188. *Constitution of Dalbergin. Part II.*[1]

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Dalbergin is shown by degradative and synthetic evidence to be a monomethyl ether of 4-phenylæsculetin, and is the first natural 4-phenylcoumarin. Its monomethyl ether is a minor component of the heartwood of *Dalbergia sissoo.*

EARLIER[1] it was shown that dalbergin $C_{15}H_8O_2(OMe)(OH)$, the chief chemical component of the heartwood of *Dalbergia sissoo,* is neither a derivative of 3-phenylæsculetin (as proposed by Dutt and Kathpalia[2]) nor of 3-phenyldaphnetin. In the present study the infrared spectrum has been found to include prominent absorption at 3200 (phenolic OH), 1680 (C=O), 1610 (-C=C-), 1540, 1505, and 1450 cm.$^{-1}$ (aromatic double bonds). The frequencies of the C=O and the C=C group suggest that they are conjugated. The behaviour of dalbergin with alkali agrees with that of an αβ-unsaturated lactone. That the phenolic hydroxyl and the methoxy-group are *ortho* to each other is shown by the ferric chloride colour of nordalbergin, which moreover forms a methylenedioxy-derivative. The methyl ether of dalbergin is stable, even on long boiling, to 20% alcoholic potassium hydroxide. Dalbergin and its methyl ether give an unusual colour reaction with magnesium and alcoholic hydrochloric acid, pink changing to blue and red. These results led to a suspicion that dalbergin was probably not a coumarin derivative,[1] but *O*-methyldalbergin with dimethyl sulphate and methanolic alkali gives an *O*-methyl ether of the corresponding cinnamic acid. Oxidation of *O*-methyldalbergin (I) with cold neutral permanganate has yielded benzoic acid, oxalic acid, and 2-hydroxy-4 : 5-dimethoxybenzophenone (II). The consequence that *O*-methyldalbergin is 6 : 7-dimethoxy-4-phenylcoumarin has been confirmed by synthesis. Nordalbergin and *O*-methyldalbergin are identical, respectively, with 4-phenylæsculetin (from 1 : 2 : 4-triacetoxybenzene and ethyl benzoylacetate) and its dimethyl ether. On the other hand, these dalbergin

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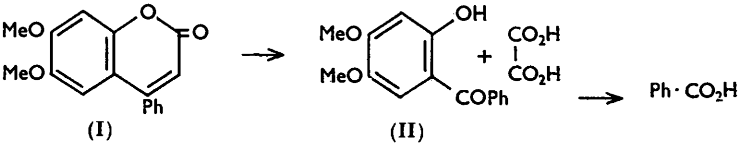
[1] Part I, Ahluwalia, Sawhney, and Seshadri, *J. Sci. Ind. Res., India,* 1956, **15**, *B*, 66.

[2] Dutt and Kathpalia, *Indian Soap J.*, 1953, **18**, 213.

derivatives differ from 4-phenyldaphnetin[3] and its dimethyl ether. The position of the methoxyl group in dalbergin is under investigation.



During the extraction of dalbergin we isolated *O*-methyldalbergin as a minor constituent, which suggests that stepwise methylation of nordalbergin takes place in the plant, possibly the more active hydroxyl group being first methylated to yield dalbergin.

Though coumarin derivatives (C_9 system) with various modifications have been found in Nature in large numbers, phenylcoumarins have not been known as natural products. Dalbergin and *O*-methyldalbergin represent naturally occurring simple members of the 4-phenylcoumarin group which are analogous to the structures found in brazilin and hæmatoxylin. Wedelolactone[4] is a 3-phenylcoumarin analogous to naturally occurring *iso*flavonoids which are fairly frequent. Dalbergin could also be considered as related to benzophenone derivatives occurring in Nature; possibly the latter are produced by the degradation of 4-phenylcoumarins. Similarly stilbenes could arise from 3-phenylcoumarins. These considerations would bring together the structural chemistry of naturally occurring flavonoids and *iso*flavonoids, 3- and 4-phenylcoumarins, benzophenones, and stilbenes.

EXPERIMENTAL

Extraction (*Dalbergin and* O-*Methyldalbergin*).—Shavings of the heartwood (2 kg.) were extracted with hot light petroleum (b. p. 60—80°; 3 × 6 hr.) to remove oils and then with boiling benzene (4 × 6 hr.). The benzene extract was concentrated to 300 c.c. and left for 2 days at 0°. Crystals (A) were deposited. The benzene solution was diluted with ether and the solution separated into alkali-soluble [mixed with the above solid (A)] and neutral components. The neutral product crystallised from methyl alcohol as colourless elongated rectangular prisms and rods (2·0 g.), m. p. 145—146° undepressed by *O*-methyldalbergin.[1] With magnesium and alcoholic hydrochloric acid it gave a feeble pink colour which changed to deep blue on addition of more magnesium; this was stable for some time and finally became deep red.

The solid (A) was passed in hot ethyl acetate (1 l.) through a column of alumina (8″) and eluted with hot ethyl acetate (2 l.). The coloured impurities were retained. The total eluate on concentration gave directly pure dalbergin (11·5 g.), m. p. 209—210°.

