

features. Firstly, on almost all the nights, the sudden onset of spread-F in the post-midnight period is closely associated with a significant increase in the height of the F-region, the onset occurring either before or after the time of reversal of the vertical uplift. There does not appear to be any particular threshold height for the onset of spread-F in the post-midnight period, as it occurred, on individual occasions, at heights ranging from 270 to 560 Km. Secondly, all the nights (with the sole exception of the one of 15/16 June 1960) correspond to either disturbed geomagnetic conditions or preceded by disturbed conditions ( $K_p > 3^\circ$ ).

The consistent increase in the F-region height noticed with the onset of spread-F in the post-midnight period bears a resemblance to the well-known post-sunset rise of equatorial F-region. This suggests that the sudden onset might be due to a sudden reversal in F-region vertical drift from its usual downward direction during the night time period. The fact that most of the events were noticed to occur during geomagnetically disturbed conditions lends support to this, as the recent observations of Fejer *et al.*<sup>14</sup> and Rastogi and Woodman<sup>15</sup> show that such night time anomalous reversals in F-region vertical drift occur during disturbed conditions, in association with sudden onsets of equatorial spread-F. However, these observations are for conditions of low to moderate sunspot activity conditions and it is yet to be seen whether such reversals do occur under high sunspot activity conditions. On the other hand, the statistical analysis of Bowman<sup>16</sup> suggests that the occurrence of equatorial spread-F, in the early morning period, is due to travelling ionospheric disturbances that originate in the auroral zones during disturbed conditions. Very recently, Bowman<sup>17</sup> presented one individual event, corresponding to high sunspot activity conditions, where in the occurrence of a sub-storm was accompanied by conspicuous increases in F-region height and sudden onset of spread-F, at stations ( $75^\circ$  W longitude) from high midlatitudes to down to the dip equator, with a delay suggesting the propagation of a travelling ionospheric disturbance with a speed of about  $740 \text{ m sec}^{-1}$ . Alternatively, it is therefore quite possible that the sudden onsets noticed might be due to travelling ionospheric disturbances. Further detailed event-wise studies are very much required to gain insight into the physical mechanisms involved and their relative role, in the sudden onset of equatorial spread-F during the post-midnight period (under high sunspot activity conditions) pointed out here.

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#### REACTION OF HALOGENOANILINES WITH ACRYLIC ACIDS

THE present communication describes a one step synthesis of some halogeno-2, 3-dihydro-4 (1H)-quinolones obtained by heating chloro- and bromo- anilines with acrylic acid and methyl acrylic acids in the presence of PPA. The halogeno quinolones are of importance because many of them are reported to possess analgesic and antibacterial<sup>2</sup> activity.

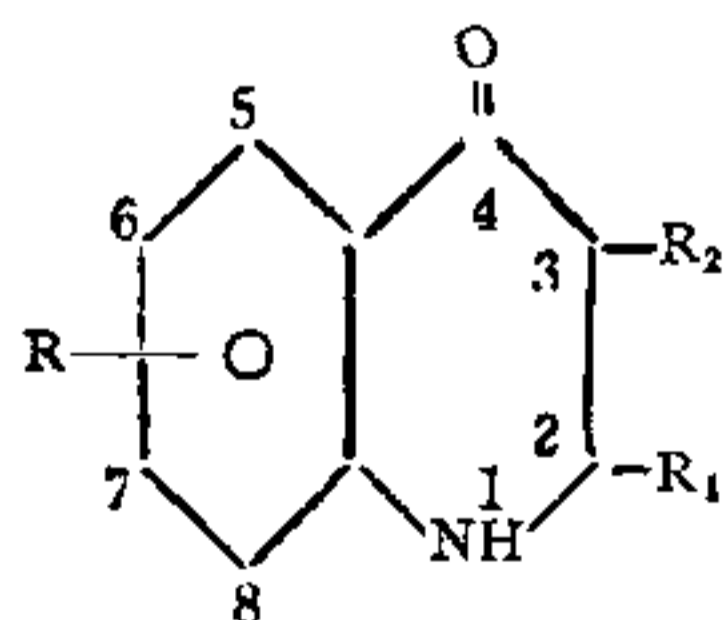
The general method<sup>1,2</sup> of preparation consists in heating the halogenoaniline (1 mole) with acrylic or methyl acrylic acid (1 mole) in the presence of PPA at  $100^\circ$ – $140^\circ$  for 3–7 hr. In some cases the acrylamides were isolated either alone or along with the quinolones. In all these experiments a large amount of tarry matter was obtained and the different compounds were purified only after column chromatography over neutral alumina (Table I).

