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行政院衛生署九十五年度科技研究發展計畫

中藥多酚配醣體定量方法之建立

Establishment of Determination Method for Polyphenol Glycosides in Herbal Medicines

研 究 報 告

計畫委託機關：中國醫藥大學

計畫主持人：溫國慶

研究人員：李珮端 徐素蘭 侯鈺琪 蕭珮玲 曹惠婷

執行期間：95 年 1 月 1 日至 95 年 12 月 31 日

＊＊ 本研究報告僅供參考，不代表本署意見 ＊＊

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行政院衛生署中醫藥委員會九十五年度

研究計畫成果報告

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溫國慶

中國醫藥大學

摘要

天然多酚配醣體廣泛存在於植物界，有關天然多酚的體內動力學真相，直到近幾年來才逐漸揭露，大多數研究顯示多酚配醣體攝食後，於腸道中必須受腸內酵素或腸道細菌水解成較低極性的非醣體，方能被腸細胞吸收。

有關中藥材之品管，於目前各國藥典對藥材規定定量者不多，且只定量非醣體或單一配醣體者為多。近年來又興起以指紋圖譜作為定性管制之另一指標，然此亦難反映活性或療效之品質。在品管上若儘量能掌握各該具活性非醣體之總配醣體含量，則更貼近實際，可再提升中藥之品質。

本計畫探討大黃、生首烏、製首烏、虎杖、蘆薈、羊蹄及決明子等七種藥材中多酚配醣體含量。藥材經煎煮後，煎煮液再以酸水解，分別

測定水解前後非醣體含量。各藥材分析之非醣體成分，分別為大黃之aloe-emodin, rhein, emodin, chrysophanol, physcion；生首烏、製首烏之emodin, physcion；虎杖之emodin, resveratrol；蘆薈之aloin, aloe-emodin；羊蹄之emodin, chrysophanol；决明子之chrysophanol, physcion。依所測定之水解前與水解後非醣體含量，就兩者之莫耳數差，求出總配醣體含量。

結果顯示大黃、生首烏、羊蹄及決明子內之上述非醣體成分及虎杖之emodin成分含量在水解之後均有明顯增加。虎杖之resveratrol則會因水解時間增加而降低。而製首烏與蘆薈並沒有顯著差異。

本研究所建立之方法，可應用於除虎杖外之上述中藥之非醣體及配醣體含量測定。

關鍵詞：中藥材，配醣體，高效液相層析法

CCMP95-RD-021

Establishment of Determination Method for Polyphenol Glycosides in Herbal Medicines

Kuo-Ching Wen

China Medical University

ABSTRACT

Polyphenol glycosides are widely distributed in natural plants. In the recent years, the fates of polyphenol glycosides in vivo are gradually understood through pharmacokinetic studies. Most of researches indicated that polyphenol glycosides are hydrolyzed to lower polar aglycones by enzymes or bacteria in the intestine after oral ingestion and then become absorbable by the intestinal cells. In the current status, there are limited items for the quality control of crude drugs, and in which only monoglycosides or aglycones are required to be assayed in pharmacopeias of many countries. Recently, chromatogramic fingerprints are used as another index of quality control. However, those quality controls could be difficult to reflect the activity or the efficacy of Chinese herbs. It will be more reasonable if the total glycosides of active ingredients could be assayed.

In this study, the contents of polyphenol glycosides in seven Chinese herbs including Rhei rhizoma, crude Polygoni multiflori radix, processed Polygoni multiflori radix, Polygoni cuspidati rhizoma, Aloe, Rumecis radix and Cassiae torae semen were studies. The contents of aglycones were determined for decoctions of the seven herbs before and after hydrolysis. The aglycones assayed were aloe-emodin, rhein, emodin, chrysophanol and physcion for Rhei rhizome; emodin and physcion for crude and processed Polygoni multiflori radix; emodin and resverstrol for Polygoni cuspidati rhizome; aloin and aloe-emodin for Aloe; emodin, chrysophanol for Rumecis radix; and chrysophanol, physicon for Cassiae torae semen. The total glycoside contents were calculated by substracting the moles of the aglycones (without hydrolysis) from those of the total moles of the aglycones (after hydrolysis). The results indicated that the contents of aglycones mentioned above for Rhei rhizome, crude Polygoni multiflori radix, Rumecis radix and Cassiae torae semen increased after hydrolysis. The content of emodin in Polygoni cuspidati rhizome increased with hydrolysis, whereas resveratrol content decreased. However, the contents of emodin and physcion in processed Polygoni multiflori radix, aloin and aloe-emodin in Aloe showed no significant difference prior to and after hydrolysis. The decrease of resveratrol content after hydrolysis might be associated with thermal decomposition.

The method developed in this study can be applied to the determinations of the contents of aglycones and their glycosides in these Chinese herbs except Polygoni cuspidati rhizome for their quality

control.

Keywords：Chinese herbs；Anthraquinone glycosides；HPLC

一、前言

天然多酚之化學結構依碳骨架可分為flavonoid、isoflavone、anthraquinone、lignan 及aromatic acid 等類，主要以配醣體之形式廣泛存在於植物界。有關天然多酚的體內動力學真相，直到近幾年來才逐漸揭露，大多數研究顯示多酚配醣體攝食後，於腸道中必須受腸內酵素或腸道細菌水解成較低極性的非醣體，方能被腸細胞吸收(1-5)。此些非醣體旋又受到腸及肝細胞之代謝，轉化成高極性的sulfates、glucuronides 等結合態代謝物循環於血流中。

本研究小組五年來致力於中藥多酚之代謝動力學研究，從所累積的動物及人體研究結果中，發現僅有少數多酚以非醣體形態存在於體循環中，如morin (6, 7)、rhein (8)；而其他多酚如quercetin、naringenin、hesperetin、baicalein、daidzein、emodin、aloe-emodin 及chrysophanol等係主要以結合態代謝物如sulfates 及glucuronides 循環於全身，其配醣體與非醣體幾乎不見存在於血中(9-13)。

由上述之科學證據，以及近年來流行病學調查研究顯示多酚類成分與多種疾病，如心血管疾病、癌症等慢性疾病成負相關(14-18)，又研究證實此等成分具生物活性。中藥材亦有很多該類成分，且其配醣體型式比非醣體更易溶解於熱水，因此對藥材之品管而言，以藥材中多酚類總

配糖體之含量，作為選材之標準，將更為貼切。

有關常用含蒽醌配醣體（anthraquinone glycosides）中藥，如大黃、何首烏、虎杖、決明子、蘆薈及羊蹄等。含黃酮類配醣體之黃芩、桑葉等。於目前各國藥典對藥材規定定量者不多，且只定量非醣體或單一配醣體者為多。 如日本藥局方（19）：大黃定量 sennoside A 不得少於 0.25%，黃芩定量 baicalin 不得少於 10%。 大陸藥典（20）：大黃定量 emodin, chrysophanol 不得少於 0.5%，何首烏定量 2, 3, 5, 4'-四羥基二苯乙烯-2-O-β-D 葡萄糖苷(2,3,5,4-tetrahydroxystilbene 2-*O*-*β*-D-glucopyranoside) 不得少於 1%。虎杖定量總蒽醌以 emodin 計不得少於 1.5 % ，蘆薈定量：庫拉索蘆薈(*Aloe barbadensis* Miller.)barbaloin 不得少於 28%，好望角蘆薈（*Aloe ferox* Miller.）蘆薈苷不得少於 18%。黃芩之 baicalin 不得少於 9 %。 台灣傳統藥典（21）：黃芩之 baicalin 不得少於 8 %。

有關常用含蒽醌配醣體（Anthraquinone glycosides）中藥：

1. 大黃(22-25)為蓼科 *Polygonaceae* 植物掌葉大黃 *Rheum palmatum* L.、唐古特大黃 *Rheum tanguticum* Maxim. ex Balf. 或藥用大黃 *Rheum officinal* Baill. 的乾燥根及根莖。含游離型之 Anthraquinones 成分，如 aloe-emodin, rhein, emodin, chrysophanol, physcion,

isoemodin, laccaic acid D, 結合型之 Anthraquinones 成分，如 aloe-emodin 1-O-β-D-gluco-pyranoside, rhein 1-O-β-D-glucopyranoside, emodin 1-O-β-D-glucopyranoside, emodin 3-O-β-D-glucopyranoside, emodin 8-O-β-D-glucopyranoside, chrysophanol 1-O-β-D-glucopyranoside, chrysophanol 8-O-β-D-glucopyranoside, physcion-8-O-β-D-gentiobioside, physcion 1-O-β-D-gluco-pyranoside。

2. 何首烏（26-27）為蓼科植物*Polygonum multiflorum* Thunb.之乾燥塊根，含phenolic compounds, flavanoids, anthraquinones (emodin and physcion), stilbenes (2,3,5,4-tetrahydroxystilbene 2-*O*-*β*-D-glucopyranoside)及tannins.

3. 虎杖(28, 29)為蓼科植物*Polygonum cuspidant* Sieb. Et Zuce.乾燥根莖和根，含anthraglycoside A (emodin-6-methoxy-8- *O*-D-glucoside), anthraglycoside B (emodin-8-*O*-D- glucoside) and resveratrol。stilbene glucosides : piceatannol glucoside (3,5,3′,4′-tetrahydroxystilbene 4′-*O*-β-D-glucopyranoside), resveratroloside (3,5,4′-trihydroxystilbene 4′-*O*-β-D-glucopyranoside), piceid (3,5,4′-trihydroxystilbene 3-*O*-β-D-glucopyranoside).

4. 蘆薈（30）為百合科植物庫拉索*Aloe barbadensis* Miller.或好望角蘆薈*Aloe ferox* Miller.及其他近緣植物葉汁液濃縮乾燥物。含aloin, aloe-emodin, aloinoside A及B, aloenin A及B, aloesin (aloeresin B), aloeresin A, homonataloin, nataloe-emodin 4-hydroxyaloin, 5-hydroxyaloin。

5. 羊蹄(31)為蓼科植物羊蹄*Rumex japonicus*含emodin, chrysophanol, emodin-8-β-D-glucoside,及chrysophanol-8-β-D-glucoside.

6. 决明子(32)為豆科植物决明 Cassia obtusifolia, 小决明 Cassia tora L. 乾燥成熟種子。含 chrysophanol, physcion, aloe-emodin, 1-hydroxy-7-methoxy-3-methylanthraquinone, 8-O-methylchrysophanol, 1-O-methylchrysophanol, 1, 2, 8-trihydroxy-6, 7-dimethoxyanthraquinone, alizarin, danthron, emodin, purpurin, quinizarin 及其配醣體。

天然物所呈現之活性或藥效常非單一成分，而是一類或幾類之混合物，對品管而言，若要逐一定量甚為繁雜，甚或無標準品而無法執行。若能指定量某些成分而回推換算，非但易於執行，且符合實際。如銀杏葉萃取物(33, 34)即是一個實例，品管上分析其所含 quercetin, kaempferol, isorhamnetin 等非醣體後再乘一係數後，求出總黃酮類成分不得低於 24%。

目前衛生署中醫藥委員會公告 (35-37) 對於中藥濃縮製劑執行指標成分之定量，藥物食品檢驗局曾建立相關之中藥濃縮製劑指標成分定量方法(38, 39)，供業界參考，研訂自家產品之品管規格，以提升中藥之品質。惟如上述中藥材之成分複雜，少數之指標成分實難以反映之活性

或療效之品質。近年來又興起以指紋圖譜作為定性管制之另一指標，然此亦難反映活性或療效之品質。筆者近年參與之研究小組致力於中藥藥物動力學之研究，以及前述之科學研究證據顯示，多酚配醣體攝食後，於腸道中被水解成非醣體後，被腸細胞吸收，因此在品管上若儘量能掌握各該具活性非醣體之總配醣體含量，則更貼近實際，以再提升中藥之品質。本計劃就大黃、生首烏、製首烏、虎杖、決明子、蘆薈及羊蹄等藥材進行水解前後之探討。

貳、材料與方法

一、 實驗材料

(一) 材料與試劑

Acetonitrile (LC Grade)	J.T. Baker, Inc. (Phillipsburg, NJ, U.S.A.)
Methyl alcohol (LC Grade)	J.T. Baker, Inc. (Phillipsburg, NJ, U.S.A.)
Ethyl acetate	J.T. Baker, Inc. (Phillipsburg, NJ, U.S.A.
Ortho-phosphoric acid (85%)	Riedel-deHaën AG (Seelze, Germany)
Hydroic acid	聯工化學廠股份有限公司(Taiwan)
Aloin	Sigma Chemical Co. (St. Louis, MO, U.S.A.)
Aloe-emodin	Sigma-Aldrich (St. Louis, MO, U.S.A.)

Chrysophanol	Aldrich Chemical Company (Milwaukee, WI, U.S.A.)
Emodin	Sigma Chemical Co. (St. Louis, MO, U.S.A.)
Resveratrol	Sigma Chemical Co. (St. Louis, MO, U.S.A.)
Physcione	Sigma-Aldrich (St. Louis, MO, U.S.A.)
Rhein	Sigma Chemical Co. (St. Louis, MO, U.S.A.)
Milli-Q® plus water (Milli-Q®)	Millipore corporation (Billerica, MA, U.S.A.)

