

similar to the naturally occurring flavan 3,4-diols and thus could be characterised as leucocyanidin. The other compound was isolated as pale yellow crystalline solid m.p. 314° , $\lambda_{\max}^{\text{EtOH}}$ (nm), 370 and 256. From the study of spectral shifts^{2,3,4}, ir and its derivatives viz., acetate and methylether it was identified as quercetin.

The residual mother liquor left after extraction with ethylacetate, was concentrated under reduced pressure to a thick brown syrup. The syrup on maceration with hot aq. ethanol (1 : 5 v/v) yielded a colourless substance crystallising as rectangular plates, m.p. 246° (d), $\lambda_{\max}^{\text{EtOH}}$ (nm), 250. On acid hydrolysis it gave ellagic acid and glucose. Quantitative hydrolysis indicated that the compound is a diglucoside. Complete methylation of the glucoside followed by acid hydrolysis gave 3,3', 4'-trimethylether of ellagic acid, m.p. 287° (lit 288°)⁵ which suggested the sugar linkage at position 4 of ellagic acid. Complete hydrolysis of the glycoside with emulsin⁶ and quantitative periodate oxidation⁷ of its methyl ether confirmed it as ellagic acid 4-O- β -gentiobioside (amritoside). This has been reported earlier in the stembark¹ and leaves⁸ of this plant.

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Chemical Constituents of *Borreria stricta* Linn.

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BORRERIA *stricta* Linn. (N.O. Rubiaceae)
commonly grows in Bundelkhand, upper gangetic

regions, in wastelands, in uncultivated fields and on crevices of rocks¹. No reference on its chemical constituents was available in literature, although sister species have been chemically investigated²⁻⁸. In view of wide availability of this plant, its chemical investigation was carried out to assess its potential as livestock feed and toxic constituents, if any. A systematic chemical investigation revealed the presence of *n*-hexacosanol, palmitic acid, free β -sitosterol, β -D-glucoside of β -sitosterol, ursolic acid, astragalin, rutin, free quercetin, two unidentified triterpenic acids and potassium oxalate. The presence of mannitol, galactose and glucose was detected in aqueous extract. The identity of all the compounds characterized, has been established by direct comparison with the respective authentic samples.

Experimental

The shade dried leaves were found to contain crude protein 10.4%, calcium 0.22% and phosphorus 0.14%. Powdered leaves (6 kg) were exhaustively extracted with 95% alcohol by cold percolation and solvent was removed under reduced pressure. The extractive was separated into petroleum ether and ethylacetate soluble fractions. Both the fractions were chromatographed over Brockmann's neutral alumina and silica gel columns respectively, which yielded following crystalline compounds.

Petroleum ether extract : On keeping deposited a residue which was filtered off. It separated into two crystalline triterpenic acids A & B, on fractionation with aqueous potassium hydroxide.

***n*-Hexacosanol** : Petroleum ether eluted fractions furnished *n*-hexacosanol, crystallised from acetone as colourless crystals m.p. $76-77^{\circ}$ (Lit. 79°)⁴. Its acetate melted at 64° .

Palmitic acid : Appeared in the benzene eluted fractions, was crystallised from methanol m.p. 62° .

β -Sitosterol : Which came in acetone fraction, crystallised from chloroform-methanol as shining needles, m.p. and m.m.p. $136-137^{\circ}$ (Lit. 136°)⁹, $(\alpha)_D^{20} -33^{\circ}$, acetate, m.p. 129° $(\alpha)_D^{20} -36^{\circ}$.

β -D-glucoside of β -sitosterol : (Ethanol) obtained as white deposition, which crystallised from excess of ethanol, (Charcoal) m.p. $265-68^{\circ}$; $(\alpha)_D^{20} -36.2^{\circ}$. On hydrolysis (alc., 7% HCl), it yielded β -sitosterol and glucose. It formed an acetate m.p. $178-79^{\circ}$.

