ± 3.3	51.5±4.2	9.2±5.51
	(30)	37.4±2.3	13.6±2.3	45.1±2.5*	20.3±2.0
25	(10)	38.1±1.3	11.7±1.3	49.5±2.2	12.7±1.4
	(30)	34.9±2.3	19.2±2.3	45.7±2.5*	19.4±1.6
28	(10)	41.6±1.9	3.6±1.8	52.2±2.0	7.8±1.4
	(30)	30.1±2.0**	30.5±3.3	44.4±2.9*	21.7±2.6
33	(10)	42.7±2.5	1.3 ± 2.2	51.1±3.1	9.9±3.2
	(30)	38.2±1.7	11.3±4.3	44.6±3.0*	21.3±2.5
34	(10)	38.4±3.0	11.4±4.7	49.1±5.6	13.7±7.3
	(30)	38.4±0.9	10.7 ± 5.4	46.5±2.5	18.0±1.5
37	(10)	40.4±2.5	6.3±6.4	47.6±3.6	16.2±3.6
	(30)	39.3±1.6	8.9±3.6	46.5±3.6	18.2 ± 3.4
mepacrine	(10)	29.9±0.6**	31.9±2.1	52.6±2.7**	24.6±4.1
	(30)	18.2±1.1**	57.8±2.9	31.6±3.4**	43.5±4.2
	(100)	5.9±0.8**	86.0±2.1	12.1±1.2**	78.2±1.4
IC ₅₀		32.2±3.6 µ	ιM	48.5±3.8	μM
Control		21.2±0.1		40.2±0.6	
6	(10)	22.3±1.4	-5.1±6.6	38.3±1.3	4.6±4.1
	(30)	22.8±1.7	-7.4±7.6	42.3±0.3	-5.3±2.4
13	(10)	21.1±0.3	0.5 ± 1.1	34.0±1.1	15.3±3.1
	(30)	18.7±0.3	12.0 ± 1.1	41.2±0.6	-2.7 ± 2.9
23	(10)	20.1±0.8	5.2 ± 4.2	34.6±0.6	13.7±2.8
	(30)	19.0±0.5	10.3 ± 2.2	33.8±0.7	15.9±0.6
mepacrine	(10)	16.2±1.5*	23.7±3.5	33.6±2.4	16.6±2.9
	(30)	12.0±1.1**	42.9±2.9	25.7±3.6**	35.8±6.0
	(100)	1.3±0.7**	93.7±1.9	4.4±1.3**	88.8±2.3
IC ₅₀		42.0±3.5 µ	ιM	50.2±4.5	μM

Table 53. Effect of compounds on the release of β -glucuronidase and histamine in mast cells (*in vitro*)

Mast cell suspensions were preincubated at 37 with 0.5% DMSO or test compounds for 3 min. Fifteen minutes after the addition of compound 48/80, the amount of β -glucuronidase and histamine activities in the supernatant were determined. Values are presented as mean \pm S. E., N=3, * *P*<0.05, ** *P*<0.01; mepacrine (as positive control).

Compounds	(µM)	Superoxide Formation			
	•	nmol/10° cells/30 min	(%inh)	N	
Control		2.39±0.28		3	
11	(3)	3.14±0.39	-31.6±9.8	3	
	(10)	3.42±0.46*	-43.5±12.7	3	
	(30)	3.62±0.46**	-52.7±17.8	3	
TFP	(3)	2.47±0.46	-3.2±5.9	3	
	(10)	0.72±0.08**	68.6±2.5	3	
	(30)	0.23±0.01**	88.5±3.3	3	
IC ₅₀		14.0±0.4	μM		
Control		1.83±0.05	·	3	
4	(10)	1.33±0.15*	27.7±6.3	3	
	(30)	1.33±0.14*	27.7±5.5	3	
12	(10)	1.31±0.20*	28.9±9.0	3	
	(30)	1.15±0.24**	37.6±11.3	3	
25	(10)	1.55±0.12	15.6±4.2	3	
	(30)	1.79±0.13	2.4±4.5	3	
28	(3)	1.48±0.14	18.7±9.3	3	
	(10)	1.08±0.12**	40.8±7.2	3	
	(30)	0.75±0.08**	58.7±5.2	3	
IC ₅₀		20.7±3.	б μМ		
33	(3)	1.15±0.18**	37.7±8.1	3	
	(10)	1.03±0.15**	43.9±6.5	3	
34	(3)	1.15±0.04**	37.2±2.5	3	
	(10)	1.02±0.03**	44.1±3.2	3	
	(30)	0.82±0.06**	55.0±3.2	3	
37	(1)	1.24±0.20**	32.7±8.7	3	
	(3)	1.06±0.13**	42.5±5.3	3	
IC ₅₀		21.3±4.1	3 μΜ		
TFP	(3)	2.50±0.42	-30.2±11.7	3	
	(10)	1.09±0.28	40.5±11.1	3	
	(30)	0.11±0.06**	93.6±3.3	3	
IC_{50}		12.9±1.	0 μM		
Control		2.81±0.19		3	
6	(10)	2.46±0.13	11.8±6.6	3	
	(30)	2.47±0.16	11.2±8.2	3	
13	(10)	2.83±0.02	-1.5±6.2	3	
	(30)	3.00±0.11	-7.4±3.3	3	
23	(10)	2.87±0.16	-3.7±12.3	3	
	(30)	2.86±0.18	-3.3±12.3	3	
TFP	(3)	2.22±0.22	20.5±5.3	3	
	(10)	1.56±0.16**	42.9±2.8	3	
	(30)	0.05±0.02**	98.2±0.9	3	
IC ₅₀		13.0±0.3 μM			

Table 54. The inhibitory effect of compounds on the superoxide formation in neutrophils

Neutrophil suspensions were preincubated at 37 with 0.5% DMSO or test compounds for 3 min in the presence of cytochalasin B (5 μ g/mL). Fifteen minutes after the addition of fMLP (0.3 μ M), the absorbance of supernatant was determined at 550 nm. Values are presented as mean \pm S. E., * *P*<0.05, ** *P*<0.01; Trifluoperazine (TFP) (as positive control).

Drugs	(µM)	1) Superoxide Formation		
		nmol/10 ⁶ cells/30 min	(% inh)	Ν
Control		2.35±0.01		3
11	(10)	2.33±0.15	0.7±5.8	3
	(30)	2.56±0.06	-8.8±2.7	3
TFP	(3)	1.49±0.15**	36.4±1.6	3
	(10)	0.64±0.14**	73.1±3.3	3
	(30)	0.20±0.24**	91.1±2.7	3
IC ₅₀		6.9±0	.7 μΜ	
Control		2.81±0.17		3
4	(10)	2.45±0.27	13.5±5.3	3
	(30)	2.17±0.41	23.7±13.4	3
12	(3)	2.20±0.12	21.3±3.7	3
	(10)	1.50±0.12**	46.6±4.1	3
	(30)	1.36±0.16**	51.8±5.5	3
IC ₅₀		24.4±	5.5 μΜ	
25	(10)	2.52±0.18	10.2 ± 5.8	3
	(30)	2.50 ± 0.30	10.5±11.2	3
28	(10)	1.74±0.09**	37.7±5.4	3
	(30)	2.14±0.22	23.6±8.5	3
33	(3)	2.66±0.19	4.1±11.0	3
	(10)	2.45±0.18	11.9±9.5	3
34	(10)	1.50±0.09	9.3±10.4	3
	(30)	2.30±0.14	16.1±13.7	3
37	(1)	2.52±0.25	8.7±13.5	3
	(3)	2.36±0.28	14.2 ± 14.2	3
TFP	(3)	2.13±0.04	23.7±3.5	3
	(10)	0.56±0.08**	79.2±4.3	3
	(30)	0.22±0.09**	91.9±4.3	3
IC ₅₀		9.7±1	.1 μΜ	
Control		3.02 ± 0.20		3
6	(10)	2.67±0.22	11.4±5.2	3
	(30)	2.76±0.34	8.8±8.5	3
13	(10)	2.64±0.17	12.4±4.2	3
	(30)	3.98 ± 0.45	-38.3±3.3	3
23	(10)	2.68±0.24	10.0 ± 11.1	3
	(30)	2.83±0.23	6.4±2.7	3
TFP	(3)	2.02±0.19**	32.5±8.6	3
	(10)	0.74±0.15**	74.9±5.7	3
	(30)	0.07±0.03**	97.6±0.9	3
IC_{50}		6.8±2	.3 μΜ	

Table 55. The inhibitory effect of compounds on the superoxide formation in neutrophils

Neutrophils were pretreated with DMSO (as control) or test compounds at 37 for 3 min before stimulation with 3 nM of PMA for 15 min, the absorbance of supernatant was determined at 550 nm. Values are expressed as means \pm S. E., N=3.* *P*<0.05, ** *P*<0.01; Trifluoperazine (TFP) (as positive control).

