THE CRYSTAL STRUCTURE OF MONO SUCCINATO TETRAAQUO NICKEL (II) MONOHYDRATE

THE title compound $[Ni(C_4H_4O_4), 4H_2O], H_2O$ was investigated in this laboratory to study the hydrated salts of carboxylic acids, scheme of hydrogen binding in them and oxygen ligands around metal ions in them.

Crystal data: The compound was prepared by the reaction of stoichiometric amounts of succinic acid with metal carbonate and crystals grown out of water solution. Monoclinic, with $a = 9{\cdot}63$, $b = 14{\cdot}61$, $c = 7{\cdot}14$ Å, $\beta = 127{\cdot}5°$, $D_{obs} = 2{\cdot}11$, $D_{calc} = 2{\cdot}18$ gm/cc, $Z = 4$, space group $P2_1/n$.

790 reflexions were collected by single crystal Weissenberg photography using CuKα radiation, usual corrections applied and data brought to approximate absolute scale by statistical methods.

Structure determination and comments: The structure was solved from a three-dimensional Patterson function. A view of the crystal structure down [001] axis is shown in Fig. 1 with hydrogen bonds shown

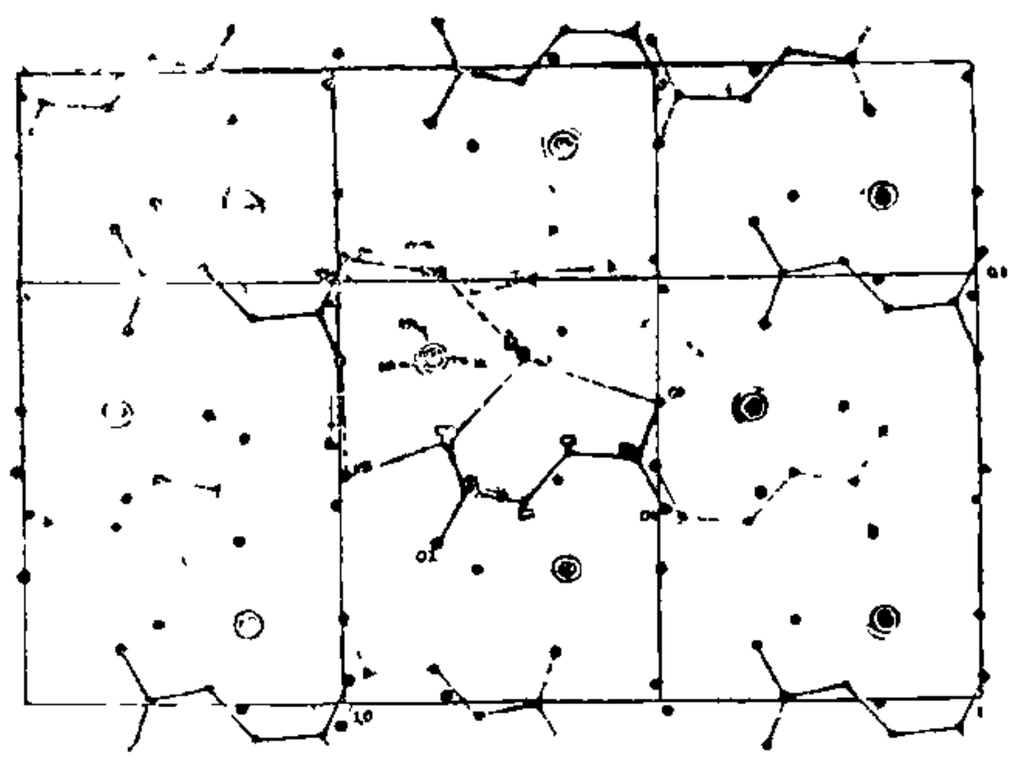

FIG. I

as dashes and dots. The metal ion has six-fold coordination with metal-oxygen distances ranging from 2·0 to 2·16 Å, giving a distorted octahedron. In the crystal the anions are hydrogen bonded *via* the water molecules, hydrogen bonds ranging from 2·7 to 3·1 Å, the chain direction being parallel to [010].

As considerable interest lies in the location of the hydrogen atoms, the structure is being refined further, details of which will be published later.

