CHEMICAL STUDIES OF *PSORALEA CORYLIFOLIA*

FYARE LAL KHANNA AND T. R. SESHADRI
Department of Chemistry, University of Delhi, Delhi-7

INTRODUCTION

PSORALEA CORYLIFOLIA (Hindi-Bavachi) is a well-known plant drug. As a legume it grows widely all over India and requires little attention. Its full utilisation has not yet been accomplished. The chemical studies on this plant started nearly 40 years ago and periodically new discoveries have been reported and yet it would appear that there is possibility of discovering more.

The seed (more correctly the fruit) is brownish-black in colour, has soft skin, pleasant odour (Sanskrit name Sugandha) and a pungent bitter taste and has been used widely in medicine. It has been reported to have antiseptic properties either in its fresh form or in the form of watery extracts prepared from it. In inflammatory diseases of the skin, leucoderma and psoriasis, it is given both as a local application and by the mouth. The seeds are frequently used in several toilet preparations because of their prophylactic and curative action against skin diseases.

CHEMICAL COMPONENTS OF *P. corylifolia*

The chemistry of the seeds has been a subject of investigation of a number of workers. Menon[1] obtained the fatty oil from the seeds and determined its physical and chemical constants. Jois *et al.*[2], besides examining in greater detail the fixed oil of the seeds, were able to isolate two crystalline compounds, psoralen and isopsoralen. The latter was identified[3] to be angelicin and psoralen was studied, its constitution established and synthesis effected[4]. In their method the whole seeds (fruits) were crushed or powdered and extracted and hence pure fractions could not be obtained easily. A method was developed by Seshadri *et al.*[5], which enabled the separation of the components more efficiently in greater purity and yield and at the same time giving information regarding the parts of the seeds in which they occur. The seed or fruit consists of a sticky oily pericarp, a hard seedcoat and a kernel. The whole seed cannot be easily powdered owing to the sticky pericarp. However, the pericarp can be removed by soaking the whole seed in ether, methylated spirit or light petroleum and gentle rubbing; this leaves the seedcoat and kernel intact. The above ether extract contains a steam volatile essential oil, an alkali soluble resin and a terpenoid liquid insoluble in alkali. Thus these are present only in the pericarp and not in the kernel.

When the ether extracted material was rubbed, the remaining pericarp could be easily removed and the seed can be conveniently powdered. This on extraction with light petroleum in a Soxhlet gave a colourless crystalline solid (1·1% of the fresh seed) found to be a mixture of psoralen and isopsoralen and also a fixed oil consisting almost completely of glycerides. The unsaponifiable portion of the fixed oil was found to contain a phytosterol. Besides these components, the kernel also contains nitrogenous and mineral matter which make it suitable as a feeding stuff and manure. The importance of this work lies in the ease with which each component of the drug is obtained practically uncontaminated by others and in highly increased yields.

That the sterol of the seed fat of *P. corylifolia* was stigmasterol was proved by Khastgir *et al.*[6]. It was also shown by Khastgir *et al.*[7] that some psoralen and isopsoralen could be obtained from the water soluble glycosidic fraction of the seed kernel after hydrolysis with alcoholic hydrochloric acid. In this connection it may be mentioned that psoralen had earlier been found[8] to occur as the glycoside of the corresponding *o*-hydroxycinnamic acid (I *a*) in the seeds of *Coronilla glauca*, a species well known for cardiac glycosides.

STUDY OF FURANOCOUMARINS AND PSORALIDIN

In general furanocoumarins produce photosensitivity and hence the presence of these coumarins in *P. corylifolia* is responsible for photodynamic activity. The active principles psoralen and isopsoralen have been identified to be isomeric furanocoumarins. In addition to these, psoralidin has been isolated from the pericarp of the seeds.

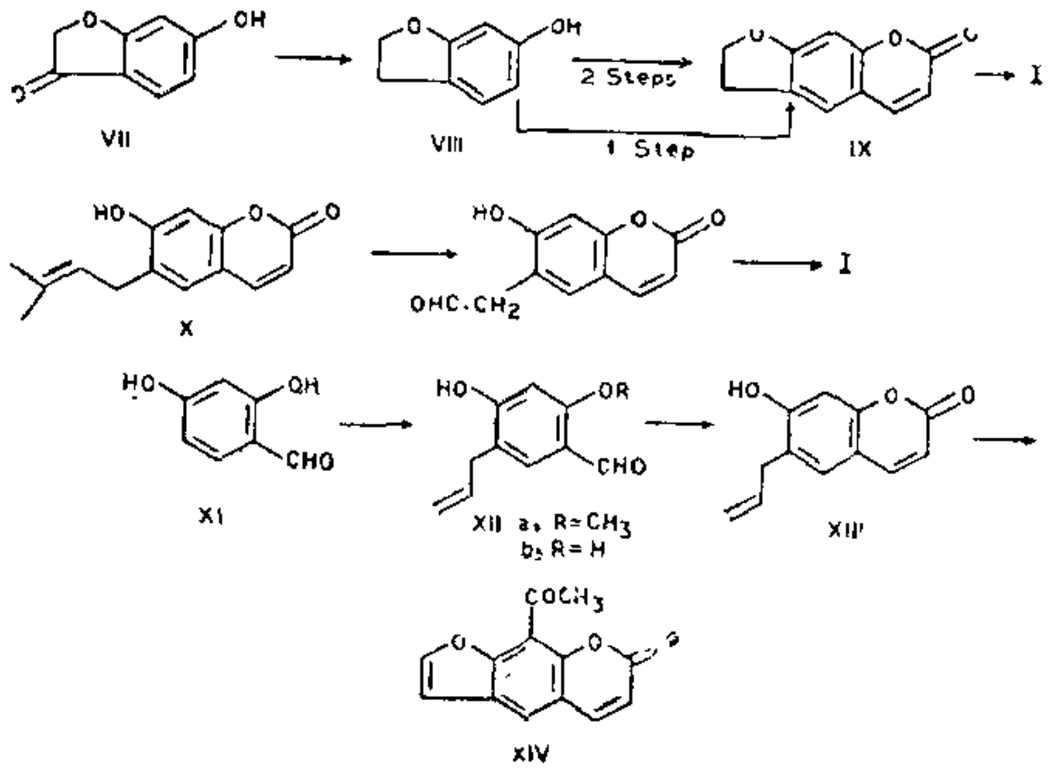
Psoralen.—It is the simplest linear furanocoumarin having high photodynamic activity and is an effective drug for the cure of leucoderma. It has been isolated from a number of other sources also. As mentioned above

β-D-glucosidofuranocoumaric acid (I *a*) occurring in Nature is readily split by emulsin or acid yielding psoralen after spontaneous lactonization.

