Pergamon 0031-9422(94)00490-0 Phytochemistry, Vol. 37, No. 6, pp. 1775–1776, 1994
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0031-9422/94 $7.00 + 0.00

A CHALCONE GLYCOSIDE FROM *CLERODENDRON PHLOMIDIS*

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(*Received* 30 *March* 1994)

Key Word Index—*Clerodendron phlomidis*; Verbenaceae; flowers; leaves; pectolinarigenin; chalcone glycoside; 7-hydroxyflavone; 7-hydroxyflavanone 7-*O*-glucoside.

Abstract—A new chalcone glycoside, together with pectolinarigenin, 7-hydroxyflavone and 7-hydroxyflavanone 7-*O*-glucoside have been isolated from the flowers and leaves of *Clerodendron phlomidis*. The structure of the chalcone glycoside has been established as 4,2',4'-trihydroxy-6'-methoxychalcone 4,4'-D-diglucoside by spectroscopic and degradative methods.

INTRODUCTION

Clerodendron phlomidis L. (Verbenaceae) is a small tree distributed throughout India and various medicinal properties are attributed to it in the Indian System of Medicine [1]. A number of compounds, namely clerodin, β-sitosterol, lupeol acetate, scutellarein, (24*S*)-ethyl cholesta, 5,22,25'-triene-3-β-ol, D-mannitol, ceryl alcohol, pectolinarigenin, palmitic acid, cerolic acid, apigenin, luteolin and hispidulin [2–7] have earlier been reported from *C. phlomidis*. We report here the isolation of flavonoids pectolinarigenin and a new chalcone glycoside from flowers and 7-hydroxyflavone and 7-hydroxyflavanone-7-*O*-glucoside from the leaves of the plant.

RESULTS AND DISCUSSION

The methanolic extract of the flowers of *C. phlomidis* yielded the chalcone glycoside (**1**), mp 186–188°, $C_{28}H_{34}O_{15}$. With Mg/HCl it developed a magenta colour. The UV spectrum showed absorption bands like that of chalcone [8]. It showed peaks in its IR spectrum at 3400 cm^{-1} (*br*) for a polyhydroxy system, at 2775 cm^{-1} for a methoxyl and at 1645 cm^{-1} for a conjugated carbonyl group. On acid hydrolysis it gave glucose and an aglycone (**2**).

The aglycone (**2**) $C_{16}H_{14}O_5$, mp 257–259°, furnished a diacetate (**3**), mp 171–173°, $C_{20}H_{18}O_7$. The ^{1}H NMR spectrum of (**2**) showed a methoxyl group signal (δ3.72), a typical four peak pattern doublet for 4'-oxygenated B ring (δ7.25, 6.80, $J = 9$ Hz each), two *meta* coupled doublets (δ5.83, 6.02, $J = 2.2$ Hz each) and ABX pattern of protons (δ2.70, *m* and 5.25 1H, *dd*, $J = 5$ Hz) like that of naringenin-5-methyl ether [9] (lit. mp 258–261°, diacetate, mp 171.5–173°). The mass spectrum showed molecular ion peak at *m/z* 286.0946 and had characteristic ion peaks (*m/z* 166 and *m/z* 120) due to retro-Diels–Alder type fragmentation indicating the presence of methoxyl group in ring A. These data suggest that **2** is naringenin 5-methyl ether.

The ^{13}C NMR of **1** showed signals at δ101.1 and 101.7 due to anomeric carbons of two D-glucose units. Compound **1** on acetylation (Ac_2O/Py) gave a nona-acetate (**4**) (δ1.95–2.42). The ^{1}H NMR spectrum of **1** showed two anomeric protons at δ5.1 and 5.3 which each appeared as doublets ($J = 3$ Hz). These data show that **1** contains two D-glucose units which have α-linkages with the aglycone. The formation of naringenin 5-methyl ether supports the structure of the aglycone as isosalipurpol 6'-methyl ether (**5**).