Drugs	(µM)	Nitrite accumulation		
	_	μM	(% inh)	Ν
Control		46.6±0.4		3
11	(1)	40.4±1.0	13.4±2.1	3
L-NAME	(0.1mM)	35.9±1.0**	23.0±2.1	3
	(0.3mM)	27.8±0.6**	40.3±1.2	3
	(1mM)	18.6±0.9**	60.2±1.9	3
IC ₅₀		0.0	58±0.01 mM	
Control		46.9±0.1		3
4	(10)	49.6±0.5	-5.8 ± 1.2	3
	(30)	47.0±0.1	-0.3 ± 0.2	3
12	(10)	50.5±0.3	-7.7±0.7	3
	(30)	49.2±0.6	-5.0 ± 1.4	3
25	(10)	47.5±0.5	-1.2 ± 1.2	3
	(30)	45.8±0.6	2.3±1.3	3
28	(10)	47.5±0.3	-1.2±0.8	3
	(30)	34.5±0.9**	26.4±1.9	3
33	(10)	49.1±0.3	-4.7±0.6	3
	(30)	47.9±0.6	-2.0 ± 1.4	3
34	(10)	48.9±0.4	-4.2 ± 0.8	3
	(30)	49.1±0.8	-4.7±1.7	3
37	(10)	49.3±0.6	-5.1 ± 1.2	3
	(30)	48.9±0.2	-4.2 ± 0.4	3
1400W	(0.1)	46.9±0.2	-0.1 ± 0.5	3
	(1)	31.0±0.4**	33.8±0.9	3
	(10)	15.3±0.1**	33.8±0.9	3
IC ₅₀		6.	1±0.06 µM	
Control		59.2±1.0		3
6	(10)	57.9±2.0	2.1±3.4	3
	(30)	58.3±1.8	1.5 ± 3.0	3
13	(10)	56.3±1.1	4.9±1.8	3
	(30)	50.6±0.8**	14.5 ± 1.4	3
23	(10)	52.2±1.0*	11.8 ± 1.8	3
	(30)	48.9±1.2**	17.4 ± 2.0	3
L-NAME	(0.1mM)	48.4±0.4**	18.3±0.6	3
	(0.3mM)	38.2±0.4**	35.4±0.7	3
10	(1mM)	25.1±1.5**	57.4±2.5	3
IC_{50}		0.7	72±0.06 mM	

Table 56. The inhibitory effect of compounds on the nitriteaccumulation in RAW 264.7 cell lines

RAW 264.7 cells were pretreated with DMSO (as control) or test compounds at 37 for 1 h before stimulation with 1 μ g/mL of LPS for 24 h. Values are expressed as means \pm S. E., N=3.* *P*<0.05, ** *P*<0.01; N^ù-Nitro-L-Arginine methylether (L-NAME) and N-(3-Aminomethyl)benzylacetamidine, 2HCl (1400W) (as positive control).

Drugs	(µM)	Nitrite	accumulation	
C		μM	(% inh)	Ν
Control		52.1±1.4		4
11	(0.3)	52.0±1.1	0.1±2.2	4
	(1)	43.7±0.3	16.1±0.5	4
	(3)	28.8±1.0**	44.6±2.0	4
L-NAME	(0.1 mM)	42.6±1.0	18.3±3.1	3
	(0.3mM)	21.1±0.4**	59.6±1.1	3
	(1 mM)	6.4±0.3**	87.7±1.1	3
IC ₅₀		0	.40±0.01 mM	
Control		37.5±0.3		3
4	(10)	38.1±0.2	-1.5±0.5	3
	(30)	37.6±0.8	-0.2 ± 2.3	3
12	(10)	39.4±0.7	-4.9 ± 2.0	3
	(30)	37.9±0.6	-1.1±1.8	3
25	(10)	35.3±0.5	5.9±1.4	3
	(30)	32.1±0.6**	14.5±1.6	3
28	(10)	38.5±0.7	-2.7 ± 1.8	3
	(30)	36.8±0.8	1.7 ± 2.2	3
33	(10)	39.3±0.5	-4.5 ± 1.5	3
	(30)	38.6±0.4	-2.7 ± 1.2	3
34	(10)	37.8±0.7	-0.8 ± 1.8	3
	(30)	37.2±0.1	0.8 ± 0.5	3
37	(10)	37.4±0.4	0.2 ± 1.2	3
	(30)	38.5±0.4	-2.5 ± 1.1	3
1400W	(0.1)	35.9±1.0	4.1±2.8	3
	(1)	26.6±0.3**	29.1±0.9	3
	(10)	13.0±0.1**	65.3±0.4	3
IC ₅₀		6	.6±0.1 μM	
Control		46.3±0.5		4
6	(10)	45.3±2.3	2.0 ± 5.0	3
	(30)	49.4±1.5	-6.8 ± 3.4	3
13	(10)	47.6±0.6	-2.8 ± 1.3	3
	(30)	45.0±0.5	2.8 ± 1.0	3
23	(10)	46.4±0.6	-0.3 ± 1.4	3
	(30)	46.9±0.2	-1.3 ± 0.5	3
L-NAME	(0.1mM)	40.2±1.3**	12.9 ± 2.5	3
	(0.3mM)	29.2±0.3**	36.2±0.6	3
	(1mM)	22.5±0.4**	50.6±0.9	3
IC_{50}		0	.84±0.01 mM	

Table 57. The inhibitory effect of compounds on the nitrite accumulation in N9 cell lines

N9 cells were pretreated with DMSO (as control) or test compounds at 37 for 1 h before stimulation with 10 ng/mL of LPS plus 10 unit/mL of IFN-ã for 24 h. Values are expressed as means \pm S. E., N=3-4.* *P*<0.05, ** *P*<0.01; N^ù-Nitro-L-Arginine methylether (L-NAME) and N-(3-Aminomethyl)benzylacetamidine, 2HCl (1400W) (as positive control).

Drugs	(µM)	% inhibition	Ν
4	(30)	-14.5±1.7	3
6	(30)	26.1±3.8*	3
11	(1)	61.6±9.6**	3
12	(30)	-8.3±0.4	3
13	(30)	15.3±2.9	3
23	(30)	-1.1 ± 2.4	3
25	(30)	7.4±1.6	3
28	(30)	-48.2±5.7**	3
33	(30)	-9.0±0.7	3
34	(30)	10.5±1.5	3
37	(30)	-2.5 ± 3.8	3
dexamethasone	(0.1)	22.0±4.2*	3
	(1)	41.0±4.7**	3
	(10)	49.9±1.7**	3

Table 58. The inhibitory effect of compounds on the TNF-áformation in RAW 264.7 cell lines

RAW 264.7 cells were pretreated with DMSO (as control) or test compounds at 37 for 1 h before stimulation with 1 μ g/mL of LPS for 24 h. Values are expressed as means ± S. E., N=3.* *P*<0.05, ** *P*<0.01; dexamethasone (as positive control).

Table 59. The inhibitory effect of compounds on the TNF-á formationin N9 cell lines

Drugs	(µM)	% inhibition	Ν
4	(30)	-8.1±3.4	3
6	(30)	12.3±4.3	3
11	(3)	70.8±3.0**	3
12	(30)	-2.2 ± 0.5	3
13	(30)	15.0±2.3	3
23	(30)	-2.2 ± 3.9	3
25	(30)	25.4±2.5**	3
28	(10)	23.8±9.1*	3
33	(30)	-21.2±4.9	3
34	(30)	-20.6±5.3	3
37	(30)	-33.2±5.8*	3
dexamethasone	(0.01)	20.1±6.1*	3
	(0.1)	74.3±3.1**	3
	(10)	82.0±3.8**	3
IC ₅₀		0.25±0.14 µM	

N9 cells were pretreated with DMSO (as control) or test compounds at 37 for 1 h before stimulation with 10 ng/mL of LPS plus 10 unit/ml of IFN- \tilde{a} for 24 h. Values are expressed as means \pm S. E., N=3.* *P*<0.05, ** *P*<0.01; dexamethasone (as positive control).