(二) 器材與儀器

高速離心機 HSIANGTAI CFT-6000	Hermle Labotechnik GmbH (Wehingen, Germany)
渦旋振盪器 Vortex Genie G-560	Scientific Industries Inc. (Bohemia, NY, U.S.A.)
超音波振盪器 Soniclean 2000HT	SONICLEAN.PTY.LTD (Australia)
氮氣濃縮裝置 N-EVAP 112 R-MT	Organomation Associates Inc. (Berlin, MA, U.S.A.)
分析天平 AB 104	Mettler Toledo (Switzerland)
微量移液管 Pipette 2-20 μL, 10-100 μL, 20-200 μL, 100-1000 μL	Gilson S.A.S.（Entrepreneurs, Villiers Le Bel, France）

水壓抽氣機 Eyela Aspirator A-2S	Tokyo Rikakikai Co. Ltd. (Tokyo, Japan)
高效液相層析儀－紫外光檢出器 (High Performance Liquid Chromatography－UV)包括:	
(1)幫浦	Shimadzu LC-10AT vp (Japan)
(2)層析管 Apollo C18 5u (4.6×250 mm)	Alltech Associates, Inc. (U.S.A)
(3)紫外光偵測器	Shimadzu UV-VIS detector SPD-10A vp (Japan)
(4)自動注射器	Shimadzu SPD -10AF (Japan)
(5)除氣裝置	ERC-3415(Japan)
拋棄式注射針及針筒 1.0 mL syringe (0.45×13 mm)	Terumo Medical Corporation (Elkton, MD, U.S.A.)
微量吸管尖 Tips (200 μL, 1000 μL)	Axygen Scientific, Inc. (Union City, CA, U. S. A.)
微量離心管 Microtubes (1.7 mL)	Axygen Scientific, Inc. (Union City, CA, U. S. A.)
針頭濾膜 Millex® (0.45 μm, 13 mm)	Millipore carrigtwohill, Co.(Cork, Ireland)

二、 實驗方法

本計畫先進行大黃、生首烏、製首烏、虎杖、蘆薈、羊蹄及決明

子等七種藥材之外觀及組織進行基原鑑定，而後分別測定各水煎劑水解前後非醣體含量，就兩者之莫耳數差，求出總配醣體含量。

大黃、生首烏、製首烏、虎杖、蘆薈、羊蹄及決明子等七種藥材進行之項目如下：

（一）酸水解條件之探討

1. 最適鹽酸溶液濃度之探討

水煎劑分別以 1.2 N、2.4 N 鹽酸溶液水解

2. 最適反應溫度之探討

水煎劑分別以 80℃、100℃加熱水解

3. 最適反應時間之探討

水煎劑分別以 0.5、1、2、4、6 小時加熱水解

4. 添加抗氧化劑之探討

添加抗壞血酸 (100 mg/ml、50 mg/ml) 之比較

5. 避光與否之探討

以避光與不避光水解反應

（二）高效液相層析(HPLC)條件之探討

1. 大黃、生首烏及製首烏之分離條件 (46)

層 析 管：Apollo C18, 5 μm (4.6 × 250 mm)

移 動 相：A：Methanol　　B：0.1% H_3PO_4（梯度沖提）

57:43 (0 min), 57:43 (3 min), 90:10 (20 min), 90:10 (35 min), 57:43 (40min), 57:43 (50 min)

流　　速： 1.0 mL/min

檢測波長： 254 nm

內 標 準： butylparaben (4 μg/mL)

2. 決明子之分離條件 (46)

層 析 管：Apollo C18, 5 μm (4.6 × 250 mm)

移 動 相：A：Methanol　　B：0.1% H_3PO_4（梯度沖提）

57:43 (0 min), 57:43 (3 min), 90:10 (20 min), 90:10 (35 min), 57:43 (40min), 57:43 (50 min)

流　　速： 1.0 mL/min

檢測波長： 254 nm

內 標 準： propylparaben (10 μg/mL)

3. 羊蹄、虎杖之分離條件

層 析 管：Apollo C18, 5 μm (4.6 × 250 mm)

移 動 相：A：Acetonitrile　　B：0.1% H_3PO_4（梯度沖提）

15:75 (0 min), 13:65 (8 min), 35:65 (12min), 75:25 (22min), 75:25 (32min), 15:75 (40 min), 15:75 (45 min)

流　　速： 1.0 mL/min

檢測波長： 254 nm

內 標 準： ethylparaben (5 μg/mL)

4. 蘆薈之分離條件

層 析 管：Apollo C18, 5 μm (4.6 × 250 mm)

移 動 相：A：Acetonitrile　　B：0.1% H_3PO_4（梯度沖提）

24:76 (0 min), 24:76 (12 min), 50:50 (22 min), 24:76 (40min), 24:76 (50 min)

流　　速： 1.0 mL/min

檢測波長： 254 nm

內 標 準： 6,7-dimethoxycoumarin (50 μg/mL)

5. 大黃、生首烏及製首烏檢量線之繪製

精確秤取 aloe-emodin、rhein、emodin、chrysophanol 及 physcion 標準品分別溶於甲醇製備各儲備溶液。以甲醇稀釋，配製一系列濃度之標準溶液如下：20.00、10.00、5.00、2.50、1.25、0.63 μg/mL。取上述標準溶液加等容含內標 butylparaben 4 μg/mL 之甲醇溶液，混合均勻後進行 HPLC 分析。

6. 決明子檢量線之繪製

精確秤取 chrysophanol 及 physcion 標準品分別溶於甲醇製備各儲備溶液。以甲醇稀釋，配製一系列濃度之標準溶液如下：25.00、12.50、6.25、3.13、1.56 μg/mL。取上述標準溶液加等容含內標 propylparaben 10 μg/mL 之甲醇溶液，混合均勻後進行 HPLC 分析。

7. 虎杖、羊蹄檢量線之繪製

精確秤取 emodin、chrysophanol 及 resveratrol 標準品分別溶於甲醇製備各儲備溶液。以甲醇稀釋，配製一系列濃度之標準溶液如下：100.00、50.00、25.00、12.50、6.25、3.13 μg/mL。取上述標準溶液加等容含內標 ethylparaben 5 μg/mL 之甲醇溶液，混合均勻後進行 HPLC 分析。

8. 蘆薈檢量線之繪製

精確秤取 aloe-emodin 及 aloin 標準品分別溶於甲醇製備各儲備溶液。以甲醇稀釋，配製一系列濃度之標準溶液如下： 200.00、100.00、50.00、25.00、12.50、6.25 μg/mL。取上述標準溶液加等容含內標 6,7-dimethoxycoumarin 50 μg/mL 之甲醇溶液，混合均勻後進行 HPLC 分析。

各指標成分層析而得之波鋒面積相對於內標準波峰面積之比值與

對應之系列濃度作圖，分別繪製檢量線。

（三）分析方法之確效

1. 精密度 (Precision)

將各濃度之標準溶液，分別於同日內早、午、晚及連續三日之異日間各進行一次層析，並以獲得之檢量線方程式，求得每次的實測濃度值。以三次同日內及三次異日間實測濃度分別求其平均值(mean)、標準偏差 (standard deviation, S.D.)及變異係數(coefficient of variation, C.V.)。

2. 準確度 (Accuracy)

三次同日內及三次異日間實測所得平均濃度與真正濃度間之相對誤差(relative error)表示之。

3. 靈敏度 (Sensitivity)

將各成分標準品濃度一再稀釋，直至其波峰面積與雜訊面積之比值為 3 時之濃度，為其偵測極限 (LOD, Limit of detection)。其波峰面積與雜訊面積之比值為 10 時之濃度，為最低可定量濃度（LOQ, Limit of Quantitation）

4. 回收率 (Recovery)

將各成分溶於甲醇，製備三種濃度之各成分標準品溶液，分別添

加於酸水解後之水煎劑，以 HPLC 定量，每種濃度各進行三重複，所測得之含量，除以理論濃度以百分比表示，即為回收率。

參、結果與討論

一、蒽醌類指標成分定量方法之建立

利用 HPLC 方法定量大黃、生首烏、製首烏、虎杖、蘆薈、羊蹄及決明子等七種藥材之蒽醌類非醣體成分之含量 (Table 1~7)。因其成分之間極性差異較大，且為避免許多成分干擾，故採用梯度沖提方式，波峰分離效果良好，均可在 50 分鐘內完成。

大黃、生首烏及製首烏各指標成分標準品與內部標準之波峰面積比值與各指標成分濃度經線性迴歸所得之檢量線顯示，aloe-emodin, rhein 及 emodin 於 0.63 ~ 20.00 μ g/mL，chrysophanol 於 1.25 ~ 20.00 μ g/mL，physcion 於 0.63 ~ 10.00 μ g/mL 濃度間均有良好之現性關係 (r > 0.999)，如 Table 8 所示。分析方法之確效顯示，各指標成分同日內及異日間之變異係數 (C.V.)、相對誤差 (relative error) 以及回收率在可接受之範圍內，結果如 Table 13~17 及 Table 25 ~ 27。

虎杖各指標成分標準品與內部標準之波峰面積比值與各指標成分濃度經線性迴歸所得之檢量線顯示，resveratrol 及 emodin 於 3.13 ~ 100.00

μg/mL 濃度間均有良好之現性關係 (r > 0.999)，如 Table 9 所示。分析方法之確效顯示，各指標成分同日內及異日間之變異係數 (C.V.) 、相對誤差 (relative error)以及回收率在可接受之範圍內，結果如 Table 20, 22, 28。

蘆薈各指標成分標準品與內部標準之波峰面積比值與各指標成分濃度經線性迴歸所得之檢量線顯示，aloin 於 12.50~ 200.00μg/mL，aloe-emodin 於 6.25~200.00μg/mL 濃度間均有良好之現性關係 (r > 0.999)，如 Table 10 所示。分析方法之確效顯示，各指標成分同日內及異日間之變異係數 (C.V.)、相對誤差 (relative error) 以及回收率均在可接受之範圍內，結果如 Table 18, 19, 29。

羊蹄各指標成分標準品與內部標準之波峰面積比值與各指標成分濃度經線性迴歸所得之檢量線顯示，emodin 及 chrysophanol 於 3.13 ~ 100.00 μg/mL 濃度間均有良好之現性關係 (r > 0.999)，如 Table 11 所示。分析方法之確效顯示，各指標成分同日內及異日間之變異係數 (C.V.) 、相對誤差 (relative error) 以及回收率均在可接受之範圍內，結果如 Table 20, 21, 30。

決明子各指標成分標準品與內部標準之波峰面積比值與各指標成分濃度經線性迴歸所得之檢量線顯示 chrysophanol 及 physcion 於 1.56 ~

25.00 μg/mL 濃度間均有良好之現性關係 (r > 0.999)，如 Table 12 所示。分析方法之確效顯示，各指標成分同日內及異日間之變異係數 (C.V.) 及相對誤差 (relative error) 均在可接受之範圍內，結果如 Table 23, 24。但其回收率在低濃度時較差，中、高濃度時在可接受範圍內，結果如 Table 31。

二、酸水解條件之探討

天然界的配醣體多以 O-glycosides 方式存在，此 O-C 的鍵結可以藉由酸催化水解或是酶解切斷，酸的作用力強，而酶的作用則較為專一。本研究選擇用酸水解，可將大部分的配醣體之糖基切除，且成本較低。各藥材酸水解條件之探討結果如下：

大黃水煎劑之成分 rhein 在水解一小時之後有明顯增加，其他成分 aloe-emodin, emodin, chrysophanol, physcion 均能在半小時內水解完成 (Fig 19)，決明子水煎劑之成分 chrysophanol 及 physcion 經酸半小時水解後有明顯增加，約 1 小時可達最大量 (Fig 25)，而鹽酸強度、反應溫度、添加抗氧化劑與否及避不避光，對於酸水解後之成分含量並無明顯差異，故選擇以 1.2N HCl 於 80℃下水解一小時。生首烏之 emodin 及 physcion 皆在半小時即可水解完全，於 100℃下可有較多的產量，而鹽酸強度、添加抗氧化劑與否及避不避光，對於酸水解後之成分含量並無

明顯差異(Fig 20)。製首烏的炮製方式通常需以黑豆汁或黃酒製，皆須經過加熱過程而破壞，致使用酸水解，其 emodin 及 physcion 之含量並無增加 (Fig 21)。與相關文獻指出，生首烏經炮製過後，其結合蒽醌衍生物的量，隨著炮製時間的延長而減少，含糖量也隨著蒸的時間延長而增加(47)。羊蹄水煎劑之成分 emodin, chrysophanol 在半小時即可水解達最大量，藉由避光及添加 ascorbic acid 的方式可減少其水解過程中成分的破壞，但較強之鹽酸酸度及較高之反應溫度無法使其產量增加 (Fig 24)。虎杖水煎劑酸水解後 emodin 顯著增加，且隨著時間、溫度、鹽酸強度增加其產率亦隨之上升，反之，resveratrol 酸水解前後並無明顯變化，且較強的酸、較高的溫度會對 resveratrol 產生破壞的現象，添加抗氧化劑亦無法保護此成分，隨著加熱時間的延長 resveratrol 呈現減少之情形(Fig 22)。然而根據文獻(29)指出虎杖具有配醣體的存在 resveratroloside (3,5,4'-trihydroxystilbene-4'-*O*-β-D-glucopyranoside) 水解後 resveratrol 理論上應增加而未增加，推測可能因為 resveratrol 對光不安定所造成的影響(48)。蘆薈水煎劑經酸水解後，其 aloin, aloe-emodin 之成分並無顯著增加，可能因蘆薈藥材為已經過加工處理所致(49)。另酸水解過程添加抗氧化劑亦無產生保護的效果，且隨著時間、溫度、鹽酸強度的增加產率明顯的下降 (Fig 23)。

三、藥材水煎劑水解前後之非醣體成分之定量

大黃水煎劑水解前後之 aloe-emodin, rhein, emodin, chrysophanol 及 physcion 之含量如 Table 1 所示。依其莫耳數差總和，回推總配醣體含量為 5.91 μmoL/g。生首烏水煎劑水解前後之 emodin 及 physcion 含量如 Table 2 所示，依其莫耳數總和，回推總配醣體含量為 111.8 nmoL/g。製首烏水煎劑含 emodin 105.6 nmoL/g，physcion 26.9 nmoL/g，水解後並無差異 (Table 3)。決明子本欲定量 aloe-emodin、chrysophanol 及 physcion，但經 diode array detector 比對後，未發現 aloe-emodin，可能其含量太低，無法定量；另外，chrysophanol 及 physcion 含量低於可定量濃度，而在水解後其含量分別為 1.65 μmoL/g 及 0.49 μmoL/g，依其莫耳數差總和，回推總配醣體含量為 2.14 μmoL/g (Table 7)。羊蹄水煎劑水解前後之 emodin 及 chrysophanol 含量如 Table 6 所示，依其莫耳數差總和，回推總配醣體含量為 1.73 μmoL/g。虎杖水煎劑水解前後之 emodin 及 resveratrol 含量如 Table 4 所示，依其莫耳數差總和，回推總配醣體含量為 8.42 μmoL/g。蘆薈水煎劑含 aloin 76.12 μmoL/g 及 aloe-emodin 8.27 μmoL/g (Table 5)。

肆、結論與建議

一、本研究選擇大黃之 aloe-emodin, rhein, emodin, chrysophanol, physcion，生首烏、製首烏之 emodin 及 physcion，虎杖之 emodin 及 resveratrol，蘆薈之 aloin 及 aloe-emodin，羊蹄之 chrysophanol，及 emodin，決明子之 chrysophanol 及 physcion 等蒽醌類成分做為指標，建立其非醣體成分之分析方法，並完成方法之確效。

二、利用酸水解上述七種中藥，並分析其水解前後之非醣體含量，結果顯示大黃、生首烏、羊蹄及決明子內之指標成分及虎杖之 emodin 在水解之後均有明顯增加。而製首烏與蘆薈並沒有顯著差異。虎杖內之 resveratrol 會因水解時間增加而減少。

三、目前各國藥點對藥材規定訂量者不多，且只定量非糖體或單一配醣體者為多，而中藥材之成分複雜，少數之指標成分實難以反映之活性或療效之品質。本研究所建立之方法，可應用於大黃、生首烏、羊蹄及決明子之水解前後非醣體之含量測定，並以其前後差值回推總配醣體含量，如此更可反映藥材活性或療效成分含量，至於製首烏及蘆薈已屬炮製過之藥材， 以直接測定其非醣體含量，供作中藥材之品質管制之參考。

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柒、表

Table 1 Comparison of contents (μmoL) of aloe-emodin, rhein, emodin, chrysophanol, physcion in the decoction of *Rheum officinale* Baill.before and after acid hydrolysis

Constituents	Decoction (μmoL/g)	After acid hydrolysis (μmoL/g)	Difference (μmoL/g)
Aloe-emodin	0.43 ± 0.00	1.09 ± 0.04	0.66 (154 %)
Rhein	6.07 ± 0.25	6.98 ± 0.35	0.91 (15 %)
Emodin	1.82 ± 0.07	4.46 ± 0.15	2.64 (145 %)
Chrysophanol	1.03 ± 0.06	2.34 ± 0.20	1.31 (127 %)
Physcion	0.41 ± 0.03	0.80 ± 0.05	0.39 (95 %)

Table 2 Comparison of contents (nmoL) of emodin and physcion in the decoction of crude *Polygonum multiflorum* Thunb. before and after acid hydrolysis

Constituents	Decoction (nmoL/g)	After acid hydrolysis (nmoL/g)	Difference (nmoL/g)
Emodin	8.3 ± 0.9	105.7 ± 4.9	97.4 (1174%)
Physcion	1.8 ± 0.1	16.2 ± 3.4	14.4 (800 %)

Table 3 The contents (nmoL) of emodin and physcion in the decoction of processed *Polygonum multiflorum* Thunb.

