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A NEW XANTHONE C-GLUCOSIDE, POSITION ISOMER OF MANGIFERIN, FROM ANEMARRHENA ASPHODELOIDES BUNGE

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Mangiferin (I) which has recently been assigned the conclusive structure 1, 3, 6, 7-tetrahydroxyxanthone 2-C-β-D-glucopyranoside (1) was first isolated from Mangifera indica L. (Anacardiaceae), later from several different families of plants (2) and the occurrence in the rhizomes and the aerial parts of Anemarrhena asphodeloides Bunge (Liliaceae) was reported by Morita et al (3). However, except mangiferin and its 3-methylether (4), no xanthone C-glycoside has been reported, while a number of flavonoid C-glucosides appear in the literatures and among them there are some pairs of coexisting position isomers, such as orientin (II) and isoorientin (III) (5).

This paper deals with a new xanthone C-glucoside, named isomangiferin (IV), which accompanies I in the aerial parts of A. asphodeloides and is defined as 1, 3, 6, 7-tetrahydroxyxanthone 4-C-β-D-glucopyranoside, a position isomer of I.

The methanolic extractives of the fresh materials collected in May were subjected to repeated fractional recrystallization from MeOH and 50% (v/v) aq dioxane to give IV, decomposed over 260° without melting, $[\alpha]_D$ + 5.5° (pyridine), Rf 0.50, $C_{19}H_{18}O_{11}$ - 1/2 H_2O,* as a minor constituent along with I, decomposed

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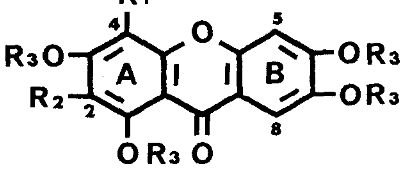
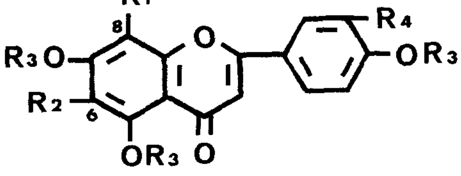
* Rf values were taken on PPC (solvent, 30% (v/v) AcOH). Analytical data were in good agreement with the molecular formulae indicated. NMR spectra were determined at 60 Mcps in $CDCl_3$ solution with TMS as an internal reference and chemical shifts (δ) are given in ppm.

over 260° without melting, $[\alpha]_D$ + 37.6° (pyridine), Rf 0.60.

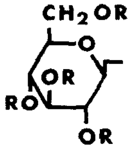
IV showed the UV spectrum and color reactions with Mg-HCl and $FeCl_3$ almost identical with those of I, and afforded octaacetate (V), $C_{35}H_{34}O_{19}$, m.p. 203-204° (from $CHCl_3$-hexane), $[\alpha]_D$ -64.7° ($CHCl_3$), tetramethylether (VI), $C_{23}H_{26}O_{11}$, m.p. 292-293° (dec) (from aq MeOH), $[\alpha]_D$ -13.2° (pyridine) and tetramethylether tetraacetate (VII), $C_{31}H_{34}O_{15}$, m.p. 142-143° (from $CHCl_3$- hexane), $[\alpha]_D$ + 9.8° ($CHCl_3$).





I : R_1=R_3=H, R_2=β-D-glc
IV : R_1=β-D-glc, R_2=R_3=H
V : R_1=β-D-glc(Ac), R_2=H, R_3=Ac
VI : R_1=β-D-glc, R_2=H, R_3=Me
VII : R_1=β-D-glc(Ac), R_2=H, R_3=Me
VIII : R_1=R_2=R_3=H
IX : R_1=H, R_2=β-D-glc, R_3=Me
X : R_1=β-D-glc(Me), R_2=H, R_3=Me
XI : R_1=H, R_2=β-D-glc(Me), R_3=Me
XII : R_1=H, R_2=β-D-glc(Ac), R_3=Me

II : R_1=β-D-glc, R_2=R_3=H, R_4=OH
III : R_1=R_3=H, R_2=β-D-glc, R_4=OH
XIII : R_1=β-D-glc(Ac), R_2=R_4=H, R_3=Me
XIV : R_1=R_4=H, R_2=β-D-glc(Ac), R_3=Me



β-D-glc (R=H, Ac, Me)

IV resisted an usual acid hydrolysis, but refluxing with HI gave 1,3,6,7-tetrahydroxyxanthone (VIII) and oxidation with $FeCl_3$ afforded arabinose and glucose (PPC). The NMR spectrum* of V exhibited three aromatic protons and four acetoxyl groups each on xanthone and sugar moieties (6, 7). Oxidation of IV, I and 1-phenyl-1-deoxy-β-D-glucopyranose with $KMnO_4$ in alkaline medium (8) provided equally D-arabonic acid γ-lactone, m.p. 92-93° (H_2SO_4- bath) or 133-134° (Kofler) (from EtOAc-benzene), $[\alpha]_D$ + 69.7° (H_2O) (9) and VI consumed, in common with I tetramethylether (IX), two moles of periodate without yielding formaldehyde.

Therefore IV is regarded as one of the C-D-glucopyranosides of VIII.

IV permethylether (X), m.p. 167° (from aq MeOH), prepared by exhaustive methylation of VI according to the Kuhn method (10) showed in its NMR spectrum (measured at 60°)** eight methoxyl groups, one α-anomeric proton of the sugar moiety (δ 4.97, d, J=10 cps) and three aromatic protons as sharp singlets (δ 7.65, 6.83 and 6.43), indicating that the D-glucopyranosyl residue is β-linked with a carbon atom of the A ring of VIII. The chemical shifts of the two aromatic protons (δ 7.65 and 6.83) of X were in good agreement with those of the C_8-H (δ 7.61) and C_5-H (δ 6.80) of I permethylether (XI), while that of the third one (δ 6.43) appeared at a significantly higher field than that of the C_4-H (δ 6.64) of XI. Since it is known that the C_2-H in many derivatives of VIII is observed at the higher field than that of C_4-H (6,7), the signal at δ 6.43 is assigned to the C_2-H and, hence, the C-glucosidic linkage in X is considered to be located at C-4. The fact that IV was negative and I was positive to the Gibbs reagent (11) supports the assignment.

Consequently IV is formulated as 1,3,6,7-tetrahydroxyxanthone 4-C-β-D-glucopyranoside.

Recently Prox (12) has reported the mass spectral differences between flavonoid 6-C- and 8-C-glucosides in the free state. Although the spectra of IV and I failed to give any particular information, VII showed in the mass spectrum the molecular ion (m/e 646) as the base peak and the $[M-59]^+$ ion with a relative intensity of 12%, and I tetramethylether tetraacetate (XII) gave the $[M-59]^+$ ion as the base peak and the molecular ion as a minor one (relative intensity, 10%). These data were in good accordance respectively with those of vitexin trimethylether tetraacetate (XIII) (M^+ 100%, $[M-59]^+$ 9%) and of the corresponding derivative (XIV) of isovitexin (M^+ 5%, $[M-59]^+$ 100%). Furthermore the empirical rules that the flavonoid 6-C-glucosides show the higher Rf values on PPC (13) and the larger optical rotations (14) than those of the isomeric 8-C-glucosides hold true in I and IV.

It is noted that the relation between xanthone 2-C- and 4-C-glucosides corresponds to that between flavonoid 6-C- and 8-C-glucosides.

** The NMR spectrum of X recorded at 22° showed the anomeric proton as a broad peak at about 5.0.

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