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ISOLATION AND STRUCTURE ELUCIDATION OF MORINGYNE – A NEW GLYCOSIDE FROM SEEDS OF MORINGA OLEIFERA LAM

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A new glycoside having the molecular formula $C_{15}H_{20}O_7$, provisionally named as *moringyne*, has been isolated from an acidic extract of the seeds of *Moringa oleifera* and its structure elucidated tentatively through spectoral analysis.

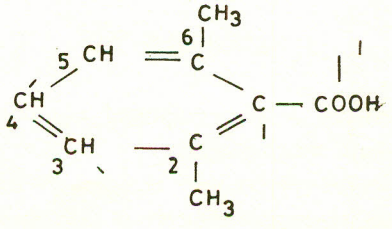
INTRODUCTION

The fruits of *Moringa oleifera* Lam. were collected in the month of April from Jamshoro (Sind University Campus). It is locally known as *Sohanjro* and the value of the plant has long been recognised in the indigenous systems of medicine [1]. It has been reported by A.G.R. Nair and S. Sankara [2] that the extraction of flowers with 95% alcohol shows the presence of three glycosides of rhamnetin and quercetin. Bennie L. Badgett [3] has reported the presence of mustard oil glucoside in *Moringa oleifera* seeds.

Moringyne was crystallised from water alcohol (95:5), and sublimed at 186°. It analysed for the molecular formula $C_{15}H_{20}O_7$. The I.R. spectrum of the moringyne showed -OH stretching vibration at 3300cm^{-1}, C-H (aromatic) stretching vibration at 3040cm^{-1}, C-H (aldehydic) at 2770cm^{-1}, C=O lactone at 1640cm^{-1}, C=C aromatic at 1510cm^{-1}, C-H (CH_2) bending vibration at 1360cm^{-1}, C-O (secondary hydroxl group) at 1040cm^{-1}, three adjacent -CH group at 780cm^{-1} and 688cm^{-1}. The number of -OH groups was confirmed through the formation of a tetra-acetyl derivative, recrystallised from chloroform as light yellow crystals, m.p. 168-169°. The I.R. spectrum of the O-acetyl derivative showed a peak at 1800cm^{-1}, and no peak for -OH group was found which confirms complete acetylation.

The proton NMR spectrum of moringyne showed a singlet at 1.63 ppm for H-3, singlet at 2.05 ppm for H-4, singlet at 2.10 ppm for H-5, singlet at 2.19 ppm assigned for 2 CH_3 groups one on each para position, i.e. C-9 and C-13, doublet at 2.54 ppm assigned for H-1 (J=4 cps) showed coupling with H-2, chemical shift at 3.71 ppm, complex multiplet assigned for H-2, singlet at 4.98 ppm assigned for H-6, chemical shift at 7.45 ppm singlet assigned for H-11, due to double *meta* coupling, singlet at 8.25 ppm, assigned for H-10 and H-12, due to *ortho* coupling of equal distance H-11. Further it was assumed that D_2O signal indicates the presence of -OH groups, these were confirmed from the proton NMR spectrum of the *O*-acetyl derivative taken in $CDCl_3$, which showed a signal at 2.30 ppm. The integral indicates the presence of four *O*-acetyl groups, i.e. moringyne contains four -OH groups.

To determine the structure of another unit, i.e. agly cone which was obtained by enzymatic hydrolysis. It was recrystallised from methanol, m.p.295-98°. It analysed for the molecular formula $C_9H_{10}O_2$, which was confirmed by mass spectrometry (M^+150). The I.R. spectrum indicated -OH stretching vibration at 3300-3040cm^{-1}, C=O group at 1650cm^{-1}, C-H vibration at 1550cm^{-1}, C-H(CH_3) vibration at 1360cm^{-1}, three adjacent C-H at 780-760cm^{-1}. The proton NMR spectrum showed a singlet at 2.34 ppm, assigned for -CH_3 group on both *p*-positions, chemical shift at 4.85 ppm singlet assigned for 1 -OH, signal at 7.45 ppm, singlet suggests H-4 due to double *meta* coupling, singlet at 8.26 ppm assumed for H-3 and H-5 due to *ortho* coupling of equal distance proton H-4. From the above information the structure of aglycone may be as follows:



