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COLEOSIDE, A MONOTERPENE GLYCOSIDE FROM *COLEUS FORSKOHLII*

BAHAR AHMED and R. A. VISHWAKARMA*

Central Institute of Medicinal and Aromatic Plants, Lucknow 226016, India

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Key Word Index—*Coleus forskohlii*; Labiatae; coleoside; cuminyl alcohol; caffeic acid.

Abstract—The alcoholic extract of the roots of *Coleus forskohlii* yielded caffeic acid and a new monoterpene glycoside, coleoside, characterised as cuminyl-*O*-β-D-glucopyranosyl(1→2)-β-D-galactopyranoside.

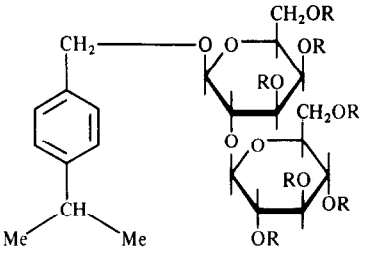
INTRODUCTION

A preliminary biological screening of root extract of *Coleus forskohlii* Briq. (syn. *C. barbatus*) indicated hypotensive and spasmolytic activities [1,2]. The benzene extract of roots afforded labdane diterpenoids [3,4], including coleonol (forskolin) a major component and potential drug for treatment of glaucoma, congestive cardiomyopathy and asthma [5] because of its unique adenylate cyclase stimulant actitivity [6]. The steam distillate of roots has been reported to contain mono- and sesquiterpenes [7]. Further examination of the polar fraction of the root extract has now furnished caffeic acid (**1**) and a new monoterpene glycoside named coleoside and characterized as cuminyl-*O*-β-D-glucosyl-β-D- galactoside (**2**).

RESULTS AND DISCUSSION

Compound **1** was characterized from spectral data (see Experimental) as caffeic acid and this was confirmed by comparison with an authentic sample (IR, ^{1}H– and ^{13}C NMR) [8]. Compound **2** gave a positive Molisch's test for a glycoside. Its ^{1}H NMR spectrum exhibited signals at δ 1.10 (6H *d*, *J* = 8 Hz, 2 × Me), 3.35–3.65 (sugar protons), 4.30 (2H, *d*, *J* = 8 Hz, benzylic protons), 4.98 (1H, *d*, *J* = 7 Hz, glucosyl H-1), 5.1 (1H, *d*, *J* = 7 Hz, galactosyl H-1) and two doublets at 6.70 and 7.65 (2H, each 2*d*, *J* = 9 Hz) for aromatic protons. On acid hydrolysis it gave an aglycone (**3**) which was characterized as cuminyl alcohol [9]. The sugars were characterized as glucose and galactose by co-PC. Acetylation of **2** gave a heptaacetyl derivative **2a** which had absorption peaks in IR at 1750 and 1230 (acetate) and a broad singlet in ^{1}H NMR at δ 1.95 (21H) for seven acetoxyl groups and a multiplet of seven peaks at 170 ppm in ^{13}C NMR indicating two sugar moieties in the molecule.

Mild hydrolysis of compound **2** with 2% H_2SO_4 [10] and subsequent co-PC of the hydrolysed product at intervals of 5 min showed that the glucose unit was removed first and the galactose afterwards, indicating that the galactose unit is involved in the glycosidic linkage with alcoholic group of cuminyl alcohol. The compound **2a** exhibited two doublets in ^{1}H NMR spectrum at δ 5.20 (1H, *d*, *J* = 7 Hz, galactosyl H-1) and 4.98 (1H, *d*, *J* = 7 Hz, glucosyl H-1) for two anomeric protons of sugars indicating the β-linkages with aglycone as well as between sugars [11]. It was also observed that the signal for acetoxyl protons at δ 1.75 ppm of 2′-position of galactose unit was not seen in ^{1}H NMR spectrum of **2a** which indicated that hydroxyl group at 2′-position is not free in galactose unit and is engaged in linkage formation with glucose moiety confirming the (1→2) glycosidic linkage with glucose [11]. Thus **2** was characterised as cuminyl-*O*-β-D–glucopyranosyl-(1→2)β-D-galactopyranoside.



2 R = H
2a R = Ac

EXPERIMENTAL

Plant material. The roots *Coleus forskohlii* Briq were procured from the market and authenticated by the Botany Division of our Institute where a voucher specimen has been preserved.

