This would result from the occurrence in vivo of bilirubin derivatives carrying a substituent on their isovinyl-neoxanthobilirubinic acid portion (as in II and III), thus causing a deficiency of the detectable isovinyl azopigments.

Riassunto. In mezzo fortemente acido la bilirubina reagisce con gli alcooli e con i tioli fornendo con alte rese prodotti di addizione identici a quelli ottenibili per via fotochimica in assenza di acidità.

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The Isolation of Dehydrodiisoeugenol from the Aril of *Myristica fragrans* Houtt[1]

Myristica fragrans Houtt. is the economically important member of the family Myristicaceae. The seed (nutmeg) and the aril (mace) are widely used as spices and have a long history of abuse in view of their reported narcotic properties[2,3]. Whilst terpenoids and fatty acids constitute the major classes of compounds found in this species, propenylphenyl ethers are also present in significant quantities[3-5]. We now wish to report the isolation of an example of a dimeric propenylphenol, the coumaran derivative, dehydrodiisoeugenol (I). This compound was isolated from the phenolic fraction of a cold petroleum ether extract of freshly ground mace, by column chromatography on silica gel [eluting solvent: benzene/hexanes (1:1)].

The dehydrodiisoeugenol (I), [mass spectrum, found: $M^{+\cdot}$ 326.1515, calculated for $C_{20}H_{22}O_4$ 326.1518, major peaks: 326 (100%), 311 (10%), 283 (6%), 202 (10%), 164 (6%), 151 (11%), 137 (18%), IR ν_{max} 3560 cm^{-1}. UV λ_{max} (EtOH) 275 nm] was obtained as white crystals m.p. 130–132° (from benzene-hexane), lit.[6]; m.p. 132–133°. The NMR-spectrum ($CDCl_3$) showed the following signals: τ 3.07–3.26, m, 5 aromatic H; 3.65, d, J = 15 Hz, 1, αH; 3,95, m, 1, βH; 4.40, s, 1, OH; 4.94, d, J = 9 Hz, 1, α'H; 6.13, s, 3, OCH_3; 6.15, s, 3, OCH_3; 6.58, m, 1, β'H; 8.15, d, J = 6 Hz, 3, γH's; 8.63, d, J = 7 Hz, 3, γ'H's. These values are in agreement with those reported by LUDWIG et al.[7], for dehydrodiisoeugenol which was prepared by oxidation of isoeugenol (II). The compound (I) was first prepared by COUSIN and HÉRISSEY[6] in 1908, its phenylcoumaran structure I proposed in 1933[8] and verified several years later[9,10]. The identification of the isolated compound as (I) was verified by formation of the acetyl derivative (m.p. 111–113°, lit.[11] m.p. 113-5°. [Mass spectrum; $M^{+\cdot}$ 368 (27%) major peaks, 326 (100%), 311 (10%), 202 (14%), 174 (5%), 164 (9%), 153 (23%), 151 (11%), 137 (14%), 91 (10%), 77 (9%), 43 (50%)].

Since isoeugenol has been reported in the essential oil of mace[11] and can be converted to dehydrodiisoeugenol by oxidation, it was therefore necessary to ensure that the dehydrodiisoeugenol isolated from mace was not an artifact formed by oxidation of isoeugenol during the extraction procedure. This was achieved by detection of I by two-dimensional thin layer chromatography [Brinkmann silica gel G plates, Rf in diethyl ether/cyclohexane (50:50) = 0.46; Rf in benzene/acetone (95:5) = 0.43] of the fresh petroleum ether extract. The identity of the thin layer spot was established by comparison of the Rf values in two solvent systems and the colour reactions (Fast Blue B and Anisaldehyde reagents) of this substance with those of a purified sample of (I), and further verified by determination of the mass spectrum of the material extracted from the appropriate spot on the plate.

Dehydrodiisoeugenol (I) has not previously been reported as a plant constituent, however the analogous compound, dehydrodiconiferol alcohol (III) has been isolated from spruce cambium sap (cf. Ref.[12]).

Dehydrodiconiferol alcohol has been proposed as an intermediate in the biosynthesis of lignin and it, as well as dehydrodiisoeugenol, has been used as a model for spectroscopic and degradative studies in lignin chemistry.

Résumé. On a pu isoler le déshydrodiisoeugénol de l'arille de *Myristica fragrans* Houtt. (fleur de muscade).

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