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SHORT COMMUNICATION

THREE FLAVONOL GLYCOSIDES FROM *RICINUS COMMUNIS*

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ABSTRACT. Chemical investigations on the roots of *ricinus communis* resulted in the isolation and characterization of a novel flavonol glycoside, kaempferol 3-O-β-D-[6'''-O-acetylglucopyranosyl [1→3)-β-D-galactopyranoside] for which the trivial name ricinitin is proposed. The structure of ricinitin was established on the basis of chemical and spectroscopic techniques. Other flavonoids that have been identified include: quercetin 3-O-glucoside and quercetin 3-O-rhamnosylglucoside (rutin).

INTRODUCTION

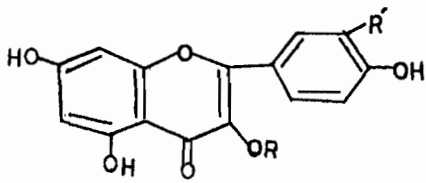
The plant is known as castor tree and used in various traditional medicines [1, 2]. In the course of physiological studies, it was observed that the aqueous solution of the root extract caused diarrhoea, loss in body weight and plasma cell volume of rats. The flavonoid profile of this plant (leaves and seeds) has been determined previously [3, 4]. In this paper, we report the isolation and identification of three flavonoid glycosides from the roots, one of which, compound (**1**), is reported for the first time from a natural source.

RESULTS AND DISCUSSION

The methanolic extract of the roots of *Ricinus communis* was chromatographed over silica gel (CC, prep. TLC) to afford three flavonoids. The identification of the known compounds, quercetin 3-O-glucoside (**2**) and quercitin 3-O-rhamnosylglucoside (**3**) were established by direct comparison (TLC, UV, ^{1}H NMR ^{13}C NMR) with the authentic samples and reported values in the literature [3-7]. Compound (1), on the basis of its solubility in polar solvents and positive colour reactions, was considered to be a flavonoid glycoside. The UV spectra of (**1**) showed bands at 265 nm and 350 nm which gave bathochromic shifts by addition of $AlCl_3$, NaOMe and NaOAc shift reagents while the aglycone of (1) showed larger bathochromic shifts with the same shifts reagents which indicated the existence of hydroxyl groups at positions C-5, C-7, C-4 in the parent compound (glycoside) and C-3, C-5, C-7 and C-4 in the aglycone. This observation led us to conclude the presence of glycosidation at position C-3 by 2.40 ppm and down field shift of the atom at ortho position (C-2) by 9.7 ppm than the shifts of similar carbon atoms in the corresponding aglycone (see experimental). The spectral data (UV, ^{1}H NMR, ^{13}C NMR, MS) observed were found quite comparable with reported values in the literature [8, 9], and, therefore, the aglycone of (**1**) was identified as 3,5,7,4'-tetrahydroxyflavone (kaempferol). Glucose and galactose were confirmed by PC after acid hydrolysis.

The negative ion FAB mass spectrum of (**1**) showed peaks at m/z 651 (M-H), m/z 609 (M-

acetyl), m/z 447 (M-hexose-acetyl) and m/z 285 (M-2 x hexose-acetyl), this observation indicated that a biose such as acetylglucosyl galactose (I) or acetylgalactosyl glucose (ii) was substituted at C-3 position of the aglycone, the presence of an acetyl group was further supported by the signals in ^{1}H NMR (δ 2.06), ^{13}C NMR (52.2 and 170.0) and by a fragment m/z 43 in the EI-mass spectrum. In ^{1}H NMR spectra, the peaks at δ 5.55 and 4.60 both as doublets (each J = 8 Hz) for two anomeric protons of inner and terminal sugar. In ^{13}C NMR spectra the down field shift by 3.1 ppm of C-6''' and upfield shift by 2.8 ppm of C-5''' was observed in comparison with those of without acetoxy group at C-6''' position of terminal sugar as glucose [8, 10]. These values were found in agreement with a biose (I) which was further supported by the comparison of ^{13}C NMR data of (**1**) with calculated values for carbons, based on the additivity rules and therefore, the biose (I) -acetylglucosyl galactose in quite preferable. Hence the compound ricinitin is a kaempferol 3-O-β-D-[6'''-O-acetylglucopyranosyl (1-3)-β-D-galactopyranoside]. To our knowledge it constitutes the first example of its natural occurrence.