Constituents	Decoction (nmoL/g)
Emodin	109.3 ± 8.6
Physcion	26.9 ± 4.2

Table 4 Comparison of contents (μmoL) of emodin and resveratrol in the decoction of *Polygonum cuspidant* Sieb. Et Zuce. before and after acid hydrolysis

Constituents	Decoction (μmoL/g)	After acid hydrolysis (μmoL/g)	Difference (μmoL/g)
Emodin	0.38 ±0.12	8.80 ±0.36	8.42 (2216%)
Resveratrol	4.16 ±0.15	4.01 ±0.90	-

Table 5 Comparison of contents (μmoL) of aloe-emodin and aloin in the decoction of *Aloe ferox* Miller. before and after acid hydrolysis

Constituents	Decoction (μmoL/g)	After acid hydrolysis (μmoL/g)
Aloin	76.12 ±5.90	77.74 ±2.83
Aloe-emodin	8.27 ±0.54	8.09 ±0.26

Table 6 Comparison of contents (μmoL) of emodin and chrysophanol in the decoction of *Rumex japonicus* before and after acid hydrolysis

Constituents	Decoction (μmoL/g)	After acid hydrolysis (μmoL/g)	Difference (μmoL/g)
Emodin	0.18 ±0.05	0.81 ±0.16	0.63 (350%)
Chrysophanol	0.16 ±0.06	1.26 ±0.24	1.10 (688%)

Table 7 Comparison of contents (μmoL) of chrysophanol and physcion in the decoction of Cassiae torae semen before and after acid hydrolysis

Constituents	Decoction (μmoL/g)	After acid hydrolysis (μmoL/g)	Difference (μmoL/g)
Chrysophanol	N.D.	1.65 ± 0.21	1.65
Physcion	N.D.	0.49 ± 0.02	0.49

Table 8 The regression equations, concentration ranges and correlation coefficients of constituents in *Rheum officinale* Baill. and *Polygonum multiflorum* Thunb.

Constituents	Regression equations	Conc. range (μg/mL)		r
Aloe-emodin	y=0.864205x+0.070187	0.63	~ 20.00	0.9999
Rhein	y=0.230382x+0.020414	0.63	~ 20.00	0.9999
Emodin	y=0.118404x+0.024871	0.63	~ 20.00	0.9999
Chrysophanol	y=0.250934x+0.058222	1.25	~ 20.00	0.9997
Physcion	y=0.184259x+0.002156	0.63	~ 10.00	0.9999

Table 9 The regression equations, concentration ranges and correlation coefficients of constituents in *Polygonum cuspidant* Sieb. Et Zuce.

Constituents	Regression equations	Conc. range (μg/mL)		r
Resveratrol	y=0.036168x-0.0234	3.13	~ 100.00	0.9999
Emodin	y=0.135202x-0.02552	3.13	~ 100.00	0.9998

Table 10 The regression equations, concentration ranges and correlation coefficients of constituents in *Aloe ferox* Miller.

Constituents	Regression equations	Conc. range (μg/mL)		r
Aloin	y=0.006603x-0.015	12.50	~ 200.00	0.9997
Aloe-emodin	y=0.060777x+0.01849	6.25	~ 200.00	0.9999

Table 11 The regression equations, concentration ranges and correlation coefficients of constituents in *Rumex japonicus*

Constituents	Regression equations	Conc. range (μg/mL)		r
Emodin	y=0.135202x-0.02552	3.13	~ 100.00	0.9998
Chrysophanol	y=0.194998x+0.208875	3.13	~ 100.00	0.9999

Table 12 The regression equations, concentration ranges and correlation coefficients of constituents in Cassiae torae semen

Constituents	Regression equations	Conc. range (μg/mL)		r
Chrysophanol	y=0.101382x+0.013816	1.56	~ 25.00	0.9997
Physcion	y=0.060731x+0.009223	1.56	~ 25.00	0.9998

Table 13 Intraday and interday analytical precision and accuracy of aloe-emodin in *Rheum officinale* Baill.

Conc. (μg/mL)	Intra-day		Inter-day	
	Precision Mean ± S.D. (CV. %)	Accuracy (%)	Precision Mean ± S.D. (C.V. %)	Accuracy (%)
20.00	19.93 ± 0.06 (0.29)	-0.36	19.89 ± 0.01 (0.05)	-0.54
10.00	10.14 ± 0.11 (1.12)	1.39	10.21 ± 0.00 (0.02)	2.07
5.00	5.05 ± 0.08 (1.64)	0.93	5.09 ± 0.06 (1.12)	1.78
2.50	2.45 ± 0.08 (3.06)	-1.90	2.39 ± 0.03 (1.42)	-4.21
1.25	1.22 ± 0.03 (2.79)	-2.47	1.20 ± 0.01 (1.04)	-3.73
0.63	0.59 ± 0.01 (1.96)	-5.56	0.59 ± 0.01 (1.61)	-5.67

Table 14 Intraday and interday analytical precision and accuracy of rhein in *Rheum officinale* Baill.

Conc. (μg/mL)	Intra-day		Inter-day	
	Precision Mean ± S.D. (C.V. %)	Accuracy (%)	Precision Mean ± S.D. (C.V. %)	Accuracy (%)
20.00	19.88 ± 0.04 (0.22)	-0.59	19.96 ± 0.03 (0.17)	-0.18
10.00	10.21 ± 0.07 (0.69)	2.15	10.06 ± 0.07 (0.71)	0.63
5.00	5.08 ± 0.09 (1.81)	1.63	5.04 ± 0.03 (0.58)	0.77
2.50	2.49 ± 0.07 (2.90)	-0.60	2.48 ± 0.08 (3.08)	-0.70
1.25	1.17 ± 0.02 (1.71)	-6.19	1.22 ± 0.03 (2.22)	-2.43
0.63	0.54 ± 0.02 (4.09)	-13.68	0.61 ± 0.06 (9.52)	-2.71

Table 15 Intraday and interday analytical precision and accuracy of emodin in *Rheum officinale* Baill. and *Polygonum multiflorum* Thunb.

Conc. (μg/mL)	Intra-day		Inter-day	
	Precision Mean ± S.D. (C.V. %)	Accuracy (%)	Precision Mean ± S.D. (C.V. %)	Accuracy (%)
20.00	19.90 ± 0.05 (0.27)	-0.48	19.90 ± 0.07 (0.33)	-0.51
10.00	10.19 ± 0.12 (1.17)	1.94	10.22 ± 0.14 (1.38)	2.16
5.00	5.03 ± 0.02 (0.40)	0.68	5.03 ± 0.03 (0.55)	0.68
2.50	2.47 ± 0.06 (2.24)	-1.36	2.42 ± 0.02 (0.83)	-3.03
1.25	1.20 ± 0.04 (3.74)	-4.26	1.18 ± 0.04 (3.42)	-5.34
0.63	0.58 ± 0.03 (4.36)	-7.05	0.62 ± 0.03 (4.93)	-0.76

Table 16 Intraday and interday analytical precision and accuracy of chrysophanol in *Rheum officinale* Baill.

Conc. (μg/mL)	Intra-day		Inter-day	
	Precision Mean ± S.D. (C.V. %)	Accuracy (%)	Precision Mean ± S.D. (C.V. %)	Accuracy (%)
20.00	19.85 ± 0.11 (0.56)	-0.76	19.92 ± 0.06 (0.29)	-0.39
10.00	10.30 ± 0.24 (2.31)	2.96	10.16 ± 0.09 (0.86)	1.56
5.00	5.10 ± 0.05 (0.99)	2.02	5.06 ± 0.10 (2.06)	1.10
2.50	2.39 ± 0.04 (1.76)	-4.22	2.41 ± 0.06 (2.55)	-3.49
1.25	1.11 ± 0.11 (10.17)	-11.22	1.20 ± 0.07 (6.15)	-3.68

Table 17 Intraday and interday analytical precision and accuracy of physcion in *Rheum officinale* Baill. and *Polygonum multiflorum* Thunb.

Conc. (μg/mL)	Intra-day		Inter-day	
	Precision Mean ± S.D. (C.V. %)	Accuracy (%)	Precision Mean ± S.D. (C.V. %)	Accuracy (%)
10.00	10.01 ± 0.02 (0.22)	0.12	10.02 ± 0.03 (0.32)	0.19
5.00	5.00 ± 0.06 (1.15)	-0.03	4.98 ± 0.08 (1.57)	-0.38
2.50	2.44 ± 0.06 (2.40)	-2.29	2.45 ± 0.05 (2.12)	-2.08
1.25	1.25 ± 0.02 (1.76)	0.09	1.26 ± 0.05 (3.96)	0.47
0.63	0.67 ± 0.03 (5.05)	7.30	0.67 ± 0.02 (2.79)	7.40

Table 18 Intraday and interday analytical precision and accuracy of aloin in *Aloe ferox* Miller.

Conc. (μg/mL)	Intra-day		Inter-day	
	Precision Mean ± S.D. (C.V. %)	Accuracy (%)	Precision Mean ± S.D. (C.V. %)	Accuracy (%)
200.00	201.28± 0.28 (0.14)	0.64	201.32 ±0.49 (0.24)	0.66
100.00	97.61 ± 0.56 (0.57)	-2.39	97.5 0± 1.00 (1.03)	-2.50
50.00	48.59 ± 0.49 (1.00)	-2.83	48.86 ± 0.41 (0.85)	-2.29
25.00	26.58 ± 0.44 (1.67)	6.30	26.09 ± 0.42 (1.59)	4.35
12.50	13.42 ± 0.65 (4.82)	7.40	13.73 ± 0.44 (3.22)	9.84

Table 19 Intraday and interday analytical precision and accuracy of aloe-emodin in *Aloe ferox* Miller.

Conc. (μg/mL)	Intra-day		Inter-day	
	Precision Mean ± S.D. (C.V. %)	Accuracy (%)	Precision Mean ± S.D. (C.V. %)	Accuracy (%)
200.00	200.70± 0.28 (0.14)	0.35	200.69± 0.80 (0.40)	0.35
100.00	98.88 ±1.20 (1.22)	-1.12	98.54 ± 1.49 (1.51)	-1.46
50.00	49.29 ± 0.34 (0.68)	-1.42	49.97 ± 1.12 (2.24)	-0.07
25.00	25.27 ±0.08 (0.32)	1.09	25.13 ± 0.27 (1.07)	0.54
12.50	12.89 ±0.37 (2.90)	3.12	12.77 ± 0.49 (3.83)	2.16
6.25	6.77 ± 0.26 (3.86)	8.35	6.65 ± 0.63 (9.49)	6.37

Table 20 Intraday and interday analytical precision and accuracy of emodin in *Rumex japonicus* and *Polygonum cuspidant* Sieb. Et Zuce.

Conc. (μg/mL)	Intra-day		Inter-day	
	Precision Mean ± S.D. (C.V. %)	Accuracy (%)	Precision Mean ± S.D. (C.V. %)	Accuracy (%)
100.00	99.47 ± 0.20 (0.20)	-0.53	100.04 ± 0.41 (0.41)	0.04
50.00	51.42 ± 0.22 (0.43)	2.83	50.13 ± 1.35 (2.70)	0.27
25.00	24.55 ± 0.10 (0.41)	-1.80	24.73 ± 0.13 (0.51)	-1.08
12.50	11.94 ± 0.02 (0.19)	-4.50	12.04 ± 0.14 (1.12)	-3.72
6.25	6.23 ± 0.05 (0.81)	-0.31	6.45 ± 0.05 (0.75)	3.21
3.13	3.27 ± 0.12 (3.69)	4.60	3.49 ± 0.05 (1.56)	11.73

Table 21 Intraday and interday analytical precision and accuracy of chrysophanol in *Rumex japonicus*

Conc. (μg/mL)	Intra-day		Inter-day	
	Precision Mean ± S.D. (C.V. %)	Accuracy (%)	Precision Mean ± S.D. (C.V. %)	Accuracy (%)
100.00	99.93 ± 0.05 (0.05)	-0.07	100.04 ±0.10 (0.10)	0.04
50.00	50.13 ± 0.12 (0.24)	0.26	49.93 ± 0.56 (1.12)	-0.14
25.00	25.24 ± 0.10 (0.38)	0.96	25.16 ± 0.03 (0.12)	0.65
12.50	12.00 ± 0.12 (1.00)	-0.42	12.07 ± 0.27 (2.25)	-3.46
6.25	6.34 ± 0.02 (0.30)	1.48	6.35 ± 0.04 (0.60)	1.66
3.13	3.24 ± 0.17 (5.37)	3.61	3.33 ± 0.13 (3.99)	6.41

Table 22 Intraday and interday analytical precision and accuracy of resveratrol in *Polygonum cuspidant* Sieb. Et Zuce.

