

AN ORSELLINIC ACID GLUCOSIDE FROM *SYZYGIUM AROMATICA*

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Key Word Index—*Syzygium aromaticum*; Myrtaceae; orsellinic acid glucoside.

Abstract—The buds of *Syzygium aromaticum* yielded two triterpenoid acids, oleanolic acid and crategolic acid, and a new phenolic glucoside, orsellinic-2-*O*- β -D-glucopyranoside, from its methanolic extract. The structure was elucidated by spectroscopic methods and acid hydrolysis. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Syzygium aromaticum (L.) Merr and Perry, a tree commonly known as clove, is indigenous to the Moluccas. In India it is cultivated in Kerala, Tamil Nadu, Karnataka, and Andaman and Nicobar Islands. Clove buds (whole or ground) are mainly used as a spice for domestic culinary purposes and for the industrial manufacture of sauces and pickles [1]. The essential oil obtained from distillation of the buds is of the highest quality and finds extensive use in the perfumery and flavouring industries and to a limited extent in the pharmaceutical industry. This oil shows antibacterial activity [2], while the acetone extract of buds shows anticholagogue activity [3]. Eugenol, a compound isolated from the ethyl acetate extract of clove buds shows antiviral activity [4]. Most studies [5–7] have been concerned with the chemical constituents of the essential oil.

Despite its great importance in Indian perfumery, flavouring and pharmaceutical industries, *S. aromaticum* had been the subject of limited investigation. This study has revealed the presence in the buds of oleanolic acid (which is already used as a drug in China [8] for the treatment of jaundice), crategolic acid and a new phenolic glucoside, orsellinic-2-*O*- β -D-glucopyranoside.

RESULTS AND DISCUSSION

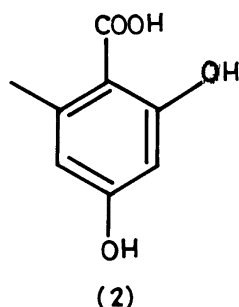
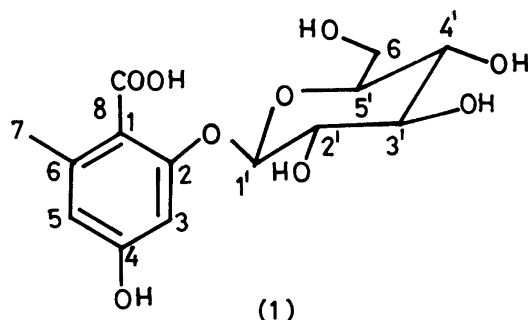
The methanolic extract of *S. aromaticum* buds yielded two triterpenoid acids, oleanolic acid and crategolic

acid [9], and a phenolic glucoside (**1**) orsellinic-2-*O*- β -D-glucopyranoside. Chemical analysis and the mass spectrum of compound **1** showed it to have the molecular formula $C_{14}H_{18}O_9$. IR absorption bands at 3490 and 1668 cm^{-1} were indicative of hydroxy and carboxyl groups, respectively. The presence of a carbonyl group was further confirmed by the presence of a signal at δ 184.34 in its ^{13}C NMR spectrum. The 1H NMR spectrum revealed the presence of two *meta* coupled aromatic protons at δ 5.93 (*d*, $J = 2$ Hz) and 6.09 (*d*, $J = 2$ Hz) and a singlet at δ 2.25 (3H) indicative of an aromatic methyl group. Signals at δ 162.80, 166.85 and 143.91 were attributed to C-2 and C-4 of the benzene ring, and a ring methyl group at C-6, respectively [10–14]. Further signals in the 1H NMR and ^{13}C NMR spectra clearly indicated the presence of a glucose moiety. A one proton doublet at δ 4.78 ($J = 7$ Hz) was assigned to the β -anomeric proton which was further supported by the chemical shift in the ^{13}C NMR spectrum at δ 104.70. Hydrolysis of compound **1** with methanolic HCl afforded two products; a sugar which was identified as glucose by paper chromatography and an aglycone identical to orsellinic acid (mp., *mmp* and Co-TLC). Thus, from the above spectroscopic and chemical data, compound **1** was concluded to be orsellinic-2-*O*- β -D-glucopyranoside.

