琉璃苣种子油中γ-亚麻酸的分析和制备

白求恩医科大学（长春 130021） 孙启良*

摘要 气质联用法分析琉璃苣种子油中8种脂肪酸，其药用成分γ-亚麻酸含量为20.01%；多级尿素包合——减压蒸馏法分离出γ-亚麻酸甲酯，其纯度为92.80%，收率50%。

关键词 琉璃苣 γ-亚麻酸 尿素包合——减压蒸馏

琉璃苣*Borago officialis* L.为紫草科草本植物，用其种子；原产日本和加拿大，目前我国已经引种，并开始出口。文献[1,2]报道其种子油主要脂肪酸成分γ-亚麻酸具有降血脂，抗血栓和抑制血小板聚集等药理作用，现采用气质联用法进一步确定琉璃苣种子油中脂肪酸类的化学结构和含量，为其药用研究提供依据。同时探讨尿素包合法分离γ-亚麻酸的效果。

1 琉璃苣种子油的提取

琉璃苣种子（由黑龙江省种子公司提供）粉碎后，按常法用石油醚（30～60℃）提取3次，回收溶剂得淡黄色油状物，收率31%。

2 琉璃苣油总脂肪酸的制备

将适量琉璃苣油，氢氧化钾，95%乙醇（W：W：V=5：3：9）混合，于沸水浴上回流皂化3h至完全。以18%盐酸酸化，水洗至中性，干燥得总脂肪酸。

3 琉璃苣油总脂肪酸甲酯的制备

将总脂肪酸、甲醇、浓硫酸（W：V：W=30：20：0.7）混合，于水浴上回流3h，水洗至中性，干燥得总脂肪酸甲酯。

4 琉璃苣脂肪酸甲酯的分离——γ-亚麻酸甲酯的制备

琉璃苣脂肪酸甲酯，尿素，95%乙醇（W：W：V=1：2：6）混合，于水浴上回流至溶，室温下放置24h抽滤。向滤液中加入适量的尿素（V：W=10：1），如上操作，同样溶解和结晶，重复2次。最后滤液浓缩至干，加15%盐酸酸化，水洗至中性，真空干燥后，减压蒸馏（162～164℃/133.32Pa）得淡黄色油状物为γ-亚麻酸甲酯，收率50%，纯度92.80%。

5 气相色谱—质谱联用分析条件和结果

5.1 色谱条件：日本岛津GC-5A型气相色谱（联数据处理机），氢火焰离子化检测器，氮气流速25ml/mi，空气流速400ml/min，氢气流速35ml/min；柱温185℃，检测室215℃，气化室250℃；柱长3m，直径3mm；载体：9%DEGS，60～80目Chromosorb W/AM DMCS。

5.2 质谱条件：VG-Quattro四极串联质谱仪；电子轰击源70eV，离子源温度200℃。

上述条件，将总脂肪酸甲酯和γ-亚麻酸甲酯进行GC-MS-计算机联用分析，测得质谱与标准图谱对照，鉴定出8种脂肪酸组分，气相色谱分析各组分的百分含量，结果见表。

6 讨论

6.1 本文阐明琉璃苣种子油中γ-亚麻酸的含量为20.01%，是月见草油和黑加仑种子油的3.08倍和1.25倍[3]，除倒提壶*Symphytum officinale* L.种子油中γ-亚麻酸的含量为27%

*Address: Sun Qiliang, Bethune Medical Uuiversity, Changchun

表 琉璃苣种子油脂肪酸甲酯尿素包合前后气质联用分析结果

峰号	脂肪酸甲酯	MS数据		GC数据		
		分子离子峰	碎片离子峰	保留时间(min)	尿素包合前(%)	尿素包合后(%)
1	软脂酸甲酯	270	239, 227, 185, 171, 149, 143, 129, 115, 101	4.269	12.25	—
2	硬脂酸甲酯	298	255, 199, 143, 129, 111, 101	8.137	4.26	—
3	油酸甲酯	296	266, 264, 222, 220, 180, 166, 151, 137, 115	8.834	19.12	—
4	亚油酸甲酯	294	263, 262, 220, 178, 164, 149, 135, 123, 110	1.5020	37.18	5.87
5	γ-亚麻酸甲酯	292	194, 175, 163, 150, 133, 117, 105	11.966	20.01	92.85
6	花生酸甲酯	326	295, 283, 241, 227, 199, 185, 143, 129, 101	15.693	0.79	1.28
7	11-廿碳一烯酸甲酯	324	293, 292, 274, 251, 250, 248, 208, 194, 141	16.862	4.14	—
8	13-廿二碳一烯酸甲酯	352	320, 278, 236, 220, 137, 123, 111	33.217	2.26	—

