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A PHLOROGLUCINOL DERIVATIVE OF *DRYOPTERIS ABBREVIATA*

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Key Word Index—*Dryopteris abbreviata*; Aspidiaceae; fern; methylene-bis-methylphlorobutyrophenone; abbreviatin BB.

Abstract—A new phloroglucinol derivative, abbreviatin BB, has been isolated from *Dryopteris abbreviata*. Its structure was elucidated to be methylene-bis-methylphlorobutyrophenone on the basis of spectroscopic data.

Dryopteris abbreviata (DC.) Newman is a diploid species which grows locally in Europe and Turkey. It is a member of the *D. filix-mas* complex. These ferns contain variable amounts of filixic acid, large amounts of flavaspidic acid, and small amounts of *para*-aspidin[1, 2]. Widén *et al.*[3] examined the rhizomes of this species from Scotland and Italy and reported the occurrence of flavaspidic acid and filixic acid. In addition, Tanker and Coşkun[2] detected the presence of *para*-aspidin and some unknown compounds in the rhizomes of *D. abbreviata* collected from Turkey.

This paper deals with the isolation of a new phloroglucinol derivative lacking the filicinic acid ring, designated abbreviatin BB(1), from rhizomes of *D. abbreviata* of Turkish origin.

The HPLC chromatogram[4] of the crude filicin obtained by the magnesium oxide method[5] is shown in Fig. 1, indicating that this material also contains much flavaspidic acid and filixic acid, and a small quantity of 1. After removal of flavaspidic acid AB, the Et₂O solution of crude filicin was subjected to CC on Si gel with a cyclohexane–tetrahydrofuran(THF)

gradient to yield 1. 1 was re-crystallized from chloroform to give pale-yellow needles, mp 200–202°. (Found: [M]⁺ at *m/z* 432.1786; C₂₃H₂₈O₈ requires: 432.1783.)

The IR spectrum showed absorption bands at 3500 (OH), 2950 (CH), 1610 (C=O), 1570 (C=C), 1480, 1160

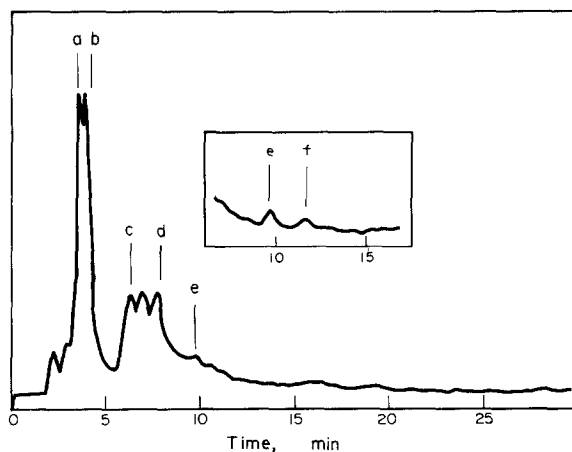
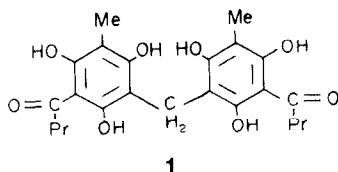


Fig. 1. HPLC chromatogram of the crude filicin. (a), Flavaspidic acid AB; (b), flavaspidic acid PB; (c), filixic acid ABA; (d), filixic acid ABB; (e), filixic acid BBB; (f), abbreviatin BB.

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and 1120 (C–O) cm^{-1} in potassium bromide. The UV spectrum showed maximum absorption at 228 ($\log \epsilon$ 4.37), 298 ($\log \epsilon$ 4.39) and 330 ($\log \epsilon$ 4.25) nm in ethanol, with a bathochromic shift to 333 nm on addition of dilute sodium hydroxide, and at 209 ($\log \epsilon$ 4.47), 228 ($\log \epsilon$ 4.45) and 289 ($\log \epsilon$ 4.48) nm in cyclohexane, indicating the presence of aromatic rings bearing free phenolic hydroxyl groups. The ^1H NMR spectrum gave signals at δ 0.99 (6H, *t*, $2 \times \text{COCH}_2\text{CH}_2\text{CH}_3$, $J = 7.6$ Hz), 1.73 (4H, *m*, $2 \times \text{COCH}_2\text{CH}_2\text{Me}$), 2.07 (6H, *s*, two-aromatic CH_3), 3.08 (4H, *t*, $2 \times \text{COCH}_2\text{CH}_2\text{Me}$, $J = 7.6$ Hz), and 3.80 (2H, *s*, =C–CH₂–C= group between two benzene rings). The signals at 5.92 (2H, *br*), 9.32 (2H, *br*) and 15.59 (2H, *br*) were all due to hydrogen bonded hydroxyl groups. The MS spectrum gave significant peaks at m/z 432 ($[\text{M}]^+ = \text{C}_{23}\text{H}_{28}\text{O}_9$), 222 ($\text{C}_{12}\text{H}_{14}\text{O}_4^+$), 210 ($\text{C}_{11}\text{H}_{14}\text{O}_4^+$), 207 ($\text{C}_{11}\text{H}_{11}\text{O}_4^+$), 181 ($\text{C}_9\text{H}_9\text{O}_4^+$), 179 ($\text{C}_9\text{H}_7\text{O}_4^+$) and 167 ($\text{C}_8\text{H}_7\text{O}_4^+$).

On the basis of the above data, structure **1** can be assigned as methylene-bis-methylphlorobutyrophenone, so far known only as a synthetic product[6]. Thus, **1** represents the first reported occurrence of a phloroglucinol derivative lacking the filicinic acid ring in European taxa of the *D. filix-mas* complex.

EXPERIMENTAL

^1H NMR spectrum was run at 200 MHz in CDCl_3 with TMS as int. standard. THF solns of the samples were

injected into a Shimadzu 841 HPLC instrument provided with a 150×4 mm i.d. Nucleosil 5 C_{18} column. UV detector was equipped with a 254 nm filter. THF– H_3PO_4 – H_2O (65:0.1:45) was used as the solvent system. The flow-rate was 0.4 ml/min, and the pressure drop 140 kg/cm².

Plant material. *Dryopteris abbreviata* (DC.) Newman was collected on 2 June, 1981 near Trabzon, Turkey. A voucher specimen is retained in Ankara Üniversitesi Eczacılık Fakültesi Herbaryumu (AEF).

Isolation. Dry powdered rhizomes (1 kg) were percolated with Et_2O . The Et_2O soln was evaporated to dryness *in vacuo* to give 148 g dark-green oil. A portion of the extract (50 g) was treated as described in a previous paper[5], giving 10.6 g crude filicin. The crude filicin was dissolved in the least possible quantity of Et_2O and allowed to stand overnight in a refrigerator to give 600 mg of flavaspidic acid AB. After the removal of flavaspidic acid AB, the mother liquor was chromatographed on 80 g Si gel with a cyclohexane–THF gradient (9:1 and 4:1). The fractions (10 ml each) were monitored by HPLC. The fractions showing a peak at R_f 12.01 min on HPLC afforded 14.5 mg of **1**.

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