EXPERIMENTAL

Mp: uncorr.; NMR: 200 MHz (1H) and 50 MHz (^{13}C) CD_3OD with TMS as int standard; MS: 70 eV (direct inlet); TLC: Merck silica gel 60 F_{254} plates, spots visualised by spraying with a 1% sol of vanillin in H_2SO_4 followed by heating at 110° for 15 min; CC: silica gel (60–120 mesh).

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Plant material

S. aromatica was purchased from the local market and a specimen voucher has been deposited at the Institute herbarium.

Extraction and isolation

Powdered buds of *S. aromatica* (1.5 kg) were extracted with *n*-hexane, CHCl_3 and MeOH. The solvents were removed *in vacuo* to give three frs weighing 112.5 g, 100.5 g and 195 g, respectively. Fifty grams of the MeOH extract on CC on silica gel using hexane, hexane-EtOAc, EtOAc and EtOAc-MeOH, afforded oleanolic acid (1 g), crategolic acid (30 mg) and compound (1) (40 mg), R_f 0.54 in CHCl_3 -MeOH (3:1).

Orsellinic-2-O- β -D-glucopyranoside (1). Colourless crystals (MeOH), mp 190–191°, $[\alpha]_D^{18} +2.4^\circ$ (*c* 1.0: MeOH). UV $[\lambda]_{\text{max}}^{\text{MeOH}}$ nm: 255 and 295; IR $[\nu]_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3490, 3279, 2921, 2912, 1668, 1615, 1542, 1457, 1421, 1386, 1320, 1268, 1220, 1028, 867, 840 and 735; ^1H NMR (200 MHz, CD_3OD): δ 2.25 (*s*, 3H, CH_3), 3.30 to 3.38 (*m*, 2H), 3.58 (*dd*, $J = 12.2$ Hz, 1H), 3.72 (*dd*, $J = 12.5$ Hz, 1H), 3.97 (*dd*, $J = 12.2$ Hz, 1H), 4.78 (*d*, $J = 7$ Hz, 1H), 5.93 (*d*, $J = 2$ Hz, 1H), 6.09 (*d*, $J = 2$ Hz, 1H); ^{13}C NMR (CD_3OD): δ 20.98 (CH_3), 62.91 (C-6'), 72.86 (C-4'), 75.49 (C-2'), 78.90 (C-5'), 80.02 (C-3'), 100.72 (C-3), 104.70 (C-1'), 105.32 (C-1), 108.75 (C-5), 143.97 (C-6), 162.80 (C-4), 166.85 (C-2), 184.34 (C-8); EI-MS m/z (rel. int.): 330 $[\text{M}]^+$ (5), 312

$[\text{M}-\text{H}_2\text{O}]^+$ (8), 168 (90) (Found: C, 51.1; H, 50.38. $\text{C}_{14}\text{H}_{18}\text{O}_9$ requires C, 50.49; H, 5.45%).

Acid hydrolysis of 1. Compound 1 (28 mg) in MeOH (2 ml) was refluxed with 5% HCl (2 ml) for 4 h in a water bath. After cooling, the reaction mixture was extracted with EtOAc. The EtOAc layer was dried over MgSO_4 and concd under reduced pressure. The extract was recrystallised from MeOH to give 2 (10 mg), mp 169–170°, which was identified as orsellinic acid by TLC, mp, and mmp. The aq. layer was processed for sugar. This sugar was identified as glucose by comparison with a standard sample on PC (BuOH-HOAc- H_2O , 4:1:5), using aniline hydrogen phthalate as the spray reagent.

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