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A CONVENIENT SYNTHESIS OF ALLO-ATHYRIOL

CONDENSATION of 4–benzyloxy–2–hydroxy–5–methoxybenzoic acid (VII) with phloroglucinol in the presence of zinc chloride and phosphorus oxychloride involved debenzylation thereby providing a convenient synthesis of allo–athyriol (I). Similar reactions of 4–benzyloxy–2, 5–dihydroxybenzoic acid (VI) with phloroglucinol and its dymethyl ether directly gave nor-athyriol (IX) and athyriol 1–methyl ether (X) respectively.

Laxanthone–II, a naturally occurring xanthone and considered[1] to be 1–hydroxy–3, 6–diacetoxy–7–methoxyxanthone (II) on deacetylation yielded 1, 3, 6–trihydroxy–7–methoxyxanthone (allo-athyriol) (I) an isomer of athyriol (III). Since an authentic sample of I was not available for comparison purposes, the same was synthesised by a more convenient method as compared to the earlier meathod that involved many steps which were cumbersome[2–4].

The present synthesis of I has been carried out using 4–benzyloxy–2–hydroxy–5–methoxybenzoic acid (VII) now made by the selective methylation of 4–benzyloxy–2, 5–dihydroxybenzoic acid[5] (VI) followed by the hydrolysis of the resulting ester (VIII). Condensation of VII with phloroglucinol in the presence of zinc chloride and phosphorus oxychloride yielded directly I instead of its expected 6–benzyl ether (IV) indicating that debenzylation had also taken place during the course of reaction. The xanthone I, thus obtained, was identical with the condensation product of phloroglucinol and 2, 4–dihydroxy–5–methoxybenzoic acid (V) now obtained by the modified method involving the catalytic debenzylation of its 4–benzyl ether (VII). Both I and its acetate (XI) were found to be identical with the hydrolysis product and the acetate of laxanthone–II (II) respectively.

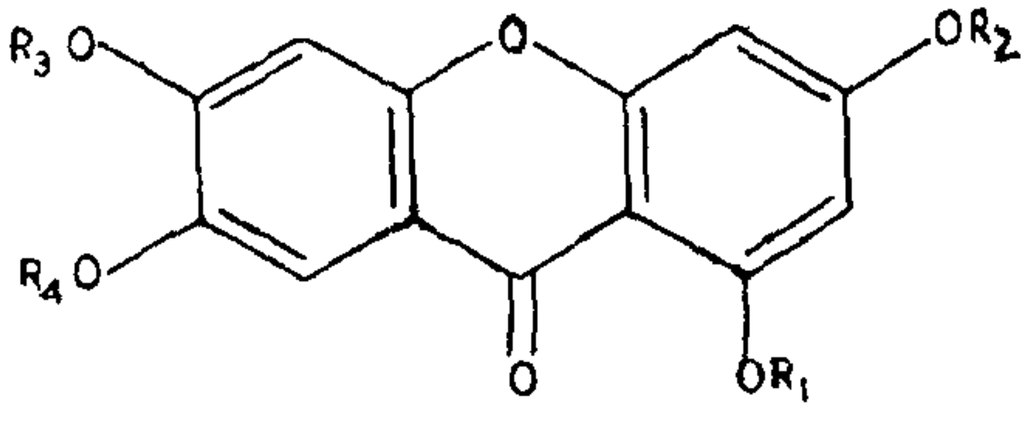
Similar condensations of 4–benzyloxy–2, 5–dihydroxybenzoic acid[5] (VI) with phloroglucinol as well as its dimethyl ether also involved debenzylations and thus, yielded directly 1, 3, 6, 7–tetrahydroxyxanthone (nor-athyriol) (IX) and its 1, 3–dimethyl ether (athyriol) 1–methyl ether) (X). The present work provides a convenient method for the syntheses of other 6–hydroxy–7–methoxyxanthones.

Experimental

Methyl 4–benzyloxy–2–hydroxy–5–methoxybenzoate (VIII):

A mixture of 4–benzyloxy–2, 5–dihydroxybenzoic acid[5] (VI) (5 g) potassium carbonate (20 g), dimethyl sulphate (3·9 ml) and acetone (120 ml) was refluxed for 10 hr. The reaction product when worked

up as usual, gave VIII which crystallised from benzene as colourless needles (4·2 g), m.p. 140–41° (Found: C, 66·5; H, 5·4. $C_{16}H_{10}O_5$ requires C, 66·66; H, 5·55%).



