Experimental

Mucochloric acid—This was prepared from furfural according to a slight modification of the previously reported method⁴⁾.

1000 cc. of concentrated hydrochloric acid was cooled to 0° by an ice-salt mixture. A mixture of 80 g. commercial furfural and 320 g. of manganese dioxide was added in small portions, care being taken that the temperature does not rise above 10°. Addition required About 3 hours. After the addition was complete, the reaction mixture was stirred at a room temperature for 0.5 hour. The reaction flask was then heated slowly with stirring at 60° in a water bath, and at this point, an additional 140 g. of manganese dioxide was added in small portions over a period of 1 hour, while the temperature was raised to 80°. After the addition, the temperature was raised to 100° and was held there until a black color of the reaction mixture turned to red brown. The reaction mixture was decanted while hot into a beaker, and allowed to cool slowly. After standing overnight in a cool place, the crystals were filtered with suction and washed with cold water. A light-colored product, m.p. 125°, was obtained, which is sufficiently pure for the next step. The yield was 85–108 g. (60–77%), which considerably depended on the quality of manganese dioxide.

2-Amino-5-chloropyrimidine—6.0 g. of dried guanidine nitrate was added to a solution of 2.5 g. of sodium in 50 cc. of absolute methanol, and the mixture was warmed at 30–40°, protected with a dry tube, with stirring for 20 minutes. To this mixture a solution of 5 g. of mucochloric acid in 30 cc. of absolute methanol was added dropwise with stirring over a period of 0.5 hour, while the temperature was gradually raised to 60°. After the addition was complete, the temperature was raised to 65° and was held there with stirring for 1.5 hours. The reaction mixture was filtered while hot and washed with warm methanol. The combined filtrate was evaporated to dryness under a reduced pressure and the dark brown residue was dissolved in 12 cc. of water. The solution was acidified with 20% sulfuric acid and the solid (III) which separated was filtered, washed and dried (4.2 g.). On dry distillation of this solid (III), 2-amino-5-chloropyrimidine sublimed to shiny, white platelets, m.p. 230–232°. The yield was 2.3 g. (60%, based on mucochloric acid). After one resublimation the melting point was 235°

(Received July 23, 1952)

Toshikazu Harada : Pharmaceutical Studies on Ferns. V. Quantitative Determination of Crude Filicin.

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As described in the preceding report, phloroglucide has histochemically been found in several ferns, which grow throughout holartic¹⁾ and neotropical²⁾ floral zone.

In the present paper, the amounts of extractives and those of phloroglucide, i.e. crude filicin, in domestic ferns are described.

I wish to express my gratitude to Dr. Y. Asahina and Dr. S. Shibata for their valuable advices.

Experimental and Results

Extractives—100 g. of the rhizome and stipes of various ferns, reduced to coarse powder and previously dried to constant weight over sulfuric acid, were digested 3 times with ether, the ethereal solution filtered, combined, and evaporated on a water bath at 50°, and the remaining ether evaporated spontaneously in a warm place to constant weight.

Amount of crude filicin.—After warming the above extractives on a water bath and stirring until thoroughly mixed, a sample of 3 g. was dissolved in ether, and the phenolic and acidic constituents comprising crude filicin removed by shaking the ether with several portions of 5% barium hydroxide solution. The barium hydroxide solutions were filtered, combined, acidified to liberate the phenolic and acidic substances, and these extracted with ether. After filtration the ethereal solution was evaporated and the residue of crude filicin dried to constant weight at 100°.

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1) This Journal, **71**, 506 (1951).

2) Ibid., **72**, 153 (1952).

Table I.