[4]外，琉璃苣是γ-亚麻酸含量较高的植物资源。

6.2 采用尿素包合法除去分子量较小的脂肪酸，再用真空蒸馏法除去分子量较大的脂肪酸，使琉璃苣种子油中γ-亚麻酸的分离适于大量制备，其纯度高达92.80%，收率50%[5]。

6.3 本文为前列腺素E_1的合成提供了新的资源，前列腺素E_1的合成路线是以γ-亚麻酸为原料经化学合成得二高-γ-亚麻酸[6]，再用羊精囊酶转化为前列腺素E_1[7]。该路线与动物中前列腺素E_1生物合成途径一致。植物中是否有相同的特点有待进一步证明，作者已阐明葱属植物中含有多种前列腺素[8~10]，Bild证明了大豆获得的脂氧酶-2使标记花生四烯酸转化为前列腺素$E_{2\alpha}$[11]，从植物中寻找出一种酶，使γ-亚麻酸或为二高-γ-亚麻酸，便可证明植物中具有相同生物合成途径。

致谢：中国科学院长春应用化学研究所测定气质联用。

参 考 文 献

1 Craig B M, et al. J Am Oil Chemist's Soc, 1964, 41(3): 209
2 Kleiman R, et al. J Am Oil Chemist's Soc, 1964, 41(7): 459
3 迟仁智, 等. 中草药, 1990, 21(2): 14
4 Traitler H, et al. J Am Oil Chemst's Soc, 1988, 65(5): 755
5 郭 煜, 等. 中草药, 1990, 21(8): 345
6 洪 盈, 等. 沈阳药学院学报, 1987, 4(4): 275
7 谷月卿, 等. 白求恩医科大学学报, 1985, 11(1): 5
8 孙启良, 等. 中草药, 1988, 19(4): 146
9 孙启良, 等. 中草药, 1988, 19(6): 249
10 孙启良, 等. 中草药, 1991, 22(4): 150
11 Bild G S, et al. J Biol Chem, 1978, 253(1): 21

(1994-12-06收稿)

ABSTRACTS OF ORIGINAL ARTICLES

Studies on the Chemical Constituents of Sagittate Epimedium (*Epimedium sagittatum*)

Wu Qinli, Zhao Yanqing, Li Zhulian

From *Epimedium sagittatum* Maxim, three compounds were isolated. They are β-sitosterol, β-sitosterolglucoside and a new flavone compound I. By spectroscopic and chemical methods, I was elucidated as 5-hydroxy-6, 7-dimethoxy-3′, 4′-methylene-dioxyflavone.

(Original article on page451)

Studies on the Chemical Constituents of Korean Epimedium(*Epimedium koreanum*)

Li Wenkui, Zhang Ruyi, Xiao Peigen

Eight compounds were isolated from the aerial parts of *Epimedium koreanum* Nakai. Their structures were identified as daucosterol(Ⅰ), icariin(Ⅱ), epimedoside-C(Ⅲ), hyperoside(Ⅳ), quercetin (Ⅴ), icariside Ⅰ(Ⅵ), baohuoside-Ⅰ(Ⅶ)and icaritin (Ⅷ) by physico-chemical properties and UV, IR, ^{1}HNMR, ^{13}CNMR and MS. Among them Ⅰ, Ⅳ, Ⅴ, Ⅵ, and Ⅷ were isolated from the plant for the first time.

(Original article on page 453)

Analysis and Preparation of γ-Linolenic Acid from Seed Oil of Common Borage (*Borago officinalis*)

Sun Qiliang

GC-MS analysis showed that seed oil of *Borago offciinalis* contains up to 20.01% γ-linolenic acid. Urea fractionation- vacuum distillation separation allowed us to obtain fractions of methyl-γ-linolenate of 92.8% purity at a yield of 50%.

(Original article on page 456)

Determination of Flavonoids in Leaf Extract Preparations of Ginkgo (*Ginkgo biloba*) by HPLC

Liu Songqing, Tang Xianzhe, Ma Wenxiu, et al

Quantitative HPLC method was developed for the determination of flavonoids in extract preparations of leaves of *Ginkgo biloba* L. YWG-C_{18} column was used with a mobile phase of methanol-water-glacial acetic acid (40∶57.5∶2.5, V/V) and detected at 254nm. The flow rate was 1.0ml/min. Ten Peaks were observed. Rutin was used as external standard and the calibration curve was linear over the rang of 0.5～2.5μg ($r=0.9996$). The extraction recovery was 104.2%(RSD=3.3%). Compared with the results of chemical colorimetric analysis, the method has a better reproducibility and more information about the flavonoids in *G. biloba* can be obtained.

(Original article on page 461)

Comparative Study on the Extraction Process for the Preparation of Maxingshigan Pill

He Qun, Luo Jieying, Deng Qingping

Influence of extraction process on the quality of Maxingshigan pills was studied. Guided by the amount of ephedrine in the extraction as determined by dual wavelength TL-