

help to induce the material to crystallise although the ethyl acetate, acetone and ethanol extracts gave tests for phenolic compounds with ferric chloride.

The hexane extract of *Amoora walluchi* answered Liebermann-Burchard test for the presence of sitosterol. The residue from the hexane extract crystallised from methanol as needles, m.p. 138° . $(\alpha)_D^{25}$; -35° (CHCl_3). The benzene, ether, ethyl acetate, acetone and ethanol extracts behaved in a similar way as in the case of the wood of *Aglaia andamanica*.

The heartwood of *Carapa obovata* was extracted and examined in a similar way. Its hexane extract gave β -sitosterol and gedunin.

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1. Kirtikar, K. R. and Basu, B. D., *Indian Medicinal Plants*, Vol. I, p. 533.
2. Akisanya, A., Bevan, C. W. L., Hirst, J., Halsall, T. G. and Taylor, D. A. H., *J. Chem. Soc.*, 1960, p. 3827.
3. Powell, J. W., *J. Chem. Soc., C Org.*, 1966, 20, 1794.

2-HYDROXY-5-METHYLACETOPHENONE SEMICARBAZONE AND THIOSEMICARBAZONE AS METAL INDICATORS FOR THE COMPLEXOMETRIC TITRATION OF IRON(III) WITH EDTA

THOUGH Variamine Blue B is the recommended indicator for the volumetric titration of iron (III) with EDTA at pH 2–3¹, it has the disadvantage that (i) even mild oxidizing agents like nitrite interfere, and (ii) a part of iron should be in bivalent state and this does not react with EDTA. The present note describes the use of 2-hydroxy-acetophenone semicarbazone and thiosemicarbazone as metal indicators for the complexometric titration of iron (III) with EDTA. The optimum conditions worked out are the following :

Adjust the pH of iron (III) solution to 2 with ammonia; and 10 ml of 1 M hydrochloric acid-sodium acetate buffer of pH 2, and 5 to 10 drops of 0.5% w/v ethanolic solution of the indicator (i) 2-hydroxy-5-methylacetophenone semicarbazone, or (ii) 2-hydroxy-5-methylacetophenone thiosemicarbazone. Dilute to 100 ml with distilled water and titrate against the standard solution of 0.005 to

0.050 M EDTA till a sharp colour change from green to colourless in the case of (i) and from bluish green to colourless in the case of (ii) is observed.

With higher amounts of iron (III), the end point is indicated by the disappearance of the last traces of greenish colour leaving behind a clear yellow solution.

The relative standard deviation for the titration has been found to be 0.3–0.5% for 1–70 mg iron (III).

With 100 mg and above of iron (III), the standard deviation was found to be nearly 1%.

Interferences

The following ions do not cause any interference even when present in quantities upto 100 times (w/w) that of iron (III): bromide, sulphate, chloride, tartrate, citrate, urea, calcium, magnesium, barium, strontium, beryllium, zinc, cadmium, mercury (II), manganese-(II), uranyl (VI) and nitrite.

The following ions can be tolerated in amounts given in parentheses, together with masking agents if any: 4.90 iron (III) (4.9 mg): aluminum (III) (200 mg tartrate), antimony (III) (50 mg, tartrate), bismuth (III) (50 mg, tartrate or urea with end point as the disappearance of green colour), chromium (III) (20 mg with end point as the disappearance of green colour), cobalt (II) (30 mg, tartrate), fluoride (50 mg), molybdate (VI) (100 mg, tartrate or citrate), oxalate (20 mg with end point as the disappearance of green colour), phosphate (200 mg), thiosulphate (200 mg), titanium (IV) (20 mg, tartrate) and zirconium (IV) (100 mg, tartrate).

The following ions interfere seriously: cyanide, sulphocyanide, copper (II), nickel (II) and vanadium (IV, V).

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1. Vogel, A. I., *A Text Book of Quantitative Inorganic Analysis*, Longmans-Green, London, 1962, (3rd. Edn.), p. 444.

FLAVANOIDS OF ACACIA SUMA HEARTWOOD QUERCETIN AND HYPERIN 3', 7-DIMETHYL ETHER

THE fine shavings of the heartwood of *Acacia suma* were extracted with boiling ethanol. The concentrated ethanolic extract was fractionated into ether and ethyl acetate soluble fractions. The ether extract gave a good yield of a flavanoid compound which was characterised as quercetin by comparison

with authentic sample. The concentrated ethyl acetate extract was subjected to fractional precipitation with petroleum ether and after removal of the resinous impurities, a chromatographically homogeneous flavanoid glycoside, could be isolated.