Conc. (μg/mL)	Intra-day		Inter-day	
	Precision Mean ± S.D. (C.V. %)	Accuracy (%)	Precision Mean ± S.D. (C.V. %)	Accuracy (%)
100.00	100.24 ±0.02 (0.02)	0.24	100.20 ± 0.06 (0.06)	0.20
50.00	49.53 ± 0.04 (0.08)	-0.95	49.65 ± 0.11 (0.22)	-0.70
25.00	25.06 ± 0.11 (0.42)	0.25	24.97 ± 0.17 (0.69)	-0.13
12.50	12.17 ± 0.05 (0.38)	-2.64	12.21 ± 0.13 (1.09)	-2.32
6.25	6.45 ± 0.01 (0.16)	3.19	6.43 ± 0.08 (1.32)	2.89
3.13	3.43 ± 0.05 (1.39)	9.61	3.42 ± 0.10 (2.87)	9.50

Table 23 Intraday and interday analytical precision and accuracy of chrysophenol in Cassiae torae semen

Conc. (μg/mL)	Intra-day		Inter-day	
	Precision Mean ± S.D. (C.V. %)	Accuracy (%)	Precision Mean ± S.D. (C.V. %)	Accuracy (%)
25.00	24.99 ± 0.18 (0.70)	-0.06	25.18 ± 0.13 (0.50)	0.72
12.50	12.60 ± 0.49 (3.92)	0.78	12.00 ± 0.42 (3.47)	-3.99
6.25	6.01 ±0.25 (4.17)	-3.81	6.43 ± 0.36 (5.55)	2.95
3.13	3.37 ±0.18 (5.27)	7.72	3.36 ± 0.17 (4.92)	7.42
1.56	1.47 ± 0.15 (10.34)	-5.61	1.46 ± 0.12 (8.10)	-6.26

Table 24 Intraday and interday analytical precision and accuracy in physcion of Cassiae torae semen

Conc. (μg/mL)	Intra-day		Inter-day	
	Precision Mean ± S.D. (C.V. %)	Accuracy (%)	Precision Mean ± S.D. (C.V. %)	Accuracy (%)
25.00	24.86 ± 0.37 (1.48)	-0.57	24.77 ± 0.30 (1.22)	-0.91
12.50	12.86 ± 0.98 (7.61)	2.84	13.08 ± 0.80 (6.08)	4.64
6.25	6.19 ± 0.58 (9.35)	-0.94	6.06 ± 0.31 (5.11)	-3.12
3.13	2.97 ± 0.23 (7.90)	-5.02	3.08 ± 0.14 (4.50)	-1.48
1.56	1.56 ± 0.15 (9.68)	0.23	1.45 ± 0.13 (8.83)	-7.08

Table 25 Recoveries (%) of constituents from *Rheum officinale* Baill. decoction

Constituents	Conc. Spiked (μg/mL)	1	2	3	Recoveries (%). Mean ± S.D
Aloe-emodin	10.0	91.8	92.9	90.8	91.8 ± 1.0
	5.0	95.5	90.8	94.9	93.7 ± 2.5
	2.5	103.0	96.4	103.9	101.1 ± 4.1
Emodin	10.0	97.9	99.5	98.9	98.7 ± 0.8
	5.0	82.6	93.6	96.2	90.8 ± 7.3
	2.5	113.8	94.1	86.5	98.1 ± 14.1
Rhein	10.0	96.2	101.7	100.9	99.6 ± 3.0
	5.0	81.3	80.4	91.8	84.5 ± 6.3
	2.5	83.5	80.5	65.2	76.4 ± 9.8

Chrysophenol	10.0	88.2	81.1	89.3	86.2 ± 4.5
	5.0	83.9	87.7	90.5	87.4 ± 3.3
	2.5	95.6	94.0	88.9	92.8 ± 3.5
Physcion	10.0	78.4	79.7	69.3	75.9 ± 5.7
	5.0	70.6	67.8	70.7	69.7 ± 1.6
	2.5	72.7	65.4	65.2	67.8 ± 4.3

Table 26 Recoveries (%) of constituents from crude *Polygonum Multiflorum* Thunb. decoction

Constituents	Conc. Spiked (μg/mL)	1	2	3	Recoveries (%). Mean ± S.D
Emodin	10.0	87.6	99.5	87.1	89.6 ± 9.1
	5.0	81.7	92.0	80.1	84.6 ± 6.5
	2.5	79.4	85.7	72.7	79.2 ± 6.5
Physcion	10.0	83.2	81.1	79.5	81.3 ± 1.8
	5.0	88.3	88.3	95.7	90.8 ± 4.3
	2.5	96.1	89.7	72.5	86.1 ± 12.2

Table 27 Recoveries (%) of constituents from processed *Polygonum multiflorum* decoction

Constituents	Conc. Spiked (μg/mL)	1	2	3	Recoveries (%). Mean ± S.D
Emodin	10.0	105.7	88.0	104.4	99.4 ± 9.9
	5.0	89.7	104.4	95.7	96.6 ± 7.4
	2.5	99.5	84.0	81.1	88.2 ± 9.9
Physcion	10.0	92.3	98.4	83.2	91.3 ± 7.6
	5.0	81.9	80.9	90.7	84.5 ± 5.4
	2.5	91.5	89.5	96.5	92.5 ± 3.6

Table 28 Recoveries (%) of constituents from *Polygonum cuspidant* Sieb. Et Zuce. decoction

Constituents	Conc. Spiked (μg/mL)	1	2	3	Recoveries (%). Mean ± S.D
Emodin	100.0	93.1	93.8	97.6	94.8 ± 2.4
	50.0	86.4	83.2	87.3	85.6 ± 2.1
	25.0	91.7	90.2	106.0	96.0 ± 8.7
Resveratrol	100.0	96.7	89.9	89.7	92.1 ± 4.0
	50.0	100.1	107.6	94.7	100.8 ± 6.5
	25.0	81.3	89.2	85.8	85.4 ± 3.9

Table 29 Recoveries (%) of constituents from *Aloe ferox* Miller. decoction

Constituents	Conc. Spiked (μg/mL)	1	2	3	Recoveries (%). Mean ± S.D
Aloin	100.0	78.4	76.4	76.8	77.2 ± 1.1
	50.0	77.2	89.4	94.1	86.9 ± 8.7
	25.0	92.8	89.9	83.1	88.6 ± 5.0
Aloe-emodin	100.0	93.6	94.1	95.1	94.3 ± 0.8
	50.0	96.8	100.8	103.8	100.5 ± 3.5
	25.0	82.8	105.2	110.3	99.4 ± 14.6

Table 30 Recoveries (%) of constituents from *Rumex japonicus* decoction

Constituents	Conc. Spiked (μg/mL)	1	2	3	Recoveries (%). Mean ± S.D
Emodin	100.0	97.8	90.2	95.9	94.6 ± 0.1
	50.0	95.5	96.2	98.4	96.7 ± 1.6
	25.0	95.7	90.7	93.8	93.4 ± 2.5
Chrysophanol	100.0	96.9	87.2	90.2	91.5 ± 5.0
	50.0	89.5	88.3	78.1	85.3 ± 6.3
	25.0	91.7	81.4	95.9	89.7 ± 7.5

Table 31 Recoveries (%) of constituents from Cassiae torae semen decoction

Constituents	Conc. Spiked (μg/mL)	1	2	3	Recoveries (%). Mean ± S.D
Chrysophanol	12.5	94.2	93.7	110.5	99.5 ± 9.6
	6.25	78.7	82.9	82.7	81.4 ± 2.4
	3.13	33.6	38.2	36.7	36.2 ± 2.4
Physcion	12.5	101.9	97.7	96.5	98.7 ± 2.8
	6.25	102.6	93.5	82.5	93.8 ± 8.7
	3.13	69.1	82.4	71.4	74.3 ± 7.1

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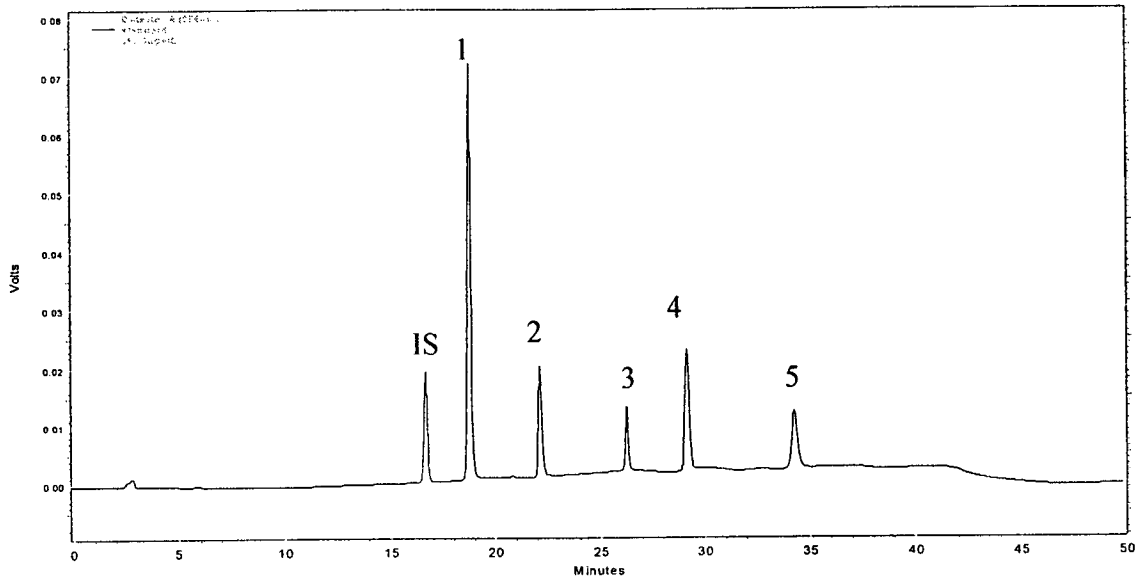

Fig 1 HPLC chromatogram of aloe-emodin, rhein, emodin, chrysophanol, physcion, and butylparaben

1. aloe-emodin 2. rhein 3. emodin 4. chrysophanol 5. physcion

IS : butylparaben

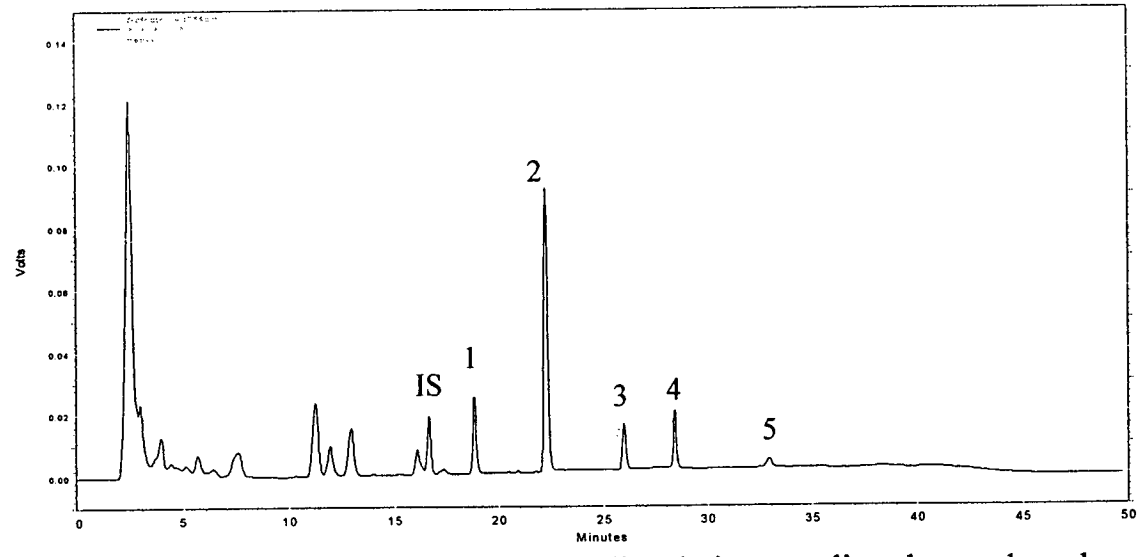

Fig 2 HPLC chromatogram of aloe-emodin, rhein, emodin, chrysophanol, and physcion in *Rheum officinale* Baill. decoction

1. aloe-emodin 2. rhein 3. emodin 4. chrysophanol 5. physcion

IS : butylparaben

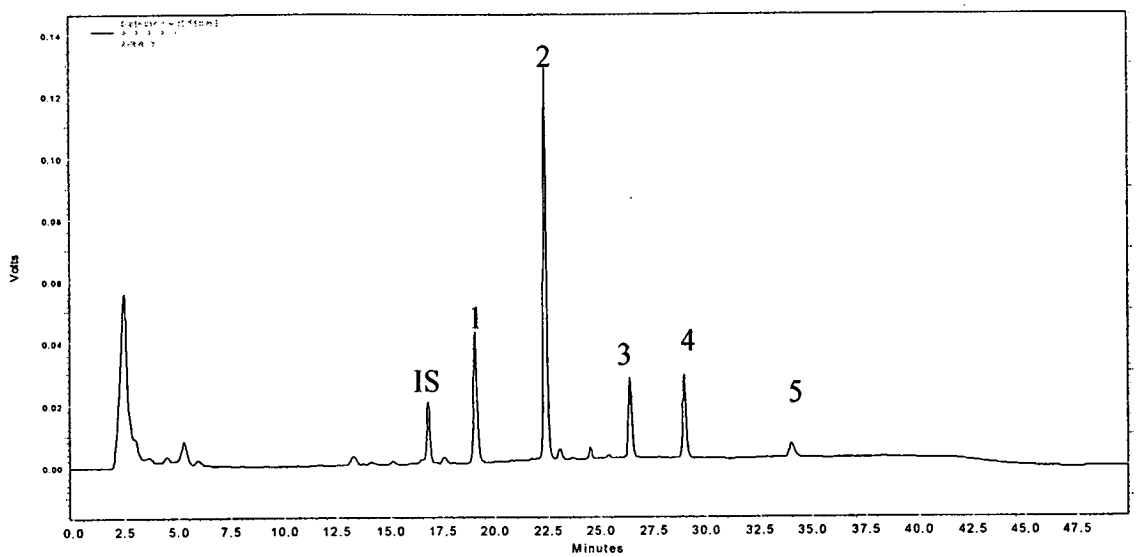

Fig 3 HPLC chromatogram of aloe-emodin, rhein, emodin, chrysophanol, and physcion in *Rheum officinale* Baill. decoction after acid hydrolysis

1. aloe-emodin 2. rhein 3. emodin 4. chrysophanol
5. physcion IS : butylparaben

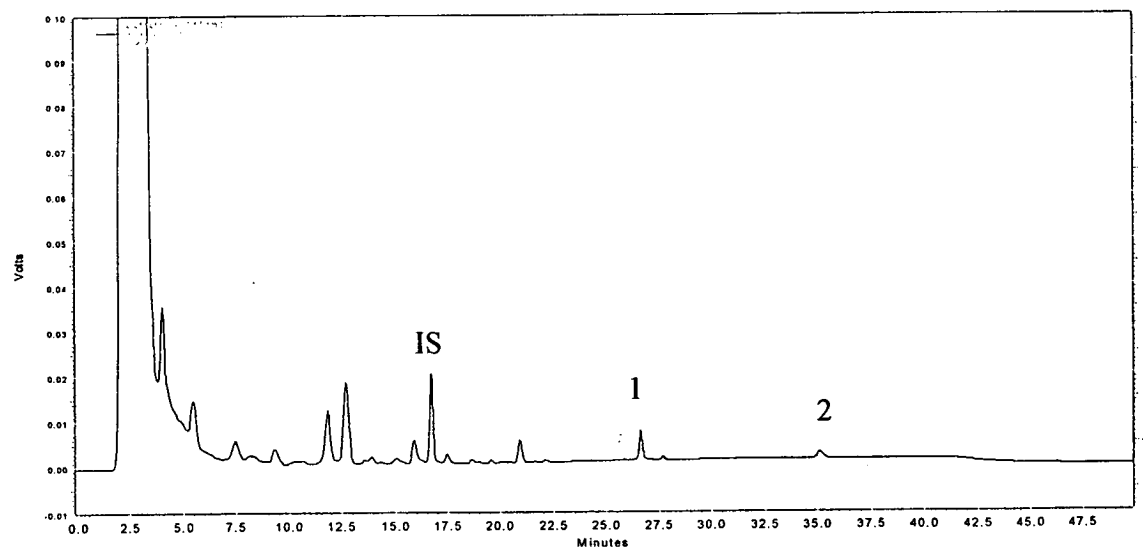

Fig 4 HPLC chromatogram of emodin and physcion in crude *Polygonum multiflorum* Thunb. decoction