Name of Plants	Date Collected	Locality Collected	Extractive %	Crude filicin %
<i>Dryopteris crassirhizoma</i> Nakai	Oct. 1949	Mt. Hiei, Japan	5.49	28.42
	July 1950	Kamiribetsu, Japan	4.83	27.70
		average	5.16	28.06
<i>Dryopteris uniformis</i> Makino	Oct. 1947	Mt. Sobo, Japan	8.13	6.02
	Aug. 1950	Cape Ashizuri, Japan	6.32	4.77
	Nov. 1951	Jinmuzi, Japan	8.58	6.14
	Nov. 1951	Inuyama, Japan	8.49	6.55
		average	7.88	5.87
<i>Dryopteris lacera</i> O. Kuntze	Aug. 1942	Yaku Is., Japan	8.92	10.97
	Oct. 1947	Mt. Amagi, Japan	9.47	11.54
	Aug. 1949	Mt. Gozaisho, Japan	8.93	10.81
	Jan. 1950	Mt. Kinka, Japan	11.32	13.64
		average	9.66	11.74
<i>Dryopteris tokyoensis</i> C. Chr.	Oct. 1949	Zyokozi, Japan	5.10	25.92
<i>Dryopteris cycadina</i> C. Christensen	July 1945	Sozan, Formosa	6.57	28.12
	Oct. 1947	Mt. Amagi, Japan	7.18	29.46
	Sep. 1950	Cape Sata, Japan	7.34	30.38
	Nov. 1950	Mt. Tanigumi, Japan	7.75	34.04
		average	7.21	30.50
<i>Dryopteris Sieboldii</i> O. Kuntze	Aug. 1942	Nagasaki, Japan	6.24	17.98
	Aug. 1947	Shimizu, Japan	6.40	18.66
		average	6.32	18.32
<i>Dryopteris Bissetiana</i> C. Christensen	Aug. 1947	Shimizu, Japan	7.98	14.38
	Nov. 1947	Mt. Amagi, Japan	8.72	15.30
	Aug. 1949	Mikkahi, Japan	8.54	14.82
	Jan. 1950	Shingu, Japan	9.12	15.38
	Nov. 1950	Jinmuji, Japan	10.51	15.82
	Oct. 1951	Mt. Hohonokawa, Jap.	8.83	15.02
		average	8.95	15.12
<i>Dryopteris Yabei</i> Hayata	April 1944	Vago, Philippines	6.42	10.96
	July 1944	Wasile, Indonesia	8.32	13.68
		average	7.37	12.32
<i>Dryopteris sordidipes</i> Tagawa	Mar. 1937	Shinten, Formosa	7.98	13.52
	Aug. 1942	Yaku Is, Japan	8.91	14.56
	July 1945	Naha, Okinawa	9.27	15.12
		average	8.72	14.40
<i>Dryopteris erythrosora</i> O. Kuntze	Mar. 1944	Baguio, Philippines	6.07	13.12
	Aug. 1947	Shimizu, Japan	5.92	12.98
	Oct. 1947	Mt. Amagi, Japan	6.22	13.34
	Jan. 1950	Shingu, Japan	6.84	15.97
	Sep. 1950	Cape Satsuma, Japan	6.12	13.18
	Jan. 1951	Kibune, Japan	7.05	15.65
		average	6.37	14.04
<i>Dryopteris cystolepidota</i> C. Christensen	Jan. 1950	Mt. Togoku, Japan	5.72	11.47
	Nov. 1950	Zushi, Japan	5.39	8.93

	Jan. 1951	Inuyama, Japan	5.50	10.98
	Nov. 1951	Mt. Kinka	4.71	8.86
		average	5.33	10.06
			5.36	8.44
<i>Dryopteris fuscipes</i> C.Christensen	May 1937	Suigen, Formosa	6.12	11.38
	Aug. 1942	Yaku Is., Japan	6.28	12.46
	Oct. 1951	Mt. Hohonokawa, Jap.	5.92	10.76
		average	4.64	12.46
<i>Dryopteris Labordei</i> C. Christensen	April 1937	Raisha, Formosa	5.50	15.28
	Jan. 1950	Kinkazan, Japan	5.07	13.87
		average	7.08	14.12
			5.47	11.32
<i>Dryopteris pseudoerythrosora</i> Kodama	Jan. 1950	Shingu, Japan	5.84	11.55
	Oct. 1950	Cape Ashizuri, Japan	6.13	12.33
	Dec. 1950	Kinkazan, Japan		
		average		

(Received June 19, 1952)

Shoji Shibata and Akira Kasahara : Studies on the Evaluation of Crude Drugs. III*. A New Detection Method for Flavanones.

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As a reagent for color reaction of flavonoids, magnesium, and hydrochloric acid are generally used¹⁾. Recently, Pew²⁾ reported that zinc and hydrochloric acid could be employed to detect 3-hydroxyflavanones (flavanonols). Shimizu³⁾ subsequently established that Pew's reagent also gives positive coloration with flavones possessing no free hydroxyl in the 3-position. By the above reactions, it should be noted that it would be difficult to distinguish flavone (including flavonol) and flavanone (including flavanonol).

We briefly describe here a specific microdetection method of flavanone, which was needed for chemico-pharmacognostical investigations. We found out that magnesium acetate which was previously reported by us on a reagent for hydroxyanthraquinones⁴⁾ gives no obvious coloration with flavonoid but exhibits a distinct sky-blue fluorescence with flavanones under ultraviolet irradiation. It should be emphasized that this reaction would enable the distinction of flavanones from other members of flavonoids.

Procedure : To a spot of the test solution on a filter paper, methanolic magnesium acetate solution was sprayed and dried on heating. The coloration under ordinary light and the color of fluorescence under ultraviolet irradiation were observed. A control test using 1% ethanolic aluminum chloride solution was also carried out.

Result :

* Part II: This Journal, **72**, (1952).

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1) cf. J. Shinoda : This Journal, **48**, 214 (1928).

2) J. C. Pew : J. Am. Chem. Soc., **70**, 3031 (1948).

3) M. Shimizu : This Journal, **72**, 338 (1952).

4) S. Shibata : This Journal, **61**, 103 (1941); S. Shibata, M. Takido, O. Tanaka : J. Am. Chem. Soc., **72**, 2789 (1950).