The constitution of psoralen (I) was established by Spath *et al.*[4-9]. It showed the properties of a lactone and on oxidation with alkaline hydrogen peroxide it gave furan-2, 3-dicarboxylic acid (II). On the other hand with potassium permanganate, it formed a hydroxycarboxylic acid (III) which on decarboxylation yielded umbelliferone (IV), thus

establishing the furanocoumarin nature of psoralen. The linear fusion of the furan and coumarin rings was indicated by methylation of psoralen in alkaline medium to a methoxycinnamic acid (V) which on oxidation gave a dicarboxylic acid (VI), identified to be 2, 4-dimethoxy-1, 5-dicarbomethoxy benzene after methylation. Further psoralen on fusion with KOH yielded directly 2, 4-dihydroxy-1, 5-dicarboxylic acid (VI).

The structure of psoralen was confirmed by its synthesis by Späth *et al.*[4-9] starting from 6-hydroxycoumaranone (VII) prepared from



resorcinol and chloroacetyl chloride. This was reduced with H_2 and Pd-charcoal to give 6-hydroxycoumaran (VIII). Condensation with malic acid and conc. H_2SO_4 gave dihydropsoralen (IX) which on dehydrogenation yielded psoralen (I). Alternatively 6-hydroxycoumaran (VIII) when subjected to Gattermann reaction followed by Perkin condensation afforded dihydropsoralen (IX) which could be converted to psoralen by dehydrogenation. This synthesis involves a number of steps and the yields are very poor.

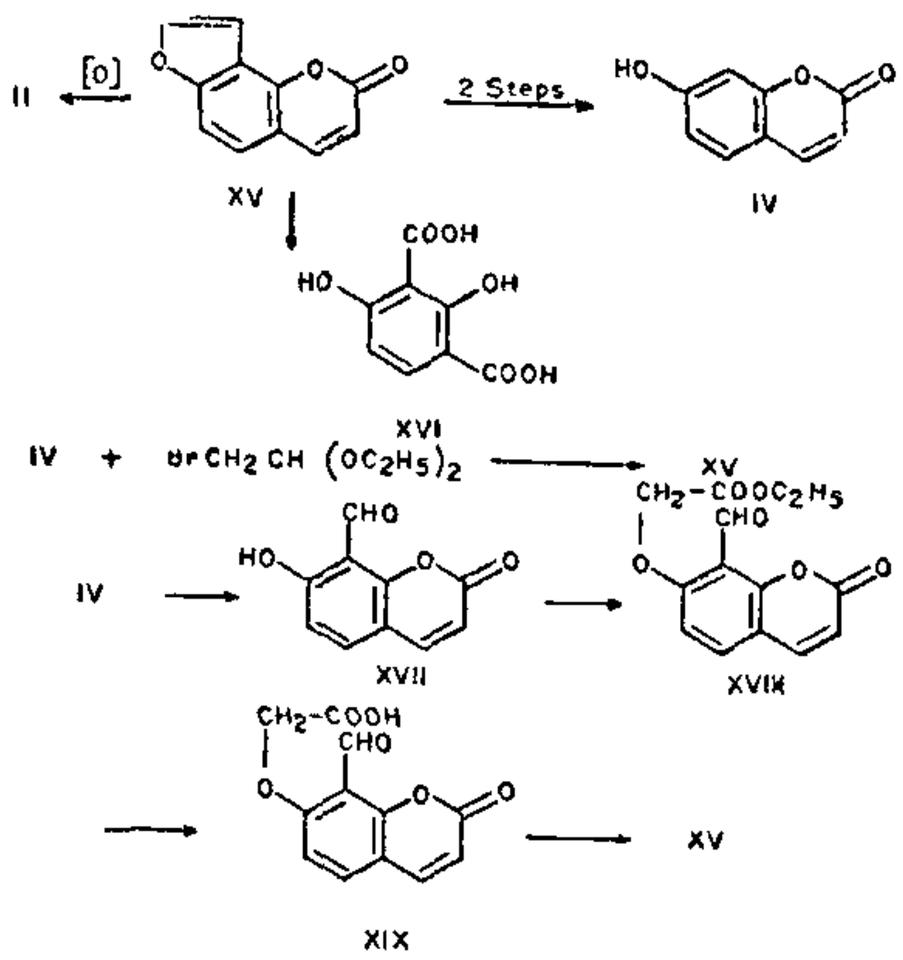
The above synthesis was improved and modified by others[10,11]. Later on Aneja *et al.*[12] synthesised psoralen following a possible path of biogenesis of a furan ring in natural products based on o-hydroxy dimethylallyl group. They were able to convert demethyl suberosin (X) occurring in Nature by ozonolysis and subsequent ring closure to psoralen (I).

Seshadri and Sood[13] modified the above synthesis using a simple allyl group in place of γ, γ-dimethylallyl group. The essential intermediate in this synthesis is 6-allyl-7-hydroxycoumarin (XIII). It could not be prepared by Claisen migration of 7-allyloxy coumarin because the reaction gives the isomeric 8-allyl-7-hydroxycoumarin. Hence the allyl group was introduced at an earlier stage. β-Resorcylaldehyde (XI) on *O*-allylation, methylation and Claisen migration gave 2-methoxy-4-hydroxy-5-allyl benzaldehyde (XII *a*); demethylation gave the hydroxy compound (XII *b*) which by Perkin condensation yielded 6-allyl-7-hydroxycoumarin (XIII). This on ozonolysis and subsequest ring closure led to psoralen (I). It is the most convenient synthesis giving good yields of psoralen.

