Procedure.—Requisite amounts of antipyrine solution and 25 ml of solution A are mixed and made up to 50 ml to give a final molarity of antipyrine ranging from 0·5 to 4·0 mM. Five ml of solution B and 10 ml of the sample solution are placed in separate boiling tubes and immersed in an ice bath. After the two solutions attain the bath temperature, a stop clock is started and the two solutions are thoroughly mixed noting the time of the first addition of the solutions. Time required for the complete disappearance of orange colour of the indicator is noted and the experiment repeated till concordant values are obtained. A blank run under identical conditions required three seconds for the bleaching and the correction is applied in all measurements. A plot of the time required for bleaching *versus* concentration of antipyrine is shown in Fig. 1. Similar results are

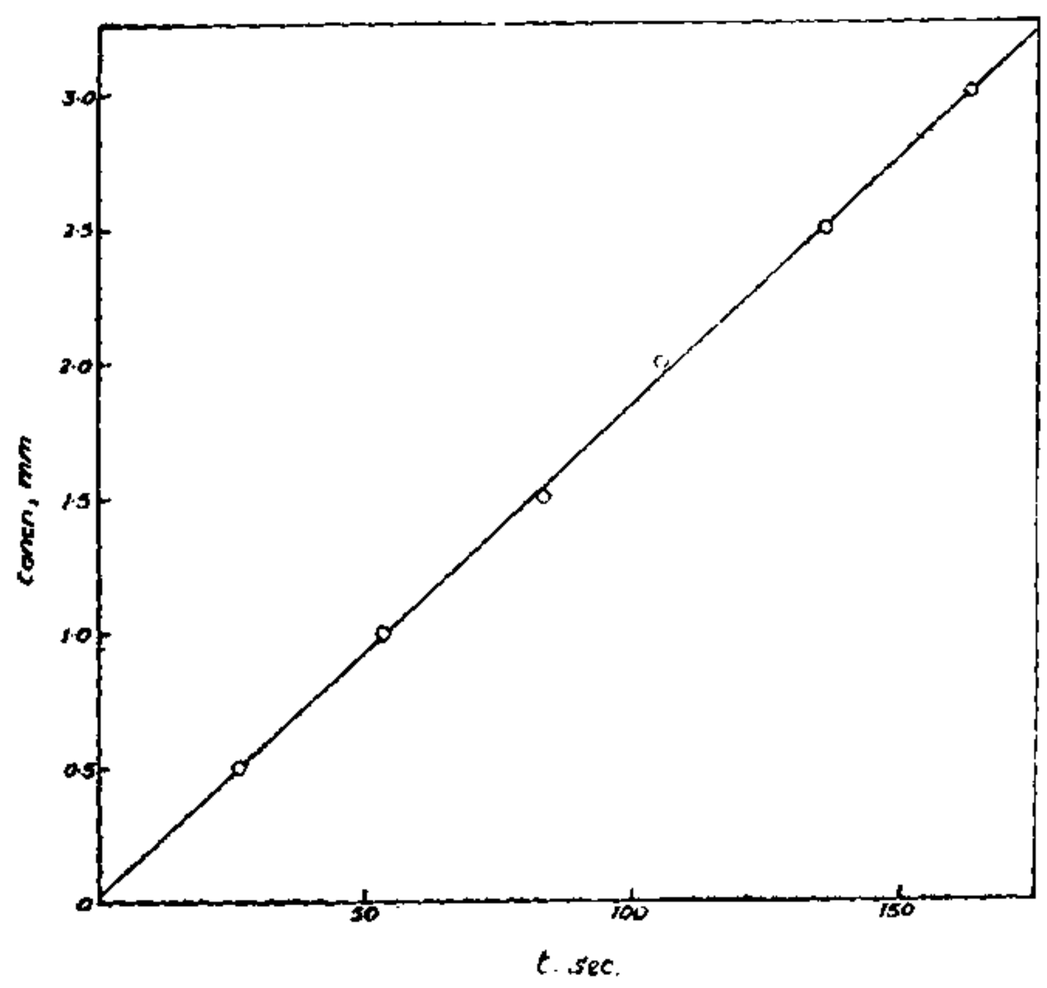

FIG. 1. Plot of time of bleaching in seconds *versus* the concentration of antipyrine (millimoles).

obtained with aniline and oxine. A low temperature is usually preferred for brominations so as to prevent side reactions. Very good results were obtained with antipyrine and aniline at room temperature also (30° C) by working with lower concentrations of bromide (0·100 M) and bromate (0·050 M) and keeping the acidity at 0·150 N. This method is quite general and can be applied for the determination of most of the organic compounds which are either brominated or oxidized by bromine at a fast rate.

