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Chemical Constituents of *Verbesina encelioides* and *Holmskioldia sanguinea*

KRISHNA C. JOSHI, PAHUP SINGH

and

(MRS.) C. L. SINGHI

Department of Chemistry, University of Rajasthan, Jaipur-302 004

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VERBESINA encelioides (Cav) (Compositae) is a much branched tall herb. It was collected from the Rajasthan University campus, Jaipur, and a voucher specimen was deposited in Rajasthan University Botany Laboratories herbarium via sheet No. 12977. A perusal of literature revealed that some work has been reported on the species[1-4]. The present work deals with the chemical examination of its aerial parts and roots separately. *Holmskioldia sanguinea* (Retz) (Verbenaceae) is a struggling shrub, 10-30 feet in height. It was obtained from the United Chemical and Allied Products, Calcutta. No work has been done so far on *H. sanguinea*, and therefore, we undertook the chemical investigation of the plant.

Experimental

Verbesina encelioides : Air dried and coarsely powdered roots and aerial parts (1.5 kg each) were extracted separately with petroleum ether-ether (2 : 1) mixture in cold for 12 hr. The extracts were concentrated under reduced pressure and chromatographed over silica gel. Fractions collected were purified over preparative silica gel glass plates using various solvents mixture as eluants. Following compounds were identified by spectral and chemical studies as well as by comparison with authentic samples.

Results and Discussion

Bornyl ferulate : It is an oily liquid and its molecular formula $C_{20}H_{26}O_4$ was established by high resolution mass spectrometry. MS : m/e 330 (M^+). IR $\nu_{max}^{CCl_4}$: 3470 (OH stretch), 1715 (unsaturated C=O stretch) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) : δ 6.30 (1H, d, J=16 Hz), 7.60 (1H, d, J=16 Hz) for $-CH=CH$ *trans* olefinic protons ; 7.05 (1H, d, J=2 Hz), 7.07 (1H, dd, J=8.5, 2 Hz), 6.9 (1H, d, J=8.5 Hz) for 3 aromatic protons ; 3.92 (3H, s, OCH_3 group), 5.00 [1H, d(br), C-2 proton], 0.93 (3H, s, C-7 Me), 0.89 (3H, s, C-9 Me), 0.88 (3H, s, C-10 Me), multiplets at 1.05, 1.6, 2.05, 2.4 ppm due to 3, 3', 4, 5, 5', 6 and 6' protons of bornyl ring. These data agree with the reported ones[5]. It was finally confirmed by comparing its nmr with that of an authentic sample.

Linolenic and linoleic acids were identified by preparation of their methyl esters[6].

Taraxasterol acetate, α- and β-amyrins, stigmasterol and β-sitosterol gave positive tests for triterpenoids and sterols and were identified by preparation of their acetyl derivatives and comparison with authentic samples.

Benzyl-2,6-dimethoxy benzoate : It is a colourless liquid and its high resolution mass spectrometry (M^+ 272) established its molecular formula $C_{16}H_{16}O_4$. IR $\nu_{max}^{CCl_4}$ cm^{-1} : 1750 (C=O stretch of ester group), 1610, 1590 (-C=CH stretch, aromatic). ^1H NMR (400 MHz, $CDCl_3$) : δ 3.8 (6H, s, $2\times OCH_3$ group), 5.37 (2H, s, benzylic protons), 6.55 (2H, d, J=8.5 Hz, C-3, 5 protons), 7.26 (1H, d, J=8.5 Hz, C-4 proton), 7.44 (2H, dd, J=8.5, 1.5 Hz, C-2', 6' protons) and 7.36 (3H, m, C-3', 4', 5' protons). These data agree with the reported values and was finally confirmed by comparing its nmr with that of an authentic material[7].

Phytol : It is a colourless liquid, MS : m/e 296 (M^+) corresponded to its molecular formula $C_{20}H_{40}O$. IR $\nu_{max}^{CCl_4}$ cm^{-1} : 3656-3580 (O-H stretch). ^1H NMR (400 MHz, $CDCl_3$) : δ 5.14 [1H, t (br), $=CH-CH_2OH$], 4.16 (2H, dd, CH_2OH protons), 0.86, 0.87, 0.88, 0.89 (3H each d, J=7 Hz, C-7, 11, 16, 17 methyl protons), 1.67 (3H, s, C-3 Me protons). These data agree with its structure and finally confirmed by preparation of its acetate (M^+ 338)[8].