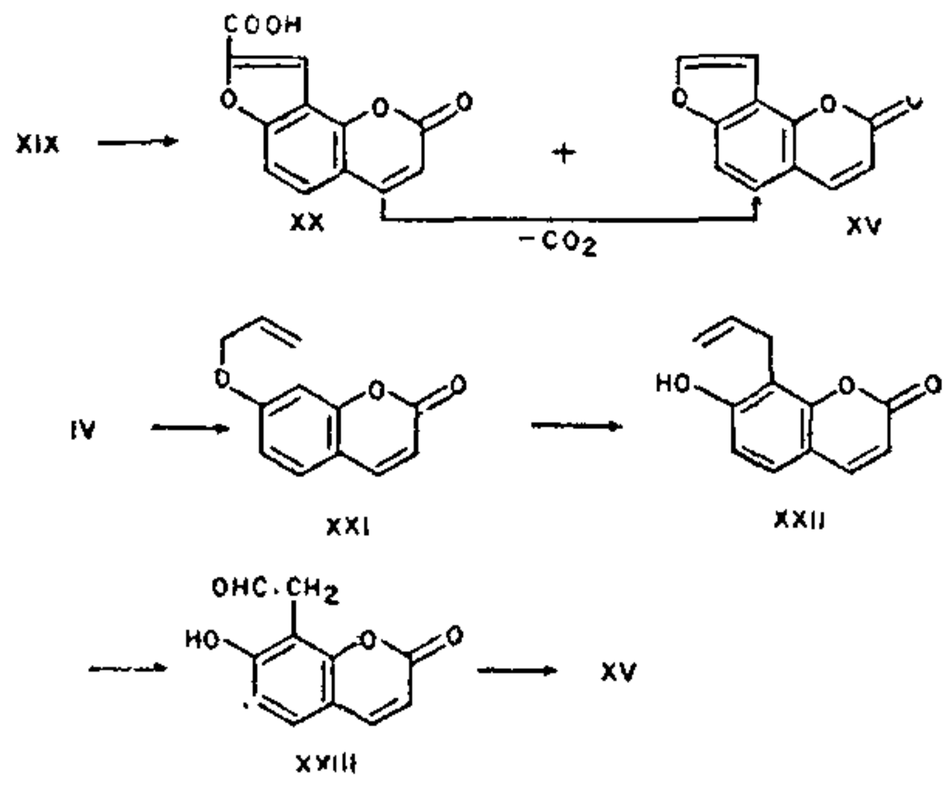
Following a similar biogenetic route, a number of other related compounds including 8-acetyl psoralen (XIV) were prepared[13]. It was observed that the introduction of an acetyl group reduces the activity of psoralen but still these compounds may be useful as they are easily made and can be used where milder action is needed.

Isopsoralen.—It is the angular isomer of psoralen and it was found to be identical with angelicin isolated earlier from the roots of *Angelica archangelica*. It is also present along with psoralen in *Angelica kiskei*. Its structure was established by Späth and Pesta[14] in 1934 based on various degradative reactions. Alkaline hydrogen peroxide oxidation gave furan-2, 3-dicarboxylic acid (II) while regulated oxidation with $KMnO_4$ yielded umbelliferone-8-carboxylic acid in poor yields which on

decarboxylation gave umbelliferone (IV). By methylation with alkaline dimethyl sulphate, isopsoralen yielded a methoxycinnamic acid ester and its oxidation with $KMnO_4$ gave 2, 4-dihydroxyisophthallic acid (XVI), thus indicating the angular fusion of the furanocoumarin ring system. All these reactions are explained in the following formulae.



The structure of isopsoralen (XV) has been confirmed by a number of synthesis carried out by Späth *et al.*[15]. In one case the dry sodium salt of umbelliferone was heated with bromoacetaldehyde diethyl acetal to give a small amount of isopsoralen (XV).



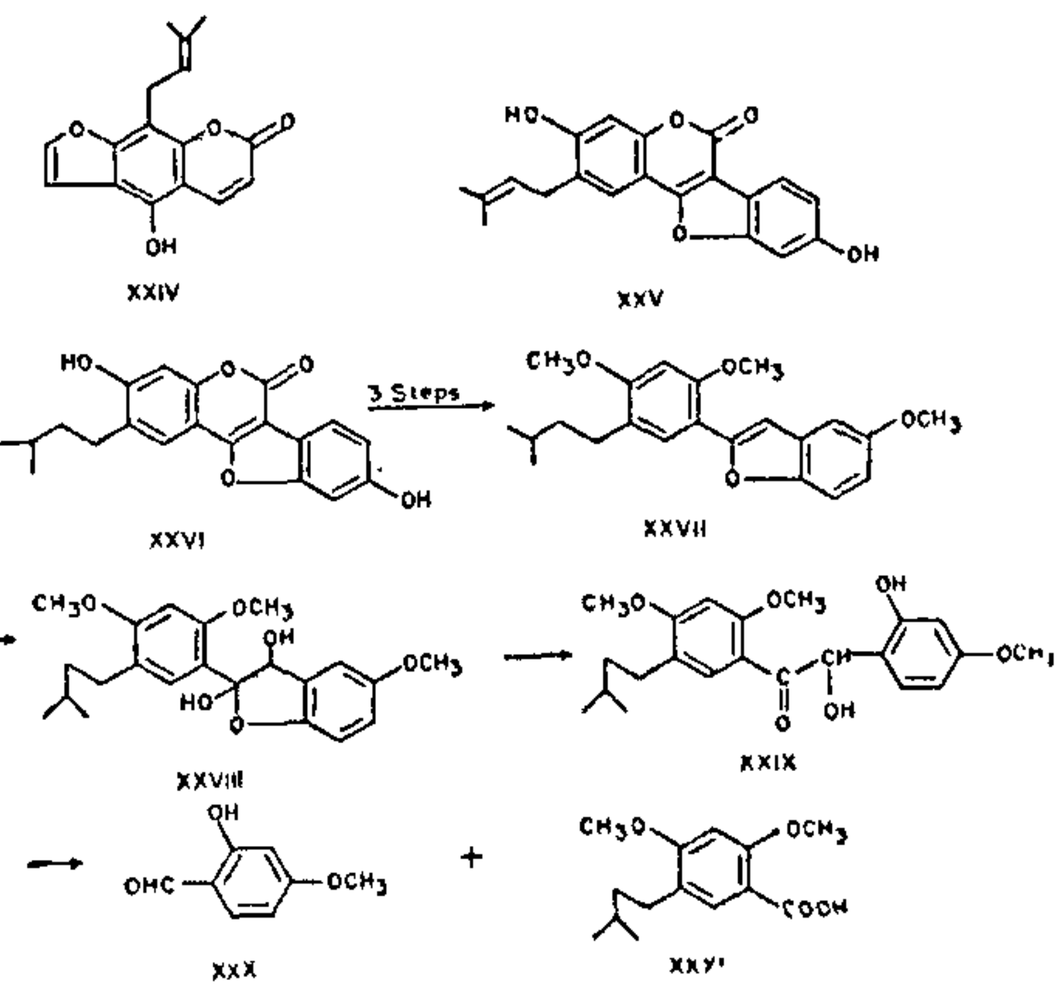
In another method umbellifferone was formylated by Duff's reaction to give 8-formyl-7-hydroxycoumarin (XVII) which on treatment with ethyl iodoacetate yielded 8-formyl-7-*O*-carbethoxy-methyl umbelliferone (XVIII). Further steps are saponification to the free glycollic acid (XIX) and boiling with sodium acetate-acetic anhydride to yield isopsoralen (XV).

