

temperature. The acids retained by the plug were eluted with ethanol and titrated with 0.01 *N* aqueous sodium hydroxide solution². Polyurethane foam was found to have good retention capacity for cinnamic (69%), indole-3-acetic (62%), β -naphthaleneacetic (85%) and β -naphthoxyacetic (78%) acids. In boiling water the retention capacity for cinnamic, indole-3-acetic and β -naphthaleneacetic acids decreases (10-20%) due to enhanced solubility of the acids in water. However, in the case of β -naphthoxyacetic acid it increases (10%) due to increase in the precipitation.

To study the effect of dilution, aqueous solutions (100 ml) of β -naphthaleneacetic acid with different concentrations were passed through the column and the acid retained was eluted and determined as before. The retention capacity of the foam plug was found to decrease sharply with the dilution of the acid, *i.e.* when concentration decreases to one-tenth, the retention decreases to one-third.

The effect of tightness and length of the foam plug in the column was studied by passing 0.0004 *N* of β -naphthaleneacetic acid (250 ml) through the column containing the foam plugs of different diameters and lengths. The acid retained was determined as before. It was observed that the retention capacity of the foam plug depends on its tightness and length in the column. When a plug of 21 mm (d.) and 45 mm length is fixed in a column of 11 mm (i.d.) the retention of β -naphthaleneacetic acid is 52% and it is 31% on using the same plug in a 17 mm (i.d.) column. The retention capacity also increases with the length of the foam plug. The retention is 99% on using four plugs and it is only 52% on using one plug of 21 mm (d.) and 45 mm length in 11 mm (i.d.) column. The rate of flow also depends on tightness and length of the foam plug. It is appreciable (23 ± 5 ml min⁻¹) with the tightest and the longest plug under study.

A known volume of the synthetic sample of water containing an acid and a foreign substance was passed through the column to study the retention of the acids from saline waters. The acids retained were eluted and determined as before. It was observed that the foam plug has fair retention (37-66%) of β -naphthaleneacetic acid from water containing 74.4 mg dm⁻³ of the acid with (units in ml dm⁻³) acetophenone (0.41), aluminium chloride (0.5), ammonium molybdate (0.5), arsenic oxide (0.05), calcium nitrate (0.7), copper sulphate (1.0), dextrin (20.0), ferrous sulphate (1.5), lead nitrate (0.1), manganese chloride (100.0), mercuric nitrate (0.001), potassium iodide (1.0), potassium sulphate (500.0), silver nitrate (0.05), sodium chloride (350.0), sodium fluoride (0.7), sodium nitrate (10.0), sodium nitrite (10.0), sodium phosphate (0.35), sodium thiosulphate (500.0), stannous chloride (0.7), strontium chloride (2.0), thiourea (2.0) and zinc chloride (5.0). The results suggest the possible use of polyurethane foam plugs for the retention of β -naphthaleneacetic acid from different types of water.

β -Naphthaleneacetic acid can be separated from acetic, benzoic, cinnamic and trichloroacetic acids in water. A definite volume of each acid (1 ml, 0.1 *N*) was taken in a 10 ml standard flask and the total volume was made up with distilled water. This mixture of acids was passed through a column of 11 mm (i.d.) containing two plugs of 21 mm (d.) at the rate of 32 ± 5 ml min⁻¹. The acids were eluted with distilled water (100 ml) and each 10 ml fraction of the effluent was titrated with 0.01 *N* sodium hydroxide solution. β -Naphthaleneacetic acid could not be eluted with water. It was eluted with ethanol (50 ml) and titrated as above. The elution curve was made by plotting the concentration of the acids against the volume of effluents. The sharp elution curve indicates that polyurethane foam plug chromatography is a very simple and fast method of separation.

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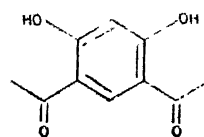
Synthesis of New Isomeric Chalcones

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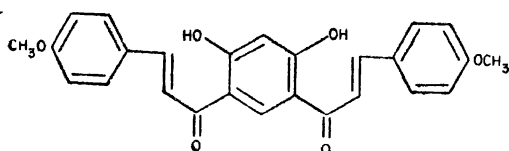
It has been reported that cinnamoylchalcones can be prepared in good yield from 4,6-diacetylresorcinol^{1,2}. This has prompted us to synthesise two new isomeric substituted derivatives of cinnamoylchalcones. Two isomeric chalcones have been synthesised in good yield from 4,6-diacetylresorcinol (1) and characterised by their uv, ir, nmr and mass spectral data. The two isomers could be differentiated only by their mass fragmentation patterns.



