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SHORT COMMUNICATION

STABILIZATION OF CAFFEYL COMPOUNDS IN ALKALINE MEDIA

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Abstract—Compounds containing a 3,4-dihydroxycinnamyl moiety can be stabilized in alkaline solutions by prior addition of Sodium borohydride. This procedure enables the determination of their alkaline spectra and also increases the yield when the isolation of these compounds after synthesis involves contact with alkaline solutions.

CAFFEIC acid (3,4-dihydroxycinnamic acid) and its congeners are unstable in alkaline media.[1,2] As a consequence, the determination of their u.v. spectra in alkaline solutions is not possible and values for their bathochromic shifts in alkali are not obtainable. Instability appears to be due to the presence of an olefinic bond since catechol and protocatechuic acid and aldehyde are stable in alkali and spectral determinations may be performed on their alkaline solutions. It is reported that esters of caffeic acid are more stable than the free acid and that their spectra in alkali can be determined. However, this property does not appear to be true for all esters; thus chlorogenic acid (3-caffeoylquinic acid) is reported to be unstable in alkali.[2] This instability of the *ortho*-dihydroxycinnamyl moiety could effect isolation of compounds containing such a structure if alkali is required in the process. As a result the isolation, purification, or even the detection of these substances may become difficult if not impossible.

The product isolated from the alkaline treatment of caffeyl alcohol has two absorption bands, at 1122 and 1070 cm^{-1}, in the i.r. region which are not present in the i.r. spectrum of caffeyl alcohol itself. Both bands indicate an ether linkage, and the 1070 cm^{-1} band is indicative of an aryl-alkyl ether. A Diels–Alder type of reaction has been reported in which substituted *ortho*-benzoquinones react with cyclopentadiene.[3] Two products were obtained, an α-diketone and a cyclic diether, indicating active participation of the *ortho*-quinone group in the reaction. The u.v. spectrum of this reaction mixture is similar to that of the alkaline treatment of caffeyl alcohol or acid. It is assumed that an *ortho*-quinone is formed when caffeyl compounds are treated with alkali and that this functional group then reacts with the olefinic double bond of another caffeyl moiety in a similar Diels–Alder type of reaction.

When excess sodium borohydride is added to a solution of a caffeyl compound before the solution is made alkaline, the caffeyl moiety appears to be stabilized. The addition of sodium borohydride apparently represses the formation of an *ortho*-quinone group from the

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[1] J. B. HARBORNE, In *Methods in Polyphenol Chemistry* (Edited by J. B. PRIDHAM), p. 25. MacMillan, New York (1964).

[2] G. K. SUTHERLAND, *Arch. Biochem. Biophys.* **75**, 412 (1958).

[3] J. A. BARLTROP and J. A. D. JEFFREYS, *J. Chem. Soc.* 154 (1954).

alkaline-treated *ortho*-dihydroxy compound. The u.v. spectra of caffeyl alcohol, ethyl caffeate and caffeic acid in neutral solutions and in alkaline solutions with prior addition of sodium borohydride are given in Figs. 1, 2, and 3. Since neither the spectrum for caffeyl alcohol nor the alkaline spectra of the other compounds has previously been published, values for λ_{max} and log ϵ are also given. These spectra are comparable with those of *p*-coumaryl, coniferyl (ferulic) and sinapyl alcohols, acids and ethyl esters. In Fig. 4, the effect of alkali upon ethyl caffeate, when borohydride is not present, is illustrated.

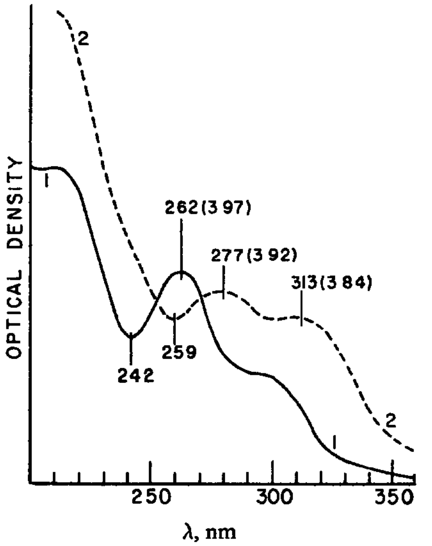

FIG. 1. ULTRA-VIOLET SPECTRA OF CAFFEYL ALCOHOL IN AQUEOUS SOLUTION: 1, NEUTRAL; 2, ALKALINE (WITH EXCESS $NaBH_4$ ADDED). LOG ϵ AT λ_{max} GIVEN IN PARENTHESES.