TOTIL	uion in KAV	v 204.7 cen mies		
Drugs	(µM)	% inhibition	Ν	
6	(3)	-1.5±1.8	3	
11	(1)	43.5±50*	3	
13	(3)	-2.5 ± 0.3	3	
23	(3)	6.1±1.2	3	
dexamethasone	(10nM)	37.5±14.2*	3	
	(30nM)	76.7±3.6**	3	
	(100nM)	98.4±0.2**	3	
IC ₅₀		29.7± 4.8 nM		

Table 60. The inhibitory effect of compounds on the PGE₂ formation in RAW 264.7 cell lines

RAW 264.7 cells were pretreated with DMSO (as control) or test compounds at 37 for 1 h before stimulation with 1 μ g/mL of LPS for 24 h. Values are expressed as means ± S. E., N=3.* *P*<0.05, ** *P*<0.01; dexamethasone (as positive control).

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第三節 化合物之光譜數據

Alkyl acetates (16)

Colorless oil.

 $R_f: 0.64$ (*n*-hexane-ethyl acetate 12:1).

EIMS m/z (%) (rel. int.): 444 [M-60]⁺ (0.4), 420 [M-60]⁺ (0.4), 392 [M-60]⁺ (1.9), 364 [M-60]⁺ (1.8), 350 [M-60]⁺ (0.3), 336 [M-60]⁺ (0.8), 153 (3), 139 (9), 124 (12), 111 (36), 97 (81), 83 (59), 69 (65), 61 (78), 57 (100).

¹H-NMR (CDCl₃, 200 MHz): 0.86 (6H, t, J=6.4 Hz), 1.23 (br s, (CH₂)_n), 2.02 (3H, s, COCH₃), 4.03 (2H, t, J=6.7 Hz, COOCH₂).

¹³C-NMR (CDCl₃, 50 MHz): 14.1 (CH₃), 21.0-32.0 ((CH₂)_n), 64.7 (COOCH₂), 171.2 (CO).

Alkyl 4´-hydroxy-*cis*-cinnamates (7)

White powder from chloroform, mp. 69-72 .

 $R_f: 0.54$ (*n*-hexane-ethyl acetate 4:1).

IR(KBr) $_{\text{max}}$: 2926, 2856, 1726, 1684, 1607, 1536, 1480, 1340, 1277, 1186, 989, 835 cm⁻¹.

UV (CHCl₃) λ_{max} : 298 nm.

EIMS m/z (%) (rel. int.): $[M]^+$, 164 (100), 147 (70), 119 (46), 107 (27), 71 (22), 57 (36).

¹H-NMR (CDC_b, 200 MHz): 見 Table 29.

¹³C-NMR (CDC_b, 50 MHz): 見 Table 29.

Alkyl 4´-hydroxy-trans-cinnamates (8)

White powder from chloroform, mp. 73-75 .

 $R_f: 0.47$ (*n*-hexane-ethyl acetate 4:1).

IR(KBr) _{max}: 3357, 2912, 2849, 1719, 1607, 1516, 1460, 1172, 835 cm⁻¹.

UV (CHCl₃) λ_{max} : 299, 248 nm.

EIMS *m*/*z* (%) (rel. int.): [M]⁺, 164 (100), 147 (70), 120 (34), 107 (28), 71 (23), 57 (55).

¹H-NMR (CDCl₃, 200 MHz): 見 Table 30.

¹³C-NMR (CDC_b, 50 MHz): 見 Table 30.

Alkyl *tran*-ferulates (5)

White powder from chloroform, mp. 57-59 .

R_f: 0.28 (benzene).

IR(KBr) _{max}: 3500, 2919, 2849, 1712, 1600, 1522, 1171, 1038 cm⁻¹.

UV (CHCl₃) λ_{max} : 320, 242 nm.

EIMS m/z (%) (rel. int.): [M]⁺, 194 (95), 177 (73), 150 (38), 137 (48), 125 (31), 83 (25), 69 (53), 57 (100).

¹H-NMR (CDCl₃, 200 MHz): 見 Table 31.

¹³C-NMR (CDC₃, 50 MHz): 見 Table 31.

p-Anisaldehyde (4)

(4-Methoxybenzaldehyde)

Pale yellow oil from chloroform, $C_8H_8O_2$.

 $R_f: 0.52$ (*n*-hexane-ethyl acetate 4:1).

IR(KBr) $_{\text{max}}$: 2947,2842, 2736, 1697, 1584, 1581, 1321, 1269, 1216, 1163, 1025, 841 cm⁻¹.

UV (CHCl₃) λ_{max} (log ϵ): 277 (4.14) nm.

EIMS *m*/*z* (%) (rel. int.): 136 [M]⁺ (37), 135 (100), 107 (22), 92 (38), 77 (53), 63 (32).

¹H-NMR (CDCl₃, 200 MHz): δ 3.88 (3H, *s*, OCH₃), 6.99 (2H, *d*, *J*=8.8 Hz, H3 and H5), 7.82 (2H, *d*, *J*=8.8 Hz, H2 and H6), 9.87 (1H, *s*, CHO).

¹³C-NMR (CDCl₃, 50 MHz): δ 55.5 (OCH₃), 114.2 (C-3, C-5), 129.8

(C-1), 131.9 (C-2, C-6), 164.5 (C-4), 190.7 (<u>C</u>HO).

Anoectolide A (42)

bi(3-*O*-ethoxybutanolide) Colorless oil, $C_{12}H_{18}O_6$. [\acute{a}]_D²⁴ +11.8 (*c* = 0.017, MeOH). R_f: 0.65 (chloroform-methanol 4:1). FABMS (positive) *m*/*z* (rel. int.): 259 [M+H]⁺, 103 [C₄H₇O₃]⁺. ¹H-NMR (CDCl₃, 500 MHz)見 Table 44. ¹³C-NMR (CDCl₃, 125 MHz)見 Table 44.

Anoectolide B (43)

bi(3-*O*-acetoxybutanolide) Colorless oil, $C_{12}H_{14}O_8$. [á]_D²⁴ +33.3 (*c* = 0.012, MeOH). R_f: 0.56 (chloroform-methanol 4:1). FABMS (positive) *m/z* (rel. int.): 287 [M+H]⁺, 103 [C₄H₇O₃]⁺. ¹H-NMR (CDCl₃, 500 MHz)見 Table 45. ¹³C-NMR (CDCl₃, 125 MHz)見 Table 45.

Bulbophyllanthrin (31)

(3,5-dihydroxy-2,4-dimethoxyphenanthrene)

yellow crystallized (*n*-hexane-ethyl acetate 10:1), mp 175 , $C_{16}H_{14}O_4$.

 $R_f: 0.29$ (*n*-hexane-acetone 2:1).

IR (KBr) _{max}: 3388, 3184, 2925, 2854, 1616, 1571, 1507, 1473, 1436, 1279, 1201, 1145, 1100, 996, 873, 847, 822, 729 cm⁻¹.

UV (CH₃OH) _{max} (log): 206 (4.14), 260 (4.55), 306 (3.84), 317 (3.84), 333 (3.48), 349 (3.54), 366 (3.61), 440 (2.51) nm.

EIMS *m*/*z* (%) (rel. int.): 270 [M]⁺ (100), 255 (24), 237 (6), 227 (15), 212 (21), 195 (36), 184 (20), 155 (19), 139 (27), 128 (19).

¹H-NMR (CDCl₃, 500 MHz)見 Table 13.

¹³C-NMR (CDC_b, 125 MHz)見 Table 13.

Confusarin (29)

(2,7-dihydroxy-3,4,8-trimethoxyphenanthrene)

pale yellow amorphous solid, $C_{17}H_{16}O_5$.

R_f: 0.51(chloroform-methanol 4:1)

UV (CH₃OH) _{max} (log): 213 (4.19), 231 (4.15), 264 (4.42), 317 (3.76), 346 (3.27), 367 (3.17) nm.

FABMS (positive) m/z (rel. int.): 301 [M+H]⁺.

¹H-NMR (acetone-d₆, 200 MHz): 3.91 (3H, *s*, OCH₃), 3.95 (3H, *s*, OCH₃), 3.99 (3H, *s*, OCH₃), 7.16 (1H, *s*, H-1), 7.24 (1H, *d*, *J*=9.3 Hz, H-6), 7.58 (1H, *d*, *J*=9.1 Hz, H-10), 7.89 (1H, *d*, *J*=9.6 Hz, H-9), 8.33 (2H, *br s*, 2-OH, 7-OH), 9.12 (1H, *d*, *J*=8.7 Hz, H-5).

Denbinobin (11)

(5-hydroxy-3,7-dimethoxy-1,4-phenanthraquinone)

Dark green solid from chloroform, mp. 190-192 , $C_{16}H_{12}O_5$.

 $R_f: 0.29$ (*n*-hexane-ethyl acetate 4:1).

IR (KBr) _{max}: 3419, 2917, 2850, 1642, 1624, 1578, 1544, 1506, 1464, 1436, 1298, 1242, 1170, 1082, 885, 725 cm⁻¹.

