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A NEW FLAVONE GLYCOSIDE FROM DICOMA TOMENTOSA

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ABSTRACT

Chemical investigations on the methanolic extract of the leaves of Dicoma tomentosa Cass resulted in the isolation and characterization of a novel flavone glycoide 5,7-dihydroxy 6,3',6'- trimethoxy flavone 4' -O-β-D-glucopyranosyl (1↦3) β-Dgalactopyranoside from which the trivial name tomentosin is proposed. The structure of tomentosin was established on the basis of chemcal and spectroscopic techniques.

KEY WORDS: Dicoma tomentosa; New Flavone glycoside, Tomentosin.

INTRODUCTION

The plant is an annual herb, usually branched from a woody base upto 2 ft high, with greenish white to pale pink florets in spinose heads and generally found in field (Hutchinson,1963). It is valued in the indigenous system of medicne and used as crude drug for the treatment of skin diseases, naso-pharyngeal febrifuge, suborifics and as an antiseptic(Burkill,1985). In a recent communication (Aqil, et al. , 1998), we reported a new flavone(Dicoma flavone) from the leaves of Dicoma tomentosa Cass. In the present paper we wish to report the isolation and identifcation of a new flavone glycoside 1 from the same extract.

EXPERIMENTAL

General melting points were detemine by using a Thomas Hoover melting point apparatus and are uncorrected. UV spectra were recorded on a Backman DU-7 spectrophotometer. NMR spetra were recorded on Varian XL-300MH_Z instrument at 300MHz for ^1H in $CDCl_3$ and 75 MH_Z for ^{13}C in DMSO-d_6, using TMS as internal reference. Column and Prep. thin layer chromatography were performed using silica gel(BDH).

Plant material:
Plant material: The leaves of Dicoma tomentosa Case were procured in January 1995 from Kukawa town, Borno State, Nigeria. A smaple was identified by Prof. B.V Gopal, Dept. of Biological Sciences, Unimaid, Maiduguri and deposited with him.

Extraction and Isolation: Air dried and powdered leaves (800g) were extracted three times with petroleum ether (40-60^0 1 lit). The residue was dried and extracted three times with 80% methanol (6lit). On evaporation of the solvent, a semi-solid gummy mass (85g) was obtained which was treated with petroleum either (40-60^0 ·, 1lit). The residue was treated with 100ml hot water, on cooling the water fraction was extracted five times with ethyl acetate(500ml), then evaporation of solvent left a solid brownish residue (10g), which was purified over silica gel by column chromatography, the fraction eluted by C_6H_6 - EtOAc(5:1,5:2,5:,4,1:1) and of EtOAc were combined and after evaporation of the solvent, a solid residue (3g) was obtained which was subjected to prep. thin layer chromatograhy, using the solvent system, $CHCl_3$-MeOH-$H_2$0,36,5,13.5:1.8 over silica gel to afford

compound1: 5,7-dihydroxy-6,3',6'-trimethoxy flavone4'-0-β-D- glucopyranosyl (1↦3) β-D galactopyranoside (Tomentosin, 140mg) as the major component. Compound**1**, yellowshi solid: mp243 - 45^0; UVλmax (MeOH)nm266,328,+$AlCl_3$ -HCl nm: 268,355; NaOMe nm: 268,330 (sh) ;+NaOAc nm:275

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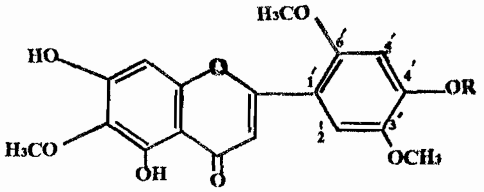
332; + NaOAc-H_3 BO_3 nm:266,332 ^{1}HNMR ($300MH_Z$) signals δ3.80,3.91,3.94. (9H,s, 3 x OMe), 3.60 (1H,m, Gal H-3),4.50(1Hd, J = 8 Hz , Glc H-1), 5.62(1H,d,J=8Hz,Gal,H.1)6.40(1H,s,H-3), 6.46(1H,s-br,OH-7)6.78(1H,s,H-5'),7.55(IH,s,H-2'), 12.72 (IH,s-br,OH-5), ^{13}CNMR($75.5MH_Z$) [Aglycone moiety]: δ164.70(C-2), 103.50(C_3), 181.50(C-4), 153.20(C-10),131.30(C-6), 156.70(C-7); 94.15(C-8), 151.25(-9), 103.90(C-10),119.45(C-1),114.95(C-2),143.70(C-3')146.40(C-4'), 103.60(C-5'),152.10(C-6'). 59.45(O$\underline{C}H_3$-6'), 56.70(O$\underline{C}H_3$-3') and 60.30(OCH_3-6)[sugar moiety] δ100.20(Gal C-1), 70.0(Gal C-2), 82.30(Gal C-3), 67.10(Gal C-4), 75.50(Gal C-5), 59.80(Gal C-6) 104.10(Glc C-1), 73.50(Glc C-2), 76.80(Glc C-3), 69.0(Glc C-4), 76.20(Glc C-5), and 60.50 (Glc C-6).