1. emodin 2. physcion IS: butylparaben

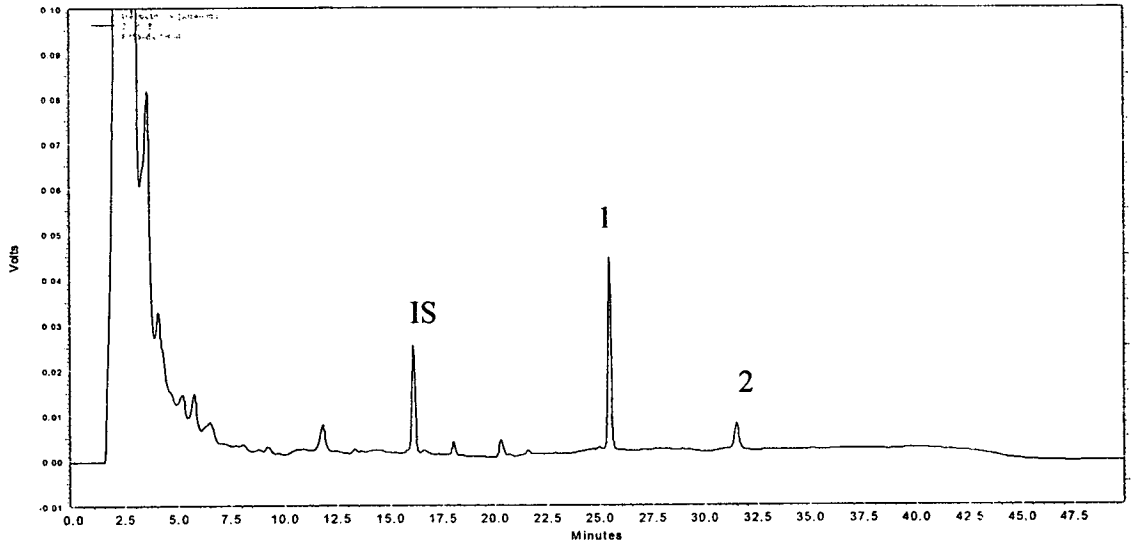

Fig 5 HPLC chromatogram of emodin and physcion in crude *Polygonum multiflorum* Thunb. decoction after acid hydrolysis
1. emodin 2. physcion IS: butylparaben

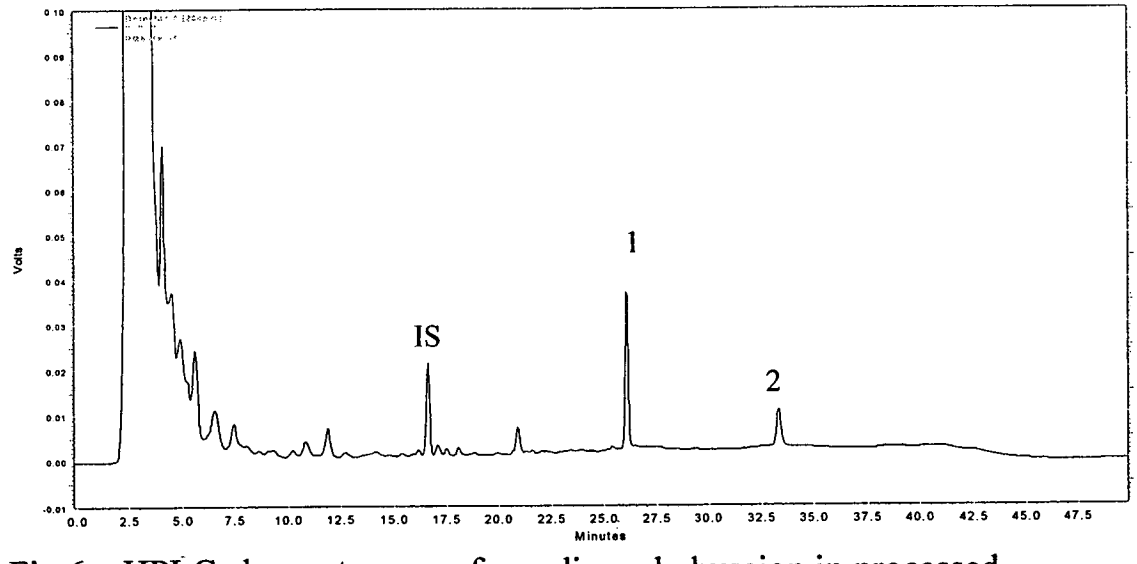

Fig 6 HPLC chromatogram of emodin and physcion in processed *Polygonum multiflorum* Thunb. decoction
1. emodin 2. physcion IS: butylparaben

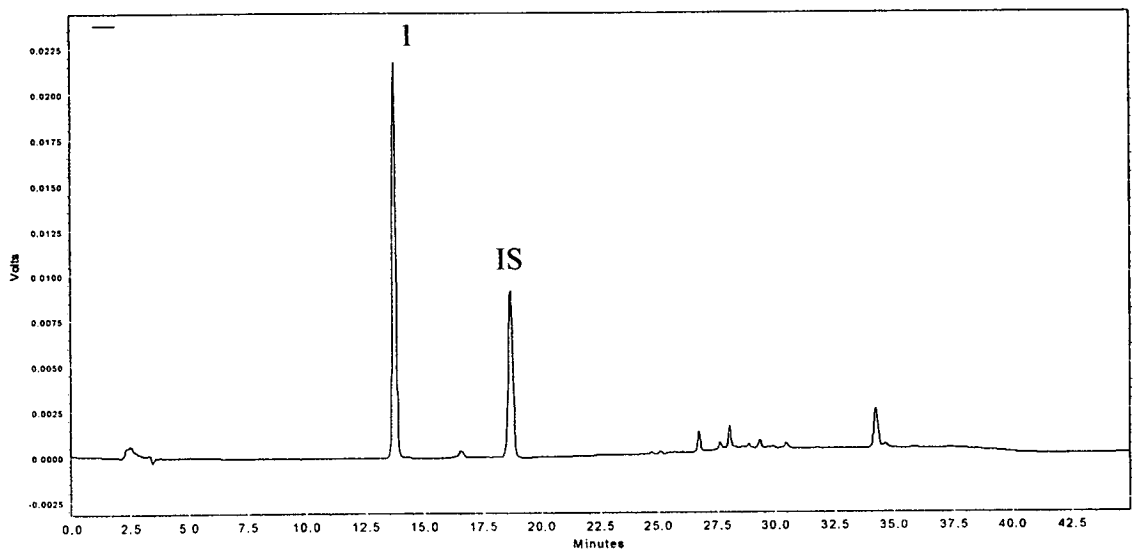

Fig 7 HPLC chromatogram of resveratrol and ethylparaben
1. resveratrol IS: ethylparaben

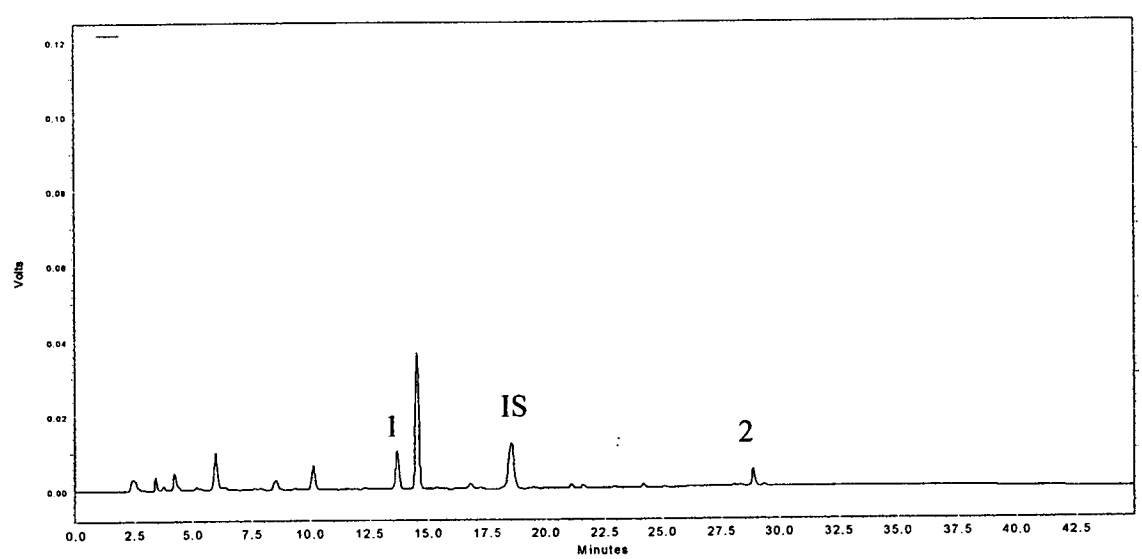

Fig 8 HPLC chromatogram of emodin and resveratrol in *Polygonum cuspidant* Sieb. Et Zuce. decoction 1. resveratrol 2. emodin IS: ethylparaben

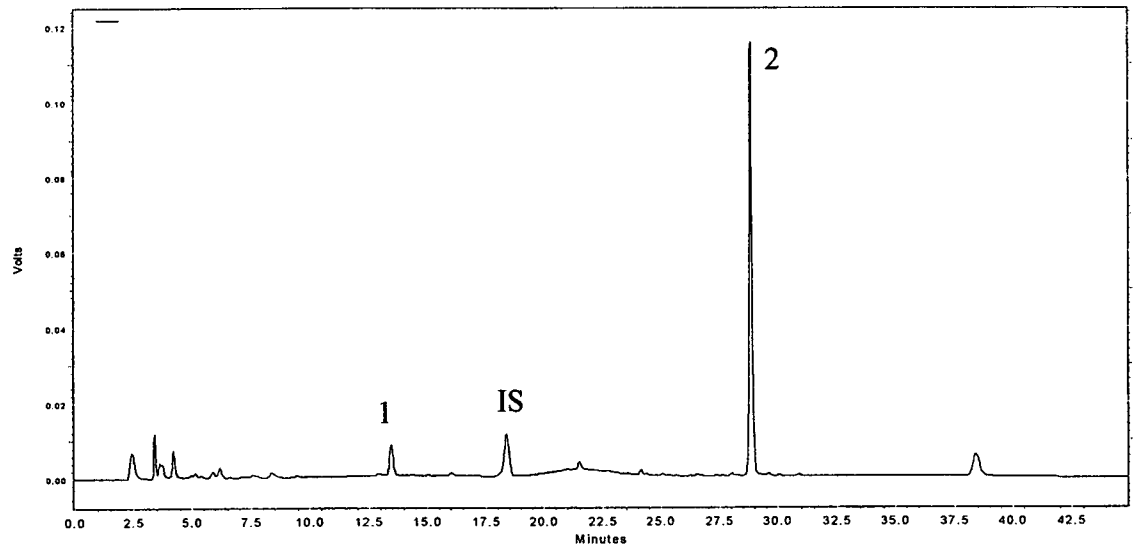

Fig 9 HPLC chromatogram of emodin and resveratrol in *Polygonum cuspidant* Sieb. Et Zuce. decoction after acid hydrolysis 1. resveratrol 2. emodin IS: ethylparaben

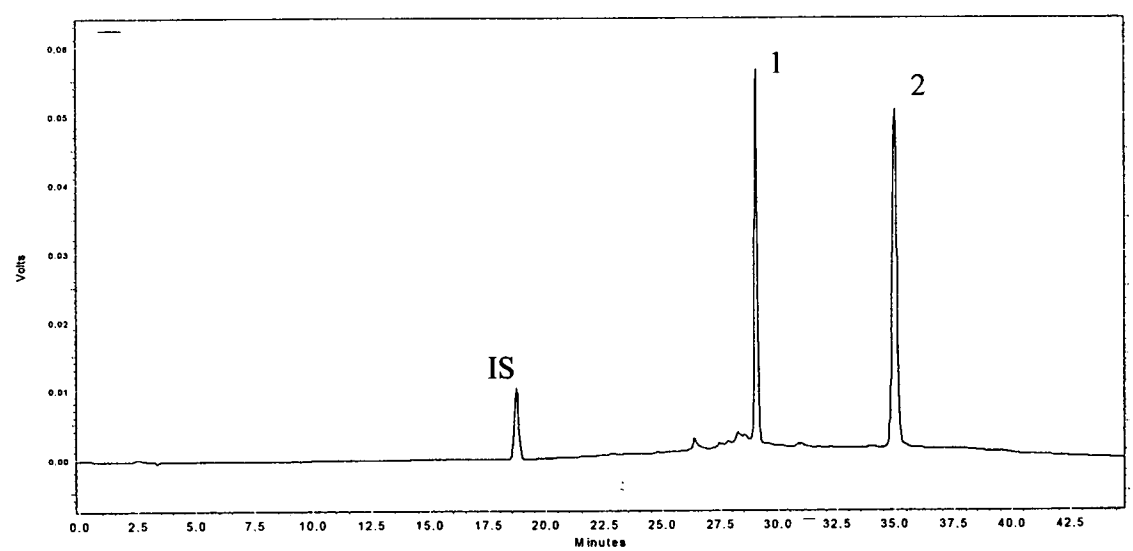

Fig 10 HPLC chromatogram of emodin, chrysophanol, and ethylparaben 1. emodin 2. chrysophanol IS: ethylparaben

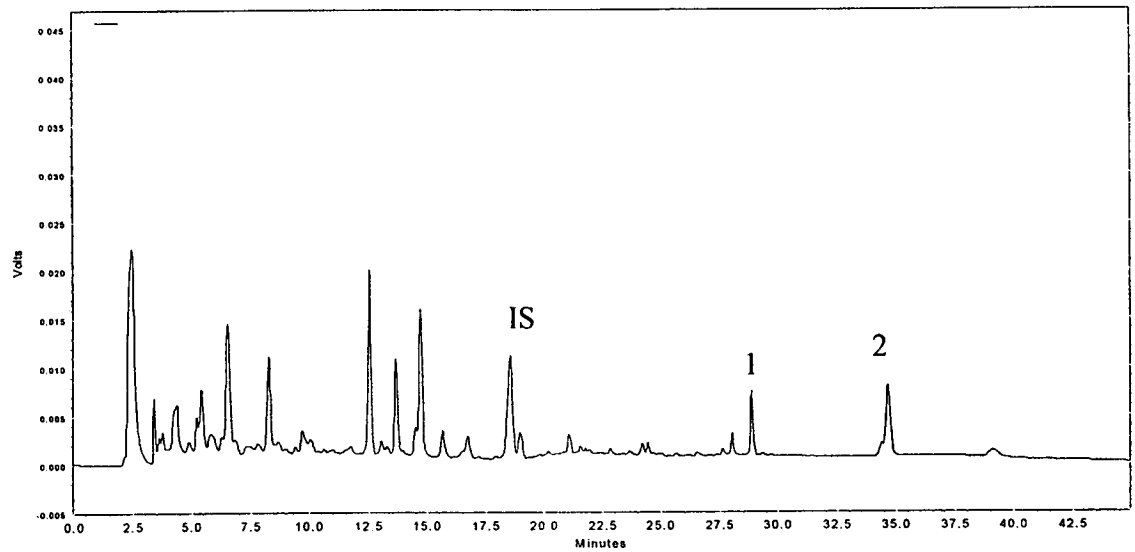

Fig 11 HPLC chromatogram of emodin and chrysophanol in *Rumex japonicus* decoction

