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ECHINATIN, A NEW CHALCONE FROM TISSUE CULTURE OF GLYCYRRHIZA ECHINATA[1]

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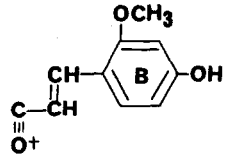
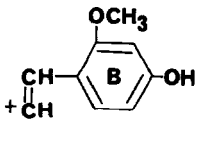
From the tissue culture of Glycyrrhiza echinata L. (Leguminosae), which was first derived in our laboratory, a new chalcone, named as echinatin, was isolated and its chemical structure was now determined.

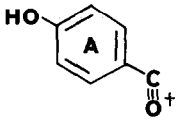
Echinatin (I) together with two phenolic compounds II and III was obtained from EtOH extract on silica gel column chromatography. I was given as yellow needles (5.6 mg, 0.01%) by crystallization from EtOH-H_2O, m.p. 209.5-212° (decomp.), $C_{16}H_{14}O_4$*, ir ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1635 (α,β-unsaturated C=O), uv λ_{max}^{EtOH} nm (log ϵ): 237 (3.79), 312 (3.94), 370 (4.20) and $\lambda_{max}^{EtOH-EtONa}$: 252 (3.79), 271 (3.80), 435 (4.41) and nmr (d_6-DMSO/D_2O) δ (ppm): 3.90 (3H, s, OCH_3), 6.40 (1H, doublet-doublet, J=8.7 and 1.5Hz), 6.49 (1H, d, J=1.5), 6.93 (2H, d, J=8.7), 7.62 (1H, d, J=15.0), 7.75 (1H, d, J=7.8), 7.95 (1H, d, J=15.0), 8.00 (2H, d, J=8.7), 10.08 and 10.29 (1H each, 2OH). The uv spectrum of I shows a characteristic absorption of chalcones[2] and the bathochromic shift and the increase of the intensity [370nm (log ϵ 4.20) ⟶ 435 (4.41)] in ethanolic EtONa indicate the presence of 4-hydroxyl group in the B-ring[3]. When aluminium chloride was added, no change was observed in the uv spectrum. This fact suggests the absence of phenolic hydroxyl groups near to the carbonyl group[4]. The mass spectrum of I shows a



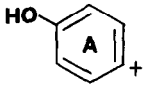
m/e 177



m/e 149



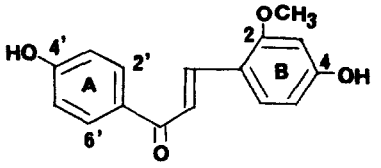
m/e 121



m/e 93

molecular peak at m/e 270 with important fragment peaks[5] at 255 ($M^+ - CH_3$), 177, 149, 121 and 93, indicating the presence of one hydroxyl group is located in the A-ring and one hydroxyl group and one methoxyl group in the B-ring. The signals at δ 6.93 and 8.00 support the presence of 4'-hydroxyl group in the A-ring and the signals at δ 6.40, 6.49 and 7.75 are due to the respective protons at 3, 5 and 6 in the B-ring. A pair of doublet signals at δ 7.62 and 7.95 (J=15.0 Hz) are also ascribed to trans protons on the double bond (CO-CH=CH-phenyl).

From these spectral data, I should be represented by 4,4'-dihydroxy-2-methoxychalcone, which was further confirmed by condensation of 4-hydroxyacetophenone with 4-hydroxy-2-methoxybenzaldehyde[6] in 70% KOH. I was the first sample of naturally occurring chalcones with the presence of



I

substituents at 2 and 4 in the B-ring and the absence of hydroxyl group at 2' or 6' in the A-ring and seems to be a significant intermediate in the biosynthesis of flavonoids and isoflavonoids.

Compound II was given as colorless needles (4.0 mg, 0.007%), m.p. 262-264°, $C_{16}H_{12}O_4$*. The structure of II was estimated as formononetin[7] (7-hydroxy-4-methoxyisoflavone) from ir, nmr and mass spectral data and identical with the authentic sample by mixed melting point and ir spectra.

Compound III gave colorless needles (5.5 mg, 0.01%), m.p. 164-165°, $C_{15}H_{14}O_4$* and the structural elucidation is now in progress.

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* Molecular formulae were measured by high resolution mass spectrometer.

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