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CHALCONE DERIVATIVES AS PRECURSORS OF 1,2,3,4-TETRAHYDRO-4-QUINOLONES

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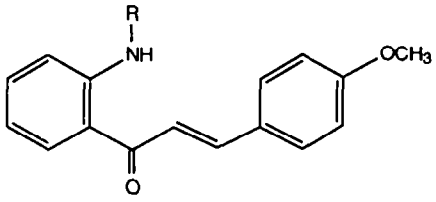
Abstract - *2-Aryl-1,2,3,4-tetrahydro-4-quinolones were synthesised from 2'-amino-4-methoxychalcone and its 2'-benzenesulphonamido derivative by acid and base catalysis, respectively. The α,β-dibromo and α-bromo-β-methoxy derivatives of 2'-benzenesulphonamido-4-methoxydihydrochalcone cyclised to 2-aryl-3-bromo-1,2,3,4-tetrahydro-4-quinolones as did the corresponding α-bromochalcones. 2'-Amino-4-methoxychalcone formed a stable epoxide.*

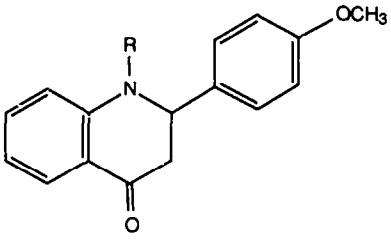
Significant and necessary improvements[1] have been made recently in the synthesis of 4-quinolones. Janzso[2], in 1975, pointed out the structural similarity between these *N*-heterocycles and certain flavonoids. As 2'-hydroxychalcones and their dihydro derivatives are the precursors[3] of a wide variety of the *O*-heterocyclic compounds, it seemed possible that derivatives of 2'-aminochalcone might serve as more readily available and synthetically flexible precursors of 4-quinolones. Except for the base-catalysed isomerisation of 2'-aminochalcone[4] and its *N*-acetyl[2] and *N*-tosyl[5] derivatives, little is known[2,4-6] of the chemistry of 2'-aminochalcones and nothing of the chemistry of 2'-aminodihydrochalcones.

As naturally occurring heterocycles are commonly substituted[3] in the *para* position by an oxy function, the parent chalcone employed was 2'-amino-4-methoxychalcone **1**. This was conveniently synthesised by Murphy and Watanasin's method[7] of aldol condensation using an ethanolic solution of 2'-aminoacetophenone

and 4-methoxybenzaldehyde containing solid sodium hydroxide. The chalcone **1** cyclised to the *N*-heterocycle, 1,2,3,4-tetrahydro-2-(4-methoxyphenyl)-4-quinolone **4**, on reaction with orthophosphoric acid in acetic acid. The benzenesulphonyl derivative **5** of this *N*-heterocycle was obtained by the base-catalysed (aqueous ethanolic sodium hydroxide) cyclisation of 2'-benzenesulphonamido-4-methoxychalcone **2**.



1 R = H
2 R = SO_2Ph
3 R = Ac

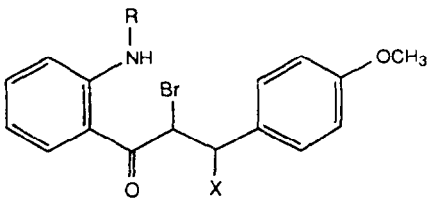


4 R = H
5 R = SO_2Ph

Bromination of 2'-acetamido-4-methoxychalcone **3** gave the chalcone dibromide **6** which eliminated bromine on standing in dry acetone, reforming the parent chalcone **3**. In aqueous acetone, the chalcone dibromide **6** was converted into the bromohydrin **7** and the chalcone **3**. The β-bromine of this 4-methoxy-substituted chalcone dibromide **6** is so labile that attempts to chromatograph it on silica gel gave the bromohydrin **7**. The 3'-hydrogen atom of the 2'-acetamidochalcone **3** and all 2'-acetamidodihydrochalcone derivatives showed the anomalous "acyl shift" (greater than 2 ppm downfield) characteristic[8] of the Hmr signal of a hydrogen atom *ortho* to an acetamido group.

