with ether and centrifuged. The solid was applied to a silica gel short column and eluted with a chloroform/methanol gradient of 20:1/4:1 and the product zone freeze-dried from dioxane/water to give 155 mg (55%). Further purification was carried out by TLC over silica gel to give **2** as light yellow crystals (mp. >100 °C dec.) from dioxane/water.

Physical data. ^{1}H-NMR (d_6DMSO/TMS = 0) 5.52 and 5.54 (2H, d), 5.88 (1H, s), 6.30 (1H, s), 6.68 (2H, s), 7.8 (4H, m) and 10.78 (1H, s). ^{31}P-NMR (d_6DMSO/85% H_3PO_4 = 0) +4.67 e and +5.91 a. UV (Methanol) ε_{256} = 4.26 TLC (chloroform/methanol 4/1) 0.31, (benzene/isopropanol 2/1) 0.24, comparable to thymidine.

$C_{17}H_{17}N_6O_9P$ (480.3) calculated: C 42.51 H 3.57 N 17.50 P 6.46
found: C 42.33 H 3.85 N 17.22 P 6.27.

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Microbiological transformation of biflavone[1]

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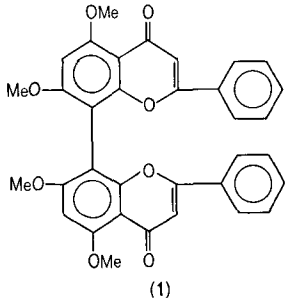
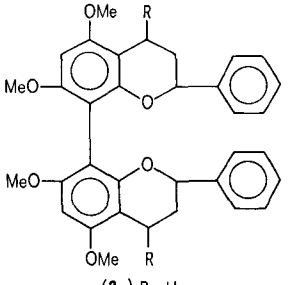
Summary. Incubation of 5,5′-7,7′-tetramethoxy-8,8′-biflavone with *Aspergillus niger* results in the formation of 4,4′-dihydroxy-5,5′-7,7′-tetramethoxy-8,8′-biflavan.

Biflavans with 4,4′ linkage and diol groupings have been synthesised by reductive dimerization of the corresponding flavanones[2]. Biflavans with –4,8– linkages are easily formed by the condensation of the respective flavan-4-ols[3]. So far biflavans with the linkage between the ring A of 2 flavan units are not known. In the present communication, we wish to report the formation of the biflavan (**2a**) from the biflavone (**1**) by the fungus *Aspergillus niger*. The fungus *Aspergillus niger* was cultured in the modified Czapeck-Dox medium[4,5] without substrate for 25 h. 5,5′-7,7′-tetramethoxy-8,8′-biflavone[6] (0.1% in alcohol) was added and incubation continued for an additional period of 103 h at 29 °C. At this time the mycelial mass was acetonised and then extracted along with the culture filtrate, with ethyl acetate. From the ethyl acetate extract compound (**2a**) was isolated in 7% yield as colourless amorphous powder (m.p. 150 °C, ν3460 cm^{-1}), besides other unidentified products by column chromatography on silica gel. The disappearance of the carbonyl group during the fermentation and the emergence of the hydroxyl group, and the characteristic colour reactions, strongly suggest that the product is a biflavan. It was acetylated and the diacetate (**2b**) was used for a detailed study (m.p. 141–143 °C, ν1780 cm^{-1}).



(1)



(**2**) R = H
(**2a**) R = OH
(**2b**) R = $OCOCH_3$

The NMR-spectrum of the biflavan diacetate (**2b**) showed the following signals: δ $CDCl_3$: 6.7 (s,2H) assigned to the protons at the 6,6′ position, 2.8 to 2.5 (m,4H) to the methylene protons, 5.6 to 4.7 (m,4H) to the methine protons, 3.7 (s,6H) to the 2 methoxy groups, 3.8 (s,6H) to the 2 methoxy groups, 7.0 to 6.8 (m,10H) to the protons of ring B and 2.5 to 1.6 (m,4H) to the protons of the 2 acetoxy groups. From the absence of ketonic absorption in the IR-spectrum of the compound (**2a**) and the NMR-spectrum of the compound (**2b**), it is concluded that *Aspergillus niger* metabolized 5,5′-7,7′-tetramethoxy-8,8′-biflavone by the reduction of the carbonyl group and the double bond at C_2 and C_3.

1 Part of this work was done at Allahabad University, Chemical Laboratories.

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Transition metals in calf thymus deoxyribonucleoprotein

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Summary: Fe, Ni, Cu and Zn were found by energy-dispersive X-ray fluorescence in calf thymus deoxyribonucleoprotein. The X-ray analyses indicated the absence of Cr, Mn and Co.

We are reporting the results of an X-ray fluorescence analysis of Cr, Mn, Fe, Co, Ni, Cu, Zn and Ga in native deoxyribonucleic acid (DNA)-chromosomal protein complex, deoxyribonucleoprotein (DNP), extracted from calf thymus by a modification of Messineo's method[2–4].

The importance of transition metals in the function of conjugated biological molecules is well established. The presence of transition metals in deoxyribonucleic acid (DNA) has been reported[5–8]. Wacker and Vallee[5] have reported the emission spectrographic analysis of Cr, Mn,