The physical constants and the spectroscopic data (u.v., i.r. and NMR) of the furanocoumarin (V) isolated from *Clausena indica* were in agreement with those described for chalepin.[4] A direct comparison however could not be made. Heliettin[7] which appears to be the racemic form of chalepin, is identical with (V) in its u.v. and i.r. spectra.

EXPERIMENTAL

Extraction of Plant Material

The dried and powdered roots (20 kg) were extracted with hexane (b.p. 60–70°) (120 l.) and the extract concentrated to give a viscous oil (180 g).

Chromatographic Separation

The oil (160 g) dissolved in hexane (300 ml) was chromatographed on a column of silica gel (0·05–0·2 mm; 1·8 kg). The column was packed with hexane and gradient eluted with hexane, hexane–benzene and benzene–$CHCl_3$. 300 ml fractions were collected and examined by TLC.

(a) Fractions 79–118 (Elution; hexane–benzene 75%) gave chalepensin (IV) (26 g) m.p. 87–88° (TLC; R_f 0·6 in benzene–$CHCl_3$, 1:1) (Found, C, 76·1; H, 5·7 Calc. for $C_{16}H_{14}O_3$, C, 76·6; H, 5·6%), M.W. by m.s. 254. Mixed m.p. with an authentic sample of chalepensin showed no depression. TLC, u.v. and i.r. spectra were superimposable.

(b) Fractions 172–206 (Elution; benzene–$CHCl_3$, 1:1) gave β-sitosterol (1 g) m.p. 138°.

(c) Fractions 209–211 (Elution; benzene–$CHCl_3$ 75%) gave phellopterin (III) m.p. 102°. (TLC; R_f 0·84 in $CHCl_3$–MeOH 2%). It was found to be identical in mixed m.p. TLC and i.r. spectra when compared with an authentic sample.

Phellopterin (20 mg) on hydrolysis with AcOH containing a drop of H_2SO_4 gave a yellow crystalline phenolic compound m.p. 223°, identified as 5-methoxy-8-hydroxypsoralen.[8]

(d) Fractions 215–235 (Elution; benzene–$CHCl_3$ 75%) gave imperatorin (I) m.p. 98–99° (TLC; R_f 0·8 in $CHCl_3$–MeOH 2%). It was found to be identical in all respects when compared with an authentic sample.

Imperatorin (40 mg) on hydrolysis with AcOH containing a drop of H_2SO_4 gave pale yellow crystals (8 mg) m.p. 245–6°, identified as xanthotoxol (II).

(e) Fractions 236–245 (Elution with $CHCl_3$) gave chalepin m.p. 118–9° $[\alpha]_D + 28°$ (TLC, R_f 0·35 in $CHCl_3$–MeOH 2%).

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3-FORMYLINDOLE FROM *MURRAYA EXOTICA*[*]

B. K. Chowdhury and D. P. Chakraborty

Bose Institute, 93/1 Achaya Prafulla Ch. Rd., Calcutta 9, India

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OUR TAXONOMIC interest in the genus *Murraya* (Rutaceae)[1–4] prompted an investigation of *M. exotica* L (Syn. *M. paniculata*) from which we reported the isolation and structure proof

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[*] Part XXII in the series "Chemical Taxonomy"; Part XXI S. P. Basak and D. P. Chakraborty (paper communicated).

[1] D. P. Chakraborty and K. C. Das, *Chem. Commun.* 967 (1968).

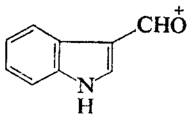
[2] D. P. Chakraborty, K. C. Das and B. K. Chowdhury, *Phytochem.* **8**, 773 (1969).

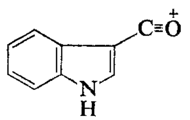
[3] B. K. Chowdhury and D. P. Chakraborty, *Chem. Ind.* 549 (1969).