TABLE I

Aniline	Acid used	Products formed	m.p./b p.	Yield %
<i>o</i> -Chloro	Acrylic	8-Chloro-2, 3-dihydro-4 (1H)-quinolone	74-5° 245°/15 mm	20
	$\alpha$ -Methyl-acrylic	no pure product	..	..
	Crotonic	2-Chloro-crotonanilide <sup>+</sup>	105-6°	20
<i>p</i> -Chloro	Acrylic	6-Chloro-2, 3-dihydro-4 (1H)-quinolone <sup>++</sup>	198-9°	10
		4-Chloro-acrylanilide <sup>+++</sup>	186-8°	3
	$\alpha$ -Methyl-acrylic Crotonic	4-Chloro- $\alpha$ -methyl-acrylanilide <sup>++</sup>	107°	5
		4-Chloro-crotonanilide <sup>+</sup>	132-3°	10
<i>o</i> -Bromo	Acrylic	8-Bromo-2, 3-dihydro-4 (1H)-quinolone	195°/6 mm	10
	$\alpha$ -Methyl-acrylic	no pure product	..	..
	Crotonic	2-Bromo-crotonanilide <sup>+</sup>	109-10°	10
<i>m</i> -Bromo	Acrylic	no pure product	..	..
	$\alpha$ -Methyl-acrylic Crotonic	3-Bromo- $\alpha$ -methyl-acrylanilide <sup>++</sup>	108-10°	10
		7-Bromo-2, 3-dihydro-2-methyl-4 (1H)-quinolone <sup>++</sup>	174-76°	10
		3-Bromo-crotonanilide <sup>++</sup>	93-4°	2
<i>p</i> -Bromo	Acrylic	no pure product	..	..
	$\alpha$ -Methyl-acrylic	6-Bromo-2, 3-dihydro-3-methyl-4 (1H)-quinolone <sup>++</sup>	145-7°	10
		4-Bromo-crotonanilide <sup>++++</sup>	174-5°	5
	Crotonic	6-Bromo-2, 3-dihydro-2-methyl-4 (1H)-quinolone <sup>++</sup>	155-6°	10

<sup>+</sup> Crystallised from petroleum ether (40-60°); <sup>++</sup> Crystallised from benzene-petroleum ether (40-60°); <sup>+++</sup> Crystallised from ether-petroleum ether (40-60°); <sup>++++</sup> Crystallised from ethyl acetate-petroleum ether (40-60°).

The 2, 3-dihydro-4 (1H)-quinolones were characterized by the formation of crystalline 2, 4-DNP derivatives and by their spectral data while the acrylanilides were non-reactive towards the usual carbonyl reagents and exhibited typical spectra.



The UV spectra of the quinolones generally showed  $\lambda_{\max}^{\text{MeOH}}$  at around 235, 255 and 375 nm, whereas the amides showed  $\lambda_{\max}^{\text{MeOH}}$  around 220 and 270 nm.

The IR spectra of the quinolones showed bands around 3350-3500  $\text{cm}^{-1}$  for -NH and the carbonyl band generally appeared around 1640-1660  $\text{cm}^{-1}$ . In case of the amides, the IR gave bands around 3300  $\text{cm}^{-1}$  and 3400  $\text{cm}^{-1}$  due to -NH and 1660-1685  $\text{cm}^{-1}$  for C=O frequencies.

