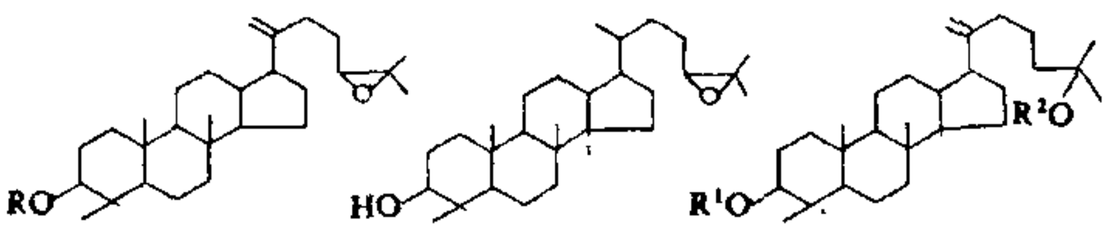

I ; R = rhamnosyl (1 → 4) xyloside
Ia; R = H
Ib; R = Ac
Ic; R = xylose

II

III; $R^1 = R^2 = H$
IIIa; R^1 = Ac; $R^2 = H$
IIIb; $R^1 = R^2$ = Ac

to Dr (Mrs.) Savitri Devi Srivastava, for her valuable suggestions and Ministry of Health and Family welfare (New Delhi) for award of fellowship to VKA.

21 May 1984; Revised 10 August 1984

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NOVEL SYNTHESIS OF BENZOFURANS

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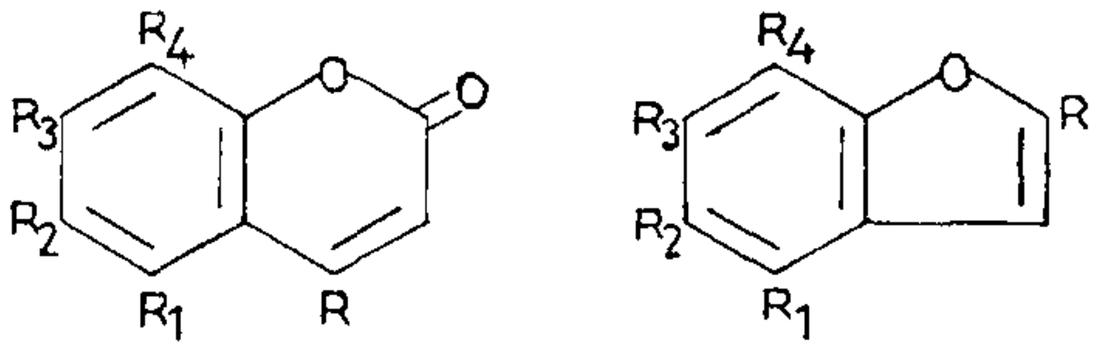
SEVERAL substituted 4-chlorocoumarins (II) have been prepared from the corresponding 4-hydroxycoumarins (I) and converted to the respective benzofuran-2-carboxylic acids (III) and then to benzofurans (IV) by Perkin-Fittig-Ebert method[1,2].



I R = OH
II R = Cl
III R = COOH
IV R = H

a, $R_1 = R_3 = H$, $R_2 = R_4$ = Me.
b, $R_1 = R_4 = H$, $R_2 = R_3$ = Me.
c, $R_2 = R_3 = H$, $R_1 = R_4$ = Me.
d, $R_2 = R_3 = H$, R_1 = Me, R_4 = i.Pr.

4-Chlorocoumarins (II) were prepared by reacting the corresponding 4-hydroxycoumarins (I) obtained by the method described earlier[3], with phosphoryl chloride in 45–60 per cent ields[4]. Respective 4-chloro-3,3′,4′,4″-tercoumarins accompanied the chlorocoumarins[5].

4-chloro-6,8-dimethylcoumarin[6] [IIa, m.p. 150–51°, UV λ_{max}^{EtOH} (log ε) 245(3.91), 288(4.19), 325(3.81), IR, KBr (cm^{-1}), 1720(m), 1660(s), 1615(s), 1575(m), 775(m)] in dioxane when refluxed for one hour with aqueous sodium hydroxide (10%) gave 5,7-dimethylbenzofuran-2-carboxylic acid [IIIa, m.p. 259–60°, UV λ_{max}^{EtOH} (log ε) 230(4.06), 270(4.16), IR KBr (cm^{-1}) 1700(s), 1566(s), 1420(s), 1315(s), 1205(s)].