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Indian Institute of Technology, R. K. GUPTA.
New Delhi-29, *July* 3, 1972.

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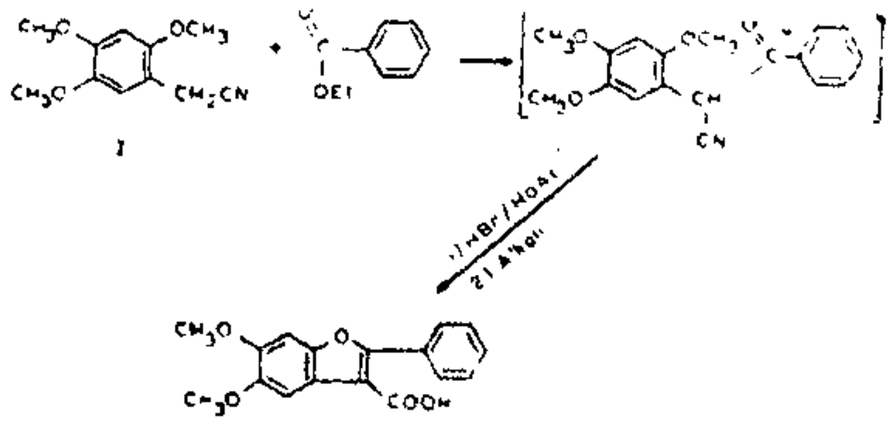
A BIOGENETIC TYPE SYNTHESIS OF (±) OBTUSAFURAN METHYL ETHER

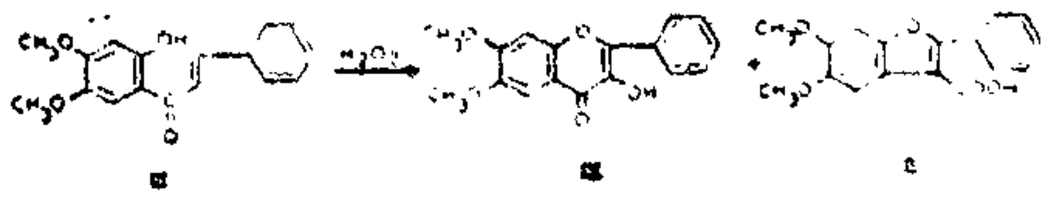
OBTUSAFURAN (IX *a*) and melanoxin are two novel 2-phenyl-3-methyl dihydrobenzofuran derivatives recently isolated[1,2] from two closely related species of *Dalbergia*. Ollis *et al.* hold the view that these novel skeletons arise by condensation of a phenol with a cinnamyl pyrophosphate. Literature however reveals that furanoid derivatives of the obtusafuran type can also arise from a number of flavonoid precursors. At least three such instances are readily available and these are: (*a*) AFO oxidation of suitably substituted chalkones to the corresponding 2-phenyl-benzofuran-3-carboxylic acids[3], (*b*) Rearrangement of catechins under solvolytic conditions[4] and (*c*) Oxidation of 3-alkoxy flavylium salts with hydrogen peroxide to 2-phenyl benzofuran-3-carboxylic esters[5]. Subsequent minor modifications of the benzofuran derivatives could easily give rise to obtusafuran type of compounds.

In order to test the above idea, a synthesis of obtusafuran methyl ether was undertaken starting from flavonoid precursors. As a preliminary step an authentic sample of the acid (II) was obtained by condensation of 2, 4, 5-trimethoxy benzyl cyanide[6] (I) with ethylbenzoate and subjecting the resulting product to demethylation-*cum*-cyclisation with HBr in acetic acid followed by alkali hydrolysis. The product had m.p. 215–16° and was obtained in good yield.