1. emodin 2. chrysophanol IS: ethylparaben

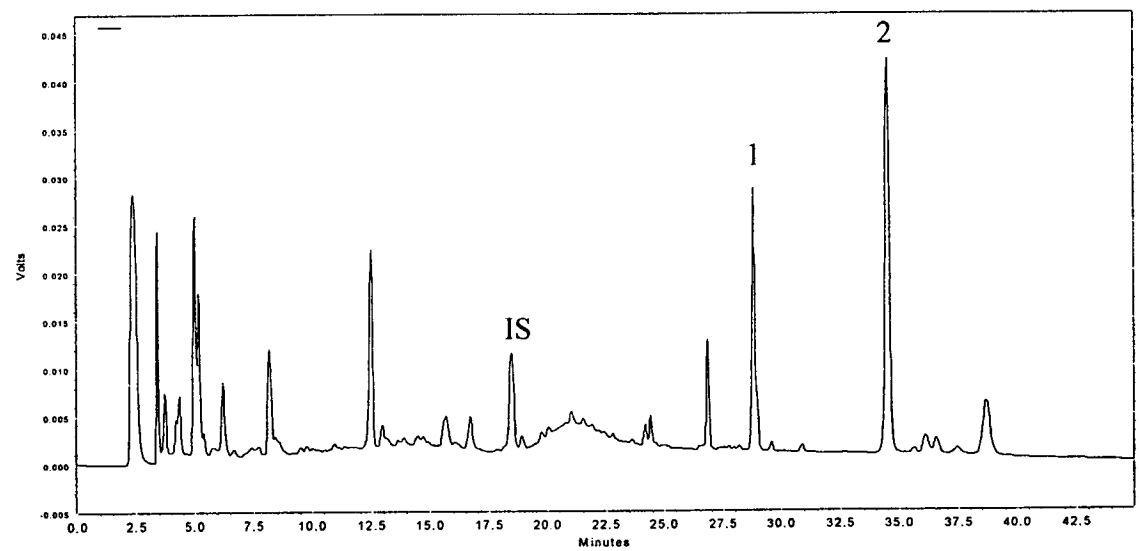

Fig 12 HPLC chromatogram of emodin and chrysophanol in *Rumex japonicus* decoction after acid hydrolysis

1. emodin 2. chrysophanol IS: ethylparaben

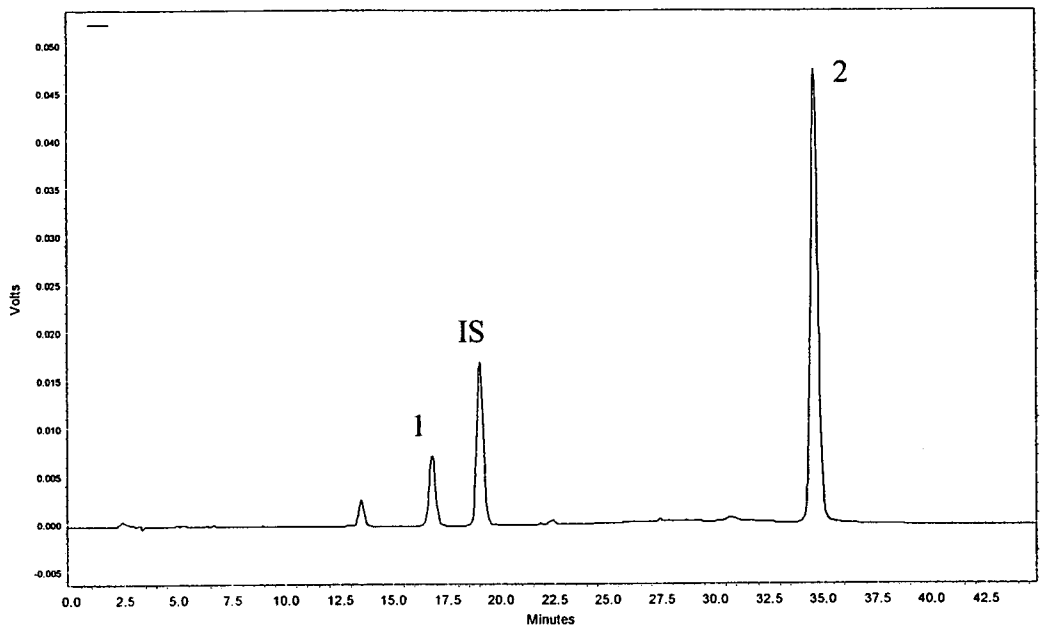

Fig 13 HPLC chromatogram of aloe-emodin, aloin, and 6,7-dimethoxycoumarin

1. aloin 2. aloe-emodin IS: 6,7-dimethoxycoumarin

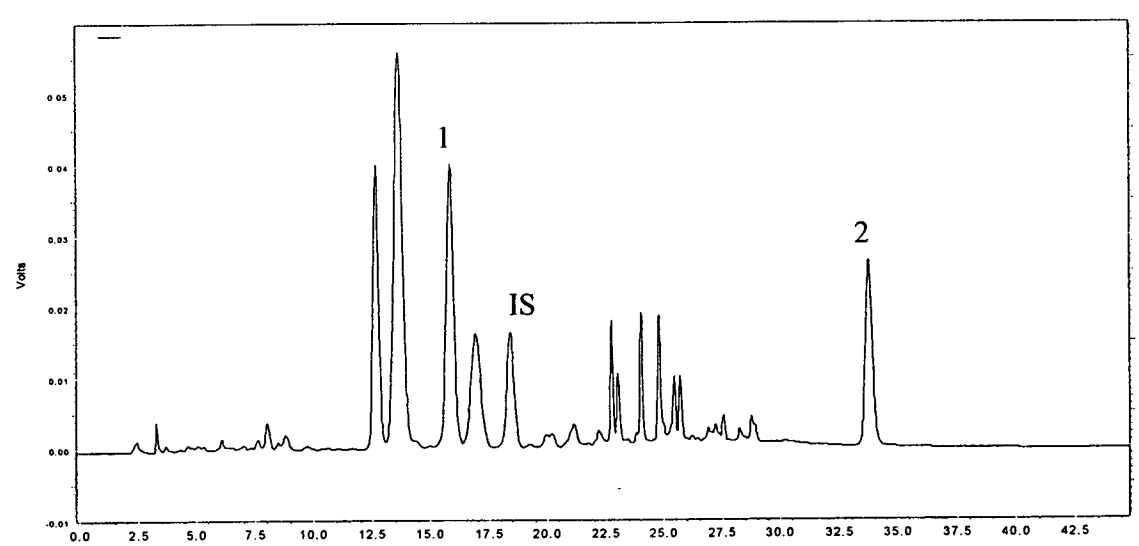

Fig 14 HPLC chromatogram of aloe-emodin and aloin in *Aloe ferox* Miller. decoction

1. aloin 2. aloe-emodin IS: 6,7-dimethoxycoumarin

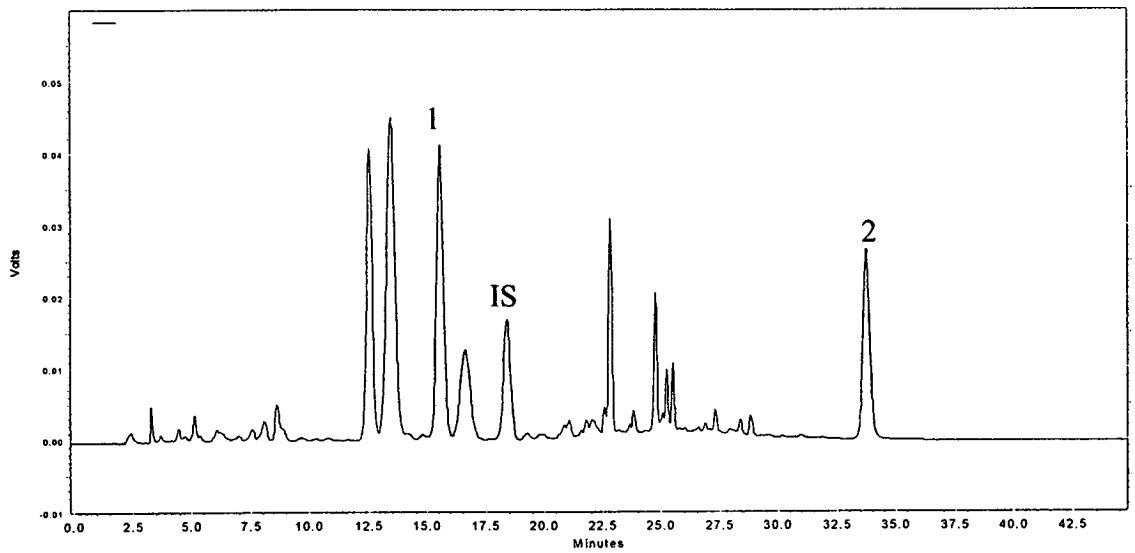

Fig 15 HPLC chromatogram of aloe-emodin and aloin in *Aloe ferox* Miller. decoction after acid hydrolysis
1. aloin 2. aloe-emodin IS: 6,7-dimethoxycoumarin

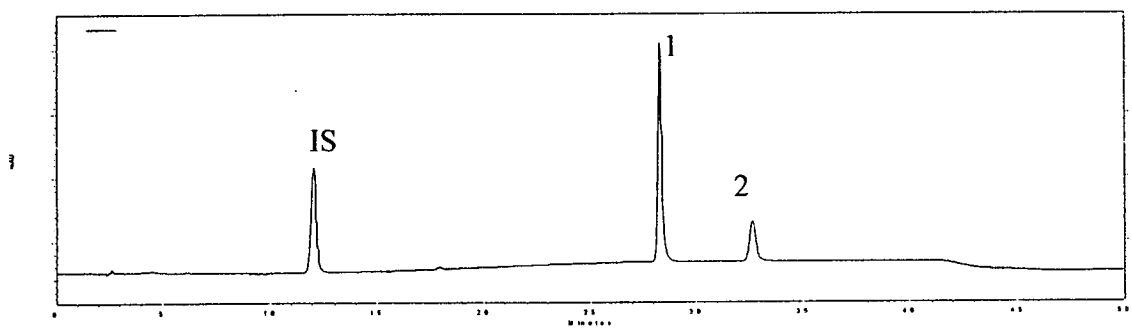

Fig 16 HPLC chromatogram of chrysophanol, physcion, and propylparaben
1. chrysophanol 2. physcion IS: propylparaben

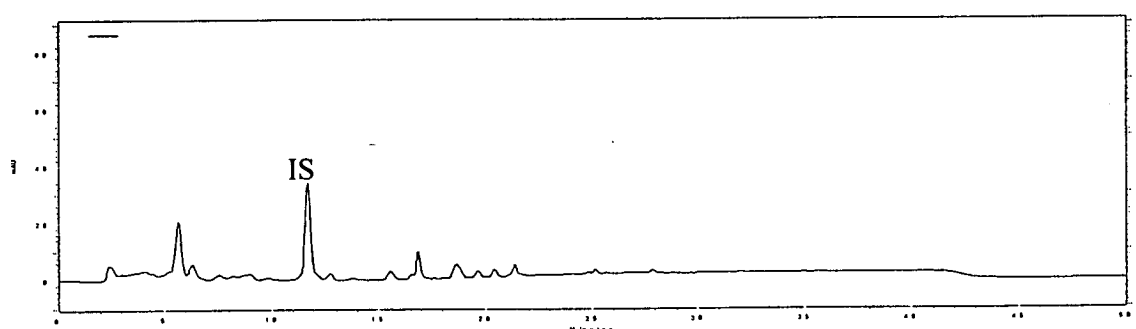

Fig 17 HPLC chromatogram of chrysophanol and physcion in Cassiae torae semen decoction IS: propylparaben

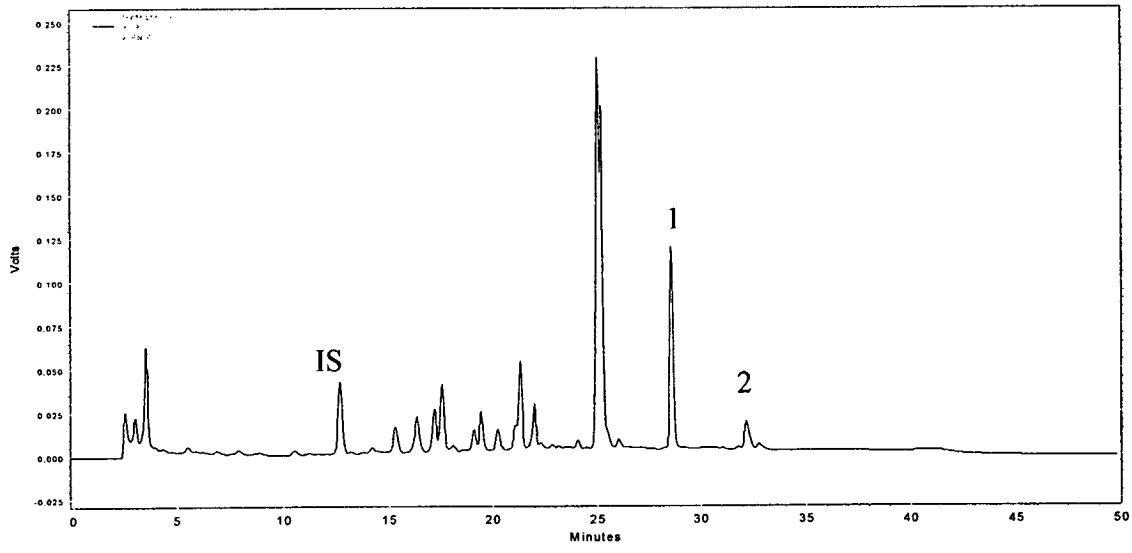

Fig 18 HPLC chromatogram of chrysophanol and physcion in Cassiae torae semen decoction after acid hydrolysis

