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Flavonoids of *Cinnamomum tamala*

V.P. Singh*, Ravi Pandey, B. Yadav and V.B. Pandey

Department of Medicinal Chemistry, Institute of Medical Sciences, Banaras Hindu University, Varanasi-221 005 (India)

Abstract – The flavonoids kaempferol, quercetin, myrecetin, kaempferol-3-O-rhamnoside and quercetrin has been isolated from the leaves of *C. tamala* and their structures were established by spectral analysis and direct comparison with authentic samples. This is the first report of occurrence of these compounds from *C. tamala.*

Keywords – *Cinnamomun tamala,* Lauraceae, leaves, flavonoids.

Introduction

Cinnamomum tamala (Hum.) Nees. and Eberm. (Family: Lauraceae) is a moderate sized evergreen tree attaining a height upto 25 ft and distributed in tropical Himalayas upto an altitude of 4000 ft. The leaves of the plant is used extensively as spices in India. In Indian System of Medicine, the plant is used in the treatment of inflammation and rheumatics. It is effective as an anthelmintic and useful in liver and spleen diseases (The Wealth of India, 1992). The chemical constituents viz. p-cymene, cinnamic aldehyde, eugenol, linalool, α and β-pinene, limonene (Upadhyay *et al.,* 1994), 3,4',5,7-tetrahydroxyflavone, 3,3,4,5,7,-pentahydoxyflavone, kaempferol-3-O-saphoroside, kaempferol-3,7-di-O-rhamnopyranoside, kaempferol-3-O-glucopyranoside and quercetin-3-O-rutenoside (Bharadwaj *et al.,* 1983) have been reported earlier from this plant. The present work deals with the isolation of further constituents from *C. tamala.*

Experimental

Plant material – The leaves of *C. tamala* was collected from Varanasi District and identified by Dr. N.K. Dube, Deptt. of Botany, B.H.U. The specimen sample is kept in the department.

Air-dried powered leaves of *C. tamala* (2 kg) were successively extracted with petroleum ether (60-80°), benzene, ethylacetate and methanol by soxhlet extraction methods. The solvents were removed from individual extracts and dried in vaccum. The ethylacetate extract (45 gm) was adsorbed on SiO_2 gel and chromatoraphed over silica gel column eluting with solvents of increasing polarity. The eluants collected were monitored by TLC technique and similar eluants were mixed together. The eluants collected from C_6H_6-$CHCl_3$ (4:1), (9:1), $CHCl_3$, $CHCl_3$ - MeOH (50:1) and (40:1) yielded compounds A, B, C, D and E by crystallization from methanol.

Compound A (kaempferol) – Compound A, crystallised from MeOH as light yellow crystals, m.p. 271-72°C showed positive Shinoda test for flavonoids. It exhibited UV : λ_{max}^{MeOH} 254 sh, 266, 294 sh, 322 sh and 367 nm. IR (KBr. cm^{-1}) ν_{max} 3000-3500 (OH), 1650-1700 (conjugated carbonyl).Its molecular formula was found to be $C_{15}H_{10}O_6$ (M^+286). The other peak m/z 284, 258, 227, 229, 213, 153, 143, 129, 121, 93, 78, 77, 69, 65, 51, 39.^{1}H NMR (90 MHz, DMSO-d_6, δ): 6.18 (1H d, J=2Hz), 6.45 (1H, d, J=2Hz), 6.93 (2H, d, J=9Hz), 8.05 (2H, d, J = 9 Hz), 10.81 (1H, br s), 12.50 (1H, br s). It was found to be identical with kaempferol on comparison with authentic sample (mixed m.p, co-TLC, and superimposable IR).

Compound B (quercetin) – Compound B, crystallized from methanol as light yellow needles, m.p. 312°C, showed positive Shinoda test for flavonoids. It exhibited UV: λ_{max}^{MeOH} 255, 269 sh, 301 sh, 370 nm and IR (KBr, cm^{-1}) : ν_{max} 3000-3300 (OH), 1640 and 1610 (conjugated carbonyl). Its molecular formula was found to be $C_{15}H_{10}O_7$ (M^+,302), and other peaks were at 301, 274, 273, 245, 229, 228, 153, 137, 128, 69. ^{1}H-NMR (90 MHz, DMSO-d_6,δ) : 6.16 (1H d, J=2Hz), 6.40 (1H, d, J=2Hz), 6.86 (1H, d, J=9Hz), 7.47 (1H, d, J=2Hz), 7.62 (1H, dd, J=2Hz and 9Hz), 9.60 (1H, br s) and 12.48 (1H, br s). It was found to be identical with authentic quercetin (mixed m.p, co-TLC, and superimposable IR).

Compound C (myrecetin) – Compound C, crystallized from methanol as yellow granules, m.p. 353°C. It showed

*Author for correspondence.