Extraction and isolation. The shade-dried powdered roots (3.5 kg) were exhaustively extracted with EtOH in Soxhlet (5 cycles). After removal of the solvent the crude extract (250 g) was dissolved in H_2O (400 ml) and extracted successively with EtOAc and *n*-butanol. After removal of solvent, the butanol fraction (15 gm) was chromatographed over a silica gel column which afforded compound **1** ($CHCl_3$–MeOH 9:1), 150 mg. Mp 190–192° (MeOH–$CHCl_3$); IR, ^{1}H and ^{13}NMR and MS data identical to those of authentic caffeic acid.

*Author to whom correspondence should be addressed

Isolation of compound **2**. The *n*-butanol fraction on subsequent column chromatography over silica gel (EtOAc–MeOH 7:3) furnished compound **2** as a viscous light yellow solid (100 mg).

Acetylation of **2**. Compound **2** (50 mg) on acetylation with Ac_2O/pyridine afforded heptaacetate **2a** (40 mg); IR ν_{max}^{neat} cm^{-1}: 2980, 2940, (Me), 1750 (OAc), 1650, 1440, 1370, 1230 (ester), 1040, 910, 920, 760, 600; ^1H NMR ($CDCl_3$): δ 1.15 (6H, *d*, $J = 8$ Hz, 2 × Me), 1.95 (21H, *brs*, 7 × Ac), 3.55 (1H, *m*, methine proton), 4.70 (2H, *d*, $J = 8$ Hz, Ar–CH_2) 4.0–4.2, 4.7–5.0 (12H, *m*, sugar protons), 4.98 (1H, *d*, $J = 7$ Hz, glycosyl H-1), 5.20 (1H, *d*, $J = 7$ Hz, galactosyl H-1), 6.70, 7.65 (2H each *d*, $J = 9$ Hz, Ar–H); ^{13}C NMR ($CDCl_3$); δ 15.0 (C-8, 9), 20.2 (7 × MeCO), 38 (C-7), 40(C-10), 62.1 (C-6′), 64.1 (C-6″), 65.8 (C-5′), 67.1 (C-3″), 69(C-4′), 73.0(C-2″), 75.9 (C-4″), 77.3, 77.5 (C-2′, 3′), 79(C-5″), 94.3, 94.8 (C-1′, 1″), 127 (C-3, 5), 128.5 (C-2, 6), 137(C-1), 145 (C-4), 170 (7 × MeCO).

Mild hydrolysis of **2**. Compound **2** (30 mg) was dissolved in 2% H_2SO_4 with addition of a few drops of MeOH and heated gently on a water bath for 1 hr. The hydrolysates were examined for sugars after each interval of 5 min. by co-PC (Whatman No. 1, *n*-BuOH–C_6H_6–pyridine–H_2O = 5:1:3:3, 48 hr) along with authentic samples of glucose and galactose. It was observed that the first sugar obtained during hydrolysis was glucose (hrf 35.0) while galactose (hrf. 30.5) was detected later.

Compound **3**. Obtained as light yellow oil by hydrolysis of compound **2** with dil. HCl on extraction with ether. ^1H NMR and MS data identical to those of cuminyl alcohol.

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FUSALANIPYRONE, A MONOTERPENOID FROM *FUSARIUM SOLANI*

WOLF-RAINER ABRAHAM and HANS-ADOLF ARFMANN

GBF-Gesellschaft für Biotechnologische Forschung mbH, Mascheroder Weg 1, D-3300 Braunschweig, F.R.G.

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Key Word Index—*Fusarium solani*; Deuteromycetes; Moniliales; fungal metabolite; monoterpenoid; α-pyrone; fusalanipyrone.

Abstract—6-(2′*Z*-butenyl)-3-Methyl-α-pyrone was isolated from the fungus *Fusarium solani* strain DSM 62416 and named fusalanipyrone. This monoterpenoid was not present in *F. solani* strain DSM 62413.

INTRODUCTION

Some species of the genus *Fusarium* are known to produce sesquiterpenes. While some strains produce sesquiterpenoids with the trichothecane skeleton, *F. culmorum* (W. G. Smith) Sacc. produces culmorin, a longicamphandiol. Up to now, no monoterpenoids have been reported from this genus.

RESULTS AND DISCUSSION

When grown on a medium containing 1% glucose, 1% universalpeptone (Merck), 2% malt extract and 0.3% yeast extract, *F. solani* (Martins) Saccardo DSM 62416 excreted an UV absorbing compound into the medium. Extraction of the medium and chromatography of the extract gave a viscous oil. The mass spectrum gave a