The attachment of sugar units at C-4 and C-4', respectively, was apparent from the UV spectrum of **1** which showed a bathochromic shift of 50 nm in presence of NaOMe without increase in intensity and no bathochromic shift with NaOAc. The ^{1}H NMR spectrum of **1** showed signals for the presence of twelve glucosyl protons (δ3.25–4.0, *m*), one methoxyl (δ3.80, *br s*), two anomeric protons, two broad singlets (δ6.35, 6.50), for C-3' and C-5' protons, two broad singlets each (δ6.50, 7.00) for C-3, C-5 and C-2, C-6 protons. It also showed two signals for one proton doublet each ($J = 16$ Hz) for C-α and C-β protons of chalcone skeleton. FAB-MS showed a molecular ion peak at *m/z* 610 and significant peaks at *m/z* 287 due to the loss of two glucose units and *m/z* 168 and 120 due to cleavage of the isosalipurpol 6'-methyl ether unit into two halves. The ^{13}C NMR data are shown on structure **1**. Thus **1** is 4,2',4'-trihydroxy-6'-methoxychalcone 4,4'α-D-diglucoside.

EXPERIMENTAL

Leaves and flowers of *C. phlomidis* were collected from Varanasi district and verified by the Department of

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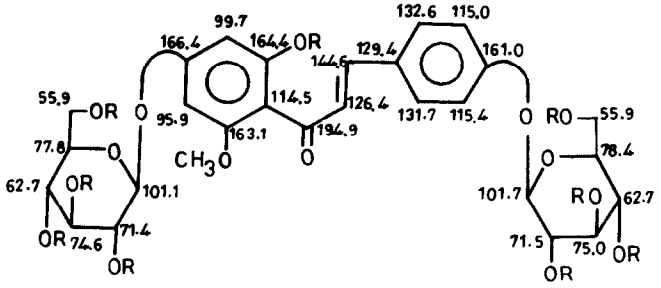
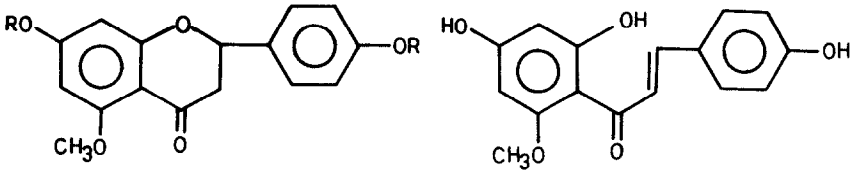


1: R = H
4: R = Ac



2: R = H
3: R = Ac

Botany, Banaras Hindu University and a specimen sample is kept in the department.

Flowers (250 g) were dried, powdered and successively extracted with EtOAc and MeOH in a Soxhlet extractor. CC resolution on SiO_2 gel of the EtOAc and MeOH extracts furnished pectolinarigenin (31 mg), mp 212–214° (lit. mp 213–215°) [10] and chalcone glycoside (**1**) (75 mg), respectively. The dried leaves (500 g) similarly extracted with MeOH and chromatographed over SiO_2 gel gave, respectively, 7-hydroxyflavone (42 mg), mp 142–144° [11] and 7-hydroxy-flavanone 7-*O*-glucoside (53 mg) [11]. The structure of the known compounds were established by a comparison with spectral data with reported data and also by authentic samples.

Chalcone glycoside (**1**) was crystallized from MeOH as yellow granules (75 mg), mp 186–188°. UV λ_{max}^{MeOH} (nm): 245 sh (log ε 4.25) and 364 (log ε 4.40), ^{1}H NMR (CD_3OD): δ 7.80 (1H, *d*, *J* = 16 Hz), 7.75 (2H, *m*), 7.60 (1H, *d*, *J* = 16 Hz), 7.00 (2H, *m*), 6.50 (1H, *br s*), 6.35 (1H, *br s*), 3.25–4.00 (12H, *m*). The acid hydrolysate showed a single spot on PC which corresponded to D-glucose (Co-PC with authentic samples). Diacetate of aglycone **3**, mp 171–173°. UV λ_{max} 273 and 320 nm, IR ν_{max} 1743 and 1682 cm^{-1}, ^{1}H NMR ($CDCl_3$): δ 2.25 (*s*, 6H), 2.70 (*dd*, *J* = 16, 5 Hz, 1H), 6.31 (*d*, *J* = 8 Hz, 1H), 7.44 (*d*, *J* = 8 Hz, 1H); (Found C, 64.66, H, 5.28, Calculated for $C_{20}H_{18}O_7$: C, 64.86, H, 4.90%).

Acknowledgements—The authors are grateful to Prof. Dr G. Rücker, Director, Pharmazeutisches Institut der Universität Bonn, Germany, for spectral analysis and R.R. wishes to thank CCRAS, New Delhi for financial assistance.

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