UV: λ_{max}^{MeOH} 254, 272 sh, 301 sh, 374 nm and IR (KBr, cm^{-1}): ν_{max} 3100-3500 (OH) and 1660, 1610 (conjugated carbonyl). Its molecular formula was found to be $C_{15}H_{10}O_8$ (M^+,318) and other peaks were at m/z: 302, 286, 261, 244,153,146,108,79,69. ^{1}H-NMR (90MHz, DMSO-d_6,δ): 6.22 (1H, d, J =2Hz), 6.43 (1H, d, J=2Hz), 7.28 (2H, br s), 10.85 (1H,, br s) and 12.55 (1H, br s). It was found to be identical with authentic myricetin (mixed m.p, co-TLC, and superimposable IR).

Compound D (kaempferol-3-O-rhamnoside) – Compound D,crystallized from methanol as yellow granules (75 mg), m.p. 178-80°C. UV: $\lambda_{max}^{(MeOH)}$ 264, 313 sh ,343 nm. $\lambda_{max}^{(MeOH+AlCl_3)}$ 274, 304, 345, 400 nm; $\lambda_{max}^{(MeOH+AlCl_3+HCl)}$ 274, 302, 342,396 nm;$\lambda_{max}^{(MeOH+NaOMe)}$ 272, 325, 388 nm; $\lambda_{max}^{(MeOH+NaOAc)}$ 273, 308 sh, 350 nm; $\lambda^{(MeOH+NaOAc+H_3BO_3)}$ 265, 313 sh, 344 nm. IR (KBr, cm^{-1}): ν_{max} 3200-3600 (OH), 1660 (conjugated carbonyl). ^{1}H-NMR (90 MHz, DMSO-d_6,δ): 6.10 (1H, d, J=2Hz), 6.28 (1H, d, J=2Hz), 6.93 (2H, d, J=9Hz), 7.75 (2H, d, J=9Hz), 12.66 (1H, br, s) and signals for protons of one molecule rhamnose: [5.32 (C-1 H).4.88 (OH), 4.00 (C-4-H). 3.46 (C-3-H), 3.13 (C-4-H and C-5-H) 0.80 (rhamnose methyl)]. Anal. calcd for $C_{21}H_{20}O_{10}$: C, 58.33; H, 4.62; O, 37.03%. Found C, 57.92; H, 4.53; O, 37.41. It was finally identified as kaempferol-3-O-rhamnoside by direct comparison with authentic sample (mixed m.p., co-TLC and superimposable IR).

Compound E (quercetin-3-O-rhamnoside) – Compound E, crystallized from MeOH as yellow granules (500 mg), m.p. 165-68°C. UV : $\lambda_{max}^{(MeOH)}$ 255, 265 sh, 301 sh, 350 nm; $\lambda_{max}^{(MeOH+AlCl_3)}$ 275, 304 sh, 330 sh, 432 nm; $\lambda_{max}^{(MeOH+AlCl_3+HCl)}$ 272, 303 sh, 350, 401nm; $\lambda_{max}^{(MeOH+NaOMe)}$ 270, 325 sh, 393 nm; $\lambda_{max}^{(MeOH+NaOAc+H_3BO_3)}$ 260, 330 sh, 365 nm. IR (KBr. cm^{-1}): ν_{max} 3200-3500 (OH), 1640, 1610 (conjugated carbonyl).^{1}HNMR (90 MHz, DMSO-d_6,δ): 6.20 (1H, d, J=2Hz), 6.38 (1H, d, J=2Hz), 6.86 (1H, d, J=9Hz), 7.22 (1H, d, J=2Hz), 7.27 (1H, d, J=9Hz), 12.66 (1H, br, s) and signals for protons of one molecule of rhamnose [5.27 (C-1-H), 5.00 (OH), 3.97 (C-2-H), 3.51 (C-3-H), 3.17 (C-4-H and C-5-H), 0.80 (rhamnose methyl)] Anal. calcd for $C_{21}H_{20}O_{11}$: C, 56.25; H, 4.46; O, 39.28. Found C, 55.81; H, 4.37; O, 39.17. It was finally identified as quercetrin from direct comparison with authentic sample (mixed m.p., co-TLC, and superimposable IR).

Results and Discussion

Chromatographic resolution of the ethylacetate extract of the leaves *Cinnamomum tamala* furnished compounds A, B, C, D and E which were characterized respectively as kaempferol , quercetin, myrecetin (Tripathi *etal*, 1985), kaempforol-3-O-rhamnoside and quercetrin (Pandey *etal*, 1985) by a detailed spectral analysis *i.e.* IR, UV, ^{1}H-NMR, mass spectrum and hydrolysis experiments wherever needed and direct comparison with authentic samples (mixed m.p., co-TLC and superimposable IR). All the above compounds are the first report from this plant.

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