Later Naik *et al.*[16] repeating this step observed that the acid (XIX) gave 2'-carboxy-isopsoralen (XX) along with some isopsoralen (XV) and separate decarboxylation of the former improved the yield of isopsoralen.

However, the most convenient synthesis of isopsoralen was that of Aneja *et al.*[12] in which 8-allyl umbelliferone (XXII) is converted into the acetaldehyde derivative (XXIII) by ozone. The aldehyde when treated with polyphosphoric acid cyclised to isopsoralen. A convenient modification for small quantities is to use KIO_4-OsO_4 as was done by Raizada *et al.*[17]. 8-Allyl umbelliferone (XXII) needed for this synthesis was prepared from 7-*O*-allyl umbelliferone (XXI) by Claisen migration.

As a result of detailed investigations, linear furanocoumarins have been found to have high photodynamic activity and angular ones much less ; isopsoralen is only $\frac{1}{4}$ as active photodynamically as its linear isomer psoralen which is the most powerful compound so far known.

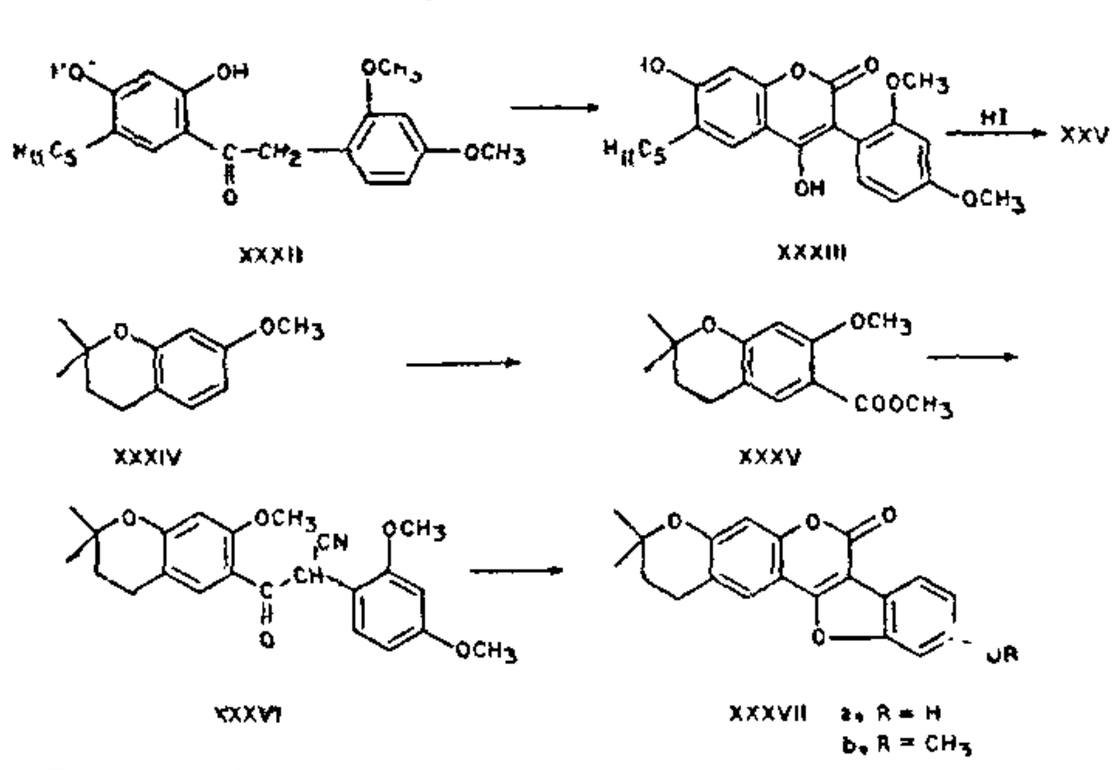
Psoralidin.—It was first isolated by Chakravarti *et al.*[18] from the pericarp of the fruit and given the molecular formula $C_{16}H_{14}O_4$. The presence in the molecule of a phenolic hydroxyl group, a lactone ring and an isopentenyl group was detected by them and they suggested the furanocoumarin structure (XXIV).



Dattagupta and co-workers[19,20] later showed that it possesses one unsaturated δ-lactone, an isopentanyl side-chain and an intramolecular ether linkage. Based on detailed chemical study supported by UV and IR data, they proposed that it had the structure of 6-isopentenyl coumestrol (XXV). Its reactions are explained below. In the presence of acid it isomerises