UV (CH₃OH) λ_{max} (log ϵ): 237 (4.25), 310 (4.05), 406 (3.15) nm.

EIMS *m*/*z* (%) (rel. int.): 284 [M]⁺ (100), 269 (4), 255 (2), 241 (5), 227 (9), 213 (61), 198 (3), 185 (44).

¹H-NMR (CDC_b, 200 MHz)見 Table 18.

¹³C NMR (CDCl₃, 50 MHz)見 Table 18.

Dengibsin (17)

(2,5-dihydroxy-4-methoxy-9-fluorenone)

red amorphous solid, $C_{14}H_{10}O_4$.

R_f: 0.44 (benzene-ethyl acetate 3:1).

IR (KBr) _{max}: 3352, 1703, 1600, 1493, 1451, 1381, 1324, 1266, 1217, 1143, 1031, 970, 739 cm⁻¹.

UV (CH₃OH) _{max} (log): 212 (4.44), 266 (4.43), 274 (4.48), 335 (3.53), 473 (3.07) nm.

EIMS *m*/*z* (%) (rel. int.): 242 [M]⁺ (100), 227 (64), 213 (2), 199 (56), 183 (2), 171 (21), 155 (5), 142 (6), 126 (8), 121 (9), 115 (22), 98 (6).

¹H-NMR (CDCl₃+CD₃COCD₃, 500 MHz)見 Table 22.

¹³C-NMR (CDCl₃+CD₃COCD₃, 125 MHz)見 Table 22.

2,5-Dihydroxy-3,4-dimethoxyphenanthrene (28)

yellow crystals, mp 118-119 , $C_{16}H_{14}O_4$.

R_f: 0.47 (*n*-hexane-ethyl acetate 3:1).

IR (KBr) $_{max}$: 3368, 3138, 2927, 2855, 1624, 1565, 1525, 1466, 1433, 1275, 1203, 1038, 992, 940, 854, 742 cm⁻¹.

UV (CH₃OH) _{max} (log): 210 (4.18), 259 (4.51), 284 (4.13), 305 (3.88), 315 (3.85), 336 (3.30), 349 (3.37), 367 (3.39) nm.

EIMS *m*/*z* (%) (rel. int.): 270 [M]⁺ (100), 255 (28), 237 (7), 227 (23), 223 (48), 212 (66), 195 (7), 184 (9), 168 (4), 155 (18), 139 (13), 128 (15), 92 (14), 77 (19), 69 (16), 63 (21), 57 (9), 51 (12).

¹H-NMR (CDCl₃, 500 MHz)見 Table 14.

¹³C-NMR (CDCl₃, 125 MHz)見 Table 14.

Diethylene glycol (20)

Brown powder, $C_4H_{10}O_3$.

¹H-NMR (CD₃OD, 200 MHz): 3.40 (*br d*, *J*=4.1 Hz), 3.46 (*br d*, *J*=4.1 Hz).

¹³C-NMR (CD₃OD, 50 MHz): 60.6, 72.5.

Ergosterol (21)

(ergosta-5,7,22E-trien-3â-ol)

White powder from chloroform, mp. 155-157 , $C_{28}H_{44}O$.

R_f: 0.64 (benzene-ethyl acetate 4:).

EIMS *m*/*z* (%) (rel. int.): 396 [M]⁺ (26), 363 (26), 337 (17), 271 (6), 253 (16), 227 (4), 211 (14), 197 (9), 183 (7), 171 (9), 157 (17), 143 (24), 131 (13), 119 (19), 105 (18), 91 (21), 81 (40), 69 (100), 55 (65).

¹H-NMR (CDCl₃, 200 MHz): 見 Table 39.

Ergosterol peroxide (22)

White powder from chloroform, mp. 177-179 , $C_{28}H_{44}O_3$.

R_f: 0.45 (benzene-ethyl acetate 4:1).

EIMS *m*/*z* (%) (rel. int.): 428 [M]⁺ (2), 410 (5), 396 (19), 337 (7), 363 (10), 337 (5), 330 (2), 301 (4), 285 (5), 267 (7), 251 (8), 211 (8), 197 (8), 185 (9), 171 (10), 152 (26), 145 (18), 133 (16), 119 (17), 107 (30), 93 (47), 81 (65), 69 (100), 55 (99).

¹H-NMR (CDCl₃, 200 MHz): 見 Table 41.

¹³C-NMR (CDC_b, 50 MHz): 見 Table 40.

Ethyl β-D-glucopyanoside (44)

Colorless oil, $C_8H_{16}O_6$.

R_f: 0.46 (chloroform-methanol 3:1).

IR(KBr) _{max}: 3388, 2975, 2926, 2877, 1648, 1639, 1379, 1076, 1037, 889 cm⁻¹.

FABMS (positive) *m/z* (rel. int.): 231 [M+Na]⁺, 209 [M+H]⁺.

EIMS *m*/*z* (%) (rel. int.): 177 (1), 163 (3), 144 (4), 131 (9), 116 (7), 97 (7), 88 (19), 73 (86), 60 (100).

¹H-NMR (CD₃OD, 200 MHz): 1.25 (3H, *t*, J=7.10 Hz, H-8), 3.21 (1H, *m*, H-2), 3.44 (2H, *m*, H-4, H-5), 3.65 (2H, *m*, H-6, H-7), 3.93 (2H, *m*, H-6, H-7), 4.29 (1H, *d*, J=7.66 Hz, H-1).

¹³C-NMR (CD₃OD, 50 MHz): 15.4 (C-8), 62.5 (C-6), 66.1 (C-7), 71.3 (C-4), 74.7 (C-2), 77.5 (C-5), 77.7 (C-3), 103.7 (C-1).

Ethyl linolenate (3b)

Yellow oil from chloroform, $C_{20}H_{34}O_2$.

 $R_f: 0.78$ (*n*-hexane-benzene 1:1).

IR (KBr) _{max}: 2926, 2863, 1710, 1650, 1467, 1186 cm⁻¹.

EIMS *m*/*z* (%) (rel. int.): 306 [M]⁺ (7), 152 (68), 143 (52), 125 (32), 111 (57), 97 (59), 83 (89), 69 (73), 57 (33), 55 (100).

¹H-NMR (CDCl₃, 200 MHz): δ 0.95 (3H, *t*, *J*=7.5 Hz, H-18), 1.23 (3H, *t*, *J*=7.2 Hz, H-2[′]), 1.28 (5 × CH₂), 2.02 (4H, *m*, H-8 and H-17), 2.28 (2H, *t*, *J*=7.3 Hz, H-2), 2.78 (4H, *t*, *J*=5.7 Hz, H-11 and H-14), 4.10 (2H, *q*, *J*=7.1 Hz, H-1[′]), 5.33 (6H, *m*, H-9, H-10, H-12, H-13, H-15 and H-16).

¹³C-NMR (CDCl₃, 50 MHz): δ 14.3 (C-18, C-2[']), 20.5-30.0 (9 × CH₂), 34.1(C-2), 60.1 (C-1[']), 127.1, 127.7, 128.3, 128.3, 130.3, 132.0 (olefinic carbon), 174.3 (C-1).

Heptacosane (1)

Colorless wax from *n*-hexane, mp. 53-56 , $C_{27}H_{56}$.

R_f: 0.26 (*n*-hexane).

EIMS *m*/*z* (%) (rel. int.): 380 [M] ⁺ (0.3), 99 (4), 84 (21), 71 (56), 57 (100).

¹H-NMR (CDCl₃, 200 MHz): δ 1.26 (*br s*), 0.88 (*t*, *J*=6.6 Hz).

¹³C-NMR (CDCl₃, 50 MHz): δ 14.1, 22.6, 29.3, 31.9.

Heptatriaconsanoic acid (14)

White solid from acetone, mp. 78-79 , $C_{37}H_{74}O_2$.

IR (KBr) _{max}: 3459, 2919, 2842, 1712, 1473 cm⁻¹.

EIMS *m*/*z* (%) (rel. int.): 550 [M] ⁺ (0.2), 213 (3), 185 (4), 129 (17), 111 (14), 96 (22), 83 (26), 73 (49), 69 (47), 60 (57), 57 (83), 55 (100).

¹H-NMR (CDCl₃, 200 MHz): δ 0.86 (3H, *t*, *J*=6.5 Hz, CH₃), 1.23 (*br* s, CH₂), 1.61 (2H, *m*, COCH₂C<u>H</u>₂), 2.32 (2H, *t*, *J*=7.5 Hz, COCH₂).

Linoleic acid (13)

(9,12(z,z)-octadecadienoic acid)

Pale yellow oil from chloroform, $C_{18}H_{32}O_2$.