Hydrolysis of Glycoside 1 :70 mg of **1** was hydrolysed in 7% B_2 SO_4(aq) at 100°C for two hours. It yielded a yellow amorphous aglycone**2**,30mg. Aglycone**2**; yellow amorphous solid, mp 232 -35° (dec) .UVλmax (MeOH)nm: 271,390; + $AlCl_3$- HCl 270,368; + NaOMe 272, 328(Sh), 410; + NaOA 280,348;+NaOAc-H_3BO_3-270,346: ^{1}HNMR(300MHz,$CDCl_3$), δ3.82,3.90,3.96(9H,s, 3xOMe). 6.40(IH,s,H-3), 6.62(1H,s,H-8), 6.70(IH,s,H-5'),7.47(IH,s,H-2'), ^{13}CNMR(DMSO-d_6) 164.60(C-2),103.40(C-3),181.45(C 4),153.40(C-5),131.35(C-6), 156.60)C-7),94.20(C-8),151.30(C-9),104.0(C-10),116.35(C-1'),114.65(C-2'), 142.20(C-3'), 147.60(C-4'), 102.10(C-5'), 151.60(C-6'), 59.60 (OCH_3-6'), 56.55 (OCH_3-3') and 60.15 (OCH_3-6).



1. R = Gal - Glc
2. R = H

[Gal = Galactose, Glc = Glucose]

Compound 1 : Tomentosin

FIGURE 1

RESULTS AND DISCUSSION

Repeated CC and Prep. TLC on silica gel of the ethyl acetate of the water soluble fraction of the methanolic extract from the leaves of Dicoma tememtosa yielded compound **1**. The solubility in polar solvents, positive colour (Finar, 1975), and λmax (Me0H) at 328,266nm in the UV spectrum, indicated compound **1** to be flavone glycoside(Mabry et al., 1970). The UV spectra of **1** gave bathochromic shifts by additon of $AlCl_3$ and Na0Ac shift reagents while the aglycone of **1** showed bathochromic shift with the same reagents as well as with NaOMe which indicated the existence of hydroxyl groups at C-5 and C-7 positions in the parent compound (glycoside) and at C-5, C-7 and C-4' positions in the aglycone **2**. This observation led us to conclude the presence of glycosidation at C-4' position (Aqil et al.,1994), which was further supported by the upfield shift of carbon atom C -4' by 1.20ppm and the down field shift by 1.50ppm of ortho carbons (Aqil et al., 1998; Mabry et al., 1970), and by 3.10pm of para carbon (C-1') of **1** than the shifts of similar carbons atoms in the ^{13}CNMR spectra of the corresponding aglycone **2** (see experimental). The solubility of compound **1** in 10% solution of Na_2 CO_3 also supported the presence of free hyrdroxyl group at C-7 position (Bharwaj et al., 1982). The spectral studies (UV, ^{1}HNMR, ^{13}CNMR, EIMS) showed the studies (UV, ^{1}HNMR, ^{13}CNMR, EIMS) showed the presence of three methoxyl groups in compound **2** which were assigned to C-6, C-3' and C-6' positions the observed spectral data were found quite comparable with the reported values in literature(Aqil et al., 1998; Markham et al.,1982 and therefore the aglycone **2** was identified as 5,7,4' -trihydoxy-6,3',6' trimethoxy flavone.

^{1}HNMR ^{13}CNMR spectra indicated the presence of one glucosyl and one galactosyl moeity in compound**1** which were further identified by PC with authentic samples after acid hydrolyis. This observation led to conclude that a biose such as glycosyl-galactoside, or galactosyl-glucoside was substituted at C-4' position of the aglycone **2**. In ^{1} HNMR spectra, two anomeric protons of an inner and terminal sugar were observed at δ5.62 and 4.50, both as doublets. A proton at 3.60 in a multiplet was assigned to H-3 of inner sugar in accord with a 4'-0-β-gluco(1↦3) β-D-galactosyl moiety which further supported by the down field shift values observed in ^{13}CNMR spectra of compound **1** for inner sugar(C-1&C-3)and

terminal sugar (C-1)(Markham et al., 1982; Mizuno et al., 1992). These results showed that compound **1** is 5,7- dihydroxy -6,3',6'-trimethoxyflavone 4' -0 - β-D-gluco-pyranosyl (1→3) β-D-galactopyranoside (Tomentosin). To our knowlegde it constitutes the first report of its occurrence.

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REFERENCES:

Hutchinson, J., 1963.Flora of west Tropical Africa Vol.II, 2nd edn. Crown Agents For Oversease Government and Administrations, Millbank, London SW1: pp.267-69.

Burkill, H.M., 1985. The useful plants for west Tropical Africa, Royal Botanical Garden, London; PP.738-59.

Aqil. M., Akinniyi, J.A and Naomi, P.N., 1998 GJPAS (Calabar, Nigeria) 4(2), 135- 37.

Finar, I.L, 1975. Stereochemisatry and Chemistry of natural products, Vol. II,2nd edn., Longoman Group Ltd., London; pp771.

Mabry, T.J., Markham, K.R and Thomas , M.B, 1970. The systematic Identification of flavonoids, Springer, New York, pp 274-78

Aqil M. Khan, I.Z, Ahmad, M.B and Ishikura, N., 1994. Discovery and Innovation (Kenya), 6,343-45.

Bhardwaj, D.K , Bishit, M.S. and Anita, R., 1982.. Phytochemistry 21(2),154-56.

Markham, K.R and Chari, V.M 1982, The Flavonoids, Advances in Research, ^{13}CNMR spectroscopy of Flavonoids (eds Harborne, J.B, Mabry, T.J.), Chapaman and Hall Ltd., U.K, pp.19-134.

Mizuno, M., Yoshida, S. Iinuma, M and Lang, A..F., 1992. phytochemistry, 31,301-303.