A Partial Structure of "Dehydro-dicatechin A"

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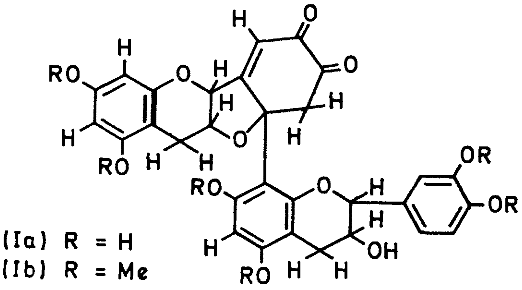
Summary Evidence is presented to establish a partial structure for "dehydro-dicatechin A."

In a recent publication, Weinges *et al.* suggested an α-diketone structure for "dehydro-dicatechin A" (Ia), the dimer formed from the oxidative condensation of (+)-catechin.[1]

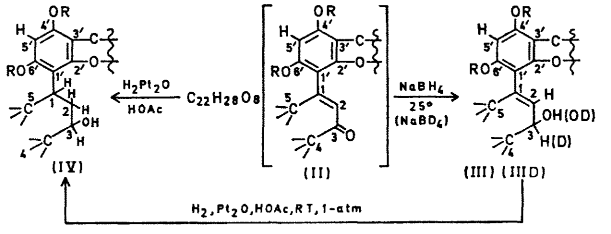


(Ia) R = H
(Ib) R = Me

We have obtained chemical evidence which conflicts with the α-diketone structure (Ia) but supports a styryl ketone structure such as (IIa).

Our "dehydro-dicatechin A" was prepared by both chemical [$K_3Fe(CN)_6$] and enzymatic (tyrosinase and polyphenol oxidase) oxidations of (+)-catechin. The physical and chemical properties of the dimer as well as those of its acetyl and methoxy-derivatives are identical to those reported by Weinges. Similarly, we found that the compound has six phenolic and one aliphatic hydroxyl groups.

The u.v. spectra of "dehydro-dicatechin A" and its monohydroxy hexamethyl ether give the following absorption bands: λ_{max} (MeOH), 385 nm (log ε = 4·26), 277 (3·70), 255 (3·86) and 376 (4·33), 277 (3·66), 257 (3·91), respectively.[3] In methanolic NaOH, the λ_{max} of "dehydro-dicatechin A" shifts to 430 nm (4·58), which is characterisric of structures such as *p*-hydroxystyryl ketones.[4] The i.r. spectrum of the monohydroxy hexamethyl ether, ν_{max} 1668m cm^{-1} [PhC=C–C(O)–] supports a conjugated carbonyl system. By treating this derivative with H_5IO_6, H_2O_2–OH^-, or 10% NaOH (H_2O-MeOH, reflux) starting material is recovered, which seems inconsistent with an α-diketone such as (Ib).



a; R = H, b; R = Me

Sodium borohydride reduction of the monohydroxy hexamethyl ether (IIb) yields (IIIb):† m.p. 173—174°; i.r. (KBr) ν_{max}, 1668w cm^{-1} (PhC=C–); n.m.r. τ 3·95 (d, *J* 2·0, 2-H) and 5·52 (d, *J* 2·0, 3-H). Reduction of (IIb) with $NaBD_4$ gives (IIIb D) whose n.m.r. spectrum shows a singlet at τ 3·95 (2-H) instead of a doublet. These data

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† Correct analysis for carbon and hydrogen was obtained.

suggest that 2-H and 3-H of (IIIb) are adjacent to each other, thus confirming an $\alpha\beta$-unsaturated ketone in (IIb). Also, because 2-H and 3-H give doublets, C-1 and C-4 of (IIb) and (IIIb) are not bonded to protons. From the τ-value of 3-H, the atom labelled C-4 must be a t-carbon rather than an oxygen atom. Compound (IIIb) has u.v. absorption bands at ν_{max} (MeOH), 319 (3·95), 308 (3·90), 288 (4·23), and 278 (4·22) which is characteristic of an *ortho-* and *para-*(OR) substituted styrene.[5] Therefore, C-1 must be bonded to an aromatic ring. It is unlikely that $NaBH_4$ reduction of (Ib) would give a product with an u.v. spectrum of this nature.

Acetylation of (IIIb) with Ac_2O–C_5H_5N gives a diacetate (τ 7·91, 8·02); one acetyl group results from the reduced carbonyl group, the other from the hydroxyl present on the original dimer.

At atmospheric-pressure hydrogenation of either (IIb) or (IIIb) over Pt_2O in HOAc at room temperature gives (IVb): *m/e* 664·2598; m.p. 147—150°, u.v. ν_{max} (MeOH), 276 (3·67). The absence of i.r. bands at 1668 cm^{-1} indicates the reduction of the carbonyl and vinyl functions. The n.m.r. spectrum of (IVb) shows the absence of the vinyl proton (2-H) in (IIb) and the presence of a singlet at τ 3·85 which can be attributed to the aromatic proton 5-H. From the absence of a low-field proton (1-H) below τ 4·0, the atom labelled C-5 must be a t-carbon rather than an oxygen atom.

Acetylation of (IVb) prepared by reduction of either (IIb) or (IIIb) yields a diacetate, m.p. 153—155°. Again, the n.m.r. spectrum shows only two aliphatic acetates (τ 8·08, 7·90); thus, "dehydro-dicatechin A" can have only one carbonyl group.

From our data, we are confident that "dehydro-dicatechin A" is a styryl ketone. We also know that the catechol ring of one molecule of catechin combines with the phloroglucinol ring of the second, but we have no chemical evidence for the position of attack. Because we can only speculate on the complete structure of "dehydro-dicatechin A," we have used partial structures which represent only the portion of the molecule for which we have chemical evidence.

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[1] K. Weinges, W. Ebert, D. Huthwelker, H. Mattauch, and J. Perner, *Annalen*, 1969, **726**, 114–124.

[2] K. Weinges and W. Ebert, *Phytochemistry*, 1968, **7**, 153–155.

[3] The u.v. absorption max of this compound is consistent with that of aflatoxin B_1 which has the same chromophore as we have postulated for "dehydro-dicatechin A"; T. Asao, G. Büchi, M. Abdel-Kader, S. Chang, E. Wick, and G. Wogan, *J. Amer. Chem. Soc.*, 1965, **87**, 882.

[4] L. Jurd, "The Chemistry of Flavonoid Compounds," ed. T. A. Geissman, Macmillan, New York, 1962, ch. 5.

[5] J. Mohandas, M. Slaytor, and T. R. Watson, *Austral. J. Chem.*, 1969, **22**, 1803.