I. $R_1 = R_2 = R_3 = H$; $R_4 = CH_3$

II. $R_1 = H$; $R_2 = R_3 = COCH_3$; $R_4 = CH_3$

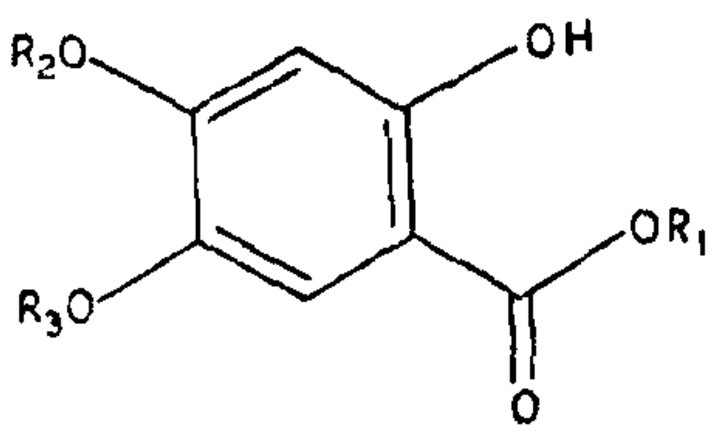
III. $R_1 = R_3 = R_4 = H$; $R_2 = CH_3$

IV. $R_1 = R_2 = H$; $R_3 = CH_2C_6H_5$; $R_4 = CH_3$

IX. $R_1 = R_2 = R_3 = R_4 = H$

X. $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$

XI. $R_1 = R_2 = R_3 = COCH_3$; $R_4 = CH_3$



V $R_1 = R_2 = H$; $R_3 = CH_3$

VI $R_1 = R_3 = H$; $R_2 = CH_2C_6H_5$

VII. $R_1 = H$; $R_2 = CH_2C_6H_5$; $R_3 = CH_3$

VIII $R_1 = R_3 = CH_3$; $R_2 = CH_2C_6H_5$

4–Benzyloxy–2–hydroxy–5–methoxybenzoic acid (VII):

A solution of the above methyl ether (VIII) (4·0 g) *in* aqueous alcoholic potassium hydroxide (120 ml; 1:1) was refluxed for 4 hr. The clear alkaline solution when acidified with hydrochloric acid, gave VII which crystallised from benzene–acetone mixture as light yellow needles (3·5 g), m.p. 191° (dec.) (Found: C, 65·4; H, 5·5. $C_{15}H_{14}O_5$ requires C, 65·69; H, 5·1%). It gave olive–green colour with alcoholic ferric chloride.

1, 3, *6–Trihydroxy–7–methoxyxanthone (Allo–athyriol) (I):*

A mixture of dry phloroglucinol (1·1 g), 4–benzyloxy–2–hydroxy–5–methoxybenzoic avid (VII) (2·0 g.) fused zinc chloride (4·5 g) and freshly distilled phosphorus oxychloride (16 ml) was heated in an oil-bath at 70–75° for 2½ hr. The reaction mixture was cooled, treated with ice, kept overnight and then heated at 100° for 30 mts. The condensation product when worked up as usual, gave I which crystallised from alcohol as pale yellow needles (0·25 g), m.p. 304° (dec.). It gave green colouration with alcoholic ferrid chloride. Aietylation (Ac_2O/Py) of I gave an acetate (XI) which crystallised from chloroform–petrol as colourless needles, m.p. 173°. NMR spectrum (δ, $CDCl_3$, TMS as internal standard): 2·33 (6H, s, 2 × $OCOCH_3$), 2·45 (3H, s, $OCOCH_3$), 3·93 (3H, s, OCH_3), 6·85 (1H, d, C_2–H), 6·91 (1H, d, C_4–H), 7·22 (1H, s, C_5–H), 7·99 (1H, s, C_8–H). It was identical with laxanthone-II acetate[1].