2'-Benzenesulphonamido-4-methoxychalcone dibromide **8** gave 4-methoxybenzaldehyde and a complex inseparable mixture when its cyclisation was attempted with aqueous ethanolic potassium hydroxide - an analogue of the Emilewicz-von Kostanecki reaction[9]. H.m.r. spectroscopy showed the mixture to be composed of the *cis* **14** and *trans* **15** 3-bromo-4-quinolones, (E)-2'-benzenesulphonamido-α-bromo-4-methoxychalcone **16**, and an ethoxy-substituted compound, unidentified but possibly the α-bromo-β-ethoxydihydrochalcone **9**.

The sulphonamido dibromide **8** formed the bromohydrin **10** in aqueous acetone. This, when subjected to the Rasoda reaction[10] conditions of aqueous ethanolic alkali, gave a complex mixture. When treated with anhydrous potassium acetate, the dibromide **8** gave the (E) **16** and (Z) **18** diastereomers of



6 R = Ac, X = Br

6a R = Ac, X = OMe

7 R = Ac, X = OH

8 R = SO_2Ph, X = Br

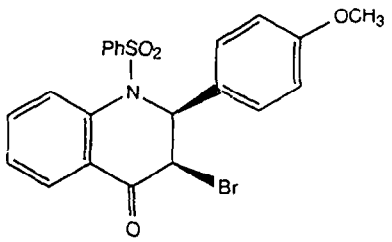
9 R = SO_2Ph, X = OEt

10 R = SO_2Ph, X = OH

11 R = SO_2Ph, X = OMe

12 R = H, X = OMe

13 R = H, X = OEt



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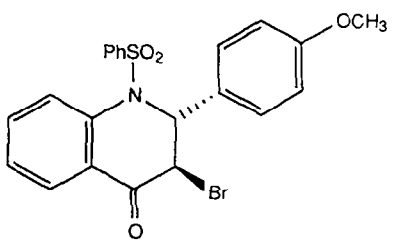

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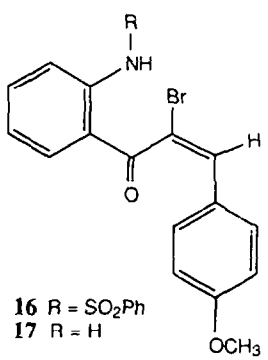
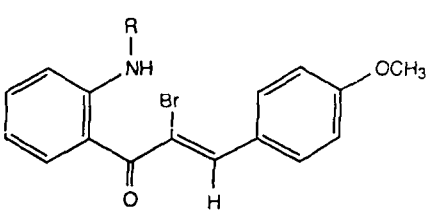
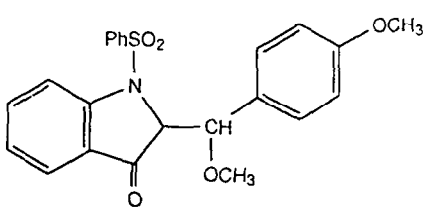


16 R = SO_2Ph
17 R = H



18 R = SO_2Ph
19 R = H



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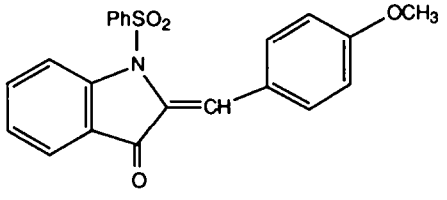
2'-benzenesulphonamido-α-bromo-4-methoxychalcone. This mixture of these isomers was cyclised by potassium hydroxide to *cis* **14** and *trans* **15** *N*-benzenesulphonyl-3-bromo-1,2,3,4-tetrahydro-2-(4-methoxyphenyl)-4-quinolone.