1.chrysophanol 2. physcion IS: propylparaben

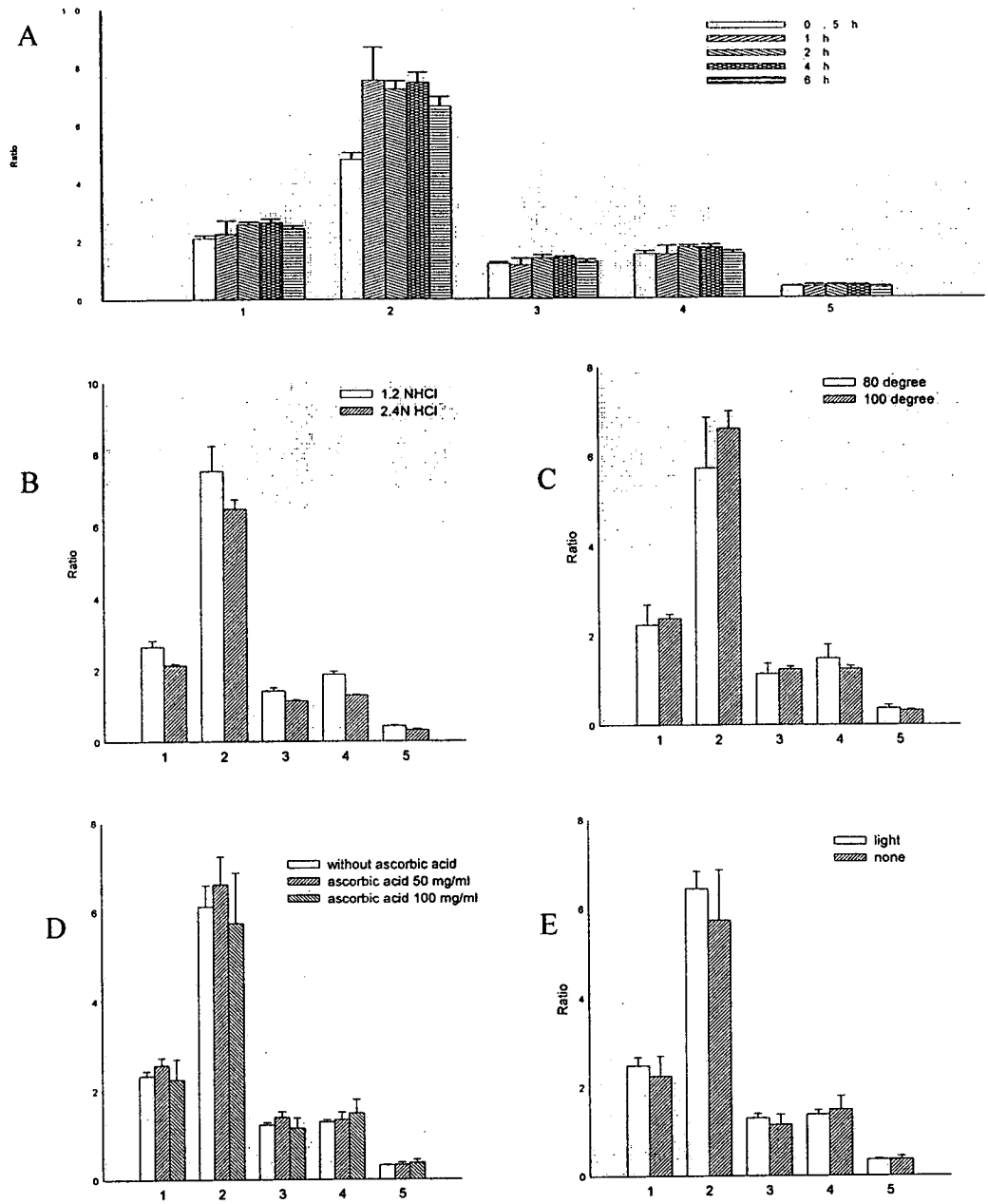

Fig 19 Histograms of aloe-emodin, rhein, emodin, chrysophanol and physcion contents in *Rheum officinale* Baill. decoction after acid hydrolysis 1. aloe-emodin 2. rhein 3. emodin 4. chrysophanol 5. physcion

A: the time effect on acid hydrolysis; B: the influence of hydrogen chloride concentration on acid hydrolysis; C: the temperature effect on acid hydrolysis D: the protection of constituent content with or without ascorbic acid; E: the influence of light on constituents

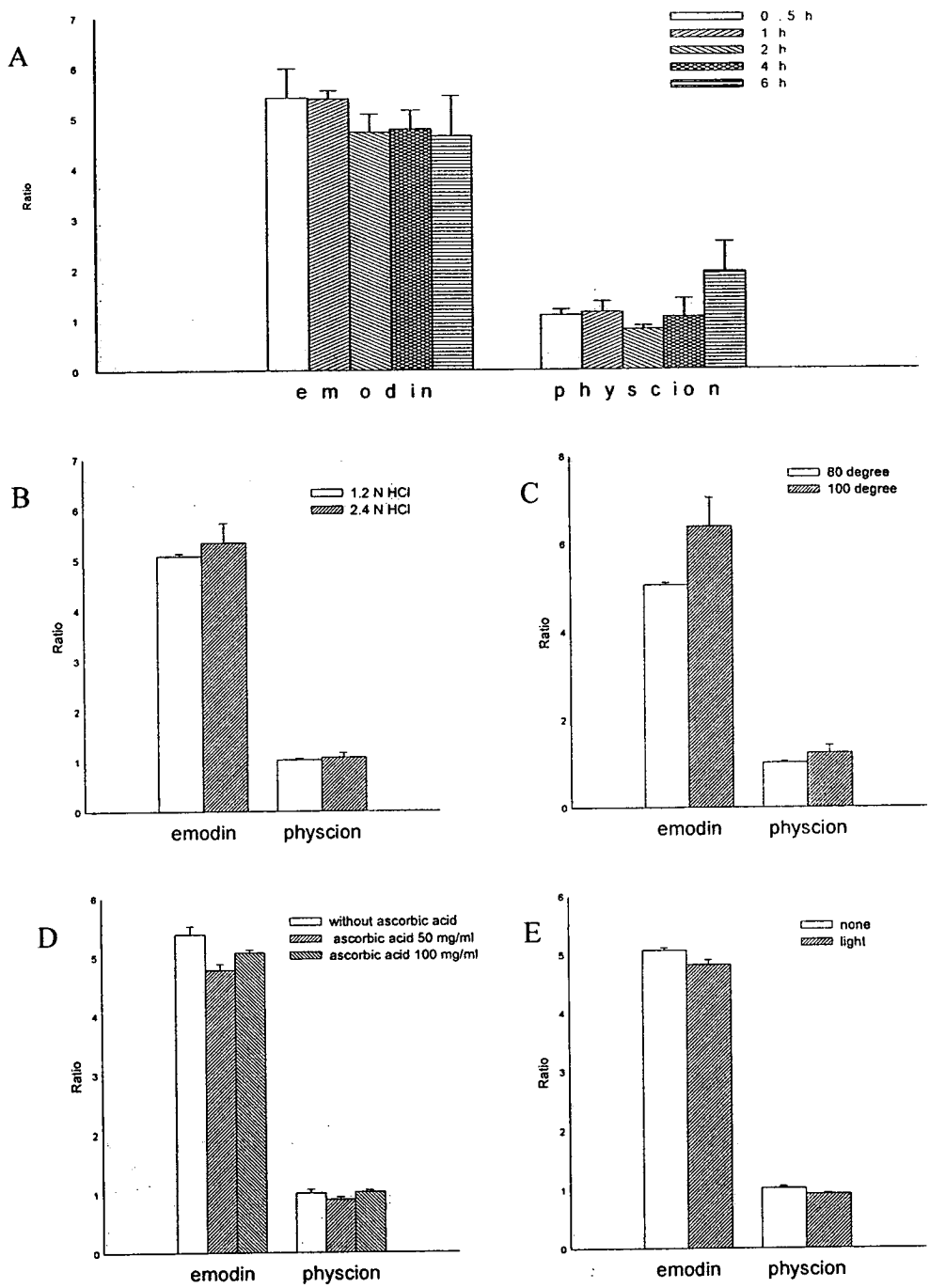

Fig 20 Histograms of emodin and physcion contents in crude *Polygonum multiflorum* Thunb. decoction after acid hydrolysis

A: the time effect on acid hydrolysis; B: the influence of hydrogen chloride concentration on acid hydrolysis; C: the temperature effect on acid hydrolysis D: the protection of constituent content with or without ascorbic acid; E: the influence of light on constituents

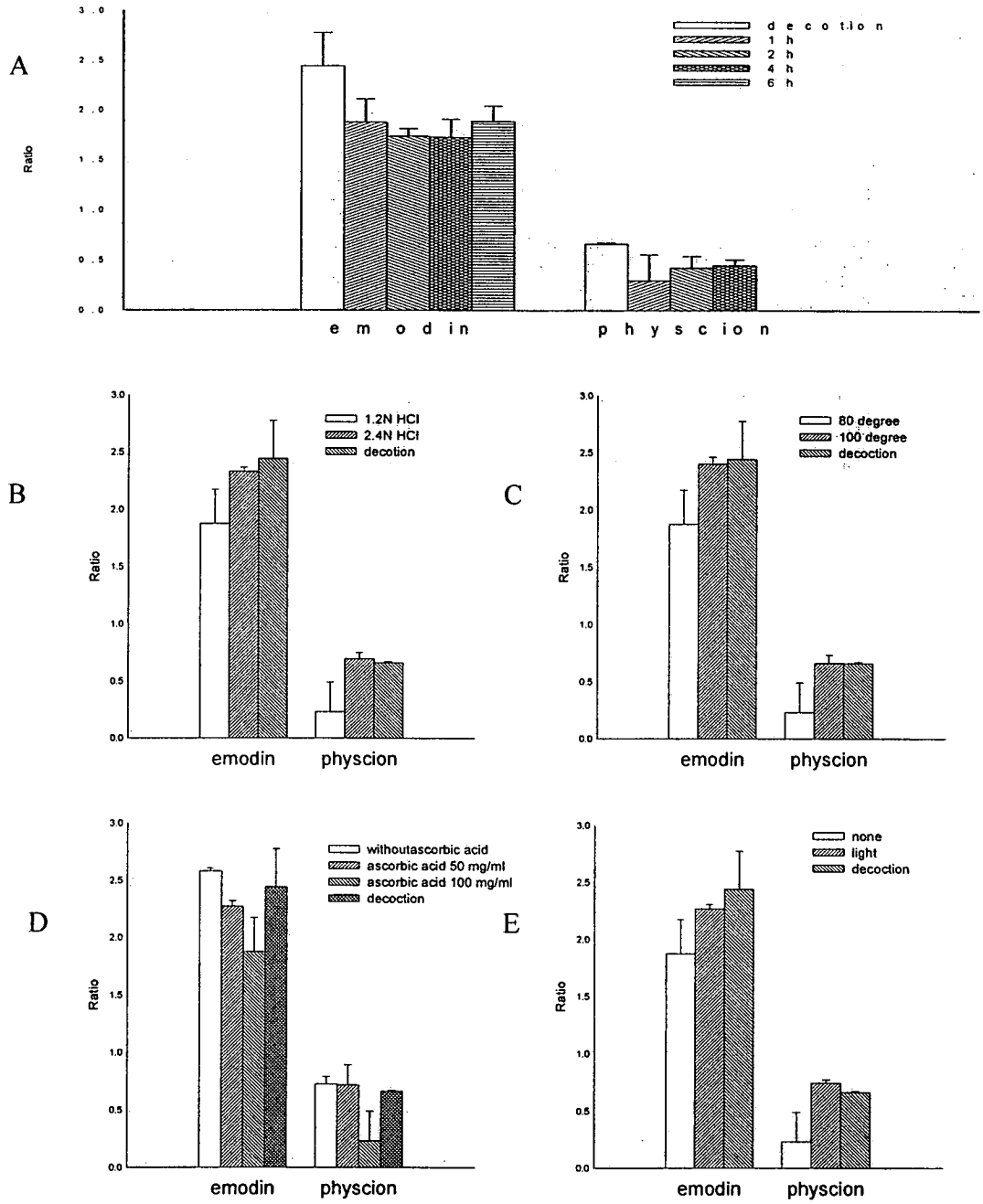

Fig 21 Histograms of emodin and physcion contents in processed *Polygonum multiflorum* Thunb. decoction after acid hydrolysis

A: the time effect on acid hydrolysis; B: the influence of hydrogen chloride concentration on acid hydrolysis; C: the temperature effect on acid hydrolysis D: the protection of constituent content with or without ascorbic acid; E: the influence of light on constituent

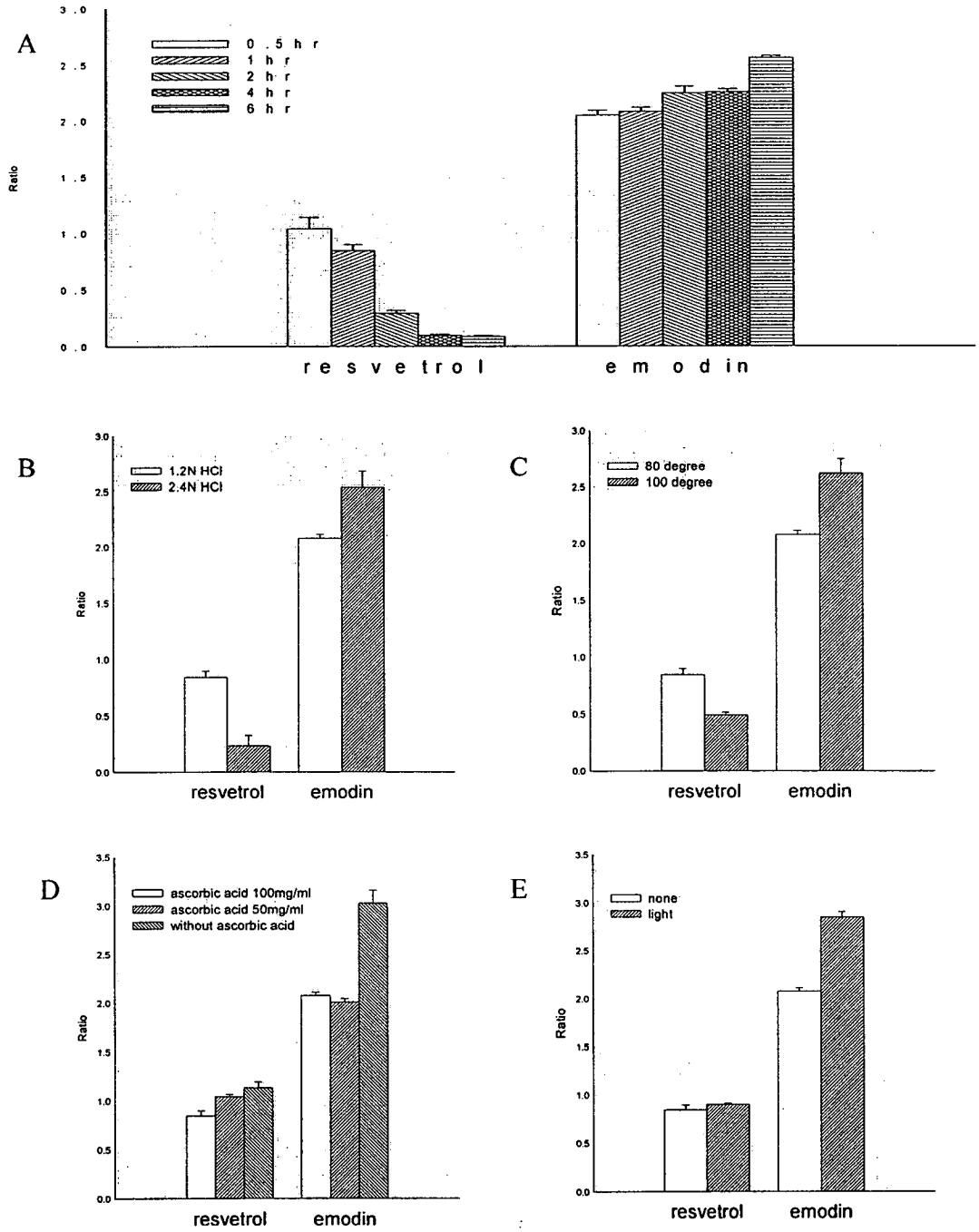

Fig 22 Histograms of emodin and resveratrol contents in *Polygonum cuspidant* Sieb. Et Zuce. decoction after acid hydrolysis
A: the time effect on acid hydrolysis; B: the influence of hydrogen chloride concentration on acid hydrolysis; C: the temperature effect on acid hydrolysis D: the protection of constituent content with or without ascorbic acid; E: the influence of light on constituents