Ursolic acid : Obtained from ethyl acetate fraction as shining needles $284-86^{\circ}$ (Lit. $285-86^{\circ}$)⁹, $(\alpha)_D^{20} +64^{\circ}$, gave an acetate crystallised from acetone as colourless needles m.p. $290-91^{\circ}$ (Lit. $293-94^{\circ}$)⁹. The methyl ester (diazomethane) and methyl ester acetate melted at $172-73^{\circ}$ (Lit. 169°)⁹ and $243-45^{\circ}$ (Lit. 245°)⁹ respectively.

NOTES

Alcoholic extract : The remaining alcoholic extractive, on chromatography over silica gel column yielded following compounds.

Astragalín : Obtained as yellow crystalline product m.p. 180° (Lit. 178°)⁴. It responded to shinoda (Mg+HCl) and Molisch's tests. On acid hydrolysis it yielded an aglycone (methanol) m.p. 275-77° (Lit. 275-76°)⁴. The aglycone was identified as kaempferol by paper chromatography and spectral data.

Rutin-Acetone : Alcohol (2 : 8) eluted fractions furnished rutin as yellow microcrystalline substance m.p. 185-86°. On hydrolysis with alc. 7% HCl, it furnished quercetin m.p. 312-15° (Lit. 313-14°)⁴. The latter gave an acetate m.p. 194-95°. The glucose and rhamnose were identified in hydrolysate by p.c.

Quercetin : On elution with alcohol quercetin was obtained as a yellow crystalline product m.p. 309-11°.

Aqueous extract : Glucose and galactose along with mannitol were detected in the aqueous extract by two dimensional p.c. The aqueous extract of the alcohol exhausted leaves gave potassium oxalate (0.001%).

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Synthesis of Some New 4-Arylhydrazono-N'-Arylthiocarbamoyl-3-Methyl-2-Pyrazolin-5-Ones as Possible Potential Antidiabetics

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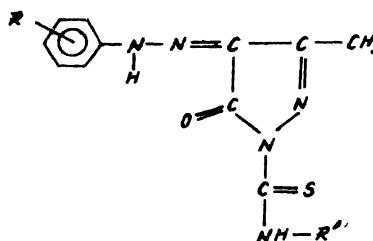
and

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A series of pyrazolin-5-one derivatives, viz., 4-arylhydrazono-N'-phenylthiocarbamoyl-(I_a), 4-arylhydrazono-N'-3-methylphenylthiocarbamoyl-(I_b), 4-arylhydrazono-N'-4-methylphenylthiocarbamoyl-(I_c), 4-arylhydrazono-N'-3-methoxyphenylthiocarbamoyl-(I_d) and 4-arylhydrazono-N'-4-methoxyphenylthiocarbamoyl-(I_e) have been synthesised as possible potential oral antidiabetics.



(I)

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| (I _a) R' = C ₆ H ₅ | (I _d) R' = <i>m</i> -OCH ₃ C ₆ H ₄ |
| (I _b) R' = <i>m</i> -CH ₃ C ₆ H ₄ | (I _e) R' = <i>p</i> -OCH ₃ C ₆ H ₄ |
| (I _c) R' = <i>p</i> -CH ₃ C ₆ H ₄ | |

The compounds described in this communication have been synthesised by reacting ethyl-2, 3-dioxobutyrate-2-arylhydrazones with different derivatives of phenylthiosemicarbazides. The structures of these compounds have been established on the basis of ir and mass spectral studies. The reactivity of ethyl-2, 3-dioxobutyrate-2-arylhydrazones was smooth and the products were obtained in good yield. The reactivity followed the expected course, diazonium chloride with electron withdrawing group in position 2 and 4 gave better yields. Colour of all these compounds ranges from yellow to orange.

Experimental

All m.p.s. are uncorrected. Ir spectra were taken in KBr film on a Beckmann IR spectrophotometer. Mass spectral studies were carried out on a Varian Mat-CH-7 mass spectrophotometer. Ethyl-2, 3-dioxobutyrate-2-arylhydrazones were prepared by the reported method¹.

Preparation of 4-arylhydrazono-N'-phenylthiocarbamoyl-3-methyl-2-pyrazolin-5-one :

Ethyl-2,3-dioxobutyrate-2-arylhydrazone (0.002 mol) was dissolved in alcohol (25 ml), a hot solution