

Chemical Examination of the Leaves of *Homonoia reparia* Lour (Euphorbiaceae)

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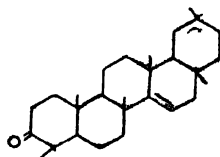
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HOMONOIA reparia Lour (Syn. *H. retusa*) is a small genus of shrubs and small trees distributed from India to new Guinea. Four species occur in India. The various parts of this genus are well-known for its medicinal properties¹. However, no work on the chemical constituents of the genus *Homonoia* has been reported. This paper deals with the first report on chemical examination of the leaves of *Homonoia reparia*.

Dried and powdered leaves of *Homonoia reparia* (0.5 kg), procured from Molim (Goa), were extracted with methanol. The methanol extract was concentrated and adsorbed on silica gel and transferred over a column of silica gel settled with petroleum ether (b.p. 60–80°). The column was eluted with petrol, petrol–benzene (1 : 1), benzene, ethyl acetate and then with methanol. Three compounds were separated out. The identification was based on spectral studies and also comparison (m.ps. and spectral data) with those of the authentic samples.

Petrol–benzene (1 : 1) elution : It gave colourless crystals on crystallisation with CHCl_3 –EtOH, (20 mg), m.p. 240°; R_f 0.25 (benzene) it afforded positive LB test; M^+ 424 analysed for $\text{C}_{30}\text{H}_{48}\text{O}$; ν_{max} (KBr) 1 690–1 700 cm^{-1} (C=O); m/e 424 (37), 409(18.3), 300(100), 285(45.4), 257(9), 232(7.3), 218(16.5), 205(62.6), 204(95), 189(10), 149(10), 133(25), 121(22), 119(10), 109(15), 107(10), 95(17), 93(10), 91(8), 67(15), 57(15) and 43(12); δ (CDCl_3) 0.83 (3H, s), 0.93(6H, s), 0.97(3H, s), 1.06(9H, s), 1.12 (3H, s), 1.32(m), 1.5–1.91 (m, methylene protons), 2.28–2.52(2H, m, methylene proton at C-2), 5.56 (1H, dd, olefinic proton). The spectral data of the compound were found identical in all respect with taraxerone (1)^{2–4}.

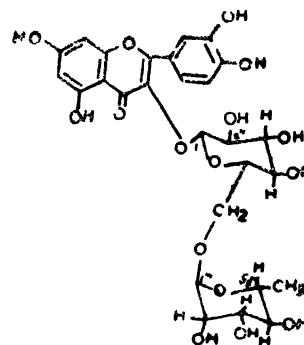


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Benzene elution : The column was eluted with benzene and eluent was crystallised from benzene–acetone; brown in uv light and gave green colour with alcoholic FeCl_3 , m.p. 253°d. It was found to be identical with the authentic sample of gallic acid.

Ethyl acetate elution : Elution of the column with ethyl acetate afforded yellow solid which was

recrystallised from ethyl acetate–acetone as yellow crystals (15 mg); R_f 0.46 (BAW), m.p. 187–88°; it gave positive Shinoda and Molisch test. The chromatographic spot appeared deep purple which turned yellow with ammonia indicating it to be a flavonoid glycoside. The uv spectral shift with diagnostic reagent indicated the presence of 7-OH, 5-OH and 3',4'-orthodihydroxyl groups⁵. On complete hydrolysis with 8% HCl it gave quercetin, glucose and rhamnose. The sugars were identified by paper chromatography and quercetin by m.m.p. comparison of its R_f value and uv spectral data with authentic sample. Partial hydrolysis with 1% H_2SO_4 yielded rhamnose and quercetin 3-O- β -D-glucoside. This indicated that the sugar must be in the disaccharide form linked to only one position of the aglycone (C-3 of quercetin) with rhamnose as the terminal sugar. Acetylation of the compound with Ac_2O /Py afforded an acetate, m.p. 135°. In ^1H nmr spectrum, the sugar region showed a multiplet at δ 0.91 and a doublet at δ 4.52 (J 2 Hz) assigned to rhamnose methyl and rhamnose C-1 proton, which indicate that rhamnose should be the second moiety of a rhamnosyl glucosyl disaccharide. The anomeric proton (H-1'') of glucose appeared as a doublet at δ 5.35 (J 7 Hz). This confirmed the direct attachment of the glucose to the aglycone and diaxial coupling between H-1'' and H-2'' indicated β -configuration. These data confirmed the rutinose moiety⁶. On methylation followed by hydrolysis it gave quercetin 5,7,3',4'-tetramethyl ether, 2,3,4-tri-O-methyl-L-rhamnose and 2,3,4-tri-O-methyl-D-glucose. From these data and by direct comparison with authentic sample it was identified as quercetin-3-O- β -D-glucopyranosyl[1 \rightarrow 6]-O- α -L-rhamnoside (2).