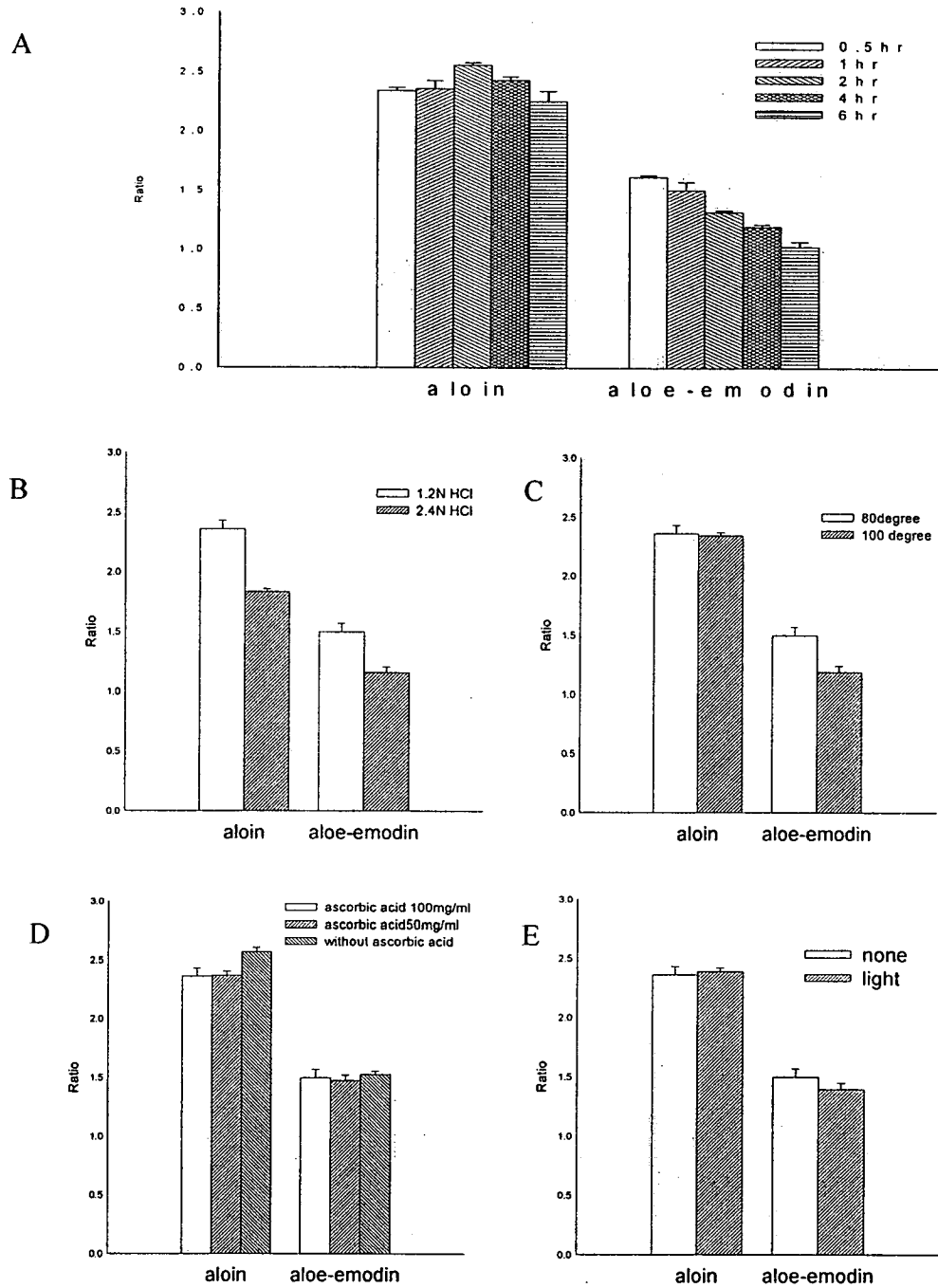

Fig 23 Histograms of aloe-emodin and aloin contents in *Aloe ferox* Miller. decoction after acid hydrolysis

A: the time effect on acid hydrolysis; B: the influence of hydrogen chloride concentration on acid hydrolysis; C: the temperature effect on acid hydrolysis D: the protection of constituent content with or without ascorbic acid; E: the influence of light on constituents

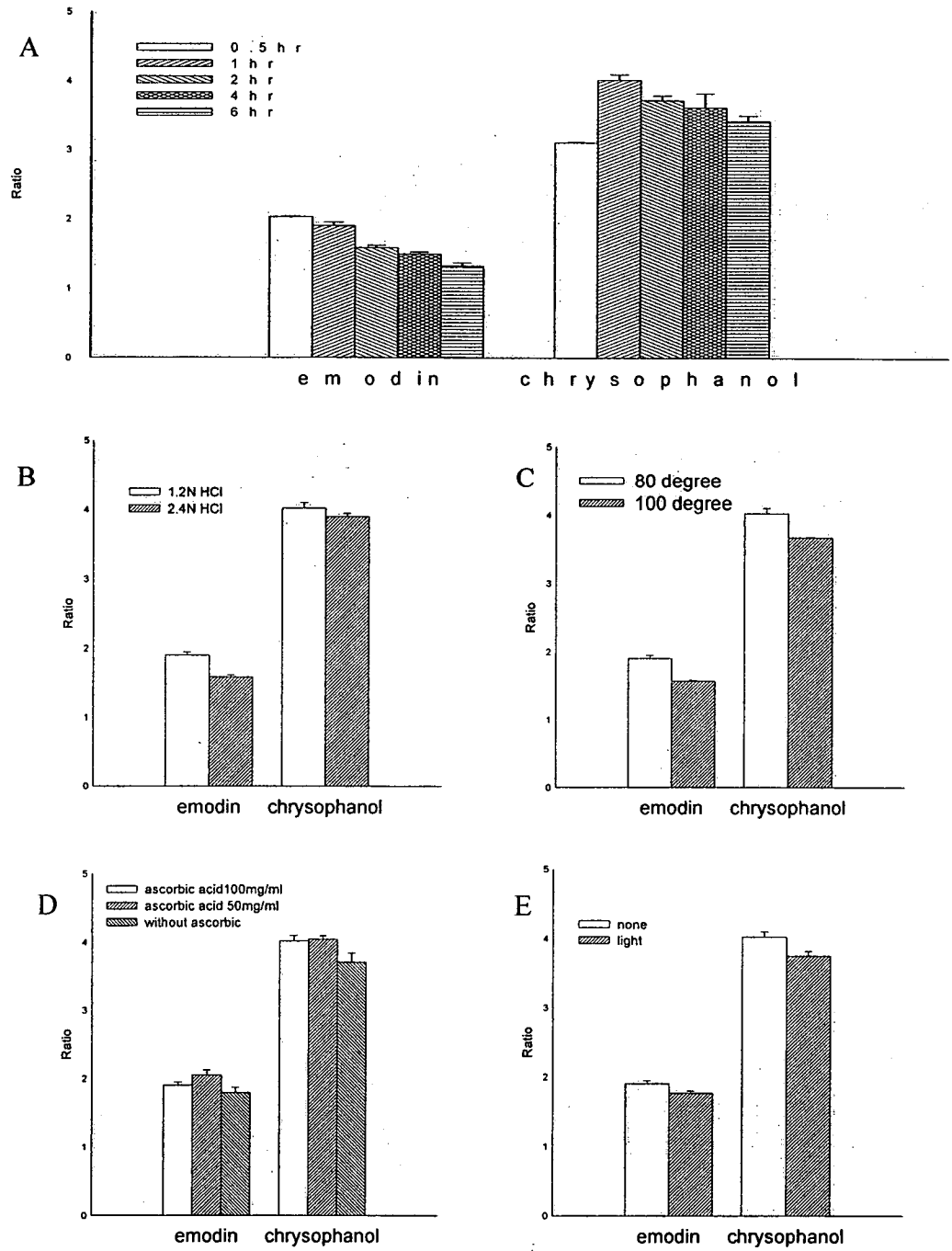

Fig 24 Histogram of emodin and chrysophanol contents in *Rumex japonicus* decoction after acid hydrolysis

A: the time effect on acid hydrolysis; B: the influence of hydrogen chloride concentration on acid hydrolysis; C: the temperature effect on acid hydrolysis D: the protection of constituent content with or without ascorbic acid; E: the influence of light on constituents

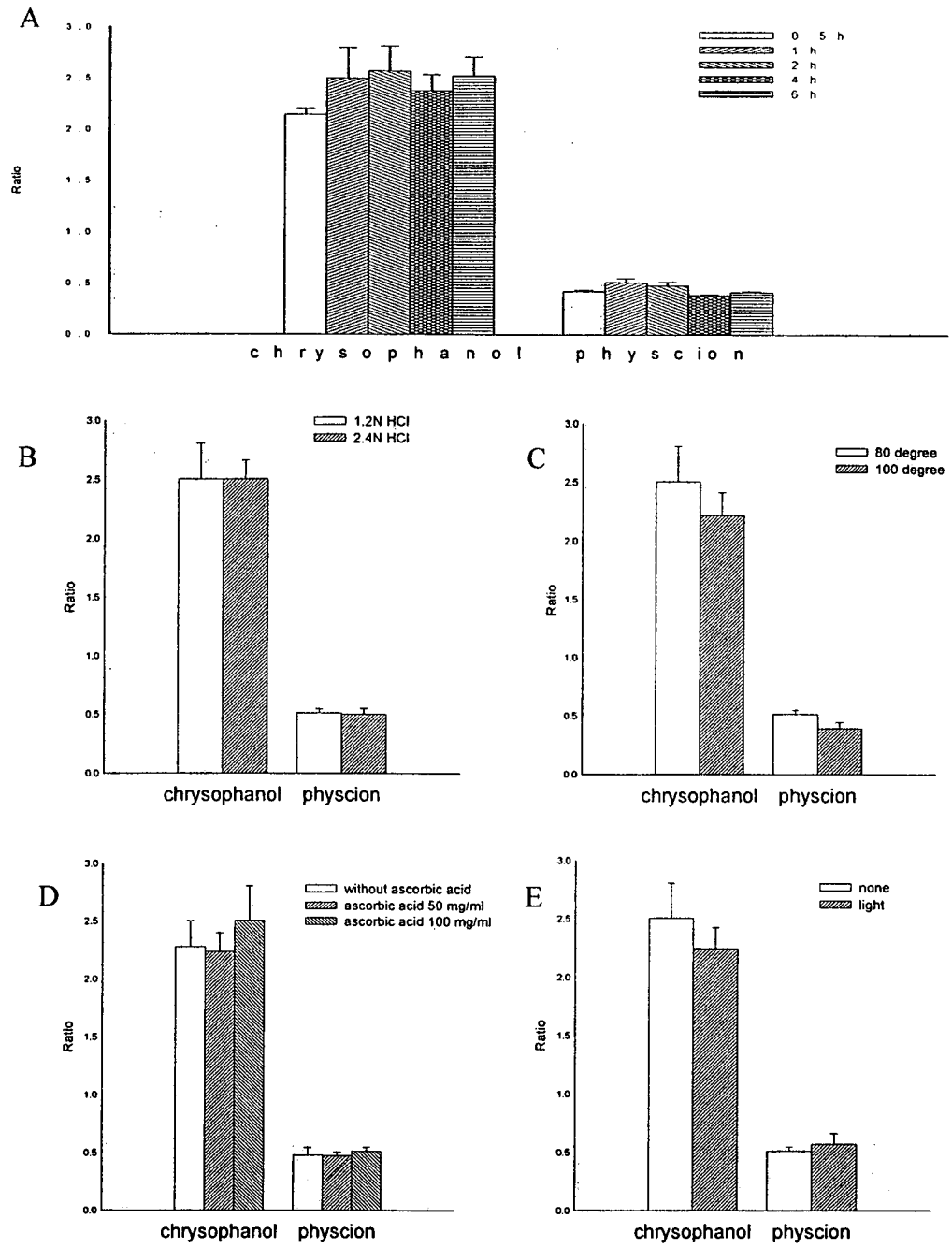

Fig 25 Histograms of chrysophanol and physcion contents in Cassiae torae semen decoction after acid hydrolysis

A: the time effect on acid hydrolysis; B: the influence of hydrogen chloride concentration on acid hydrolysis; C: the temperature effect on acid hydrolysis D: the protection of constituent content with or without ascorbic acid; E: the influence of light on constituents

行政院衛生署中醫藥委員會95年度委辦研究計畫成果報告自我評估表

計畫名稱	中藥多酚配醣體定量方法之建立	計畫編號	CCMP95-RD-021
執行機構	中國醫藥大學 藥用化妝品系	主 持 人	溫國慶

自我評估項目：

一、研究方法是否與原計畫之設計相同

■完全相同 □少部分不同 □ 大部分不同 □ 完全不同

未"完全相同"者請說明不同之項目與原因：

二、研究成果內容與原計畫書目的之相符程度

■ 完全相符 □ 少部分不符 □ 大部分不符 □ 完全不符

未"完全相符"者請說明不符之項目與原因：

三、研究成果是否達成預期目標

□ 已達成且超過預期目標 ■ 已達成預期目標 □ 部分未達成 □ 均未達成

均請說明，未達成目標請務必說明原因：

四、對該研究成果應用價值之自我評估：（可複選）

□ 可列為中醫師或中藥從業人員在職繼續教育專題演講之內容

□ 具出版專籍參考之價值

■ 具發表於學術期刊之價值

□ 具備申請專利或技術移轉之潛力

□ 其他 _____

五、其他

計畫主持人簽章	溫國慶	日 期	95年11月日

註：本表電腦檔案可於"http://www.ccmp.gov.tw"上取得