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COUMARINOLIGNOIDS, CLEOMISCOSIN A AND CLEOMISCOSIN B, FROM *AESCULUS TURBINATA*

HITOSHI TANAKA, ICHIRO KATO, KAZUHIKO ICHINO, and KAZUO ITO*

Faculty of Pharmacy, Meijo University, Yagoto, Tempaku, Nagoya 468, Japan

Aesculus turbinata B. (Hippocastanaceae) is a tall deciduous tree widely distributed in the moutains of Japan. Seeds of *A. turbinata* have been used as food. Previous chemical studies have shown that this plant contains β-sitosterol, four simple coumarins (fraxetin, fraxin, esculetin, and esculin) (1), a flavonoid (2), and triterpenoids (3). We now describe the isolation of the coumarinolignoids, cleomiscosin A and cleomiscosin B, from the bark of *A. turbinata*. Cleomiscosin A was identical with an authentic sample (4,5) by direct comparison (mmp, ms, ^{1}H-nmr, ^{13}C-nmr, and ir spectra), and cleomiscosin B was identified by direct comparison with an authentic specimen (6), which we synthesized. Cleomiscosin A has cytotoxic activity (7) and has been previously isolated from *Cleome viscosa* (Capparidaceae) (4,5), *Simaba multiflora, Soulamea soulameoides* (Simaroubaceae), and *Matayba arborecens* (Sapindaceae) (7). Cleomiscosin B is recently shown to have antihepatotoxic activity (8) and has been isolated from *C. viscosa* (5). This is the first reported isolation of the coumarinolignoids from a member of the Hippocastanaceae.

EXPERIMENTAL

PLANT MATERIAL.—*A. turbinata* was collected near Takayama, Gifu Prefecture, Japan, in July 1984. A voucher specimen is deposited at our department.

EXTRACTION AND ISOLATION.—Air-dried bark (7.56 kg) of *A. turbinata* was extracted with MeOH. The extract was evaporated, and a small amount of the concentrate was extracted with EtOAc to give fraxin (50 mg). The major portion of the concentrate was partitioned between H_2O/MeOH and hexane, and between H_2O/MeOH and EtOAc. The EtOAc soluble fraction was chromatographed on a silica gel column using C_6H_6-EtOAc (5:1) to afford scopoletin (2.4 g), esculetin (30 mg), fraxetin (1.0 g), and isoscopoletin (50 mg), mp 185-186° [lit. (9): mp 185°, lit. (10): mp 185-187°, lit. (11): mp 187-190°]. These coumarins (fraxin, fraxetin, esculetin, and scopoletin) were identified by direct comparison (mmp, ir, ms, and ^{1}H nmr) with authentic specimens. A mixture of coumarinolognoids was further purified by chromatography over silica gel using $CHCl_3$-MeOH-EtOAc (9:1:1) to provide cleomiscosin A (150 mg), mp 250-252° [lit. (4,5): mp 247-249°, lit. (7): mp 250-252°, lit. (12): mp 257°] and cleomiscosin B (15 mg), mp 273-275° [lit. (5): mp 274°, lit. (6): mp 275-276°, lit. (12): mp 275-278°].

Full details of the isolation and identification of the compounds are available on request to the senior author.

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AUCUBIN FROM *SUTERA DISSECTA*

P. FORGACS, J. PROVOST, and A. JEHANNO

Centre de Recherches, Laboratoire Roger Bellon 90, rue Marcel Bourdarias, 94140 Alfortville, France

Scrophulariaceous species are known to contain iridoids (1). Several species used medicinally have been examined for their chemical constituents. In the literature, nothing could be found concerning the constituents of *Sutera dissecta* Roth (Scrophulariaceae). We report the isolation and identification of aucubin.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Uv spectra were run in MeOH on a Perkin-Elmer 137 uv recording spectrophotometer and ir spectra in KBr pellets on a Perkin-Elmer 237; mps were determined on a Köfler hot-stage and microscope and were uncorrected; ^{1}H-nmr spectra were determined in D_2O using TMS as internal standard on a Brüker spectrospin 80; optical rotations were determined on a Zeiss polarimeter; elementary analyses were determined on a Perkin-Elmer 240 CHN; silica gel 60 Merck was used for column chromatography.

PLANT MATERIAL.—The plant was collected in January 1982, by Bhogilal C. Shah in the Indore district, India, and anthenticated by Dr. J. Guedes, Museum National d'Histoire Naturelle, Paris, France (82/207). An herbarium specimen of the plant material is being preserved in the laboratory.

EXTRACTION AND ISOLATION OF AUCUBIN.—The air-dried and powdered aerial parts (1 kg) of *S. dissecta* were defatted with hexane, extracted with EtOH-H_2O (8:2), and the solvent evaporated. The portion of the crude mixture soluble in absolute EtOH (76 g) was chromatographed on silica gel (60 Merck, 700 g) and eluted with EtOAc/MeOH mixtures of increasing polarity.

Fractions 11-13: eluent EtOAc-MeOH (9:1), gave a solid which crystallized from EtOH, yielded pure aucubin. Mp, ir, ^{1}H nmr, optical rotation and elemental analysis values are in agreement with those in the literature (2-3).

ENZYMATIC HYDROLYSIS OF AUCUBIN.—Aucubin (100 mg) was incubated with emulsin at 37° for 24 h. The aqueous layer afforded D-glucose which was identified by co-tlc and by analytical gc as its trimethylsilyl derivative.

ACETYLATION OF AUCUBIN.—Aucubin (500 mg) was treated with Ac_2O-pyridine, worked up in the usual manner to afford aucubin hexa-acetate.

Mp, ir, $[\alpha]_D$, ^{1}H nmr, of aucubin and aucubin hexa-acetate were found identical with authentic samples kindly supplied by Prof. F. Bailleul, U.E.R. de Pharmacie, Laboratoire de Pharmacognosie, Lille-Cedex 59045, France.

Full details of the isolation and identification of the compounds are available on request to the senior author.

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