2, *4–Dihydroxy–5–methoxybenzoic acid (V):*

The acid (VII) (3·2 g) in ethyl acetate (100 ml) and Pd–C (0·8 g; 10%) was stirred in an atmosphere of hydrogen at room temperature and atmospheric pressure till the absorption of hydrogen completed. The catalyst was filtered out and the reaction product when worked up as usual, gave V which crystallised from water as bright yellow needles (2·0 g) m.p. 201–2° (dec.) (Lit.[2] 201° dec.).

1, 3, *6–Trihydroxy–7–methoxyxanthone (allo–athyriol) (I):*

Condensation of dry phloroglucinol (1·1 g) with 2, 4–dihydroxy–5–methoxybenzoic acid (V) (1·0 g) in the presence of fused zinc chloride (4·0 g) and freshly distilled phosphorus oxychloride (14 ml) at 70–75° for 2½ hr yielded I which crystallised from alcohol as pale yellow needles (0·3 g), m.p. 304° (dec.) [Lit.[2] m.p. 304°d). It gave green colour with alcoholic ferric chloride and was found to be identical with the condensation product obtained above as well as with the hydrolysis product of laxanthone-II[1].

1, 3, 6, 7–*Tetrahydroxyxanthone (nor-athyriol) (IX):*

Condensation of phloroglucinol (0·6 g) with 4–benzyloxy–2, 5–dihydroxybenzoic acid[3] (VI) (1·0 g) in the presence of fused zinc chloride (3·0 g) and freshly distilled phosphorus oxychloride (12 ml) at 70° for 3 hr as described earlier gave IX which crystallised from alcohol as yellow needles (0·2 g), m.p. 323° (dec.) It was found to be identical with an authentic sample of nor-athyriol.

1, 3–*Dimethoxy–6, 7–dihydroxyxanthone* (X):

As described above, VI (1·0 g) on condensation with phloroglucinol dimethyl ether (0·7 g) gave X which crystallised from aqueous alcohol as pale

yellow needles (0·2 g) m.p. 278–80°. It was found to be identical with an authentic sample of **1, 3**-dimethoxy-6, 7-dihydroxyxanthone (athyriol 1-methyl ether[5]).

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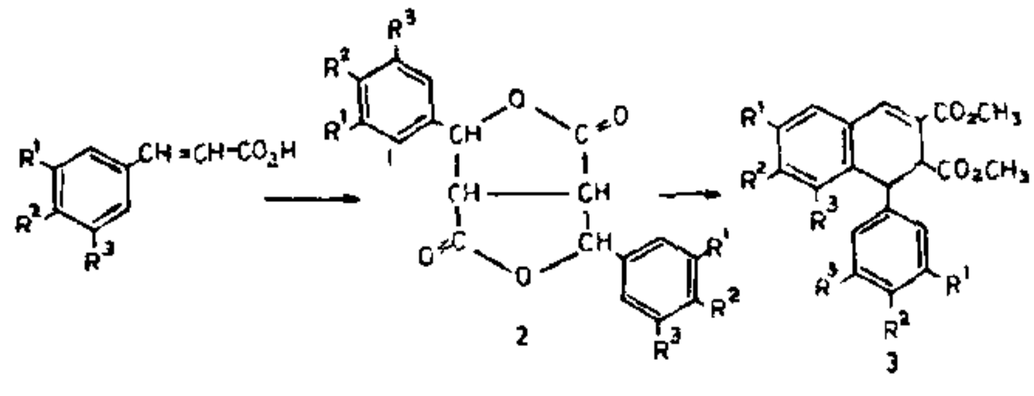
CYCLOLIGNANS THROUGH STOBBE CONDENSATION

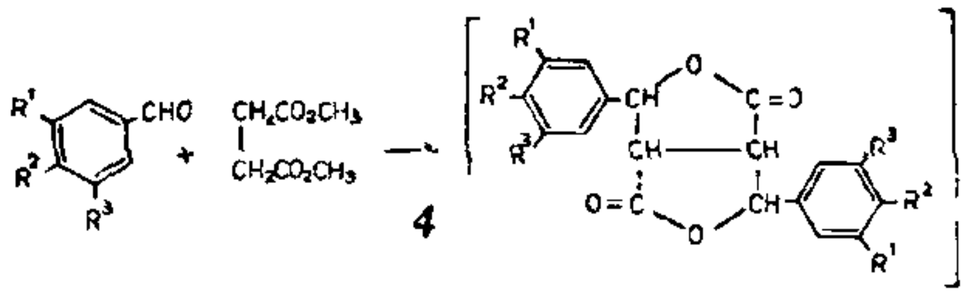
II.* Synthesis of Thomasidioic Acid Dimethyl Ester Dimethyl Ether

