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CONSTITUTION OF DALBERGIN—IV

A NOVEL TRANSFORMATION OF O-METHYLDALBERGIN

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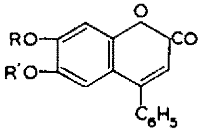
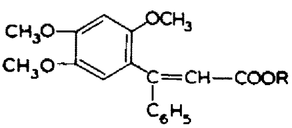
Abstract—O-methyldalbergin and related 4-phenylcoumarins are markedly different from ordinary coumarins in their behaviour towards alkali. They are stable in boiling alkali and on addition of mercuric oxide yield coumarilic acids. Phenyl-coumarilic acids undergo decarboxylation readily when boiled with aqueous alcoholic mercuric chloride to yield phenyl substituted coumarones.

In part III[1] it was shown that dalbergin is 4-phenyl-6-hydroxy-7-methoxy-coumarin (I). O-methyldalbergin (II) was reported earlier[2] to be stable to boiling aqueous alkali and give an O-methyl ether of the corresponding cinnamic acid (III) which can be esterified to (IV) and demethylated to nordalbergin (V). According to Seshadri and co-workers,[3] mercuric chloride converts an *ortho*-methoxy *cis*-acid into the trans form, and as (III) is unchanged by mercuric chloride, it is considered to have the trans structure.

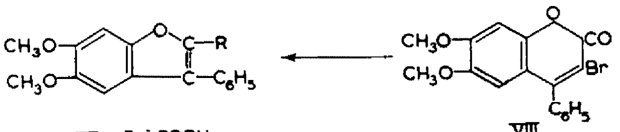


I; $R=CH_3$, $R'=H$
II; $R = R' = CH_3$
V; $R = R' = H$



III; $R=H$
IV; $R=CH_3$

Attempts to prepare *ortho*-hydroxy *trans*-cinnamic acid from (II) gave unexpected results. Treatment of (II) with mercuric oxide in alkaline medium for a long period gives a non-phenolic acid, $C_{17}H_{14}O_5$, which may be decarboxylated to a non-phenolic neutral substance, $C_{16}H_{14}O_3$. As mercury is formed during the reaction, oxidation has taken place. This suggested that the acid is 3-phenyl-5:6-dimethoxycoumarone-2-carboxylic acid (VI) and the neutral substance 3-phenyl-5:6-dimethoxy-coumarone (VII).



VI; $R=COOH$
VII; $R=H$
VIII

These conclusions were confirmed by comparison with authentic samples. (II) was monobrominated to (VIII) which when refluxed with aqueous alkali, formed

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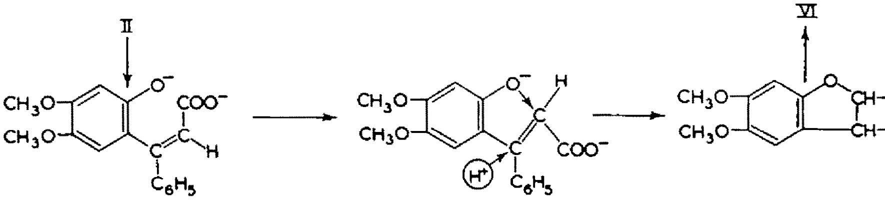
[1] V. K. Ahluwalia, A. C. Mehta and T. R. Seshadri, *Proc. Indian Acad. Sci.* A **45**, 15 (1957).
[2] V. K. Ahluwalia and T. R. Seshadri, *J. Chem. Soc.* 970 (1957).
[3] S. Rangaswami and T. R. Seshadri, *Proc. Indian Acad. Sci.* A **5**, 249 (1937).

3-phenyl-5:6-dimethoxycoumarone-2-carboxylic acid (VI). Decarboxylation with copper and quinoline gave the corresponding coumarone (VII).

Mercuric oxide is an efficient catalyst for *cis–trans* inversion of hydroxycinnamic acids derived from coumarins.[4] Coumarin, 6-nitro coumarin and 4-methyl-7-methoxy coumarin, yield only the corresponding coumaric acids (*trans*-cinnamic acids) by this treatment.[4,5] The transformation of (II) with mercuric oxide involves dehydrogenation which has also been observed in other 4-phenyl coumarins such as 4-phenyl-7-methoxy- and 4-phenyl-7:8-dimethoxy-coumarins, although the amount of conversion into coumarilic acids is much lower as compared with (II).



