## The Constitution and Stereochemistry of Obtusafuran

By M. GREGSON, W. D. OLLIS,\* B. T. REDMAN, and I. O. SUTHERLAND

(Department of Chemistry, The University, Sheffield S3 7HF)

and H. H. DIETRICHS

(Bundesforschungsanstalt für Forst- und Holz-wirtschaft, Institut für Holzchemie, Hamburg, Germany)

In addition to two neoflavanoids and two cinnamylphenols,<sup>1</sup> the heartwood of *Dalbergia obtusa* Lecomte (syn. *D. retusa*) has yielded a novel natural product, obtusafuran, which is of interest in that it contains a  $C_{15}$ -(1,2-diarylpropanoid)skeleton associated in a very unusual way with a dihydrobenzofuran residue. This constitution has direct implications regarding our biogenetic proposals.<sup>2</sup> The determination of the constitution and absolute configuration of obtusafuran and the synthesis of its racemate are now reported.

Obtusafuran,  $C_{16}H_{16}O_3$ , m.p. 110–113°, was optically active,  $[\alpha]_{20}^{20} + 47^\circ$ , and had a u.v. spectrum  $[\lambda_{max} \text{ (EtOH) } 235 \ (\epsilon 2940; \text{ infl)} and$  $305 m\mu \ (\epsilon 4600)]$ , which suggested an oxygenated benzene chromophore without additional conjugation. The n.m.r. spectrum of obtusafuran indicated the presence of a phenyl group  $[\tau 2.63]$ (s, 5H)], two *para*-related aromatic protons  $[\tau 3.30]$ 

(s, 1H),  $\tau$  3.53 (s, 1H)], a >CH-CH<sub>3</sub> unit [ $\tau_{A}$  4.90 (d, 1H),  $\tau_{M}$  6.4—6.9 (m, 1H),  $\tau_{X}$  8.63 (d, 3H), AMX<sub>3</sub> system,  $J_{AM}$  8.0 c./sec.,  $J_{MX}$ 7.0 c./sec.], a methoxy-group [ $\tau$  6.20 (s, 3H)], and

a hydroxy-group [ $\tau 4.77$  (broad s, 1H)] (i.r.  $v_{max}$ 3500 cm.<sup>-1</sup>), thus leading to the partial structure (II) for obtusafuran. The relative positions of the hydroxy- and methoxy-substituents were determined by the hydrogenolysis (10% Pd-C catalyst in acetic acid) of obtusafuran followed by aerial oxidation which yielded a yellow quinone (III), m.p. 120°,  $[\alpha]_{D}^{25} - 11.0^{\circ} [\tau 2.80 \text{ (s, 5H)}; \tau 3.56$ (d, 1H), J = 1 c./sec.;  $\tau = 4.10$  (s, 1H);  $\tau = 6.4 - 7.6$  (m, 3H);  $\tau$  6·20 (s, 3H);  $\tau$  8·91 (d, 3H), J 7.0 c./sec.]. This constitution (III) for the optically active quinone was confirmed by synthesis of its racemate. 2-Benzyloxy-4-methoxyacetophenone<sup>3</sup> reacted with benzylidinetriphenylphosphonium ylid to give the olefin (IV) and catalytic reduction (10% Pd-C in acetic acid) of (IV) gave the 1,2-diarylpropane (V) which was oxidised by Frémy's salt giving the racemic quinone (cf. III). Obtusafuran must therefore be 2,3-dihydro-5-hydroxy-6-methoxy-3methylbenzofuran, and the definition of its stereochemistry is now considered.

The relative stereochemistry of obtusafuran was determined by comparison with the synthetic racemic cis-2,3-dihydrobenzofuran derivative (VI), prepared by controlled catalytic hydrogenation (10% Pd-C in ethyl acetate) of the benzofuran (VII) which was synthesised by the reaction of 2,5-dihydroxyanisole<sup>4</sup> with 1-bromo-1-phenylpropan-2-one. cis-2,3-dihydrobenzofuran The (VI), m.p. 110–111°, had i.r. and n.m.r. spectra different from those of (+)-obtusafuran, particularly with respect to the chemical shifts of the proton on C(2) [ $\tau$  4.27 for (VI) and  $\tau$  4.90 for (I)] and the methyl group on C(3) [ $\tau$  9.26 for (VI) and  $\tau$  8.63 for (I)]. The trans-2,3-dihydrobenzofuran structure (I) could therefore be assigned to obtusafuran, and this opinion was confirmed by the isomerisation of the cis-2,3-dihydrobenzofuran (VI) by heating (100°; 16 hr.) it with potassium tbutoxide in dimethyl sulphoxide. This isomerisation gave racemic obtusafuran (I), whose n.m.r. spectrum was identical with that of natural (+)-obtusafuran.

Ozonolysis of the (-)-quinone (III), from natural (+)-obtusafuran, and decomposition of the ozonide with hydrogen peroxide gave (-)-(S)methylsuccinic acid (VIII).<sup>5</sup> The (-)-quinone therefore has the (S)-configuration (III), and it



follows that (+)-obtusafuran has the (2R,3R)absolute configuration (I).

This (2R,3R)-configuration of (+)-obtusafuran may be compared with the (2S,3S)-configuration recently discussed<sup>6</sup> for melanoxin [2,3-dihydro-5hydroxy-2-(3-hydroxy-4-methoxyphenyl)-6-methoxy-3-methylbenzofuran] isolated from Dalbergia melanoxylon.

The n.m.r. spectral characteristics of the cis- and trans-2,3-dihydrobenzofurans have the same vicinal coupling  $(J_{2H-3H} \ 8 \text{ c./sec.})$ . This result is of general interest in relation to considerable recent discussion<sup>7</sup> of the deduction of the stereochemistry of 2,3-dihydrobenzofurans from n.m.r. coupling constants.

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