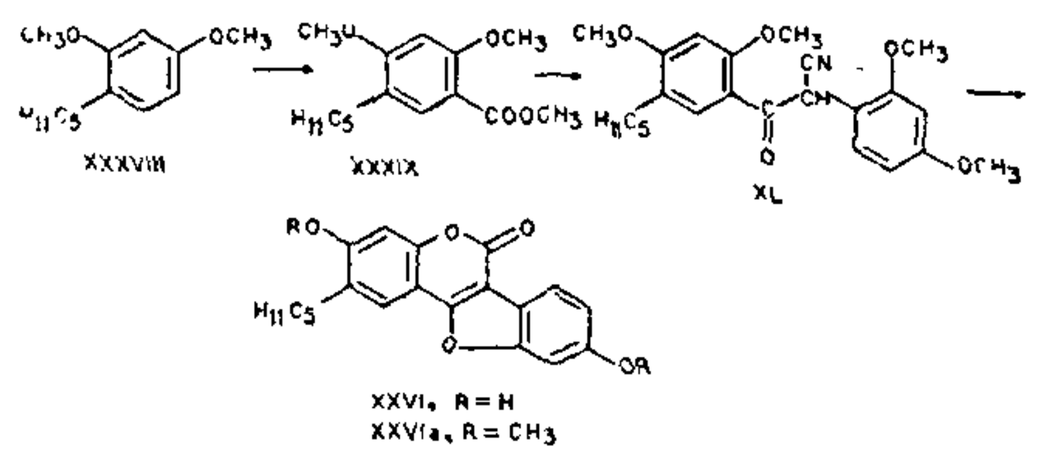
into the related 2, 2-dimethylchroman. After saturation of the isopentenyl side-chain, the dihydro compound (XXVI) is stable to acids. But on hydrolysis with alkali and methylation followed by decarboxylation it gave the benzofuran (XXVII). The later steps involve treatment with osmium tetraoxide to give hydroxylated product (XXVIII) isomerising to the ketonic alcohol (XXIX), which is cleaved with periodic acid giving 2-hydroxy-4-methoxybenzaldehyde (XXX) and the isopentyl benzoic acid (XXXI).

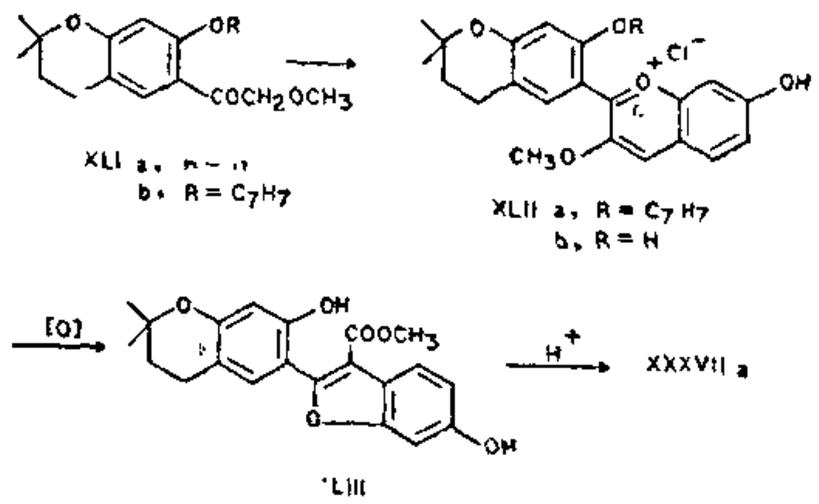
The above structure of psoralidin (XXV) has been confirmed by the synthesis of its dihydroderivative by Nasipuri and Pyne[21,22]. The isopentyldesoxybenzoin (XXXII), prepared by Hoesch condensation of isopentyl resorcinol and 2, 4-dimethoxybenzyl cyanide, was condensed with ethyl chloroformate and potassium carbonate. The product was 4, 7-dihydroxy-6-isopentyl-3-(2, 4-dimethoxyphenyl) coumarin (XXXIII). This on demethylation with HI underwent ring closure also to give dihydropsoralidin (XXVI).



Isopsoralidin (XXXVII *a*) was synthesised later by Chatterjea *et al.*[23]. The synthesis started from 7-methoxy-2, 2-dimethylchroman (XXXIV) and involved the following steps. Formylation, oxidation and esterification gave 6-carbomethoxy-7-methoxy-2, 2-dimethylchroman (XXXV). Condensation with 2, 4-dimethoxybenzyl cyanide in the presence of sodium hydride gave the α-cyanodesoxybenzoin (XXXVI). Further treatment with pyridine hydrochloride gave isopsoralidin (XXXVII *a*) which was isolated as its methyl ether (XXXVII b).

Similar steps were used by the same authors for the synthesis of dihydropsoralidin (XXVI) starting from 4-isopentyl-1, 3-dimethoxybenzene (XXXVIII). The resulting product, after treatment with pyridine hydrochloride, gave dihydropsoralidin which was isolated as its dimethyl ether (XXVI *a*).