The NMR spectrum of the 2- or 3-methyl-2, 3-dihydro-4 (1H)-quinolones gave a doublet around

$\delta$  1.0-1.3 for the  $\text{C}_2\text{-CH}_3$  or the  $\text{C}_3\text{-CH}_3$ . For the  $\alpha$ -methyl-acrylanilides the methyl protons were obtained as a singlet while in the case of the crotonanilides the methyl protons were seen as a doublet, and in both the cases they appeared in the region  $\delta$  1.7-2.1. The methylene and methine protons of the quinolones appeared as a doublet and a multiplet at  $\delta$  2.4-3.8 respectively while the amides showed no signals in this region. The  $\alpha$ -methyl-acrylanilides showed singlets at  $\delta$  5.5-5.9 for  $\text{C}=\text{CH}_2$  while the crotonanilides gave a doublet at  $\delta$  6.66 due to  $\text{CH}_3\text{-CH}=\text{CH-CO-}$  grouping and a multiplet at  $\delta$  7.5 corresponding to  $-\text{CH}=\text{CH-CH}_3$ . The quinolones showed doublets at  $\delta$  6.5 and 7.33 ( $\text{C}_6$ ) and ( $\text{C}_5$ ) and a singlet at  $\delta$  7.0 ( $\text{C}_8$ ) for the aromatic protons. In case of the  $\alpha$ -methyl-acrylanilides and crotonanilides four aromatic protons were observed as two doublets or a broad multiplet around  $\delta$  6.4-7.9. The (-NH) proton of the quinolones was usually found around  $\delta$  4.2-4.6 as a broad singlet while the amide proton (-NH) appeared at about  $\delta$  8.0-10.0.

All the compounds gave satisfactory elemental analyses.

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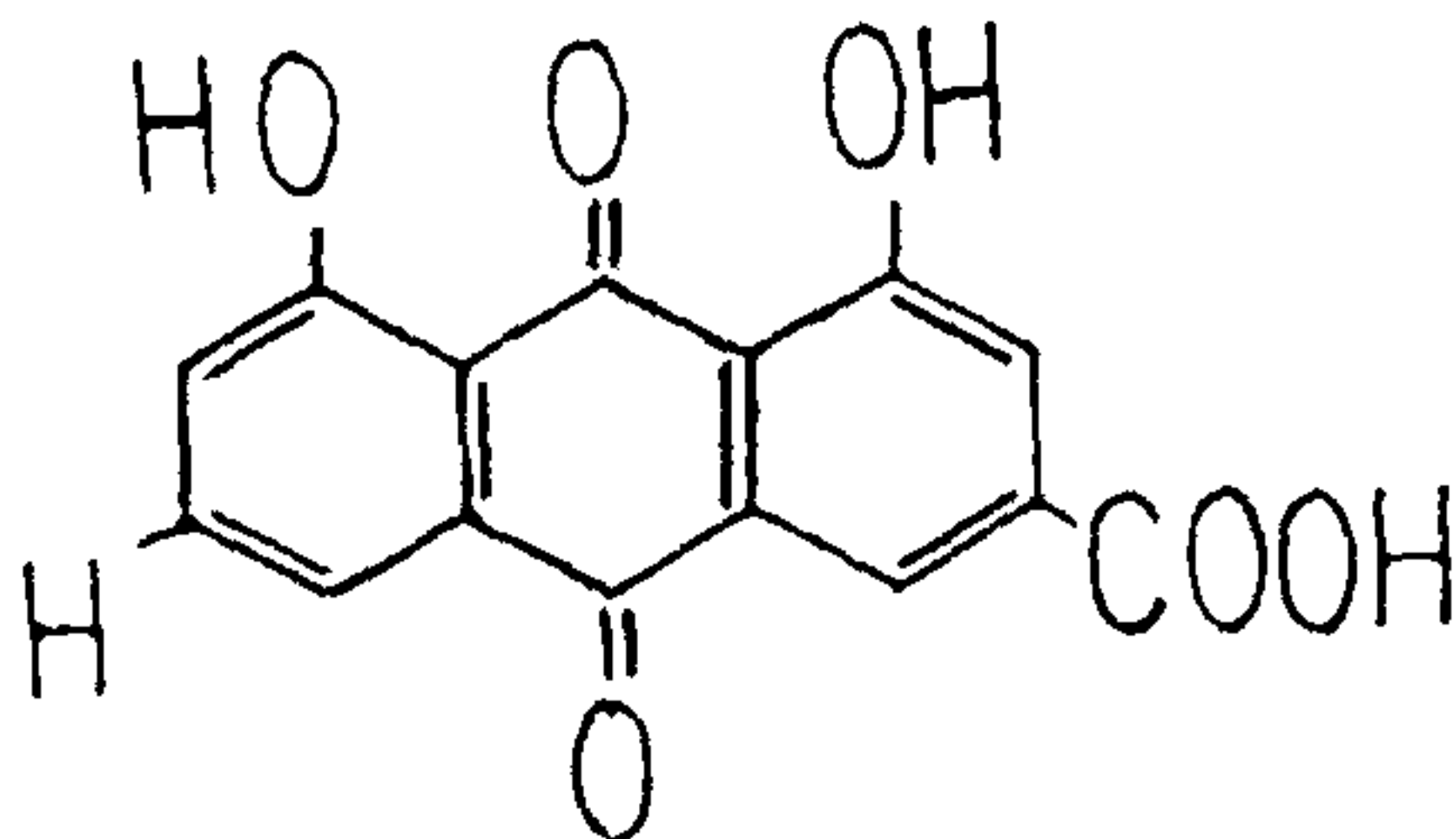
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### RHEIN FROM THE LEAVES OF *CASSIA NODOSA*