Hyperin 3', 7-dimethyl ether

It was isolated as a pale yellow solid, m.p. 190–192°. It gave positive Molisch test suggesting the presence of a carbohydrate moiety in the molecule. It neither reduced Fehling solution nor gave any positive colour with aniline hydrogen phthalate, which showed that the reducing group of the sugar is involved in the glycosidic linkage. Acid hydrolysis of the glycoside gave a water insoluble aglycone and a reducing sugar which was identified as D (+) galactose by mixed paper chromatography, R_f value of its benzyl amine derivative and mixed m.p. of its osazone.

The pale brown aglycone $C_{17}H_{14}O_7$; m.p. 214°, was found to be flavanoid in nature by its characteristic colour reactions and positive colour reaction with zirconium oxychloride in presence of citric acid. The aglycone was analysed for two methoxyl groups (Zeisel's method) as supported by the IR peak at 2850 cm^{-1} . With acetic anhydride and pyridine the aglycone formed a triacetate thereby the presence of three hydroxyl groups was indicated. The relative positions of the methoxyl and hydroxyl groups was determined by the colour reactions, spectral shifts² and degradative studies. The tetramethyl ether of the glycoside on oxidation with neutral potassium permanganate gave veratric acid as one of the oxidation products, which suggested that the side phenyl is a 3:4 substituted nucleus. The absence of a free phloroglucinol unit in the aglycone was indicated by the absence of a positive colour reaction with vanillin-hydrochloric acid reagent. However, its positive test with ethanolic boric acid in the presence of citric acid showed the presence of a free hydroxyl group at 5 position. No bathochromic shift on addition of sodium acetate indicated that probably 7 hydroxyl group is substituted. Therefore, one of the methoxyl groups eventually was located at position 7. A bathochromic shift was observed on addition of ethanolic aluminium chloride which showed the presence of free hydroxyls at position 3 and 5. On addition of sodium ethylate (0.002 M) long wavelength band at 374 nm disappeared which indicated the presence³ of free hydroxyls at 3 and 4'. Therefore, 5, 3, and 4' positions carry free hydroxyls and conclusively one of the two methoxyl groups must be present in position 3' of the side phenyl.

The position of glycosidic linkage was ascertained by comparing the colour reactions of the aglycone

with those of the glycoside. The glycoside failed to give reaction with zirconium oxychloride in presence of citric acid⁴ whereas aglycone responded to it, indicating thereby that 3-hydroxyl of the aglycone is involved in glycosidic linkage.

The glycoside could be hydrolysed to give free sugar and aglycone with emulsin isolated from almonds. Hence it is concluded that the substance is a β -glycoside. The ring structure of the galactose moiety was found to be pyranose, as the glycoside methyl ether with all the free phenolic hydroxyls methylated on periodate oxidation consumed two molecules of periodate with liberation of one molecule of formic acid.

Thus, it has been found to be 5, 4'-dihydroxy-7, 3'-dimethoxy flavone 3-O- β -D-galactopyranoside or 3', 7-dimethyl flavone ether of hyperin.

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1. Briggs, L. H., Colebrook, L. D., Fales, H. M., Wildman, W. C., *Anal. Chem.*, 1954, 29, 904.
2. Jurd, L. and Geissman, T. A., *J. Org. Chem.*, 1956, 21, 1395.
3. —, In: *Chemistry of Flavonoid Compounds*, Edited by T. A. Geissman, Pergamon Press, Oxford, 1962, p. 107.
4. Hörhammer, L. and Hänsel, R. M., *Arch. Pharm.*, 1955, 288, 315.

SOME METAL BISTHIOSALICYLATO MERCURATES

THE preparation and studies on mercuric thiosalicylate has already been described¹. In the present communication, preparation and analysis of cerium, chromium and thallium bithiosalicylato mercurates are reported. The preparation² and other studies³ on disodium bithiosalicylato mercurate have also been discussed.

Chromium solution was prepared from $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ which was a 'Baker Analyzed' reagent. Thiosalicylic acid was from Evans Chemetics (U.S.A.). All other chemicals and reagents were of B.D.H. (India) Analar quality. Cerium and chromium bithiosalicylato mercurates were obtained on mixing the equivalent quantities of 0.01 M solutions of disodium bithiosalicylato mercurate and the metal ions. Thallium mercurate precipitated only after adding tenfold excess of the thallium solution. Cerium gave a buff coloured precipitate and a light-grey chromium mercurate was obtained.