GALIEPEIN, A COUMARIN FROM GALIEPA TRIFOLIATA

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Key Word Index—Galipea trifoliata; Rutaceae; coumarins; ramosin; phebalosin; 7-isopentenyloxy-8-(trans-1',2'-epoxy-3'-methyl-3'-butenyl)coumarin; galipein.

Abstract—In addition to phebalosin and ramosin, the air-dried stem and root barks of Galipea trifoliata contain a third previously unreported coumarin identified as 7-isopentenyloxy-8-(trans-1',2'-epoxy-3'-methyl-3'-butenyl)coumarin.

INTRODUCTION

In our continuing phytochemical studies of Rutaceae, we report here coumarins from stem and root barks of Galipea trifoliata.

RESULTS AND DISCUSSION

The petrol extracts of the root bark and of the stem bark from Galipea trifoliata, on chromatographic separation, each afforded, three coumarins. Two were identified as ramosin (7-isopentenyloxy-8-isopentenylcoumarin) [1] and phebalosin 7-methoxy-8-(trans-1',2'-epoxy-3'-methyl-3'-butenyl)coumarin) [2]. The third (1), a new natural compound, was isolated as colourless prisms from acetone.

The UV spectrum of 1 in methanol exhibited maxima at 223, 246, 257, 312 (sh) and 324 nm. There was no bathochromic shift on addition with sodium hydroxide. The IR spectrum afforded strong peaks at 1740, 1710, 1605 and 1220 cm⁻¹. This suggested that

Isopentenyloxy-8-(trans-1'-2'-epoxy-3'-methyl-3'-butenyl)coumarin, mp 88-90; IR νmax cm⁻¹: 1740, 1710, 1605, 1280, 1220, 1090, 780; MS m/z (rel. int. %): 312 [M]+ (2) (C₁₉H₂₂O₄), 244 [M-C₅H₈] (32), 230 [M-C₆H₆O] (50), 215 [244-CHO] (33), 175 [244-C₆H₆O] (100); 1H NMR: 87.29 and 6.85 (each, 1H, d, J = 9 Hz, H-5 and H-6 in the aromatic nucleus. A 7-isopentenyloxy group was revealed by two methyl singlets at δ 1.76 and 1.78, a doublet at δ 4.62 for methylene protons and a multiplet at δ 5.44 for an olefinic proton. An 8-isoprenoid side chain was characterized by a vinylic methyl group at δ 1.86 and two multiplets at δ 5.02 and 5.26 corresponding to the presence of C=CH₂ as in phebalosin. An AB quartet centred at δ 3.93 (1H, d, J = Hz), 3.97 (1H, d, J = 2 Hz) revealed the presence of the epoxy oxime methine protons, the vicinal coupling constant of 2 Hz indicating a trans configuration [4].

The UV, IR and 1H NMR spectra suggested that 1 was 7-isopentenyloxy-8-(trans-1',2'-epoxy-3'-methyl-3'-butenyl) coumarin for which we propose the name of galipein.

EXPERIMENTAL

Materials. Stem bark and root bark of Galipea trifoliata Aublet (voucher samples. No. 47, are deposited at the Herbarium of O.R.S.T.O.M. Center of Cayenne in French Guyana) collected near Säul (French Guyana) were sliced, then air-dried and powdered.

Centrifugal thin layer chromatographic (CTLC) separations were carried out using a Chromatotron from Harrison Research. All mps are uncorr. 1H NMR were measured at 90 MHz in CDCl₃ using TMS as int. standard. EIMS were recorded at 70 e.V.

Extraction, isolation and purification. The air-dried powdered material were separately stirred at room temp. with petrol (68-80°C). Filtration, followed by removal of petrol, gave a residue which was chromatographed on a silica gel column using hexane containing increasing amounts of EtOAC. The coumarins collected were isolated and purified by CTLC on silica gel with hexane-EtOAC as eluent (9/1 to 7/3).

Isopentenyloxy-8-(trans-1',2'-epoxy-3'-methyl-3'-butenyl)coumarin, mp 88-90;

REFERENCES
of 6 except for a (—) signal at δ 5.60 due to a methoxy group.

**EXPERIMENTAL**

Mps: uncorr. 1H NMR was run at (CD$_2$Cl$_2$) 100 MHz and 400 MHz and 13C NMR spectra (CD$_2$Cl$_2$) at 74.2 MHz. HRMS, 13C NMR and micro-analysis were performed at the Department of Chemistry, University of British Columbia, Canada.

**Isolation and identification of phenolics.** The dried powdered seeds (500 g) of *M. dactyloides* Gaertn., from Hanguranketa, Sri Lanka, were extracted with Me$_2$CO. The concd Me$_2$CO extract was defatted with petrol giving a viscous brown solid (165 g), which after CC on silica gel using petro1:EtOAc mixtures of increasing proportions yielded compounds 1–6, which were purified by prep. TLC.

1-(2,6-Dihydroxyphenyl)-9-(4-hydroxy-3-methoxyphenyl)nonan-1-one (1). Needles mp, 91–91.5° (petrol, lit [3] 91–92°; Found: C, 74.89%; H, 9.96%; C$_{20}$H$_{19}$O$_3$ requires: C, 74.96%; H, 10.06%, nm 386, 283, 238; IR ν$_{max}$ cm$^{-1}$ 3450 (br), 3340, 1640 (s), 1510, 1450 (s), 1370, 1260, 1100, 1030, 810, 750, 680 (s); 1H NMR (400 MHz, CD$_2$Cl$_2$) 69.37 (2H, d, δ = 7 Hz, H-13), 6.98 (1H, d, δ = 8 Hz, H-15), 6.73 (1H, d, δ = 8 Hz, H-16), 6.65 (1H, d, δ = 8 Hz, H-17), 6.22 (2H, t, δ = 8 Hz, H-19), 6.98 (1H, d, δ = 8 Hz, H-15), 6.73 (1H, d, δ = 8 Hz, H-16), 6.65 (1H, d, δ = 8 Hz, H-17), 6.22 (2H, t, δ = 8 Hz, H-19), 6.98 (1H, d, δ = 8 Hz, H-15), 6.73 (1H, d, δ = 8 Hz, H-16), 6.65 (1H, d, δ = 8 Hz, H-17), 6.22 due to a methoxy group.

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