(2)

Acknowledgement

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Spectrophotometric Determination of Vanadium(v) with *N*-Hydroxy-*N*,*N*'-diarylbenzamidine in Presence of *p*-Hydroxybenzaldehyde†

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N-Hydroxy-*N*,*N*'-diarylbenzamidines have been found to be potential analytical reagents for determination of various transition elements¹. The present paper reports the use of a newly synthesised reagent *N*-hydroxy-*N*-*p*-chlorophenyl-*N*'-(2,3-dimethyl)phenyl-*p*-toluamidine hydrochloride for the extractive photometric determination of vanadium(v). The proposed method based on the chloroform-extraction of vanadium as V-HCPDMPH-*p*-hydroxybenzaldehyde complex and its subsequent photometric determination is rapid and better in sensitivity and selectivity than the other established methods².

Experimental

Uv spectra were recorded on a Carl-Zeiss GS-865 Specord spectrophotometer equipped with 1-cm matched silica cuvettes for all photometric measurements.

A stock solution of vanadium(v) was prepared by dissolving ammonium metavanadate (A.R.) in double-distilled water, and its vanadium was evaluated volumetrically using potassium permanganate solution³.

N-Hydroxy-*N*-*p*-chlorophenyl-*N*'-(2,3-dimethyl)phenyl-*p*-toluamidine hydrochloride was synthesised by coupling an equimolar mixture of *N*-(2,3-dimethyl)phenyl-*p*-toluimidoyl chloride and *N*-*p*-chlorophenylhydroxylamine in ether medium at 5°. The resulting hydrochloride was crystallised from absolute ethanol containing few drops of HCl (A.R.). C, H, and N values of the compound

were found satisfactory. A 0.003 *M* solution of HCPDMPH and 0.2 *M* solutions of the *p*-hydroxybenzaldehyde were prepared in chloroform and used in extraction.

Procedure : A known aliquot of vanadium(v) solution containing 100 µg of V was transferred to a separatory funnel, diluted to 25 ml with distilled water and adjusted the pH 1.5–5.2 with 2 *M* HCl and dilute ammonia. A 0.003 *M* reagent solution (15 ml) and 0.2 *M* *p*-hydroxybenzaldehyde solution (5 ml) were then added. After shaking the funnel for 2 min, the chloroform layer separated and dried over anhydrous sodium sulphate. The aqueous phase was then washed with chloroform (2×4 ml). The coloured extracts were transferred to a 25 ml volumetric flask and the volume made up with chloroform. The absorbance was then measured at 590 nm against chloroform as a blank.

Results and Discussion

Absorption spectra : The absorption spectra of vanadium(v)–HCPDMPH complex in the absence and presence of *p*-hydroxybenzaldehyde were scanned. The vanadium–HCPDMPH complex shows a flat peak at 570–590 nm with molar absorptivity of about 900 dm³ mol⁻¹ cm⁻¹. In the presence of *p*-hydroxybenzaldehyde, a 1:2:1 (metal–HCPDMPH–*p*-hydroxybenzaldehyde) bluish green mixed-complex is formed with molar absorptivity of 7 900 dm³ mol⁻¹ cm⁻¹.

Effect of variables : Various non-polar organic solvents were tried and chloroform was found to be most satisfactory because it gives high distribution ratios for the reagent and mixed complexes. The optimum pH range was found to be 1.5–5.2. A 4-fold molar excess of reagent and at least 250-fold molar excess of *p*-hydroxybenzaldehyde was necessary for the complete extraction of vanadium. The order of addition of reagents was not critical. Sodium, potassium and ammonium sulphates and chlorides were tried as salting out agents in the concentration range 0.5–3.0 *M* but did not enhance the extraction. The extracts were stable for at least 40 h at 27±2°.

Characteristics of complexes : The system obeyed Beer's law in the range 0.8–6.4 ppm of V. The optimum concentration range on the basis of Ringbom plots was found to be 1.2–5.8 ppm of V. The relative standard deviation was found to be 0.84% (10 measurements were made, each containing 4 ppm V in 25 ml). In vanadium–HCPDMPH–*p*-hydroxybenzaldehyde mixed-complex the ratio of vanadium to HCPDMPH was determined by the mole-ratio⁴ and Job's method of continuous variation⁵. The ratio of vanadium to *p*-hydroxybenzaldehyde was determined by curve-fitting method⁶, i.e. plots of log absorbance vs log[*p*-hydroxybenzaldehyde]. The results obtained show the formation of a 1:2:1 (metal–HCPDMPH–*p*-hydroxybenzaldehyde) complex.

Effect of foreign ions : Chloride, bromide, nitrate and sulphate do not interfere. Urea,

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