(1)

Experimental

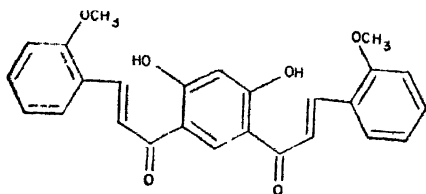
4,6-Diacetylresorcinol (1) was prepared by the reaction of acetic anhydride and resorcinol in the presence of $ZnCl_2 \cdot 1$ on condensation with *p*-methoxybenzaldehyde in presence of ethanolic potassium hydroxide³ gave 2',4'-dihydroxy-5'-(4-methoxy)cinnamoyl-4-methoxychalcone (2). Its isomer 3 was prepared by similar condensation with *O*-methoxybenzaldehyde.



(2)

2',4'-Dihydroxy-5'-(4-methoxy)cinnamoyl-4-methoxychalcone (2): 1 (1 g) was mixed with *p*-methoxybenzaldehyde (2 ml) in ethanol (20 ml) and aqueous potassium hydroxide (10 g in 10 ml of water) and allowed to stand for 24 h. The yellow solid that resulted on acidification with 1:1 hydrochloric acid was filtered and recrystallised from acetone-ethanol as yellow needles (1.5 g), m.p. 184-86°, $C_{26}H_{22}O_6$; ν_{max} (MeOH) 241, 288, 354 and 387 nm; ν_{max} (KBr) 3600-3400 (br), 3060, 2980, 2900, 1650, 1600, 1540, 1230, 1060, 850 and 740 cm^{-1} ; δ (60MHz, $CDCl_3$) 4.0 (6H, s, OMe), 8.65 (1H, s, C_{α} -H), 6.65 (1H, s, C_{β} -H), 8.1 (2H, d, C_{β} -H) and 7.1-7.85 (10H, m, 8Ar-H + 2 C_{α} -H); m/z (%) 430 (M^+ , 50.5), 399 (3.87), 296 (12.34), 281 (5.38), 268 (9.47), 161 (12.83), 134 (100), 121 (60.74), 108 (7.18) and 91 (15.53).

2',4'-Dihydroxy-5'-(2-methoxy)cinnamoyl-2-methoxychalcone (3): A similar reaction of 1 with *O*-methoxybenzaldehyde gave a light orange coloured product which was recrystallised from acetone-ethanol as orange coloured needles (1.5 g), m.p. 187-9°, $C_{26}H_{22}O_6$; ν_{max} (MeOH) 252, 312, 355 and 384 nm; ν_{max} (KBr) 3520 (br), 3040, 2980, 2900, 1670, 1590, 1520, 1500, 1220, 1060, 840 and 750 cm^{-1} ; δ (60MHz, $CDCl_3$) 4.0 (6H, s, OMe), 8.8 (1H, s, C_{α} -H), 6.65 (1H, s, C_{β} -H), 8.4 (2H, d, C_{β} -H), and 7.1-8.0 (10H, m, 8Ar-H + 2 C_{α} -H); m/z (%) 430 (M^+ , 72.18), 399 (100), 323 (12.66), 296 (12.09), 281 (12.8), 265 (68.1), 189 (13.3), 163 (45.8), 134 (37.26), 119 (39.77), 91 (36.8), 77 (18.6) and 51 (5.01).



(3)

Results and Discussion

The ions located at m/z 399, 161 and 121 arise from characteristic fragmentation pattern expected of a chalcone. But the appearance of ions at m/z 296 and 134 with higher intensities shows greater degree of isomerisation of the chalcone 2 to the flavanone⁴. Compound 3 shows the molecular ion at m/z 430 with higher intensity (72.18) than that for compound 2. It ejects methoxyl radical easily as evident from the peak at m/z 399 which happens to be the base peak too. The ions appearing at m/z 296, 265 and 134 arise from the isomerised flavanone.

From the above spectral characteristics, it is clear that the two isomers can be distinguished only from the mass fragmentation data. The base peaks of 2 and 3 appear at m/z 134 and 399, respectively which are suggestive of the fact that the isomerisation, of the chalcone to the flavanone is much faster in 2 than in 3. The loss of the methoxyl group from the molecular ion to give the base peak at m/z 399 in 3 indicates the steric hindrance to isomerisation to flavanone. Hence, 3 must have the methoxyl group in 2-position in the B-ring and 2 will have the methoxyl group in 4-position.

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Biflavones from *Picea morinda* Linn.

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PICEA *morinda* Linn. (Syn. *P. smithiana*, Boiss; Fam.: Pinaceae) is a genus of tall evergreen trees, commonly known as *Spruce*, distributed in a temperate and cooler region of the Northern hemisphere