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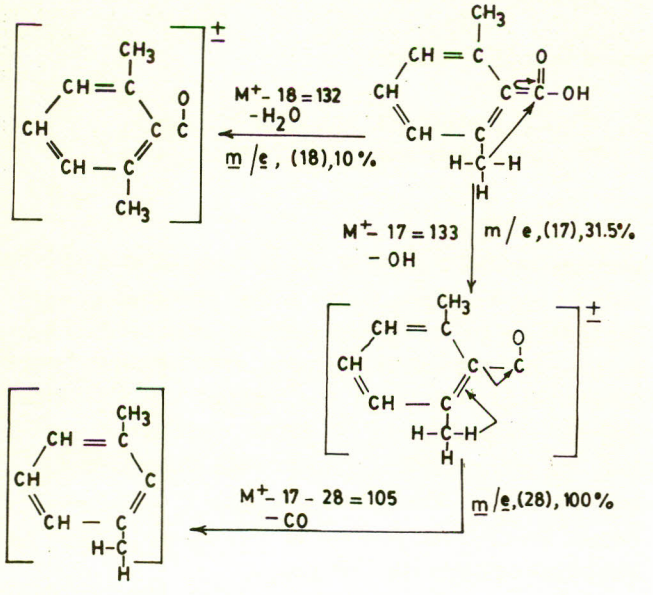
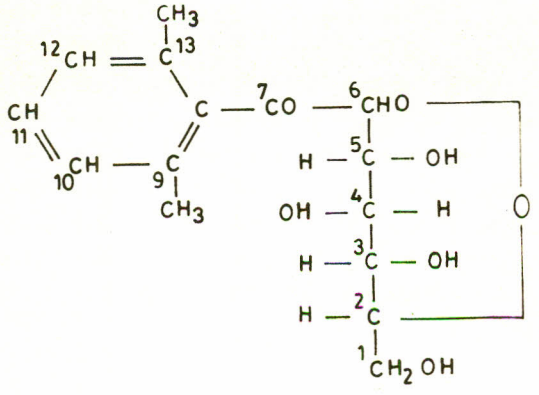
The mass spectrum of the aglycone showed peak at m/e 133, and m/e 132 which were assumed to be due to the loss of -OH and H_2O respectively from C-1[1]. In the second cleavage $C_8H_9^+$ ion was obtained at m/e 105 after the loss C=O (-28 m/e).



From the above data, the structure of moringyne can be concluded to be:



EXPERIMENTAL

Microanalysis of the compound was done on Perkin Elmer automatic micro analyser.

The infra-red spectra were recorded on a Perkin Elmer double beam spectrophotometer in KBr pellets. Nuclear magnetic resonance were recorded on Bruker WP-80 (80 MHZ) spectro spin. All chemical shift values (δ) are measured from tetra-methyl-silane (TMS) as standard. The mass spectra were taken on ZAB-2F vacuum generator Manchester. The procedure adopted is described below:

630 g of semi dried seeds of *Moringa oleifera* were extracted with 0.1N HCl followed by the addition of an ammonia solution (for neutralisation), 4 g of the precipitated brownish material were subjected to partial purification on silica gel plates (silica gel 250-300μ) by using ethanol: water (5:95) as a solvent. Further purification by repeated T.L.C. was carried out by using same solvent system and the same binder. Moringyne was crystallised from the same solvent ratio as colourless crystals which sublimed at 186^o (the yield was 450 mg) Moringyne was highly soluble in water and slightly soluble in alcohol. It analysed for $C_{15}H_{20}O_7$ (found C: 57.65%, H: 6.35%, O:36%, calculated for $C_{15}H_{20}O_7$ requires C:57.69%, H: 6.45%, O: 35.90%) ν max 3300cm^{-1}, 1430cm^{-1}, 3100-2980cm^{-1}, 2700cm^{-1}, 2220cm^{-1}, 1640cm^{-1}, 1510cm^{-1}, 1475cm^{-1}, 1430cm^{-1}, 1410cm^{-1}, 1360cm^{-1}, 1330cm^{-1}, 1280cm^{-1}, 1190cm^{-1}, 1140cm^{-1}, 1115cm^{-1}, 1070cm^{-1}, 1040cm^{-1}, 960cm^{-1}, 935cm^{-1}, 890cm^{-1}, 825cm^{-1}, 780cm^{-1}, 688cm^{-1}, δ= ppm, 1.63 ppm, 2.05 ppm, 2.10 ppm, 2.19 ppm, 2.54 ppm, 3.71 ppm, 4.98 ppm, 5.20 ppm, 7.45 ppm, 8.25 ppm.

Acetylation of moringyne

50 mg of moringyne were taken in 2 ml of pyridine and 2 ml of acetic anhydride, kept for 15 hr at room temperature [4]. It was crystallised from $CHCl_3$ as light yellow crystals melting at 168-69^o, showed no hydroxylic absorption in I.R. spectrum but displayed a weak broad peak at 1800cm^{-1} due to *O*-acetyl group. It showed no signal for hydroxalic group in NMR.

Hydrolysis of moringyne

20 mg of moringyne were taken in 10 ml of β-emulsin solution which was obtained from almonds [5].

The flask was placed in a water bath, maintaining a temperature of 45^o for two hr. The mixture was shaken well from time to time. Then the mixture was extracted with chloroform, 3 to 4 times, dried over sodium sulphate and the solvent evaporated. It was crystallised from methanol as light yellow crystals, m.p. 295-98^o. The aglycone gave molecular ion peak at m/e 150 in agreement with the formula $C_9H_{10}O_2$ (found C, 71.88%, H, 6.7%, O, 21.40%, calculated for $C_9H_{10}O_2$ requires C, 72.00%, H, 6.33%, O, 21.67%). ν max. 3300-3040cm^{-1}, 3020-2680cm^{-1},

1120-1108cm^{-1}, 1050-980cm^{-1}, 930cm^{-1}, 890cm^{-1}, 840cm^{-1}, 780cm^{-1}, Mol. Wt. 150 δ = ppm, 2.3 ppm, 4.85 ppm, 7.45 ppm, 8.26 ppm.

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