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NEW TYPE CHALCONES FROM LICORICE ROOT

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During the course of studies on the chemical principles of the root bark of licorice, a commercially available herb drug consisting of various species of Glycyrrhiza (Leguminosae), we isolated some new flavonoid compounds which are characteristic of the species[1].

From Sinkiang licorice, presumably the roots of a variety of Glycyrrhiza glabra L , we obtained two new peculiar chalcones named licochalcones A and B.

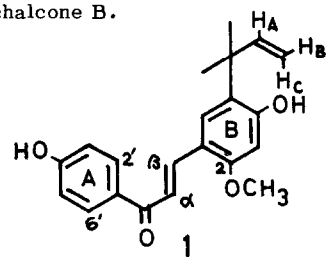
Licochalcone A (1), yellow needles, m p 101-102°, $C_{21}H_{22}O_4$ (M^+ 338), IR λ_{max}^{KBr} cm^{-1} 3440 (OH), 1640 (C=O). The UV spectrum of licochalcone A suggested a close similarity in the structure with echinatin (3), a chalcone which was isolated by Furuya et al.[2] from a tissue culture derived from the seedling of Glycyrrhiza echinata L. The NMR spectrum (in $CDCl_3$) of licochalcone A showed the presence of an α, α-dimethylallyl side chain (δ 1.41 (s, 2 x CH_3), 6.19 (q, J=10 and 18 Hz, H_A) , 5.31 (d, J=10 Hz, H_B), 5.34 (d, J=18 Hz, H_C)), a methoxyl group (δ 3.81), six aromatic protons and two olefinic protons of trans-α, β-unsaturated ketone (δ 7.53 (d, J=15 Hz, H_α), 8.03 (d, J=15 Hz, H_β)). Of six aromatic protons four compose A_2B_2 signals (δ 6.97 (d, J=8.5 Hz, 2H), 7.97 (d, J=8.5 Hz, 2H)) and the others appear as two singlets (δ 6.43 and 7.45, 1H each). From these results, two alternative structures, (1) and (2), can be presumed for licochalcone A. The A_2B_2 signals (δ 7.97) are assigned to $H_{(2')}$ and $H_{(6')}$ showing a good agreement with those of echinatin

Echinatin gave a characteristic mass fragment (M^+ -31 (m/e 239)) as the base peak, which corresponds to the peak (m/e 307) observed in the mass spectrum of licochalcone A

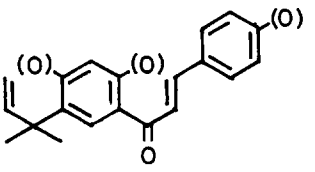
The appearance of M^+-31 ion reveals the location of methoxyl at the 2 -position by the mechanism as shown below[3].

Licochalcone B (4), yellow needles, m p 195-197°, $C_{16}H_{14}O_5$ (M^+ 286), UV · λ_{max}^{EtOH} nm 262, 360. The NMR spectrum (d_6-acetone) of licochalcone B revealed the presence of a methoxyl and six aromatic protons, of which four appeared as A_2B_2 signals (δ 6.98 (d, J=8.5 Hz, 2H), 8.07

(d, J=8 5 Hz, 2H)) and two as AB signals (δ 6 73 (d, J=8.5 Hz), 7.31 (d, J=8.5 Hz)). A pair of doublet signals at δ 7.69 (J=16 Hz) and 8.03 (J=16 Hz) were assigned to H_α and H_β of trans-α, β-unsaturated ketone. The appearance of M^+-31 (m/e 255) ion peak in the mass spectrum and the deshielding effect of C=O on $H_{(2')}$ and $H_{(6')}$ in the NMR spectrum led a formula (4) for licochalcone B.



1



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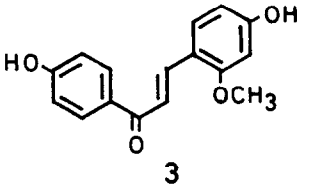

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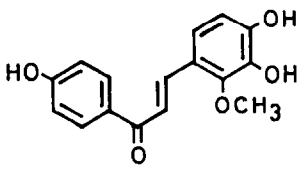

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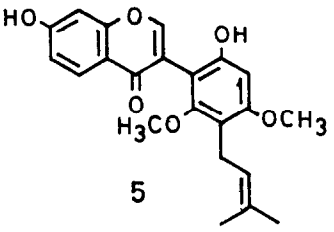

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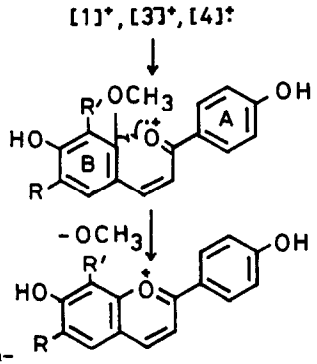

In addition to echinatin (3), licochalcones A and B (1 and 4) are noted to be unusual as having no hydroxyl at the position 2' (or 6'). Furthermore licoricone (5), an isoflavone isolated from North-Eastern Chinese Licorice (the root of G. uralensis Fischer et DC.), is also different from usual flavonoid to possess a phloroglucinol structure in B-ring instead of A-ring.

These facts suggest that there might be a new biosynthetical system in flavonoid, which should be designated biogenetical retroflavonoid, in which, contrary to the usual flavonoid, the A-ring would be derived from shikimate and the B-ring from polyketide of malonate origin

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b) T.Saitoh, T.Kinoshita and S.Shibata, Chem. Pharm. Bull.(Tokyo), in press. Ref. are cited therein
2) T.Furuya, K.Matsumoto and M.Hikichi, Tetrahedron Letters, 2567 (1971).
3) It has been proved that chalcones having a methoxyl in the 2-position show M-31 ion in their mass spectra The details are to be published soon