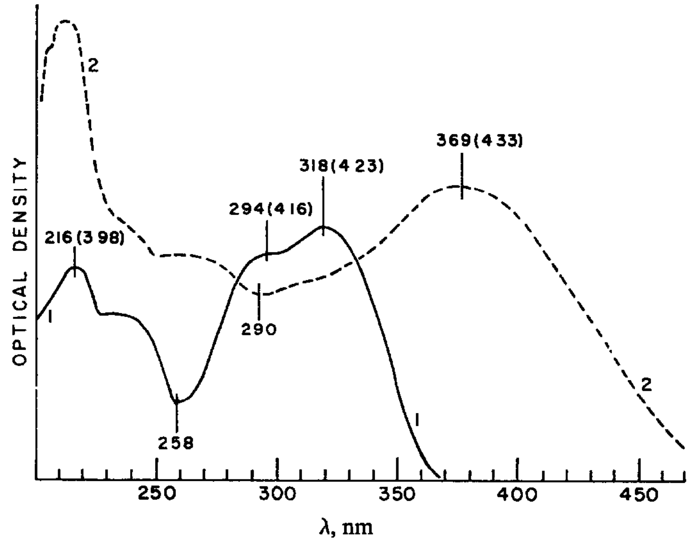

FIG. 2. ULTRA-VIOLET SPECTRA OF ETHYL CAFFEATE IN AQUEOUS SOLUTION: 1, NEUTRAL; 2, ALKALINE (WITH EXCESS $NaBH_4$ ADDED). LOG ϵ AT λ_{max} GIVEN IN PARENTHESES.

In the preparation of caffeyl alcohol from ethyl caffeate by lithium aluminum hydride reduction, considerable difficulty is experienced in isolation of the product.[4, 5] The yield is low and the desired compound is difficult to crystallize due to oily by-products being present. In the process of isolating the alcohol the reaction mixture is made alkaline as a result of

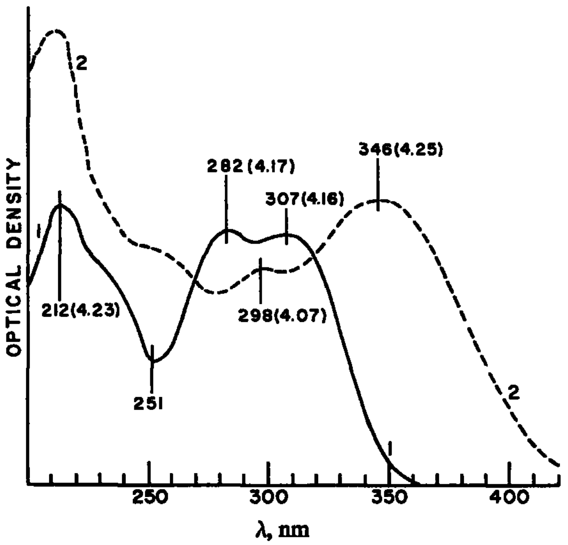

Fig. 3. Ultra-violet spectra of caffeic acid in aqueous solution: 1, neutral; 2, alkaline (with excess $NaBH_4$ added). Log ε at λ_{max} given in parentheses.

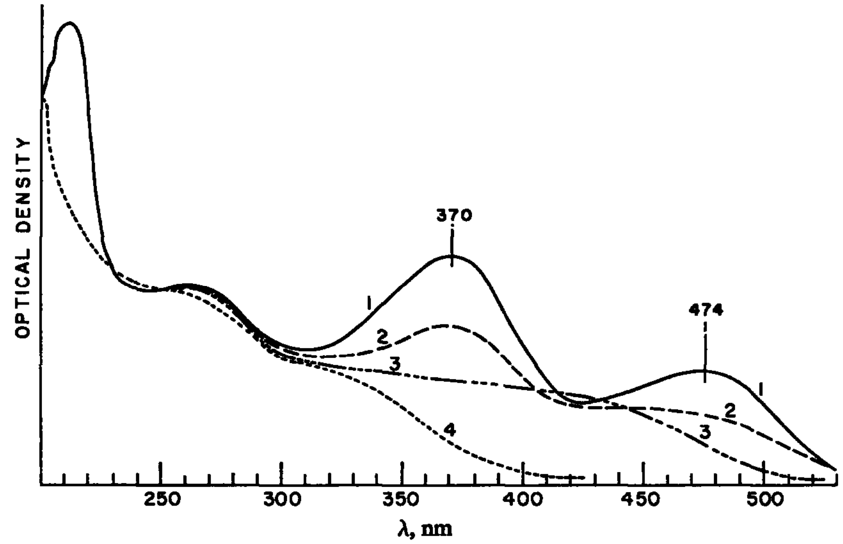

Fig. 4. Ultra-violet spectra of ethyl caffeate in alkaline aqueous solution when $NaBH_4$ is not present after (1) 2 min, (2) 5 min, (3) 30 min, and (4) after neutralization of the alkaline solution.

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[4] K. Freudenberg and W. Heel, *Chem. Ber.* **86**, 190 (1953).

[5] K. Hermann, *Pharmazie* **8**, 303 (1953).

destroying the excess lithium aluminum hydride present and of liberating the product from its reduction-complex by the addition of water. If the water added to the reaction mixture contains an excess of sodium borohydride, and subsequent neutralization is performed with caution in order to avoid acidic conditions, the yield of caffeyl alcohol is excellent. When the dried ethereal extract solution is evaporated under a nitrogen stream, the caffeyl alcohol crystallizes without difficulty in 90 per cent yield. Caution must be exercised when neutralizing because the decomposition of the borohydride causes excessive foaming.