The formation of coumarilic acids from 4-phenylcoumarins may depend on the capacity of the α-carbon atom of the *trans*-cinnamic acid produced to develop a positive charge and the β-carbon atom a negative charge. This effect may be attributed to the combined influence of two phenyl groups as coumaric acids with one phenyl group alone do not undergo the change.

Decarboxylation in the presence of mercuric chloride has been observed in certain cases of furan α-carboxylic acids by Gilman and Wright[6] who came to the conclusion that this decarboxylation is of general utility for halogen and alkyl substituted 2-furoic acids. They found that the reaction failed with 5-nitro-2-furoic acid. Experiments carried out using coumarilic acids have not produced any marked decarboxylation, but with the phenyl-substituted coumarilic acids the decarboxylation is complete.

EXPERIMENTAL

3-*Phenyl-5:6-dimethoxy-coumarone-2-carboxylic acid* (VI)

(i) *Action of mercuric oxide and alkali on* O-*methyldalbergin.* O-methyldalbergin[1,2] (2 g) dissolved in hot aqueous potassium hydroxide (30 cm^3, 20%) was diluted with water (70 cm^3) and refluxed with freshly prepared yellow mercuric oxide (15 g) for 10 hr. The mixture was filtered, the filtrate saturated with hydrogen sulphide to remove mercury, filtered again and acidified. The acid product obtained was purified (sodium hydrogen carbonate) and crystallised from methanol; colourless rectangular plates (1·5 g), m.p. 224–225° (Found: C, 68·4; H, 5·1; $C_{17}H_{14}O_5$ requires C, 68·4; H, 4·7%). It gave an orange red colour with alcoholic ferric chloride. Mixed m.p. with a sample prepared by method (ii) was undepressed.

(ii) 3-*Bromo-4-phenyl-6:7-dimethoxy-coumarin* (VIII). To a hot solution of O-methyldalbergin[1,2] (2·8 g) in glacial acetic acid (20 cm^3) a solution of bromine in

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[4] P. S. Rao and T. R. Seshadri, *Proc. Indian Acad. Sci.* A 3, 293 (1936).
[5] K. S. Murty, P. S. Rao and T. R. Seshadri, *Proc. Indian Acad. Sci.* A 6, 316 (1937).
[6] H. Gilman and G. F. Wright, *J. Amer. Chem. Soc.* 55, 3303 (1933).

glacial acetic acid (16 cm^3; 10%) was added with shaking (10 min). Bromine was absorbed immediately and on cooling, colourless crystals (2·8 g) separated which crystallised from glacial acetic acid as colourless rectangular plates, m.p. 190–91°; diluting the mother liquor with water gave (0·2 g) more (Found: C, 56·4; H, 3·7; $C_{17}H_{13}O_4Br$ requires C, 56·5; H, 3·6%).

Action of alkali on the bromo-coumarin. The bromo compound (3 g) was refluxed with aqueous NaOH (150 cm^3; 10%) for 4 hr. The solution was cooled, the insoluble portion filtered, and the filtrate acidified with dilute hydrochloric acid. The product was purified by treatment with sodium hydrogen carbonate and it crystallised from methanol as colourless rectangular plates (1·9 g), m.p. 224–225°.

The *methyl ester* prepared from (VI) (obtained by both methods) by methylation with dimethyl sulphate, acetone and potassium carbonate or sodium bicarbonate crystallised from methanol as small colourless prisms, m.p. 135–36° (Found: C, 69·6; H, 5·3; $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·2%). It was insoluble in cold 5% sodium hydroxide and gave no colour with alcoholic ferric chloride. On hydrolysis it gave the original acid m.p. and mixed m.p. 224–25°.

3-*Phenyl*-5:6-*dimethoxy-coumarone* (VII)

(i) *Action of mercuric chloride on the coumarone-carboxylic acid.* (VI) (0·5 g) and mercuric chloride (1 g) were refluxed with aqueous alcohol (50 cc; 50%) for 6 hr. The solution was acidified with hydrochloric acid to make the strength 1%, and alcohol removed under reduced pressure and the residue extracted with ether. The ether solution was washed with aqueous sodium hydrogen carbonate and the solvent distilled. The residue (0·35 g) crystallised from methanol as clusters of colourless needles, m.p. 94–95°. Mixed m.p. with a sample prepared as given below (ii) was undepressed (Found: C, 75·5; H, 5·7; $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5%).