THE Stobbe condensation presents the most fascinating and prolific entry to syntheses of lignans. Fulgenic acids, the dicondensation product in the Stobbe reaction obtained in one-step or two-step sequence has been used for several approaches to the open-chain lignan systems[1]. Photochemical cyclization of the fulgides, anhydride of fulgenic acids, leads to the 1-arylnaphthalene systems of cyclolignans[2]. Benzylsuccinic compounds, from reduction of the mono-condensation products (itaconic acids) of the Stobbe reaction, after a second Stobbe condensation have been used for the syntheses of the 7, 8-dihydrolignans[3]. Benzhydrylidenesuccinates, from the Stobbe condensation of substituted benzophenones and *o*-carbethoxybenzophenones, are the starting materials for several of the cyclolignan syntheses[4].

On a different route[5] to 1-aryl-1, 2-dihydronaphthalenes, dehydrodiferulic acid dilactone (2*a*), obtained by oxidative coupling of ferulic acid (1*a*), was cleaved and recyclized with methanolic hydrogen chloride to 1-aryl-1, 2-dihydronaphthalene (3*a*)[5a].

A similar dilactone (5) has been considered as an intermediate in the formation of fulgenic acid in the Stobbe condensation[6]. Hence a practical *in situ* treatment of an interrupted Stobbe reaction mixture with methanolic hydrogen chloride was expected to result in the formation of 1, 2-dihydronaphthalene, and consequently be a proof of the formation of such intermediate in the Stobbe reaction.





a, $R^1 = OCH_3$, $R^2 = OH$, $R^3 = H$
b, $R^1 = OCH_3$, $R^2 = OH$
c, $R^1 = R^2 = R^3 = OCH_3$

3, 4, 5-Trimethoxybenzaldehyde (4) and dimethyl succinate were reacted in the presence of dry sodium methoxide in ether at −10° for 24 hr and the reaction mixture which would contain the dilactone was treated with methanolic hydrogen chloride. After working up, it afforded a neutral fraction (94%) which on chromatographic separation and crystallization yielded 1-(3, 4, 5-trimethoxyphenyl)-2, 3-dicarbomethoxy-6, 7, 8-trimethoxy-1, 2-dihydronaphthalene (thomasidioic acid dimethyl ester dimethyl ether) (3*c*) as a white crystalline material, mp 121–122°. Its NMR spectrum showed four singlets at 3·70, 3·77, 3·80 and 3·93 δ for methoxyl and carbomethoxyl groups. The proton at C_2 appeared as a doublet ($J = 1·5$ Hz) at 4·13 δ and that at C_1 appeared as a broad singlet at 5·07 δ. The olefinic proton showed a singlet at 7·77 δ. The aromatic protons at C_2' and C_6' showed a singlet at 6·37 δ and that of C_5 showed a singlet at 6·80 δ.

This data is in agreement with that reported by Stevenson *et al.*[5a] for (3*c*), obtained through the dilactone (2*b*)[5] [prepared by oxidative coupling of sinapic acid (1*b*)] by treatment with methanolic hydrogen chloride.

Experimental

A solution of 3, 4, 5-trimethoxybenzaldehyde 1·37 g (7 mm) and dimethyl succinate, 0.51 g (3.5 mm) in dry ether (20 ml) was added to a suspension of dry sodium methoxide (7 mm) in ether (20 ml) at −5 to −10° and the mixture was kept at −10° for 24 hr with occasional stirring. Then it was poured into methanol (40 ml) saturated with dry hydrogen chloride at 0° and refluxed for 4 hr under a slow stream of dry hydrogen chloride. The reaction mixture was cooled, diluted with water (150 ml) and extracted with benzene (3 × 50 ml). The combined organic layer

* Part I : Ganeshpure, P.A., *Curr. Sci.*, 1976 **45**, 494.