Journal of Natural Products
Vol. 53, No. 2, pp. 498-499, Mar-Apr 1990

A NEW PTEROCARPAN FROM THE HEARTWOOD OF *CLADRASTIS PLATYCARPA*

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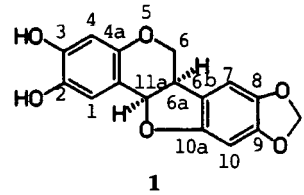
ABSTRACT.—A new pterocarpan, (−)-2,3-dihydroxy-8,9-methylenedioxypterocarpan [**1**], was isolated from the heartwood of *Cladrastis platycarpa* (Leguminosae), in addition to the known compounds maackiain, medicarpin, medicagol, daizein, genistein, prunetin, orobol, and piceatannol.

The genus *Cladrastis* (Leguminosae, subfamily Faboidae, tribe Sophoreae) has primitive characters and a close relationship to the genera *Maackia* and *Sophora* on the basis of morphology. The genus includes about six species, one of which is distributed in North America, the rest in East Asia (1). Two species, *Cladrastis platycarpa* (Maxim.) Makino and *Cladrastis sikokiana* (Makino) Makino, are known in southern Japan. The constituents of the Japanese species have been examined, and many isoflavones and their glycosides were characterized by Ohashi *et al.* (2). As part of our series of chemotaxonomic studies on the Leguminosae (3), especially directed to the genus *Sophora*, we describe in this paper the isolation and structure determination of phenolic constituents in the heartwood of *C. platycarpa*.

The dried and ground heartwood of *C. platycarpa* was extracted with CH_2Cl_2 followed by MeOH. The MeOH extract was fractionated between EtOAc and H_2O. The CH_2Cl_2 extract and the EtOAc-soluble portion were combined and subjected to cc on Si gel; further purification was made by repeated chromatography, and preparative tlc of the crude eluents resulted in the isolation of nine phenolic compounds (three pterocarpans, one coumestan, four isoflavones, and one stilbene) in addition to some other phenolics previously isolated. One of the pterocarpans, compound **1**, is new.

Compound **1** was obtained as a colorless powder. The spectral data are as follows: $[\alpha]^{24}D$ −25.6° (c = 0.1, MeOH); hrms m/z $[M]^+$ 300.0626 (calcd 300.0633 for $C_{16}H_{12}O_6$); uv (nm, MeOH) 305. In the ^1H-nmr spectrum, a characteristic set of four protons [δ 3.46–3.61 (2H, m), 4.15 (1H, dd), 5.42 (1H, d)] due to hydrogens at C-6 (2H), C-6a, and C-11a, respectively, suggested **1** had a pterocarpan skeleton. Furthermore, a methylenedioxy group (δ 5.91), four singlet protons in the aromatic region (δ 6.24, 6.44, 6.73, and 6.89), and two phenolic hydroxyl groups (δ 8.57 and 9.08) indicated that **1** had oxygen functions at C-2, C-3, C-8, and C-9. In the eims, two fragments at m/z 163 and 175 were regarded as the ions **1a** and **1b**, which led to the conclusion that the two hydroxyl groups were substituted at C-2 and C-3, and the methylenedioxy group was located at C-8 and C-9. The ^{13}C-nmr data shown in



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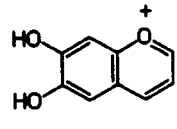
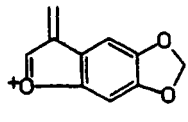


1a m/z 163



1b m/z 175

Table 1, the chemical shifts of which were confirmed by comparison with those of maackiain and medicarpine (4), support the proposed oxygenation pattern. Therefore, the structure of **1** was determined to be (−)-2,3-dihydroxy-8,9-methylenedioxypterocarpan [(−)-2-hydroxymaackiain], which is a new pterocarpan.

TABLE 1. ^{13}C-nmr Spectral Data of Compound **1** and Maackiain.

Carbon	Compound	
	1	Maackiain
C-1	116.2	132.3
C-2	140.2	109.9
C-3	146.9	160.8
C-4	103.5	103.1
C-4a	147.3	156.6
C-6	65.8	66.2
C-6a	40.2	40.4
C-6b	118.2	118.7
C-7	105.5	105.6
C-8	140.9	141.4
C-9	148.3	147.7
C-10	93.1	93.5
C-10a	153.7	154.0
C-11a	78.1	78.4
C-11b	110.2	111.6
OCH_2O	100.9	101.3

The other compounds, new to this species, were determined as maackiain, medicarpin, medicagol, daizein, genistein, prunetin, orobol, and piceatannol by spectral analysis.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Ms was obtained on JEOL JMS-D300 operating at 70 eV. ^{1}H- and ^{13}C-nmr spectra were taken on a JEOL JNM-GX 270 instrument at 270 MHz; chemical shifts were given in δ (ppm) with TMS as an internal standard. Tlc was carried out with Kiesel-gel 60F-254 (Merck). Fuji gel BW820-MH was used for cc.

PLANT MATERIAL.—The heartwood of *C. platycarpa* was collected at Miyama-cho, Gifu Prefecture, September 12, 1987, and the voucher specimen is on deposit in the Herbarium of Gifu Pharmaceutical University.

EXTRACTION AND ISOLATION.—The dried and powdered heartwood of *C. platycarpa* (1.5 kg) was extracted with CH_2Cl_2 (3 liters × 4) and MeOH (3 liters × 4) under reflux, successively. The MeOH-soluble portion was separated between EtOAc and H_2O. The CH_2Cl_2-soluble (15 g) and EtOAc-soluble (25 g) portions were separately subjected to cc on Si gel eluted with C_6H_6/EtOAc systems. Repeated rechromatography on Si gel and preparative tlc gave **1** (100 mg) as well as the other eight compounds. The known compounds identified by eims, ^{1}H nmr, and/or uv spectra are daizein (15 mg), prunetin (5 mg), orobol (8 mg), and piceatannol (22 mg) from the EtOAc extract, and maackiain (2.5 g), medicarpin (800 mg), medicagol (10 mg), and genistein (12 mg) from the CH_2Cl_2 extract.

(−)-2-HYDROXYMAACKIAIN [**1**].—A colorless amorphous powder: $C_{16}H_{12}O_6$; $[M]^+$ 300.0626 (calcd 300.0633); uv (nm, MeOH) 305; eims (*m/z*) (rel. int.) $[M]^+$ 300 (100), 175 (7), 163 (12), 162 (45); ^{1}H nmr (DMSO-d_6) δ 3.46–3.61 (2H, m, H-6β and -6a), 4.15 (1H, dd, J = 10.6, 5.1 Hz, H-6α), 5.42 (1H, d, 6.2 Hz, H-11a), 5.91 (2H, m, OCH_2O), 6.24 (1H, s, H-4), 6.44 (1H, s, H-10), 6.73 (1H, s, H-7), 6.89 (1H, s, H-1), 8.57 and 9.08 (1H, each s, OH); ^{13}C nmr see Table 1.

ACKNOWLEDGMENTS

The authors are grateful to Dr. J. Murata, Botanical Gardens, Faculty of Science, The University of Tokyo for identification of plant material.

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Received 17 July 1989