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A NEW SAPONIN FROM MATURE TUBERS OF *CYPERUS ROTUNDUS*

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A triterpenoid acid and its glycoside have been isolated from the benzene extract of the tubers of nutgrass (*Cyperus rotundus*). The aglycone was identified as oleanolic acid (mp, mmp, colour reactions, derivatization, UV, IR, NMR and MS). The glycoside gave characteristic colour reactions of triterpenoids and on acid hydrolysis produced glucose and rhamnose. By methylation (CH_2N_2) the sugars were shown to be in the form of bioside linked to position 3 of the aglycone. The NMR spectrum of the glycoside had a doublet at δ 1.30, typical of a rhamnose methyl group. The nature of the sugar–sugar linkage was deduced by comparison of the rhamnose methyl signal with corresponding signals of neohesperidoside (δ 1.20(*d*)) and rutinoside (δ 0.80–0.95 (*br*) [1, 2]) to be of the neohesperidoside type. Thus the glycoside is oleanolic acid-3-*O*-neohesperidoside which has not been isolated previously from any plant source. Sitosterol was also detected in the same source.

EXPERIMENTAL

Mature tubers of nutgrass, collected from the University campus, were extracted with petrol and C_6H_6, respectively. The petrol fraction yielded sitosterol (mp, mmp, derivatives and spectral data.) While the C_6H_6 fraction on TLC showed two compounds separated by column chromatography (Si gel G) first with C_6H_6 giving oleanolic acid, then with $CHCl_3$ and finally with $CHCl_3$–MeOH (3:2) giving a colourless saponin crystallized from EtOH, mp 120° (d). UV λ_{max}^{EtOH} nm: 236; IR ν_{max}^{KBr} cm^{-1}: 3650–3100 (broad band –OH), 2980 (C–H), 1710 (C–O), 750–720 (sugar).

Acetylation (Py–Ac_2O) gave a product, mp 180°. UV λ_{max}^{MeOH} nm: 235; IR ν_{max}^{KBr} cm^{-1}: 3670, 3000, 1740, 1700, 1460, 1370; ^1H NMR ($CDCl_3$): Me signal at 0.98 and 1.08, OMe signals at 2.1, methylene proteins of sugar moieties, i.e. OAc at 4.28, a vinylic proton at 5.4; MS *m/e*: 563 (acetylated hexo hexose), 456. An intense peak at *m/e* 503 indicated the presence of two sugar moieties attached to the aglycone. Peaks at 248, 208 and 133 are the characteristic peaks for a pentacyclic triterpenic acid with a double bond at C_{12}–C_{13} and a carboxylic group at C_{17}. Therefore, *m/e* 456 seems to be the molecular ion peak for the sapogenin. The sapogenin (5% H_2SO_4 hydrolysis) followed by TLC (Si gel G; developing solvent: C_6H_6–EtOAc, 4:1) showed the presence of one spot which was crystallized (EtOH) with mp 306°, $C_{30}H_{48}O_3$. The IR showed peaks at 3452 (OH), 1686 (acid carbonyl), 1380 and 1365 (gem-dimethyl group and 815 cm^{-1} (trisubstituted double bond) and formed a monomethyl ester, mp 197°, which could not be easily saponified to the original acid, indicating the hindered nature of the carboxyl function [3]. The acid formed a monoacetate (Py–Ac_2O), mp 267°, $C_{32}H_{50}OH$. The acetate was converted to the methyl ester acetate, mp 224°. Its NMR spectrum confirmed the presence of one double bond (5.30), an acetoxy (2.00), a carbomethoxy (3.65) and seven methyl (0.78–1.10) groups [4] and its MS (*m/e* 262, 249, 203 and 133) indicated the presence of a C_{12}–C_{13} double bond, a C_{17} carbomethoxy and an acetoxy group at C_3 in the molecule [5]. All these findings clearly indicate the identity of the acid as oleanolic acid which was confirmed by co-chromatography with an authentic sample.

Isolation of the sugar moieties of the saponin. The hydrolysate was neutralized with $BaCO_3$, concd at 40° under red. pres. The sugar moieties D-glucose and L-rhamnose were identified by PC.

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