*Cassia nodosa* (Fam. Ceasalpinaceae) is a tree of upto 30-40 feet high. Leaves are mentioned to function as purgatives<sup>1</sup> but yet there is no report of isolation of any active principle from leaves which may be responsible for its purgative action. This note describes the isolation and identification of the active principle rhein, which is found in free as well as in the combined state in leaves.

#### Experimental

Isolation of (I) Free rhein :—About 1 g of the dried powdered leaves was completely extracted with chloroform, (II) Combined rhein :—The marc after extraction of free rhein was heated with dilute HCl + FeCl<sub>3</sub> (20%) for 30 minutes on water-bath. Solution was cooled and the liberated aglycone (rhein) was extracted with chloroform.



## RHEIN

Chloroform extracts from (I) and (II) were concentrated under reduced pressure and used for TLC studies with silica gel G using solvent system benzene, chloroform, glacial acetic acid (90 : 10 : 0.5). Extracts (I) and (II) both produced single spots (R<sub>f</sub> 0.15)

which were identical to the R<sub>f</sub> of authentic sample of rhein developed on the same chromatogram.

15 mg of pure rhein was obtained by preparative TLC<sup>2</sup> (orange needle crystals), M.P.—321, I.R. spectra (cm<sup>-1</sup>) in Nujol—1630; 1670; 1705; 1570 u.v. spectra max (in methanol)—(nm) 228; 260; 432.

Physical properties and the chromatographic studies confirmed the presence of rhein, the compound which is responsible for purgative action of the leaves.

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### 2-(2'-LEPIDYL AZO)-1-NAPHTHOL-4-AMMONIUM SULPHONATE (LANAS) AS VISUAL METALLO-CHROMIC INDICATOR IN COMPLEXOMETRIC DETERMINATION OF LEAD(II)

HETEROCYCLIC azo dyes introduced recently<sup>1</sup> find extensive use in complexometric<sup>2-4</sup> and spectrophotometric<sup>5</sup> determination of micro amounts of metal ions in solution. Only very few water soluble heterocyclic azo dyes have been used so far. We have synthesised 2-(2'-lepidyl azo)-1-naphthol-4-ammonium sulphonate (LANAS) and have used for micro determination of mercury(II) complexometrically<sup>6</sup>. In this present communication LANAS has been employed as metallo-chromic indicator for complexometric determination of lead(II) alone or in the presence of large number of other bivalent metal ions.

LANAS gives deep blue colour complex with lead(II) which is readily discharged on adding dilute solutions of EDTA. The observation has been made the basis for the present investigations. The formation of blue coloured Pb-LANAS complex is quantitative and completely discharged in the pH range 6.0 to 7.5 (hexamine-nitric acid buffer). The titration can be successfully performed in the temperature range 0 to 95°C with two to three drops of 0.01% (w/v) LANAS solution as indicator. The best results are obtained when solutions containing lead(II) 0.207 to 41.440 mg per 20 ml are titrated.

#### Recommended Procedure

To suitable aliquots containing 0.207 to 41.440 mg of lead(II), add two to three drops of 0.01% (w/v) LANAS solution. Add few drops of dilute nitric acid till yellow colour is obtained. Add 10% hexamine solution dropwise till blue colour is obtained. Raise the value to 20 ml and titrate with EDTA solution at room temperature till a sharp colour change blue to