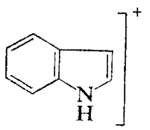
[4] D. P. Chakraborty, B. K. Chowdhury and B. C. Das, *Tetrahedron Letters* 3471 (1966).

of a new coumarin mexoticin.[4] The present communication relates to the isolation of a nitrogenous constituent C_9H_7NO (I) m.p. 196° which has been identified as 3-formylindole. After the separation of the basic and phenolic fractions with cold dilute 5% HCl and 1 per cent NaOH respectively, a neutral fraction was obtained from the alcoholic extract of the stem bark of the plant. From this neutral fraction, a compound, m.p. 196° was obtained by chromatographic separation over silica gel. The compound gave a 2,4-dinitrophenylhydrazone. The i.r. spectrum of the compound in the nujol phase showed peaks at 3180 (—NH— function), 1632 (—CHO group) 1612, 1575, 1520 (aromatic system and unsaturation), 785 and 755 cm^{-1} (substituted benzene derivative).

The NMR spectrum of the compound showed signals for —CHO group (10·02), NH-proton (12·11), one aromatic proton (8·22–8·00) and 3 aromatic protons, (7·65–7·17). The doublet of proton at 2 position of the indole nucleus collapsed to a singlet (8·3) upon irradiation at δ 12·11, showing its coupling with the H on nitrogen. Besides the molecular ion peak (I; M^+ 145), the mass spectrum of the compound showed peaks at *m/e* 144 (M-1) and another peak at *m/e* 117 (M-28) which could be explained by structures (II) and (III).


(I)


(II)


(III)

All these data showed that the compound might be 3-formylindole which has been confirmed by comparison with a synthetic specimen of 3-formylindole prepared by the formylation of indole using the method and procedure of Smith.[5]

The occurrence of simple indoles have been encountered in members of the Rutaceae, including *M. exotica.*[6] 3-Formylindole is uncommon in plant kingdom, and is considered to originate from tryptophan *via* indole acetic acid.

It is also known that photolysis of indole-3-acetic acid, *in vitro* gives rise to 3-formylindole.[7] Recent investigations[3] on the carbazole alkaloids from *Murraya koenigii* Spreng. have revealed the presence of carbazole alkaloids with methyl, formyl and carboxylic acid groups at 3-position, the most electrophilic centre of carbazole nucleus as evidenced in murrayanine, mukoeic acid, girinimbine, murrayacine etc. The demonstration of biological oxidation[8] of *p*-toluidine to *p*-hydroxymethylaniline lends support to the concept that the methyl group in these carbazoles may be biologically oxidized to formyl and carboxylic acid groups. Whether the oxidation of the aromatic methyl group to the formyl group takes place in the genus *Murraya*, is not yet known, but the occurrence of 3-formylindole in *M. exotica* may have some significance.

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SALICACEAE

HOT WATER PHENOLIC EXTRACTIVES OF THE BARK AND LEAVES OF DIPLOID *POPULUS TREMULOIDES**

IRWIN A. PEARL and STEPHEN F. DARLING

The Institute of Paper Chemistry, Appleton, Wisconsin 54911, U.S.A.

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Abstract—The hot water extractives of the fresh smooth green bark, leaves, and leaf stem twigs of a diploid *Populus tremuloides* tree cut in June were fractionated by ethyl acetate extraction and polyamide chromatography. Crystalline components isolated in quantity included salicin, salicortin, 1-*O*-*p*-coumaroylglucose, tremuloidin, tremulacin, and salireposide.

IN THE course of our studies on the barks and leaves of *Populus* species, the continuous evolutionary changes in processing employed in the laboratory suggested that organs of species investigated more than a decade ago be reinvestigated in the light of the newer knowledge. Accordingly, the smooth green bark, leaves, and leaf stem twigs of a diploid *P. tremuloides* tree cut in June were studied.

The fresh organs were processed immediately by the Waring Blendor and gradient elution polyamide chromatography procedures as detailed in an earlier paper on *Salix purpurea* bark.[1] The crystalline components isolated are presented in Table 1.

The recovery of crystalline products as noted in Table 1 represented a comparatively small proportion of the total products recovered from the chromatograms. TLC of filtrates from the crystals noted in the table in all instances indicated more of the specific compound together with one or more components, some in substantial amount. Further fractionation is necessary to separate these components in order to obtain crystalline compounds for identification. This is especially true in the case of compounds which are exceedingly soluble in water as represented by salicortin in the present study. The tremulacin noted in Table 1 was obtained by silica gel column chromatography as described earlier for salicortin.[1]

* Part XXVII in the series "Studies on the Barks of the Family Salicaceae" and Part XIV in the series "Studies on the Leaves of the Family Salicaceae."

[1] I. A. PEARL and S. F. DARLING, *Phytochem.* 9, 1277 (1970).