2'-Benzenesulphonamido-α-bromo-β,4-dimethoxydihydrochalcone **11**, formed from the chalcone dibromide **8** by reaction with anhydrous methanol, was cyclised to the *cis*-3-bromo-4-quinolone **14** by potassium hydroxide; H.m.r. showed the product to be contaminated by a trace of an unisolable, unidentified ethoxy compound, probably the α-bromo-β-ethoxy derivative **9**. This reaction, the *N*-heterocyclic version of the Wheeler aurone synthesis[11], might have been expected to cyclise the α-bromo-β-methoxydihydrochalcone **11** to the five-membered ring compound **21** *via* the intermediate **20**. That it **11** produced a six-membered heterocycle **14** is probably due to a slow rate of formation of the conjugate base of the benzenesulphonamido group which allows side-chain elimination of methanol - forming the 4-quinolone precursors, the α-bromochalcones **16, 18** - to predominate over cyclosubstitution of the 2'-nitrogen atom for the α-bromine atom. The presence of the *para*-methoxyl substituent would increase the susceptibility to side-chain elimination of methanol and, therefore, the rate of 4-quinolone **14** formation.



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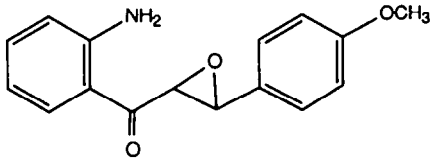

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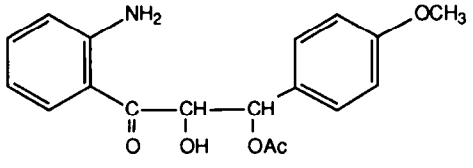

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2'-Acetamido-4-methoxychalcone dibromide **6** was solvolysed by dry methanol, and simultaneously deacylated by the liberated hydrogen bromide, to form 2'-amino-α-bromo-β,4-dimethoxydihydrochalcone **12**.

This dihydrochalcone **12** was transformed into the diastereomers of the corresponding α-bromo-β-ethoxydihydrochalcone **13** on reaction with aqueous ethanolic potassium hydroxide; also formed in this reaction were the (E) **17** and (Z) **19** isomers of 2'-amino-α-bromo-4-methoxychalcone but these could not be freed from a trace of an unknown compound.

2'-Amino-4-methoxychalcone **1** was readily epoxidised by aqueous alkaline hydrogen peroxide. This formation of a stable epoxide **22** is remarkably different from the Algar-Flynn-Oymada reaction of 2'-*hydroxy*chalcones which, under the same reaction conditions, form[12] dihydroflavonols without the intermediacy of chalcone epoxides; 2'-hydroxychalcone epoxides are very unstable[13] compounds. 2'-Amino-4-methoxychalcone epoxide **22** reacted with acetic acid and formed the α-hydroxy-β-acetoxydihydrochalcone **23**. No useful reaction was observed when the epoxide **22** reacted with aqueous sulphuric acid in tetrahydrofuran.

EXPERIMENTAL

Melting points were determined with a Reichert Thermovar hot-block and are uncorrected. All Hmr spectra were recorded at 60 MHz on a Perkin-Elmer R12 spectrometer in $CDCl_3$ solutions containing Me_4Si as an internal standard. Mass spectra were recorded on a VG Micromass 7070H spectrometer. Precoated Merck silica gel $60F_{254}$ plates were used for thin layer chromatography (TLC). Merck silica gel $PF_{254+366}$ was used for preparative TLC (PLC).

2'-Amino-4-methoxydihydrochalcones

2'-Aminoacetophenone (6.97 g), in a solution of 4-methoxybenzaldehyde (7.00 g) in EtOH (60 ml) containing 3 pellets of NaOH (0.28 g), was stirred for 12 h and diluted with iced water (30 ml). The precipitate gave 2'-amino-4-methoxychalcone **1**, orange needles (7.55 g), m.p. 91-92°C (cyclohexane/EtOH). Hmr δ 3.76 (s, Me), 6.40 (bs, NH_2), 6.52-8.00 (m, 10 H). Found: C, 75.6; H, 6.0; N, 5.2. $C_{16}H_{15}NO_2$ requires: C, 75.9; H, 6.0; N, 5.5%.

The chalcone **1** (4.00 g), dissolved in acetic acid (20 ml) and orthophosphoric acid (90%; 20 ml), was refluxed for 1 h and diluted with iced water (100 ml). The orange/red waxy solid,

2-(4-methoxyphenyl)-1,2,3,4-tetrahydro-4-quinolone **4**, could not be crystallised. Found: C, 75.7; H, 5.9; N, 5.2. $C_{16}H_{15}NO_2$ requires: C, 75.9; H, 6.0; N, 5.5%.