 $R_f: 0.55$ (benzene-ethyl acetate 4:1).

IR (KBr) $_{\text{max}}$: 3010, 2919, 2856, 1712, 1473, 1445, 1424, 1291, 954, 736 cm⁻¹.

EIMS m/z (%) (rel. int.): 280 [M]⁺ (21), 123 (14), 109 (20), 96 (53), 81 (95), 67 (100).

¹H-NMR (CDCl₃, 200 MHz): δ 0.88 (3H, *m*, H-18), 1.25 (14H, *s*, 7 × CH₂), 1.64 (2H, *m*, H-3), 2.04 (4H, *m*, H-8 and H-14), 2.35 (2H, *t*, *J*=7.5 Hz, H-2), 2.77 (2H, *t*, *J*=5.7 Hz, H-11), 5.35 (4H, *m*, H-9, H-10, H-12 and H-13).

 $^{13}\text{C-NMR}$ (CDCl₃, 50 MHz): δ 14.1 (C-18), 22.7-33.7 (12 \times CH₂), 127.9, 128.0, 130.0, 130.2 (olefinic carbon), 177.8 (C-1).

Lutein (40)

Yellow solid, C₄₀H₅₆O₂.

 $R_f: 0.70$ (*n*-hexane-ethyl acetate 1:1).

EIMS *m*/*z* (%) (rel. int.): 568 [M]⁺ (6), 550 (12), 275 (2), 237 (4), 223 (7), 209 (15), 197 (14), 183 (13), 173 (21), 157 (34), 145 (50), 133 (33), 119 (56), 105 (58), 91 (71), 81 (49), 69 (65), 55 (100).

¹H-NMR (CDC_b, 200 MHz): 見 Table 35.

¹³C-NMR (CDC_b, 50 MHz): 見 Table 35.

2-Methoxy-4-vinylphenol (38)

Colorless oil, C₉H₁₀O₂.

R_f: 0.50 (benzene).

IR(KBr) _{max}: 3513, 2944, 2844, 1600, 1514, 1463, 1430, 1368, 1271, 1241, 1209, 1152, 1122, 1031, 990, 906, 860, 823, 793 cm⁻¹.

UV (CHCl₃) λ_{max} : 213 (4.30), 264 (4.09) nm.

EIMS m/z (%) (rel. int.): 150 [M]⁺ (98), 135 (100), 107 (35), 89 (6), 77 (33), 63 (6), 51 (9).

¹H-NMR (CDCl₃, 300 MHz): δ 3.90 (3H, *s*, 2-OCH₃), 5.10 (1H, *dd*, *J*=0.9, 10.8 Hz, *cis* H-8), 5.53 (1H, *dd*, *J*=0.9, 17.5 Hz, *trans* H-8), 5.59 (1H, *s*, 1-OH), 6.62 (1H, *q*, *J*=10.8, 17.4 Hz, H-7), 6.85 (1H, *d*, *J*=7.8 Hz, H-6), 6.90 (1H, *dd*, *J*=1.8, 8.7 Hz, H-5), 6.92 (1H, *d*, *J*=1.8 Hz, H-3).

¹³C-NMR (CDCl₃, 75 MHz): δ 55.9 (2-OCH₃), 108.0 (C-3), 111.4 (C-8), 114.3 (C-6), 120.1 (C-5), 130.2 (C-4), 136.6 (C-7), 145.6 (C-2), 146.6 (C-1).

Methyl linolenate (3a)

Yellow oil from chloroform, $C_{19}H_{32}O_2$.

 $R_f: 0.78$ (*n*-hexane-benzene 1:1).

IR (KBr) _{max}: 2926, 2863, 1710, 1650, 1467, 1186 cm⁻¹.

EIMS *m*/*z* (%) (rel. int.): 292 [M]⁺ (32), 152 (68), 143 (52), 125 (32), 111 (57), 97 (59), 83 (89), 69 (73), 57 (33), 55(100).

¹H-NMR (CDCl₃, 200 MHz): δ 0.95 (3H, *t*, *J*=7.5 Hz, H-18), 1.28 (5 × CH₂), 2.02 (4H, *m*, H-8 and H-17), 2.28 (2H, *t*, *J*=7.3 Hz, H-2), 2.78 (4H, *t*, *J*=5.7 Hz, H-11 and H-14), 3.64 (3H, *s*, OCH₃), 5.33 (6H, *m*, H-9, H-10, H-12, H-13, H-15 and H-16).

¹³C-NMR (CDCl₃, 50 MHz): δ 14.3 (C-18), 20.5- 30.0 (9 × CH₂), 34.1 (C-2), 51.4 (OCH₃), 127.1, 127.7, 128.3, 128.3, 130.3, 132.0 (olefinic carbon), 174.3 (C-1).

Moniliquinone (18)

(moniliformin; 2,6-dimethoxy-1,4,5,8-phenanthradiquinone)

yellow amorphous solid, $C_{16}H_{10}O_6$ (298).

 R_{f} : 0.41(benzene/ethyl acetate 3/1).

IR(KBr) $_{\text{max}}$: 3454, 3290, 2963, 2922, 2847, 1694, 1653, 1598, 1469, 1346, 1237, 1189, 1135, 1087 cm⁻¹.

UV (CH₃OH) _{max} (log): 230 (3.06), 241 (3.12), 273 (3.62), 329 (3.13), 445 (2.36) nm.

EIMS *m*/*z* (%) (rel. int.): 298 [M]⁺ (76), 283 (34), 269 (4), 255 (28), 240 (17), 225 (7), 214 (23), 199 (15), 184 (8), 171 (27), 156 (16), 143 (15), 128 (25), 113 (17), 100 (39), 87 (57), 74 (51), 69 (100).

HREIMS 298.0474 for C₁₆H₁₀O₆ (required 298.0477)

¹H-NMR (CDC_b, 600 MHz)見 Table 21.

¹³C-NMR (CDCl₃, 150 MHz)見 Table 21.

Moniliformol (19)

(hydroxyethyl 3-methoxy-6-hydroxybenzoate)

colorless amorphous solid, mp 160-162 $\,$, $C_{10}H_{12}O_5$.

R_f: 0.56 (chloroform-methanol 5:1)

UV (CH₃OH) _{max} (log): 212 (4.29), 253 (4.06), 286 (3.76) nm.

EIMS *m*/*z* (%) (rel. int.): 212 [M]⁺ (?), 168 (100), 153 (78), 136 (3), 125 (45), 108 (15), 97 (90), 79 (23), 63 (16), 52 (32).

¹H-NMR (CDCl₃, 600 MHz)見 Table 32.

¹³C-NMR (CDCl₃, 150 MHz)見 Table 32.

Nakaharain (25)

(5-hydroxy-1,2,3,4-tetramethoxyphenanthrene)

yellow solide, C₁₈H₁₈O₅.

 R_f : 0.42 (benzene).

IR (KBr) _{max}: 3131, 2980, 2934, 2842, 1591, 1558, 1460, 1400, 1394, 1302, 1262, 1196, 1098, 1058, 999, 933, 828, 762, 558 cm⁻¹.

UV (CH₃OH) _{max} (log): 215 (4.00), 256 (4.34), 285 (3.99), 308 (3.67), 320 (3.71), 350 (3.02), 368 (3.01), 752 (1.37) nm.

EIMS *m*/*z* (%) (rel. int.): 314 [M]⁺ (100), 299 (47), 256 (34), 212 (57), 169 (29), 141 (28), 125 (41), 113 (62).

HREIMS: 314.1146 for C₁₈H₁₈O₅ (required 314.1154).

¹H-NMR (CDCl₃, 500 MHz)見 Table 15.

¹³C-NMR (CDCl₃, 125 MHz)見 Table 15.

Nakaharaiquinone (32)

(7-hydroxy-2,5,6-trimethoxy-9,10-dihydrophenanthraquinone)

red amorphous solid, C₁₇H₁₆O₆.

R_f: 0.48 (*n*-hexane-ethyl acetate 1:1).

IR (KBr) _{max}: 3441, 2947, 2855, 1657, 1639, 1620, 1580, 1552, 1466, 1368, 1229, 1163, 1085, 1052, 959, 841, 624 cm⁻¹.

UV (CH₃OH) _{max} (log): 218 (4.46), 261 (4.12), 334 (3.81), 479 (3.51) nm.

EIMS *m*/*z* (%) (rel. int.): 316 [M]⁺ (100), 300 (10), 285 (5), 273 (13), 257 (8), 241 (10), 213 (8), 201 (7), 185 (8), 173 (7), 159 (7), 129 (10), 115 (23), 102 (10), 89 (14), 77 (14), 69 (42), 55 (22).