1 R = Gal-Glc, R^1 = H
2 R = Glc, R^1 = OH
3 R =Glc- Rha, R^1 = OH

Compound **1**: Ricinitin.

EXPERIMENTAL

General. Melting points were determined by using a Thomas-Hoover melting point apparatus and uncorrected UV spectra were recorded on a Beckman DU-7 spectrophotometer. NMR spectra were recorded on Varian XL-300 instrument at 300 MHZ for ^{1}H and 75.5 MHZ 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. The roots of *Ricinus communis* was procured from the campus, College of Agriculture, Maiduguri, Borno State, Nigeria in November 1993 and was identified by Mrs Shabana Khan, Department of Biological Sciences of the same college. A sample of the collection was deposited in the Herbarium of the College.

Extraction and isolation. Air-dried and powdered roots of *R. communis* (500 g) were extracted three times with petroleum either (40-60°, each 1.5 L, the residue was dried and extracted three times with 80% methanol (3 x 1.5 L). On evaporation of the solvent, a semi-solid gummy mass (40 g) was obtained which was treated with petroleum either (40-60°, 2 x 400 mL. The residue was treated with ethylacetate (500 mL). The evaporation of the solvent left a solid residue (8.0 g) which was purified over silica gel by column chromatography, the fractions 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 (2.0 g) was obtained which was subjected to prep. thin layer chromatogrpahy, using the solvent system, $CHCl_3$-MeOH-H_2O, 36.5:13.5:1.8 over silica gel to afford compound (**1**), kaempferol 3-O-β-D-[6'''-O-acetylglucopyransoyl (1→3)-β-D-galactopyranoside], (*Ricinitin*, 120mg), Compound (**2**), quercetin 3-O-glucoside (30 mg) and compound (**3**), quercetin 3-O-rhamnosylglucoside (60 mg).

Compound (**1**). Yellow powder m.p. 241-43, UV λ_{max} (MeOH) nm: 265, 350; +$AlCl_3$ nm: 270, 395; + NaOMe nm: 268, 330 sh, 398; + NaOAc nm: 275, 355; + H_3BO_3 nm: 266, 352: EIMS m/z (%): 286 (100), 285(22), 258(18), 153(6), 151(3), 151(3), 43(18). Negative ion FAB-MS m/z (%): 651 (M-H) (50), 609(30), 447(18), 285(100) ^{1}H NMR (300 MHZ, DMSO-d_6) signals: δ 6.20 (1 H, d, J = 2 Hz, H-6), 6.45 (1 H, d, J = 2 Hz, H-8), 6.90 (2H, d, J= 9 Hz, H-3, 5), 7.90 (2 H, d, J = 9 Hz H-2, 6), 2.06 (3H, s, Ac), 4.60 (1 H, d, J = 8 Hz, Glc H-1), 5.55 (1 H, d, J = 8

Hz, Gal H-1); ^{13}C NMR (DMSO-d_6) δ (aglycone moiety): 156.5 (C-2), 133.2 (C-3), 177.8 (C-4), 160.6 (C-5), 98.5 (C-6), 164.4 (C-7), 94.5 (C-8), 156.3 (C-9), 104.4 (C-10), 121.5 (C-1), 131.2 (C-2), 115.5 (C-3), 160.0 (C-4), 115.5 (C-5), 131.2 (C-6) (sugar moiety) 100.8 (Gal C-1), 70.3 (Gal C-2), 83.2 (Gal C-3), 67.1 (Gal C-4), 75.8 (Gal C-5), 60.2 (Gal C-6), 104.2 (Glc C-1) 73.5, 73.7 (Glc C-2,5) 76.2 (Glc C-3), 70.2 (Glc C-4), 63.8 (Glc C-6), 20.5 (COMe), 170.2 (COMe).

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