Similarly, 6,7-dimethyl- [IIb, m.p. 143–44°, UV λ_{max}^{EtOH} (log ε), 235(3.90), 288(4.24), 325(3.81)], 5,8-dimethyl- [IIc, m.p. 82–83°, UV λ_{max}^{EtOH} (log ε) 242(3.89), 303(4.13)] and 5-methyl-8-isopropyl- [IId, m.p. 83–84°, UV λ_{max}^{EtOH} (log ε) 245(4.01), 297(4.25), IR KBr (cm^{-1}) 1720(s), 1600(m), 1575(s), 780(m)]-4-chlorocoumarins gave respectively 5,6-dimethyl- [IIIb, m.p. 243–44° UV λ_{max}^{EtOH} (log ε), 272(3.97)], 4,7-dimethyl- [IIIc, m.p. 205–07° UV λ_{max}^{EtOH} (log ε), 270(4.25), 285(4.15), IR KBr (cm^{-1}), 1685(s), 1570(s),

1300(m), 1200(s)] and 4-methyl-7-isopropyl- [IIId, m p. 189–90°, UV λ_{max}^{EtOH} (log ε) 282(4.23)] benzofuran-2-carboxylic acids.

These acids were decarboxylated to 5,6-dimethyl-benzofuran [IVb, b p. 220–22°, picrate, m p. 63–64°], 4,7-dimethyl benzofuran[7] [IVc, b p. 217–18°, picrate m p. 102–03° UV λ_{max}^{EtOH} (log ε), 253(4.23), 300 (4.24)], 5,7-dimethylbenzofuran[7] [IVa, b p. 222–24°, picrate, m p. 78–79] and 4-methyl-7-isopropyl benzofuran[7] [IVd, b p. 235–37°, picrate m p. 97–98°].

Elemental analyses of all the compounds agree with the expected structural formulae.

AKS and RVR are grateful to UGC and NSB to Gujarat Government for fellowships.

7 August 1984

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TERREIC ACID—A DIABETOGENIC MYCOTOXIN IN RATS

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ASPERGILLUS TERREUS, a common food contaminant, grows on foods and feeds when storage conditions are poor, and produces a number of secondary metabolites like terreic acid, terrein and terremutin[1]. Among these, terreic acid has been reported to be toxic to man and laboratory animals[2].

Eventhough many mycotoxins appear to disturb the carbohydrate metabolism, the effect of mycotoxins on the serum insulin levels which is a major factor controlling the blood glucose level has not been reported. Hence the effect of terreic acid ingestion on blood glucose, liver glycogen and serum insulin levels in rats has been reported here.

A. terreus was grown on Czapek-Dox liquid culture medium for 15 to 20 days, terreic acid extracted from the culture filtrate by the method of Kaplan *et al*[2] and purified using preparative thin layer chromatography. It was crystallised using absolute alcohol and the purity tested by comparing with an authentic sample. Bread, 400 g, containing calcium propionate as preservative was mixed with water to have 30 % moisture, sterilized, cooled, inoculated with spores of *A. terreus* (10^6 spores/ml) and allowed to get incubated at 27–28°C for 20 days. After this, the contaminated material was sterilised free of the fungus using chloroform and dried well to remove any traces of chloroform. This material was mixed with the normal diet in the ratio of 1:3 and fed as the contaminated diet.

Weanling albino rats of Wistar strain weighing about 35–40 g were divided into three groups. The first group received normal diet and served as control while the second group of animals was injected intraperitoneally with the pure terreic acid at a dosage of 0.2 mg/rat, dissolved in 0.5 ml of sterile water, and the third group of rats was fed with the contaminated diet containing terreic acid in a concentration such that each rat consumed 50 μg of terreic acid daily. Toxicity studies were carried out on rats for a period of 24 weeks, which is a long term experiment on a mycotoxin with a high LD_{50} value. At the end of the experimental period, the rats were starved overnight

Table 1 *Fasting blood glucose level and liver glycogen level in control and experimental rats. The values are expressed as mean ± S.D. for six animals in each group.*

Experimental animals	Tests carried out: Fasting blood glucose level mg/dl of blood	Tests carried out: Liver glycogen mg/gm of wet tissue
Control	68.8 ± 5.1	30.5 ± 2.1
Toxin injected	91.9 ± 3.9[a]	18.8 ± 1.2[a]
Contaminated diet fed	78.5 ± 4.4[b]	25.1 ± 1.8a

[a] $p < 0.001$; [b] $p < 0.01$