Holmskioldia sanguinea : The coarsely powdered plant material (1 kg) was extracted with petroleum ether and benzene over steam bath for 3×12 hr, separately. Both the extracts were mixed together, being similar in tlc behaviour, and chromatographed over silica gel when the following compounds were obtained.

Docasane, tetracosanol, friedelin and friedelinol were identified by comparison with authentic samples and by preparing their suitable derivatives.

Wogonin : It is a yellow crystalline solid, m.p. 203-04°. It gave colour with $FeCl_3$ and positive Wilson's boric test. Elemental analysis and mass measurements (284, M^+) assigned[9] its molecular formula as $C_{16}H_{12}O_5$. UV λ_{max}^{MeOH} : 270, 330 nm. IR ν_{max}^{KBr} cm^{-1} : 3400-3200 (O−H stretch hydrogen bonded), 1660 (C=O stretch), 1610 and 1580. ^1H NMR (400 MHz, acetone D_6) : δ 3.97 (3H, s, OCH_3), 6.32 (1H, s, C−6H), 6.82 (1H, s, C−3H), 11.31 [1H, s (br), C−5 OH], 9.4 (1H, s, C−7 OH), 8.13 (2H, dd, C−2', 6' protons), 7.63 (3H, m, C−3', 4', 5' protons). The above data indicated the compound to be 5,7-dihydroxy-8-methoxy flavone (wogonin), finally confirmed by preparation of its diacetate, m.p. 151° and comparison with an authentic sample.

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Possible Anthelmintic Compounds. Part-II : Mannich Bases from 2-Aryl/alkyl-3-(aryl/alkyl-benzimidazolyl)-quinazolin-4(3H)-ones

Y. D. KULKARNI, BASANT KUMAR and S. H. R. ABDI

Department of Chemistry, Lucknow University, Lucknow-226 007

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SUBSTITUTED quinazolones[1-3] and benzimidazoles[4,5] have been found to possess high anthelmintic activity. These observations have prompted the authors to synthesise a series of new compounds having both the quinazolone and benzimidazole moieties in their molecules and to evaluate their anthelmintic activity.

Experimental

All the melting points were taken in open capillaries and are uncorrected. IR spectra were recorded on Perkin Elmer spectrophotometer in KBr pellets.

2-Aryl-6,8-substituted benzoxazinone (**I**) *:* These were prepared by the action of anthranilic acids[6-9] and acid chlorides in presence of pyridine[10,11] and substituted anthranils were obtained by following the published work[12].

2-Aryl/alkyl-2-alkyl/phenyl carboxy substituted quinazolone (**II**) *:* A mixture of 2-substituted benzoxazinones (0.01 mole) and amino acids (0.01 mole) in dry pyridine was refluxed at 150° for 6 hr. Pyridine was removed by washing with dil.HCl (5 *N*) and the residue was extracted with saturated aqueous $NaHCO_3$. Crude product (**II**) obtained on acidification was purified by recrystallization from aqueous ethanol.

2-Alkyl/aryl 3-[2'-alkyl/aryl-benzimidazolyl]-3,1 (4H)quinazolinones (**III**) *:* They were obtained by the condensation of II and *o*-phenylenediamine in presence of excess of polyphosphoric acid[13].

Mannich bases of 2-alkyl/aryl 3-[2'-alkyl/aryl-benzimidazolyl]-3,1(4H) quinazolin-4-one (**IV**) *:* A mixture of III (0.01 mole), an amine (0.015 mole) and formalin (0.25 mole ; 40%) was refluxed in ethanol for 10 hr. The solvent was removed *in vacuo* and the residue recrystallised from aqueous ethanol.

Bio-assay :

LD_{50} for the compounds was determined[14] and was found to be in the order of 680-700 mg/kg of the animals (rat). The compounds were screened for their anthelmintic activity against *H. nana*[15] and *N. brasinellis*[16].

Results and Discussion

The compounds were found to be well tolerated and were devoid of any toxic manifestation. Substitution of morpholine, piperidine and pyrrolidine residue resulted in compounds with high activity.