HREIMS: 316.0953 for C₁₇H₁₆O₆ (required 316.0947)

¹H-NMR (CDCl₃, 500 MHz)見 Table 20.

¹³C-NMR (CDC₃, 125 MHz)見 Table 20.

Nakaharoside A (35)

(apigenin 8-C-(6"-O-acetyl)-â-glucopyranoside)

yellow amorphous solid, $C_{23}H_{22}O_{11}$.

R_f: 0.49 (chloroform-methanol 4:1)

IR (KBr) _{max}: 3381, 1729, 1657, 1611, 1512, 1460, 1433, 1380, 1249, 1177, 1111, 1085, 1045 cm⁻¹.

UV (CH₃OH) _{max} (log):270 (4.19), 332 (4.08) nm.

UV (CH₃OH+NaOCH₃) _{max} (log): 279 (4.23), 329 (3.95), 391 (4.11) nm.

UV (CH₃OH+AlCl₅) _{max} (log): 277 (4.11), 305 (4.00), 347 (4.07), 384 (3.94) nm.

UV (CH₃OH+AlCl₃/HCl) _{max} (log): 278 (4.09), 303 (4.00), 346 (4.05), 384 (3.87) nm.

UV (CH₃OH+NaOAc) _{max} (log): 279 (4.25), 306sh (3.95), 386 (4.04) nm.

UV (CH₃OH+NaOAc/H₃BO₃) _{max} (log): 272 (4.18), 345 (4.01) nm.

FABMS (positive) m/z (rel. int.): 475 [M+H]⁺.

HRFABMS 475.1253 [M+H]⁺, for C₂₃H₂₃O₁₁ (required 475.1240).

¹H-NMR (DMSO, 500 MHz)見 Table 24.

¹³C-NMR (DMSO, 125 MHz)見 Table 24.

Nakaharoside B (36)

(apigenin 6-*C*-(6"-*O*-acetyl)-â-glucopyranoside)

yellow amorphous solid, $C_{23}H_{22}O_{11}$.

R_f: 0.63 (chloroform-methanol 4:1)

IR (KBr) _{max}: 3381, 1719, 1708, 1655, 1624, 1509, 1459, 1439, 1369, 1245, 1114, 1088, 1029 cm⁻¹.

UV (CH₃OH) _{max} (log):272 (4.39), 335 (4.19) nm.

UV (CH₃OH+NaOCH₃) _{max} (log): 277 (4.46), 328 (4.91), 395 (4.30) nm.

UV (CH₃OH+AlCl₃) _{max} (log): 278 (4.33), 305 (4.22), 346 (4.19), 386 (4.05) nm.

UV (CH₃OH+AlCl₃/HCl) _{max} (log): 279 (4.31), 303 (4.22), 346 (4.17), 384 (3.99) nm.

UV (CH₃OH+NaOAc) $_{max}$ (log): 279 (4.41), 307 (4.17), 388 (4.17) nm.

UV (CH₃OH+NaOAc/H₃BO₃) _{max} (log): 272 (4.37), 323sh (4.15), 343 (4.30) nm.

FABMS (negative) m/z (rel. int.): 473 [M-H]⁻.

HRFABMS 475.1236 [M+H]⁺,for C₂₃H₂₃O₁₁ (required 475.1241). ¹H-NMR (CD₃OD, 500 MHz)見 Table 26. ¹³C-NMR (CD₃OD, 125 MHz)見 Table 26.

Nakaquinone (27)

(5-hydroxy-2,3-dimethoxy-1,4-phenanthraquinone)

red amorphous solid, C₁₆H₁₂O₅.

R_f: 0.58 (benzene-ethyl acetate 10:1).

IR (KBr) _{max}: 3454, 2967, 2927, 2848, 1644, 1591, 1512, 1433, 1348, 1282, 1223, 1170, 1045 cm⁻¹.

UV (CH₃OH) _{max} (log): 221 (4.34), 305 (4.21) nm.

FABMS (positive) m/z (rel. int.): 285 [M+H]⁺.

¹H-NMR (CDC_b, 500 MHz)見 Table 19.

¹³C-NMR (CDCl₃, 125 MHz)見 Table 19.

Nudol (30)

(2,7-dihydroxy-3,4-dimethoxyphenanthrene)

pale yellow amorphous solid, $C_{16}H_{14}O_4$.

R_f: 0.28 (chloroform-methanol 4:1).

IR (KBr) _{max}: 3418, 2964, 2923, 2853, 1613, 1572, 1467, 1414, 1401, 1263, 1213, 1097, 1067, 1025, 804 cm⁻¹.

UV (CH₃OH) _{max} (log): 213 (3.91), 231(3.84), 259 (4.20), 346 (2.90), 365 (2.87) nm.

EIMS *m*/*z* (%) (rel. int.): 270 [M]⁺ (100), 255 (28), 237 (7), 227 (29), 223 (48), 212 (66), 195 (7), 184 (10), 168 (5), 155 (18), 139 (13), 128 (15), 92 (14), 77 (19), 63 (21).

¹H-NMR (acetone-d₆, 200 MHz): $3.95(3H, s, 4-OCH_3)$, $3.98(3H, s, 3-OCH_3)$, 7.13(1H, d, J=2.7 Hz, H-8), 7.48(1H, d, J=9.0 Hz, H-9), 7.51(1H, d, J=9.0 Hz, H-10), 8.46(1H, s, 2-OH), 8.80 (1H, s, 7-OH, 9.30(1H, d, J=9.2 Hz, H-5).

Octacosanyl hexadecanoate (2)

White powder from chloroform, mp. 63-65 $C_{44}H_{88}O_2$.

 $R_f: 0.60$ (*n*-hexane-benzene 4:1).

IR (KBr) _{max}: 2920, 2851, 1736, 1474, 1187, 716 cm⁻¹.

EIMS *m*/*z* (%) (rel. int.): 648 [M]⁺ (1), 396 (5), 369 (6), 341 (6), 313 (6), 285 (8), 257 (5), 111 (18), 97 (32), 83 (41), 71 (63), 57 (100).

¹H-MR (CDCl₃, 200 MHz): δ 0.86 (6H, *t*, *J*=6.4 Hz, 2 × CH₃), 1.23 (*br s*, CH₂), 1.65 (2H, *m*, CH₂), 2.27 (2H, *t*, *J*=7.5 Hz, CH₂COO), 4.03 (2H, *t*, *J*=6.6 Hz, COOCH₂).

¹³C-NMR (CDCl₃, 50 MHz): δ 14.1 (CH₃), 22.7-31.9 (CH₂), 34.4 (<u>CH₂COO</u>), 64.4 (COO<u>C</u>H₂), 174.0 (C=O).

本化合物為酯類化合物,經由皂化反應可以得到 hexadecanoic acid 和 octacosanol 來印證其結構。

皂化(Saponification):本化合物 10 毫克在 5 毫升的 5% 氫氧化鉀乙醇 溶液中迴流 4 小時 再經矽膠管柱層析法分離,結果獲得 hexadecanoic acid ($[M]^+ m/z 256$)和 *n*-octacosanol ($[M]^+ m/z 410$)。

Pheophytin a (6)

green amorphous solid, C₅₅H₇₄N₄O₅.

R_f: 0.69 (benzene-ethyl acetate 12:1).

IR (KBr) _{max}: 3448, 2954, 2937, 1738, 1697, 1619, 1557, 1500, 1455, 1367, 1222, 1162, 1037 cm⁻¹.

UV (CH₃OH) _{max} (log): 208 (4.24), 229 (4.23), 272 (4.04), 329 (4.28), 372 (4.64), 408 (4.84), 506 (3.88), 536 (3.85), 608 (3.82), 665 (4.51) nm.

FABMS (positive) m/z (rel. int.): 871 [M+H]⁺.

¹H-NMR (CDCl₃, 500 MHz)見 Table 37.

¹³C-NMR (CDCl₃, 125 MHz)見 Table 37.

Pheophytin b (41)

green amorphous solid, C₅₅H₇₂N₄O₆.

R_f: 0.69 (*n*-hexane-benzene-ethyl acetate 2:2:1).

IR (KBr) _{max}: 3448, 2952, 2928, 2864, 1737, 1702, 1663, 1616, 1544, 1497, 1458, 1378, 1224, 1161, 1034 cm⁻¹.

UV (CH₃OH) _{max} (log): 207 (4.13), 233 (4.11), 281 (4.03), 328 (4.16), 373 (4.25), 4.17 (4.56), 435 (4.74), 525 (3.71), 600 (3.61), 655 (4.14) nm.