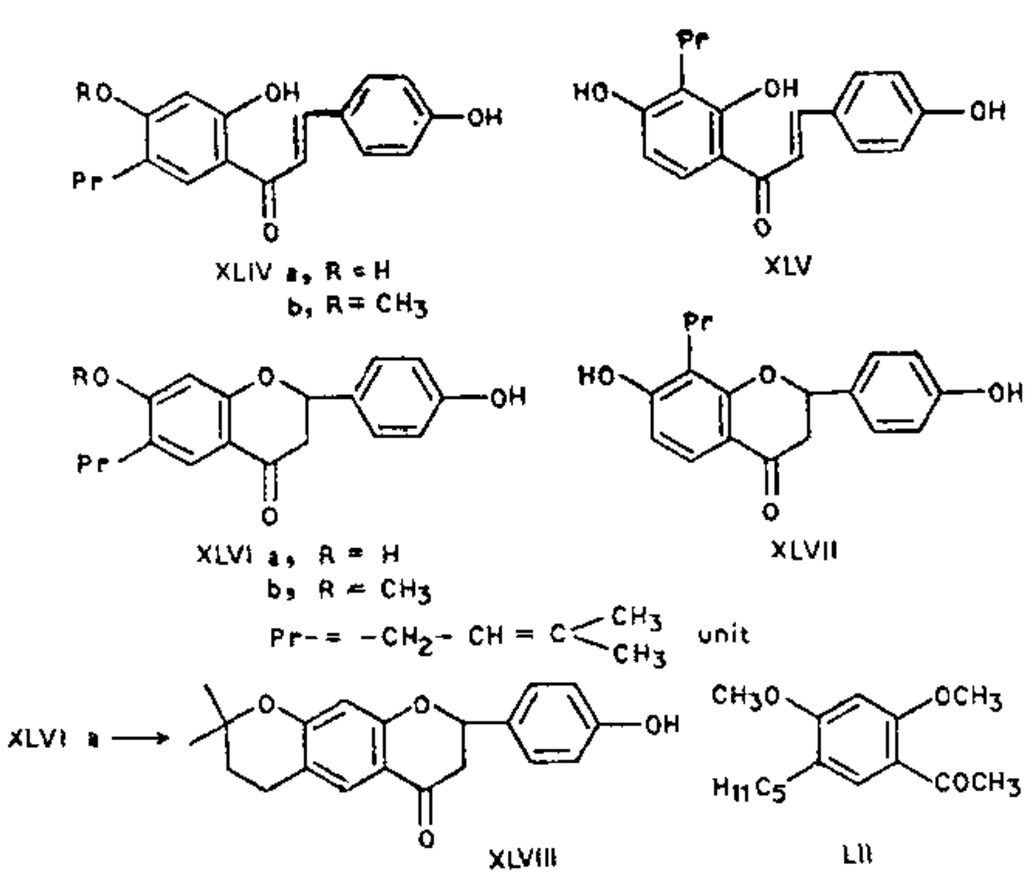


Very recently isopsoralidin has also been synthesised by Molyneux and Jurd[24] employing a novel route. The essential method is the oxidation of a flavylium salt to give a benzofuran derivative. A Hoesch reaction between 7-hydroxy-2, 2-dimethylchroman and methoxyacetonitrile gave ω-methoxyacetophenone (XLI *a*), the phenolic hydroxyl group of which was protected by the formation of the benzyl ether (XLI *b*). Its condensation with 2, 4-dihydroxybenzaldehyde in ether solution saturated with gaseous HCl gave the flavylium salt (XLII *a*) which was readily debenzylated by a mixture of glacial acetic acid and conc. hydrochloric acid to yield the phenolic flavylium salt (XLII *b*). Oxidation of the flavylium salt with 30% aqueous hydrogen peroxide resulted in ring contraction to the furan (XLIII) which on acidification readily lactonized to isopsoralidin (XXXVII *a*).

Chalcones and Flavanones

A recent closer examination by Bhalla *et al.*[25] of the chloroform extract of the petroleum ether exhausted whole seeds of *P. corylifolia* has revealed the presence of three *C*-prenylated flavanones along with two corresponding chalcones. These are likely to be the components of the resin part of pericarp. The names assigned to them by the discoverers were not free from ambiguity. In order to make them more rational Seshadri and co-workers[26] considered the chalcones as the primary products which underwent change into flavanones. Bavachalcone (XLIV *a*) would then be the

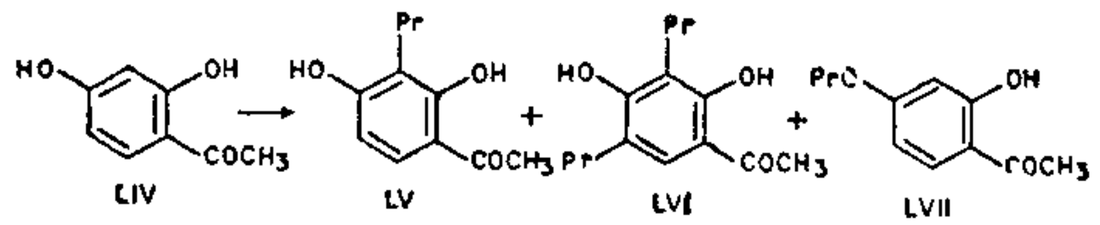
primary member of this group but it has not been so far isolated from this plant. But its related flavanone bavachin (XLVI *a*) is present, which is an indication that the chalcone is also likely to be present. Its 4′-*O*-methyl derivative (XLIV *b*, *O*-methylbavachalcone) is however found to occur in this plant. The corresponding flavanone 7-*O*-methylbavachin (XLVI *b*) has also the synonym bavachinin. Isobavachalcone (XLV) and isobavachin (XLVII) have rational names since they are isomers of bavachalcone and bavachin.

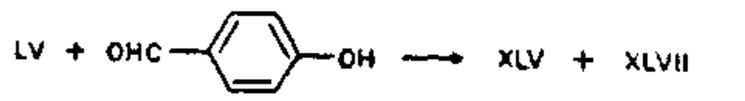


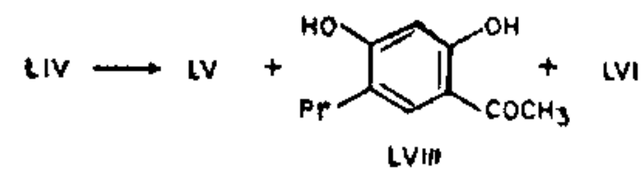
The structures of these closely related flavonoids were established on the basis of spectroscopic evidence. A study of the UV spectra indicated the coloured compounds *O*-methylbavachalcone (XLIV *b*) and isobavachalcone (XLV) to have chalcone structures. The position of the hydroxyl group in the side phenyl was established by a study of bathochromic shifts in UV with alkali and also by the characteristic A_2B_2 pattern in the NMR. The C_5 unit was also located in the nucleus by NMR spectra. Thus in the compounds *O*-methyl bavachalcone (XLIV *b*), bavachin (XLVI *a*) and *O*-methylbavachin (XLVI *b*) there were only two para coupled aromatic protons of ring A, one of them being deshielded by the carbonyl group. The vicinal nature of the hydroxyl and C_5 unit was established by acid treatment of the compounds bavachin (XLVI *a*) and isobavachin (XLVII) when the corresponding chromans (XLVIII) and (XLIX) were obtained.

These findings were supported by the conversion of the chalcones into the corresponding prenylated acetophenones. Thus the compounds 7-*O*-methylbavachin (XLVI *b*) and isobavachin (XLVII) on degradation with alkali gave the corresponding ketones (L *a*) and (LI) besides *p*-hydroxybezoic acid. The structures of the ketones were supported by spectral evidence and further that of former was confirmed by catalytic hydrogenation of its methyl ether (L *b*), when the product obtained was found to be identical with (LII) prepared synthetically from 5-isopentyl-2, 4-dimethoxybenzoic acid (LIII) by treatment with methyl lithium.

An unambiguous synthesis of these compounds has been recently carried out by Jain *et al.* [26,27]. It has been done following a possible biogenetic route, which involves C-prenylation either at the ketone stage or at the chalcone stage. Both the approaches were successful. In this work nuclear prenylation of β-resacetophenone was carried out under alkaline[27] as well as acidic conditions[26]. β-resacetophenone (LIV) on nuclear prenylation with prenyl bromide and alkali gave a mixture of 3-*C*-prenyl (LV), 3, 5-di-*C*-prenyl (LVI) and 4-*O*-prenyl derivatives (LVII) among which 3-*C*-prenyl compound was in maximum amount.