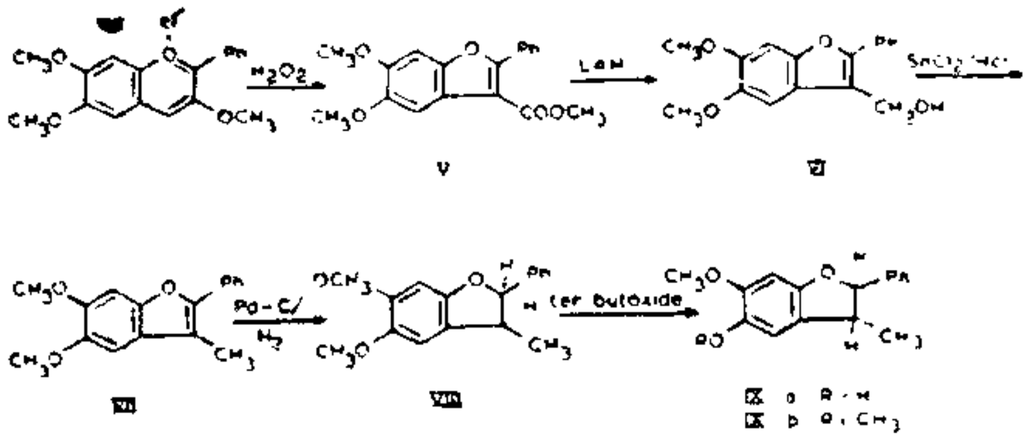
I II

The same acid was also obtained by AFO reaction of 2-hydroxy-4, 5-dimethoxy chalkone[7] (III) which gave, in addition, the corresponding flavonol (IV) as a major product.



III IV V

Similarly H_2O_2 oxidation of 3, 6, 7-trimethoxy flavylium chloride furnished the methyl ester of the acid (II). LAH reduction of the ester (V) gave the coumaryl alcohol (VI) which was further reduced with $SnCl_2$/HCl to give 2-phenyl-3-methyl-5, 6-dimethoxy benzofuran (VII) as the sole product. Subsequent catalytic hydrogenation gave *cis* (±)-obtusafuran methyl ether (VIII). This was isomerised to the *trans*-compound (IX *b*). The latter was identical in IR and NMR with an authentic sample of trans (+) obtusafuran methyl ether.



We wish to thank Prof. W. D. Ollis, Department of Chemistry. University of Sheffield, for a natural sample of obtusafuran used for comparison and the C.S.I.R. (India) for financial assistance to one of us (S. B.).

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A NEW ISOFLAVONE, NEO-BAVA-ISOFLAVONE, FROM THE SEEDS OF *PSORALEA CORYLIFOLIA*

In a recent communication[1], the isolation of a new compound from the alcoholic extract of the pericarp of the fruits of *P. corylifolia* was reported. Its structural elucidation is reported in this paper.

The 5% Na_2CO_3 soluble fraction of the alcoholic extract when subjected to silica gel column chromatography gave a new compound in addition to the known compounds bavachin and psoralidin. It crystallised from ethyl acetate-benzene mixture as colourless long needles, m.p. 195–96° ; M^+ 322 ; no ferric colour ; $\lambda_{max.}^{MeOH}$ 247, 305 s, $\lambda_{max.}^{MeOH\text{-}NaOMe}$ 252. 310, $\lambda_{max.}^{MeOH\cdot NaOH}$ 253, 330 ; $\nu_{max.}^{KBr}$ 1625 cm^{-1}. It gave acetate m.p. 120–21°. Its NMR spectrum taken in $CDCl_3$ showed the signals of a *C*-prenyl unit (a broad singlet at δ 1·70 for six protons, a doublet at δ 3·30 for two protons of Ar-CH_2- and a triplet at δ 5·25 ppm for an olefinic proton of the prenyl unit), two singlets at δ 2·30 and 2·33 ppm for two acetoxyl groups, a singlet at δ 7·98 for one proton, two ortho-coupled doublets at δ 6·85 and 8·33 ppm (J = 10 cps) and a multiplet (δ 7·1–7·4) for four protons. It did not give Mg/HCl test but gave a positive Na/Hg test. This along with the presence of a singlet at δ 7·98 in the NMR spectrum suggested that the compound was an isoflavone. It has therefore been named neo-bavaisoflavone.

The close similarity of the UV spectrum of neo-bavaisoflavone with that of diadzein along with the general hydroxylation pattern of other compounds occurring in this source indicated that it was a *C*-prenyl derivative of diadzein. For locating the position of the prenyl group, the compound was heated with formic acid when the *C*-prenyl unit was converted into the corresponding 2, 2-dimethyl chroman (II) as shown by the NMR spectrum of its acetate : two triplets at δ 1·83 and 2·86 for four H, a singlet at δ 1·38 for six protons and a singlet at δ 2·35 ppm for one acetoxyl group.