FABMS (positive) m/z (rel. int.): 884 [M]⁺.

¹H-NMR (CDC_b, 500 MHz)見 Table 38.

¹³C-NMR (CDCl₃, 125 MHz)見 Table 38.

Phytosterols (10)

(Campesterol (a), Stigmasterol (b) and β -sitosterol (c))

White powder from chloroform, mp. 138-140 , $C_{29}H_{50}O,\ C_{29}H_{48}O,\ C_{28}H_{48}O.$

 R_{f} : 0.41 (benzene-ethyl acetate 4:1).

IR (KBr) _{max}: 3417, 2940, 2863, 1460, 1375, 1053 cm⁻¹.

EIMS *m*/*z* (%) (rel. int.): 414 [M]⁺ (34), 412 [M]⁺ (17), 400 [M]⁺ (7), 396 (18), 369 (3), 255 (27), 213 (28), 145 (57), 81 (92), 69 (86), 55 (100).

¹H-NMR (CDCl₃, 200 MHz): 見 Table 42.

氣相層析-質譜儀(GC-MS)分析條件為:HP-20 毛細管柱, 25 m× 0.32 mm (i.d.) × 0.52 μ m, 載氣為氦氣, 流速為 1 mL/min, 管柱溫度 110 到 300 ,每分鐘升溫 5 。結果顯示滯留時間在 24.6 分鐘為 campesterol (分子量 *m*/*z* 為 400), 滯留時間在 25.6 分鐘為 stigmasterol (分子量 *m*/*z* 為 412)而滯留時間在 27.4 分鐘為β-sitosterol (分子量 *m*/*z* 為 414)。

Protocatechuic acid (33)

(3,4-dihydroxybenzoic acid)

Colorless amorphous solid, C₇H₆O₄.

R_f: 0.49 (chloroform-methanol 2:1)

IR (KBr) max: 3263, 1677, 1604, 1407, 1387, 1289, 1256, 1196, 1131, 1104, 946, 762 cm⁻¹.

UV (CH₃OH) _{max} (log): 208 (4.19), 255 (3.80), 291 (3.54) nm.

EIMS m/z (%) (rel. int.): 154 [M]⁺ (24),, 137 (25), 110 (32), 97 (12), 92 (30), 81 (100), 63 (98), 53 (86).

¹H-NMR (CD₃OD, 200 MHz)見 Table 33.

¹³C-NMR (CD₃OD, 50 MHz)見 Table 33.

Stigmast-4-en-3-one (9)

White powder from *n*-hexane, mp. 87-89 , $C_{29}H_{48}O$ (412).

 $R_f: 0.62$ (*n*-hexane-ethyl acetate 4:1).

IR (KBr) _{max}: 2936, 2856, 1677, 1621 cm⁻¹.

UV (CHCl₃) λ_{max} (log ϵ): 246 (4.20) nm.

EIMS m/z (%) (rel. int.): 412 [M]⁺ (20), 370 (8), 289 (12), 271 (10), 229 (31), 147 (29), 124 (100).

¹H-NMR (CDCl₃, 200 MHz): 見 Table 43.

¹³C-NMR (CDC_b, 50 MHz): 見 Table 43.

2,3,4,7-Tetramethoxyphenanthrene (24)

Pale yellow solid, $C_{18}H_{18}O_4$.

 $R_f: 0.44$ (benzene)

IR (KBr) max: 2929, 2857, 1614, 1475, 1455, 1432, 1385, 1348, 1281, 1223, 1152, 1082, 1003, 870, 804, 685 cm⁻¹.

UV (CH₃OH) _{max} (log): 212 (3.78), 232 (3.81), 257 (4.34), 281 (3.69),

291 (3.58), 303 (3.36), 342 (2.75), 359 (2.76) nm.

EIMS *m*/*z* (%) (rel. int.): 298 [M]⁺ (100), 283 (43), 258 (6), 255 (17), 240 (57), 225 (13), 197 (25), 169 (35), 154 (11), 149 (11), 137 (10), 126 (27).

¹H-NMR (CDCl₃, 500 MHz)見 Table 17.

¹³C-NMR (CDCl₃, 125 MHz)見 Table 17.

Trans-ß-carotene (23)

Deep yellow solid, $C_{40}H_{56}$.

R_f: 0.49 (*n*-hexane).

IR(KBr) $_{max}$: 3034, 2950, 2920, 2859, 2821, 1728, 1719, 1674, 1649, 1656, 1561, 1451, 1363, 1260, 1172, 964 cm⁻¹.

UV (CHCl₃) λ_{max} (log): 281 (3.54), 465 (4.25), 492 (4.19) nm.

EIMS *m*/*z* (%) (rel. int.): 536 [M]⁺ (100), 444 (25), 268 (9), 209 (14), 183 (14), 171 (19), 157 (25), 145 (33), 133 (32), 119 (63), 105 (67), 91 (46), 81 (34), 69 (85), 55 (100).

¹H-NMR (CDCl₃, 200 MHz): 見 Table 36.

¹³C-NMR (CDC_b, 50 MHz): 見 Table 36.

Uracil (34)

Colorless needles (CH₃OH), mp > 300, C₄H₄N₂O₂.

R_f: 0.22 (chloroform-acetone 1:2)

IR (KBr) max: 3105, 3040, 2980, 2927, 1716, 1670, 1420, 1387, 1236, 992, 861, 828, 545 cm⁻¹.

UV (CH₃OH) _{max} (log): 206 (3.58), 259 (3.58) nm.

EIMS m/z (%) (rel. int.): 112 [M]⁺ (94), 105 (3), 85 (3), 69 (100), 55 (13), 53 (15).

¹H-NMR (CD₃OD, 200MHz): 5.60 (1H, *d*, *J*=7.6 Hz, H-5), 7.38 (1H, *d*, *J*=7.6 Hz, H-6).

¹³C-NMR (CD₃OD, 50MHz): 101.7 (C-5), 143.6 (C-6), 153.6 (C-2), 167.4 (C-4).

Vanillin (38)

(4-hydroxy-3-methoxybenzaldehyde)

White powder from chloroform, mp. 78-81 , $C_8H_8O_3$.

R_f: 0.56 (benzene-ethyl acetate 9:1).

IR (KBr) _{max}: 3171, 1664, 1585, 1512, 1466, 1462, 1302, 1262 cm⁻¹.

UV (CH₃OH) λ_{max} (log ϵ): 208 (4.08), 231 (4.14) , 278 (3.99), 306 (4.00), 350 (3.65) nm.

EIMS *m*/*z* (%) (rel. int.): 152 [M]⁺ (100), 151 (97), 137 (3), 123 (10), 109 (16), 93 (4), 81 (54), 65 (20).

¹H-NMR (CDCl₃, 200 MHz): 見 Table 34.

¹³C-NMR (CDC_b, 50 MHz): 見 Table 34.

4-Vinylphenol (39)

Colorless oil, C_8H_8O (120).

R_f: 0.61 (benzene-ethyl acetate 6:1).

IR(KBr) _{max}: 3283, 1610, 1512, 1454, 1412, 1380, 1261, 1171, 1111, 992, 897, 833, 495 cm⁻¹.

UV (CH₃OH) λ_{max}: 208 (4.44), 259 (4.47), 293 (3.63) nm.

EIMS *m*/*z* (%) (rel. int.): 120 [M]⁺ (100), 91 (41), 65 (12).

¹H-NMR (CDCl₃, 300 MHz): δ 4.94 (1H, *br s*, 1-OH), 5.10 (1H, *dd*, *J*=0.9, 10.9 Hz, *cis* H-8), 5.58 (1H, *dd*, *J*=0.9, 17.6 Hz, *trans* H-8), 6.63 (1H, *q*, *J*=10.9, 17.6 Hz, H-7), 6.77 (2H, *t*, *J*=2.0, 2.8, 7.8 Hz, H-2, H-6), 7.28 (2H, *t*, *J*=1.9, 2.8, 8.7 Hz, H-3, H-5).

¹³C-NMR (CDCl₃, 75 MHz): δ 111.6 (C-8), 115.3 (C-2, C-6), 127.6 (C-3, C-5), 129.9 (C-4), 136.1 (C-7), 155.3 (C-1).

Vitexin (37)

(apigenin 8-C-â-glucopyranoside)

yellow amorphous solid, $C_{21}H_{20}O_{10}$.

R_f: 0.25 (chloroform-methanol 4:1)

IR (KBr) _{max}: 3388, 3237, 1657, 1611, 1572, 1512, 1429, 1361, 1289, 1229, 1179 cm⁻¹.

UV (CH₃OH) _{max} (log): 271 (4.07), 305 (3.95), 333 (4.03) nm.