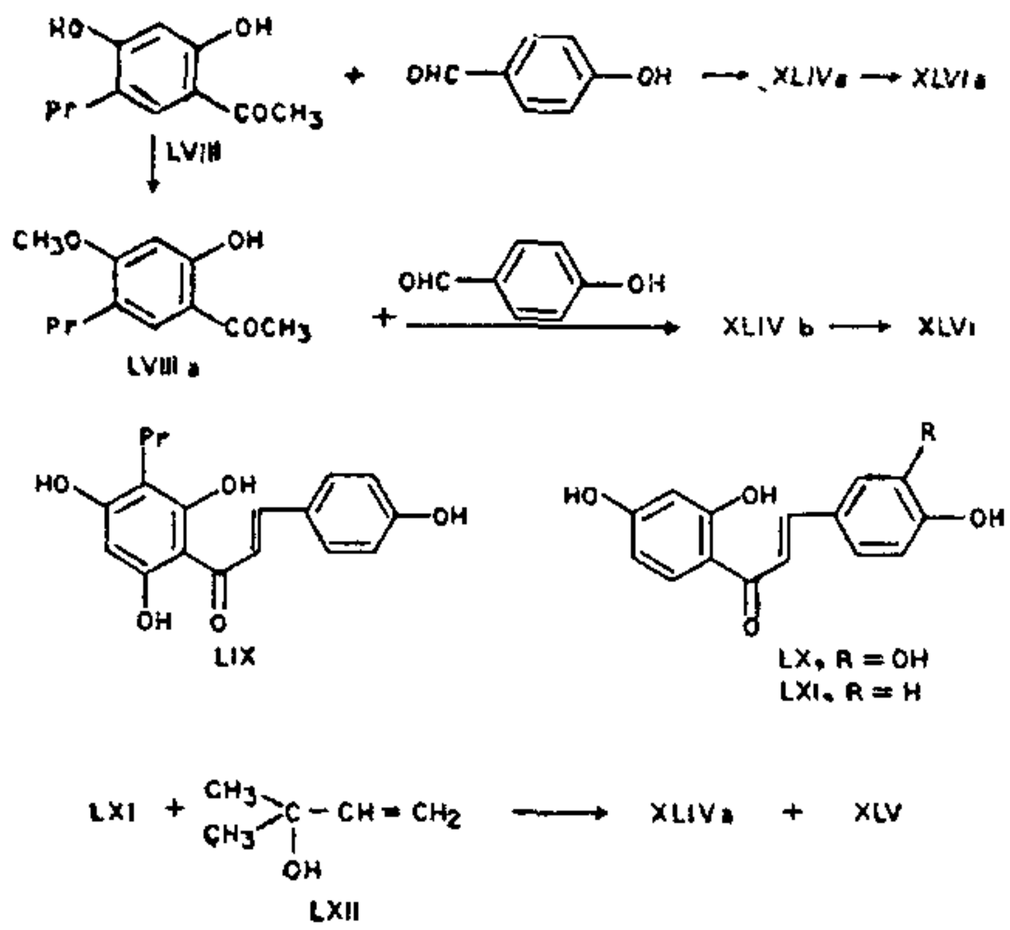


Condensation of the 3-*C*-prenyl resacetophenone (LV) with *p*-hydroxybenzaldehyde in the presence of conc. alcoholic alkali[27] gave a mixture of isobavachalcone (XLV) and isobavachin (XLVII), identical in properties with the natural compounds. The former was also converted to the latter by treatment with dilute alkali.

In the above prenylation experiment no 5-*C*-prenyl derivative was obtained. In order to obtain this isomer also, the nuclear prenylation of β-resacetophenone was studied under

acidic conditions using 2-methyl-but-3en-2-ol in the presence of boron trifluoride etherate. Here a mixture of 5-*C*-prenyl (LVIII), 3, 5-di-*C*-prenyl (LVI) and 3-*C*-prenyl derivatives (LV) was obtained, the first being in maximum amount.

5-*C*-Prenyl resacetophenone (LVIII) and its 4-*O*-methyl derivative (LVIII *a*) were condensed with *p*-hydroxybenzaldehyde separately to give bavachalcone (XLIV *a*) and 4′-*O*-methyl bavachalcone (XLIV *b*) respectively and these on isomerisation with dilute alkali gave corresponding flavanones, bavachin (XLVI *a*) and 7-*O*-methyl bavachin (XLVI *b*) respectively.



Biogenetic Consideration and Interrelationship

The fruit (seed) of *P. corylifolia* contains a large number of components. They belong to different groups, furano-coumarins, coumestrol group (isoflavonoid), chalcones and flavanones. They contain the following structural units, C_9, C_6 and C_5. The simple coumarins are derived from C_9 units and the furan rings in psoralen and isopsoralen have been considered to arise[13] from C_5 (isoprene) units. This C_5 unit is also present in psoralidin as a open chain substituent. The main structure in psoralidin is that of coumestrol whose skeleton is isoflavonoid in Nature. In an earlier publication[28] the evolution of coumestrol type of compounds from related isoflavanones was discussed and hence it is justified to include these compounds under isoflavonoids. Chalcones and flavanones mentioned above also carry terpenoid C_5 units and details of their biogenesis are discussed below.

Bhalla *et al.*[25] suggested that an intermediate (LIX) with phloroglucinol A-ring is first formed which undergoes ring closure in different ways and subsequent dehydroxylation in order to produce bavachin and isobavachin. Since resorcinol derivatives are very common among chalcones, *e.g.*, butein (LX) and isoliquiritigenin (LXI), Seshadri and co-workers[26] considered isoliquiritigenin (LXI), as the primary member of this series. Analogous to β-resacetophenone, it should undergo prenylation at both 5′- and 3′-positions yielding bavachalcone and isobavachalcone, which by ring closure would yield bavachin and isobavachin. The partial methylation of the 4′-position of the chalcones of this type and 7-position of the flavanones is an easy reaction both in Nature and in the laboratory and accounts for the presence of 4′-*O*-methyl bavachalcone and 7-*O*-methyl bavachin.

In support of the above scheme for the evolution of prenylated chalcones, isoliquiritigenin (LXI) was condensed[26] with 2-methyl-but-3-en-2-ol (LXII) in the presence of a Lewis acid. The resulting product, a mixture of two compounds, was separated into 5′ C-prenyl isoliquiritigenin (or bavachalcone, XLIV *a*) and 3′-C-prenyl isoliquiritigenin (or isobavachalcone XLV).