(ii) *Decarboxylation of* (VII). 3-Phenyl-5:6-dimethoxy-coumarone-2-carboxylic acid (1 g) was heated at 220° in quinoline (10 cm^3) solution with copper powder (0·4 g) until the evolution of carbon dioxide ceased (30 min). The cooled mixture was poured into ether, the solution filtered and washed with dilute hydrochloric acid to remove quinoline and then with aqueous sodium hydrogen carbonate, dried and the solvent distilled. The viscous residue crystallised from methanol as clusters of colourless needles (0·8 g), m.p. 94–95°.

Methyl 2:4:5-*trimethoxy-β-phenylcinnamate* (IV) was prepared by heating (III)[2] with dimethyl sulphate and potassium carbonate in acetone for 3 hr. It crystallised from methanol as colourless rectangular plates, m.p. 92–94° (Found: C, 69·7; H, 5·9; $C_{19}H_{20}O_5$ requires C, 69·5; H, 6·1%).

Action of hydriodic acid on 2:4:5-*trimethoxy-β-phenylcinnamic acid* (III)[2]. (III) (0·5 g) was refluxed with acetic anhydride (10 cc) and hydriodic acid (5 cm^3) for 2 hr. The mixture was poured into cold saturated aqueous sodium bisulphite (75 cm^3). The solid product was filtered and crystallised from ethyl acetate-petroleum ether mixture yielding colourless small rectangular plates and small prisms (0·3 g), m.p. 268–69°, undepressed by an authentic sample of nordalbergin (V).[1,2] The acetate and the methyl ether melted at 157–58° (O-acetyl nordalbergin) and 144–45° (O-methyldalbergin) respectively.

3-*Phenyl*-6-*methoxy-coumarilic acid,* prepared from 4-phenyl-7-methoxy-coumarin,[1] mercuric oxide and sodium hydroxide (20 hr refluxing) as in the case of (II) crystallised from methanol as colourless plates and needles, m.p. and mixed m.p. with an authentic sample[7] 204–6°. Yield, 14%.

3-*Phenyl*-6-*methoxy-coumarone* obtained by the decarboxylation of the above acid either with mercuric chloride in aqueous alcoholic medium or with copper-quinoline, crystallised from petroleum ether as colourless needles, m.p. 41–42°. Motylewski[8] recorded the same m.p. for this product.

2:4-*Dimethoxy-β-phenyl-cinnamic acid*, prepared from 4-phenyl-7-methoxy-coumarin by the action of dimethyl sulphate and methanolic potash, crystallised from methanol as pale yellow plates, m.p. 170–71° (Found: C, 71·9; H, 6·0; $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·7%).

3-*Phenyl*-6:7-*dimethoxy-coumarilic acid* was prepared from 4-phenyl-7:8-dimethoxy-coumarin[2] by heating with mercuric oxide and sodium hydroxide solution; the acid crystallised from methanol as clusters of colourless needles, m.p. 196–198°. Yield 33% (Found: C, 69·0; H, 4·5; $C_{17}H_{14}O_5$ requires 68·4; H, 4·7%). Mixed m.p. with a sample prepared by the method given below was undepressed.

3-*Bromo*-4-*phenyl*-7:8-*dimethoxy coumarin*, prepared by bromination of 4-phenyl-7:8-dimethoxy-coumarin[2] in acetic acid medium, crystallised from hot glacial acetic acid as colourless rectangular plates and small prisms, m.p. 231–33° (Found; C, 57·0, H, 4·0; $C_{17}H_{13}O_4Br$ requires C, 56·5; H, 3·6%). It was refluxed with sodium hydroxide solution and the product, 3-*phenyl*-6:7-*dimethoxy-coumarilic acid* crystallised from methanol as colourless needles m.p. 196–198°.

3-*Phenyl*-6:7-*dimethoxy-coumarone*, obtained by decarboxylation of the above acid crystallised from alcohol as small colourless leaflets, m.p. 83–84°, as recorded previously.[8]

2:3:4-*Trimethoxy-β-phenyl-cinnamic acid*, prepared from 4-phenyl-7:8-dimethoxy-coumarin[2] crystallised from methanol as aggregates of small prisms, m.p. 168–70° (Found: C, 68·7; H, 5·8; $C_{18}H_{18}O_5$ requires C, 68·8; H, 5·8%). The methyl ester crystallised from methanol as colourless prisms, m.p. 89–90° (Found: C, 70·0; H, 5·9; $C_{19}H_{20}O_5$ requires C, 69·5; H, 6·1%).

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[7] T. R. Seshadri and S. Varadarajan, *J. Sci. Ind. Res. (India)* B **11**, 59 (1952).

[8] S. Motylewski, *Ber. Dtsch. Chem. Ges.* **42**, 3148 (1909).