UV (CH₃OH+NaOCH₃) _{max} (log): 279 (4.15), 327 (3.91), 390 (4.15) nm.

UV (CH₃OH+AlCl₃) _{max} (log): 277 (4.01), 305 (3.95), 346 (4.06), 386 (3.95) nm.

UV (CH₃OH+AlCl₃/HCl) _{max} (log): 278 (3.99), 304 (3.94), 346 (4.05), 382 (3.87) nm.

UV (CH₃OH+NaOAc) _{max} (log): 280 (4.18), 300 (3.90), 385 (4.06) nm.

UV (CH₃OH+NaOAc/H₃BO₃) _{max} (log): 272 (4.06), 329 (3.97), 346 (3.98) nm.

FABMS (positive) m/z (rel. int.): 433 $[M+H]^+$.

¹H-NMR (DMSO, 200 MHz)見 Table 28.

¹³C-NMR (DMSO, 50 MHz)見 Table 28.

第四節 分離之成分的化學結構

石斛、連珠石斛及臺灣金線連所分離得到 44 個化合物之結構如 下:











26 R = OH, n = 15-23

14

R = COOH, n = 14-28, 35

RCOOR'

 $R = C_{15}H_{31}$, R' = alkyl, C_{22} - C_{28} 15 $R = CH_3$, R' = alkyl, C_{24} - C_{31} 16











20







22

23



24 $R_1, R_5, R_6, R_8 = H, R_2, R_3, R_4, R_7 = OCH_3$ 25 $R_1, R_2, R_3, R_4 = OCH_3, R_5 = OH, R_6, R_7, R_8 = H$ 28 $R_1, R_6, R_7, R_8 = H, R_2, R_5 = OH, R_3, R_4 = OCH_3$ $R_1, R_5, R_6 = H, R_2, R_7 = OH, R_3, R_4, R_8 = OCH_3$ 29 $R_1, R_5, R_6, R_8 = H, R_2, R_4 = OCH_3, R_3, R_7 = OH$ 30 $R_1,\,R_6,\,R_7,\,R_8=H,\,R_2,\,R_4=OCH_3,\,R_3,\,R_5=OH$ 31

34 $R_1, R_6, R_7, R_8 = H, R_2, R_5 = OH, R_3, R_4 = OCH_3$







35 $R_1 = H, R_2 = 6"-O$ -acetyl- β -D-glucopyranosyl **36** $R_1 = 6"-O$ -acetyl- β -D-glucopyranosyl, $R_2 = H$ **37** $R_2 = H$







40









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第四章 結論

本研究之結論依植物化學成分和藥理之抗發炎及抗過敏活性試 驗分為兩節。

第一節 植物化學成分

本研究首先針對蘭科石斛屬和開唇蘭屬植物的化學成分進行考察。在石斛屬植物成分考察結果有三十八種植物,二十一種成分類別和一百零七個成分,整理如 Table 1,在開唇蘭屬植物成分考察結果有二種植物,六種成分類別和三十二個成分,整理如 Table 2。

其次植物成分的分離和純化方面的結果為:總共分離得到四十四 個化合物,其中石斛(D. moniliforme)莖的正己烷粗抽物分離得到十四 個化合物,乙酸乙酯粗抽物分離得到十一個化合物,根部的正己烷粗 抽物分離得到六個化合物;連珠石斛(D. nakaharai)正己烷粗抽物分離 得到十七個化合物,乙酸乙酯粗抽物分離得到十個化合物;臺灣金線 連正己烷粗抽物分離得到六個化合物,乙酸乙酯粗抽物分離得到五個 化合物,甲醇粗抽物分離得到四個化合物。以上所分離得到之化合物 依結構主要分為十四個類別:

1. Phenanthrene 類化合物:

由連珠石斛分離到六個此類化合物 - bulbophyllanthrin (31), confusarin (29), 2,5-dihydroxy-3,4-dimethoxyphenanthrene (28), nakaharain (25), nudol (30)和 2,3,4,7-tetramethoxyphenanthrene (24), 其中 25 為新化合物。

2. Phenathraquinone (phenanthrene-1,4-quinone)類化合物:

此類化合物 denbinobin (11)由石斛分離得到,而連珠石斛分離 得到一個新化合物 nakaquinone (27)。

3.9,10-Dihydrophenanthraquinone 類化合物:

由連珠石斛分離得到一個新的此類化合物 nakaharaiquinone (32)。

4. Phenathradiquinone 類化合物:

由石斛分離得到一個新的此類化合物 moniliquinone (18)。

5. Fluorenone 類化合物: 由連珠石斛分離得到一個的此類化合物 dengibsin (17)。 6. Flavonoid 類化合物:

由連珠石斛分離得到三個的此類化合物, nakaharoside A (35), nakaharoside B (36)和 vitexin (37), 其中 35 和 36 為新化合物。

7. Benzene 和 Phenol 類化合物:

在石斛中分離到六個此類化合物, alkyl 4´-hydroxy-*cis*-cinnamates (7), alkyl 4´-hydroxy-*trans*-cinnamates (8), alkyl *trans*ferulates (5), *p*-anisaldehyde (4), moniliformol (19)和 vanillin (12), 其中 19 為新化合物;在連株石斛分離得到 4 個此類化合物 alkyl 4´-hydroxy-*cis*-cinnamates (7), alkyl 4´-hydroxy-*trans*-cinnamates (8), alkyl *trans*-ferulates (5)和 protocatechuic acid (33);而在金線連 中分離得到 3 個此類化合物 2-methoxy-4-vinylphenol (38), protocatechuic acid (33)和 4-vinylphenol (39)。

8. Carotenoid 類化合物:

在臺灣金線連中分離得到二個此類的化合物 lutein (40)和 *trans*-β-carotene (23), 在石斛中也有發現化合物 23 的蹤跡。

9. Chlorophyll 類化合物:

在臺灣金線連中分離得到二個此類化合物 pheophytin a (6)和 pheophytin b (41)。

10. Sterol 類化合物:

在石斛中分離得到 ergosterol (21), ergosterol peroxide (22), phytosterol (campesterol, stigmasterol, -sitosterol) (10)和 stigmast-4-en-3-one (9), 連珠石斛和臺灣金線連均有分離到化合物 10。

11. Fatty acid or ester 類化合物:

在石斛中分到 5 個此類化合物, alkyl acetate (16), linoleic acid (13), methyl and ethyl linolenates (3)和 octacosanyl hexadecanoate (2);在臺灣金線連中,正己烷的抽出物經 GC,GC/MS 檢測,結果如 Figure 4,主要以此類化合物為主,在分離過程中,則有分離 到化合物 13。

12. Pyrimidine 類化合物:

在連珠石斛和臺灣金線連中均分離得到一個 pyrimidine 類之核酸化合物 uracil (34)。

13. Sugar 類化合物:

在臺灣金線連分離得到一個此類化合物 ethyl â-D-glucopyra-noside (44)。
14. 其它:

由石斛分離得到化合物 diethylene glycol (20),臺灣金線連分離 得到新化合物 anoectolide A (42)和 anoectolide B (43)。

第二節 抗發炎及抗過敏活性試驗

石斛、連珠石斛和臺灣金線連等植物的粗抽物或其分離純化之 化合物的抗發炎及抗過敏活性試驗結果如下述。

石斛分離純化的化合物顯示:

- 1. *p*-Anisaldehyde (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。
- 2. Denbinobin (11)有好的中樞和周邊抗發炎及抗過敏活性。
- 3. Vanillin (12)對嗜中性白血球的抗發炎可能有活性。

連珠石斛的三種粗抽物的抗發炎及抗過敏活性有顯著的抑制作 用,而其中以乙酸乙酯粗抽物最佳。進一步由連珠石斛乙酸乙酯粗抽 物所分離得到的五個化合物,進行抗發炎及抗過敏活性試驗,分別顯 示其不同模式的活性作用:

- 1. 新化合物 nakaharain (25)對於抗發炎及抗過敏活性不佳。
- 2. 2,5-Dihydroxy-3,4-dimethoxyphenanthrene (28)對嗜中性白血球的 抗發炎有不錯的活性。
- 3. Protocatechuic acid (33)、uracil (34)和 Vitexin (37)對嗜中性白血球 所引發的發炎可能有抑制效果。

臺灣金線連的三種粗抽物的抗發炎及抗過敏活性以正己烷粗抽物最好。而由正己烷粗抽物所分離得到的主要化合物 pheophytin a (6), linoleic acid (13)和 *trans*-â-carotene (23)進行抗發炎及抗過敏活性試驗,顯示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還在進行中。

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學術著作目錄

一、學術期刊發表:

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