OO-*Methylenenordalbergin*.—Nordalbergin[1] was refluxed with an excess of methylene iodide and potassium carbonate in acetone for 8 hr. The *product* crystallised from methyl alcohol as thick tablets, m. p. 142—143° (Found: C, 72·2; H, 3·8. $C_{16}H_{10}O_4$ requires C, 72·2; H, 3·8%).

Permanganate Oxidation.—A solution of *O*-methyldalbergin (2 g.) in acetone (100 c.c.) was treated with potassium permanganate (10 g.) in small quantities and left for 24 hr. at room temperature (occasional shaking); acetone was distilled off, and the residue suspended in water (100 c.c.) and saturated with sulphur dioxide. The mixture was extracted with ether [aqueous mother-liquor (A)], and the extract washed with water. The ether extract was extracted with 5% aqueous sodium hydrogen carbonate (B), 10% aqueous sodium hydroxide (C), and then water, and the solvent distilled off (residue D). The carbonate extract (B), on acidification, ether-extraction [the remaining aqueous solution was mixed with the above aqueous mother-liquor (A)], and removal of the solvent, gave benzoic acid (0·7 g.), m. p. and mixed m. p. 120—121° (from water). The sodium hydroxide extract (C), worked up similarly, gave a small amount of oil. Its dinitrophenylhydrazone crystallised from acetic acid as deep red elongated rectangular plates, m. p. 254—256° alone or mixed with 2-hydroxy-4 : 5-dimethoxybenzophenone 2 : 4-dinitrophenylhydrazone (Found: C, 57·3; H, 4·5. $C_{21}H_{18}O_7N_4$ requires C, 57·5; H, 4·2%). The neutral residue (D) (0·1 g.) on crystallisation from methanol melted at 144—145° (unchanged methyldalbergin).

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[3] Kostanecki and Weber, *Ber.*, 1893, **26**, 2906.

[4] Govindachari, Nagarajan, and Pai, *J.*, 1956, 629.

The aqueous mother-liquor (A) was distilled under reduced pressure, and the residue dried and extracted with hot ethyl acetate (3 × 25 c.c.). After evaporation of the extract the residue of oxalic acid crystallised from ether–light petroleum as prisms (50 mg.), m. p. and mixed m. p. 100—101°.

Degradation of O-*Methyldalbergin to* 2 : 4 : 5-*Trimethoxy*-β-*phenylcinnamic Acid*.—*O*-Methyldalbergin (2 g.) was heated with dimethyl sulphate (22·5 c.c.), methyl alcohol (30 c.c.), and 10% aqueous potassium hydroxide (80 c.c.).[5] The *product* crystallised from methanol as pale yellow plates (1·0 g.), m. p. 170—171° (Found : C, 68·6; H, 5·7. $C_{18}H_{18}O_5$ requires C, 68·8; H, 5·8%).

7 : 8-*Dimethoxy*-4-*phenylcoumarin*.—7 : 8-Dihydroxy-4-phenylcoumarin[3] was methylated by use of dimethyl sulphate, potassium carbonate, and acetone. The *product* crystallised from alcohol as rectangular prisms, m. p. 135—136° (Found : C, 71·9; H, 5·3. $C_{17}H_{14}O_4$ requires C, 72·4; H, 5·0%).

6 : 7-*Dihydroxy*-4-*phenylcoumarin* (*Nordalbergin*).—This was prepared from hydroxyquinol triacetate[6] (55 g.), ethyl benzoylacetate[7] (42 g.), and 75% sulphuric acid (400 c.c.), under conditions similar to those adopted for 4-methylæsculetin,[8] the *product* being purified through the borate complex. It crystallised from alcohol as rectangular tablets and tiny prisms (30 g.), m. p. 267—268° undepressed by nordalbergin,[1] and gave a deep green colour with alcoholic ferric chloride and with magnesium and hydrochloric acid a pink colour which changed to blue and finally red (Found : C, 70·5; H, 3·7. $C_{15}H_{10}O_4$ requires C, 70·9; H, 3·9%).

The diacetate (acetic anhydride and pyridine) crystallised from alcohol as rectangular prisms and rods, m. p. and mixed m. p. 157—158°.

6 : 7-*Dimethoxy*-4-*phenylcoumarin* (O-*Methyldalbergin*).—6 : 7-Dihydroxy-4-phenylcoumarin was methylated by use of methyl sulphate, potassium carbonate, and acetone. The *product* crystallised from methyl alcohol as prisms and rods, m. p. and mixed m. p. 145—146° (Found : C, 72·9; H, 5·1. $C_{17}H_{14}O_4$ requires C, 72·4; H, 5·0%). With magnesium and hydrochloric acid it gave the same colour reaction as *O*-methyldalbergin. The trimethoxy-β-phenylcinnamic acid obtained as above melted at 170—171°, undepressed by a sample obtained from *O*-methyldalbergin.

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[5] Cf. Robertson, Waters, and Jones, *J.*, 1932, 1683.
[6] *Org. Synth.*, 1925, **4**, 35.
[7] *Ibid.*, 1943, **23**, 35.
[8] *Ibid.*, 1925, **4**, 45.