1. Menon. *Agricultural Ledger*, 1911–12, **17**, 139.
2. Jois, H. S., Manjunath R. L. and Venkatarao, *J. Ind. Chem Soc.*, 1933, p. 41.
3. — and —, *Ber.*, 1936, **69**, 964
4. Späth, E., Manjunath, B. L., Jois H. S. and Pailer, M., *Ibid.*, 1936, **69**, 1087.
5. Seshadri, T. R. and Venkatarao, C, *Proc. Ind. Acad. Sci*. 1937, **5 A** 351.
6. Khastgir, H. N., Datta Gupta, P. C and Sengupta, P., *Ind. J. App Chem*, 1959, **22**, 35.
7. —, — and —, *Ibid.*, 1959. **22**, 82.
8. Stoll, A., Pereira, A. and Renz, J., *Helv. Chim. Acta*, 1950, **33**, 1637.
9. Späth, E, Okahara, K. and Kuffner, F., *Ber.*, 1937, **70**, 73.
10. Foster, R. T., Robinson, A. and Bushra, A., *J. Chem. Soc.*, 1948. p. 2254.
11. Horning, E C. and Reisner, D. B., *J. Am. Chem. Soc.*, 1948, **70**, 3619.
12. Aneja, R., Mukerjee, S. K. and Seshadri, T. R., *Tetrahedron*, 1958. **4**, 256; 1958, **2**, 203.
13. Seshadri, T. R. and Sood, M. S., *Int. J. Chem*, 1963. **1**, 291.
14. Späth, E. and Pesta, O., *Ber.*, 1934. **67**, 853.
15. — and Pailer, M, *Ibid.*, 1934, **67**, 1212; 1935, **68 B**, 941.
16. Naik R M. and Thakor, V. M., *J. Org. Chem.*, 1957, **22**, 1096.
17. Raizada, K. S., Sarin, P. S. and Seshadri, T. R., *J. Sci. Ind. Res.*, 1960, **19 B**, 76.

18. Chakravarti, K. K., Bose A. K. and Siddiqui, S., *J. Sci. Ind. Res.*, 1948, **7 B**, 21.
19. Dattagupta, P. C., Khastgir, H. N. and Sengupta, P., *Chem and Ind.*, 1960, p. 48.
20. —, — and —, *Tetrahedron*, 1961, **14**, 275.
21. Nasipuri, D. and Pyne, G., *J. Sci. Ind. Res.*, 1962, **21 B**, 51.
22. — and —, *J. Chem. Soc.*, 1962, p. 3105.
23. Chatterjea, J. N., Banerji, K. D. and Prasad, N., *Ber.*, 1963, **96**, 2356.
24. Molyneux, R. J. and Jurd, L., *Tetrahedron*, 1970, **26**, 4743.
25. Bhalla, V. K., Naik, U. R. and Sukhdev, *Tetrahedron Letters* 1968, **20**, 2401.
26. Jain, A. C., Pyare Lal and Seshadri, T. R., *Tetrahedron*, 1970, **26**, 2631.
27. — — and —, *Ind. J. Chem*, 1969, **7**, 1072.
28. Krishnamurti, M. and Sesnadri, T. R., *Curr Sci.*, 1966, **35**, 167.

STUDIES ON OPTICAL BLEACHING OF X-RAY IRRADIATED NaCl CRYSTALS

K. VIJAYALAKSHMI AND K. N. KUCHELA

Physics Department, Central College, Bangalore University, Bangalore

ABSTRACT

The regions of fast first stage bleaching and the slow second stage bleaching of F-centres in 'as cleaved' X-ray irradiated NaCl crystals at room temperature are not clearly separated out in the optical bleaching curves. These curves are explained by a simple relation of the form $\Delta \alpha_F / \alpha_{F0} = k \log t$, $\Delta \alpha_F$ being the change in absorption coefficient at the F-band peak after bleaching the colored crystal for t minutes, α_{F0} being the absorption coefficient at the F-band peak before bleaching and k being the constant dependent on the time of X-ray irradiation. The two regions are distinctly separated out in the case of heat-treated NaCl crystals. A possible mechanism of bleaching is suggested to explain the results of optical bleaching.

INTRODUCTION

IT is well established by several authors[1-8] that F-centres are formed in alkali halides by X-rays by two distinct processes. In one of them the negative ion vacancies initially present in the crystal, trap electrons liberated by X-rays and these are uniformly distributed in the volume of the crystal. In the other process, new vacancies are generated during irradiation and these in turn may trap electrons and form additional F-centres. These F-centres are formed perhaps near some defects and are highly localized in small regions of the crystal having very high concentration of these F-centres.

The optical bleaching of F-centres also supports the idea of two stages of coloration. The studies on optical bleaching of F-centres by Markham *et al.*[9] on additively colored KBr crystals at low temperatures, by Ueta and Werner Kanzio[10] on additively colored, deformed KCl crystals, and by Bron[5] on the relation between X-ray coloration and optical bleaching indicate that optical bleaching of F-centres also takes place in two stages. During the first stage of bleaching the F-band decreases rapidly and this can be attributed to the bleaching of first type F-centres. During the second stage of bleaching, the decrease in F-band is much slower and this can be attributed to the bleaching of second type F-centres.

In the present paper optical bleaching curves of F-centres have been studied systematically to investigate the nature of these two stages of bleaching at room temperature in X-irradiated Harshaw NaCl crystal (as cleaved and heat-treated crystals).

EXPERIMENTAL

Sodium chloride crystals used in the present study were aged about 8 to 10 years. Systematic experiments were conducted to find the origin of these crystals. Rabin and C. C. Klick[11] have studied the F-band growth curves for NaCl crystals of different origins. The F-band growth curve obtained from our experiments agreed well with that obtained by Rabin and Klick for Harshaw NaCl crystals.

NaCl crystals were cut and cleaved to the size required from a big block. The thickness of the crystals used was less than 0·4 mm.

Heat treatment of NaCl crystals consisted in raising their temperature to about 600° C and maintaining them at that temperature for 7 to 8 hours, then quenching immediately by withdrawing them from the furnace and cooling on a copper plate.

The continuous X-ray spectrum from a copper target tube operated at 39 kV and 10 mA