Hydrogen peroxide (30% w/v; 15 ml) was added to a solution of the chalcone **1** (4.00 g) in MeOH (120 ml) containing aqueous NaOH (20%; 15 ml), stirred for 1 h, and diluted with water (100 ml). The yellow precipitate gave 2'-amino-4-methoxychalcone epoxide **22**, yellow crystals (2.72 g), m.p. 146-148°C (EtOH). Hmr δ 3.89 (s, Me), 4.06 (d, β-H, J 2.0 Hz), 4.33 (d, α-H, J 2.0 Hz), 6.30 (bs, NH_2), 6.65-7.97(m, 8 H). Found: C, 71.6; H, 5.6; N, 5.3. $C_{16}H_{15}NO_3$ requires: C, 71.4; H, 5.6; N, 5.2%.

A solution of the epoxide **22** (0.56 g) in acetic acid (6 ml) was diluted after 4 h with water (30 ml). The orange solid (0.29 g) was purified by PLC giving the β-acetoxy-α-hydroxydihydrochalcone **23**, an orange oil (76 mg). Hmr δ 2.14 (s, OAc), 3.80 (s, OMe), 5.64 (d, β-H, J 3.5 Hz),5.64 (bs, OH), 6.14 (d, α-H, J 3.5 Hz), 6.14 (bs, NH_2), 6.74-7.75(m, 7 H), 8.15 (q, 6'-H, J 8 and 1.5 Hz). M/z 329.

Aqueous KOH (4.0 M; 3 ml) was added to a solution of the α-bromo-β-methoxydihydrochalcone **12** (217 mg) in EtOH (15 ml), stirred for 1 h, diluted with water (20 ml), and extracted with $CHCl_3$. The extract was washed, dried , and evaporated to dryness. The residual oil (197 mg) was fractionated by PLC into two components. The one with the larger R_F value gave a diastereomer of the α-bromo-β-ethoxydihydrochalcone **13**, an orange oil (61 mg). Hmr δ 1.02 (t, OEt, J 7.0 Hz), 3.47 (q, CH_2, J 7.0 Hz), 3.91 (s, OMe), 4.98 (d , β-H, J 10.0 Hz), 5.31 (d, α-H, J 10.0 Hz), 6.25 (bs, NH_2), 6.50-8.15 (m, 8 H). M/z 377, 379. Found: C, 57.1; H, 5.3; Br 21.4; N, 3.7. $C_{18}H_{20}BrNO_3$ requires: C, 57.2; H, 5.3; Br 21.1; N, 3.7%. The second component gave the other diastereomer of **13**, an orange oil (57 mg). Hmr δ 1.23 (t, OEt, J 7.0 Hz), 3.65 (q, CH_2, J 7.0 Hz), 3.75 (s, OMe), 4.91 (d , β-H, J 10.0 Hz), 5.51 (d, α-H, J 10.0 Hz), 6.10-8.90 (m, 8 H). M/z 377, 379. Found: C, 56.9; H, 5.3; N, 3.7. $C_{18}H_{20}BrNO_3$ requires: C, 57.2; H, 5.3; N, 3.7%.

2'-Benzenesulphonamido-4-methoxydihydrochalcones

A solution of 2'-amino-4-methoxychalcone **1** (5.10 g) in pyridine (7 ml), containing benzenesulphonyl chloride (3.56 g) was stirred for 3 h and diluted with iced water (100 ml). The precipitate gave 2'-benzenesulphonamido-4-methoxychalcone **2**, yellow crystals (6.63 g), m.p. 124-125°C (EtOH). Hmr δ 3.89 (s, Me), 6.86-8.10 (m, 10 H), 11.38 (bs, NH). Found: C, 67.5; H, 5.0; N, 3.5; S, 8.2. $C_{22}H_{19}NO_4S$ requires: C, 67.2; H, 4.9; N, 3.6; S, 8.1%.

Warm (70°C) aqueous NaOH (1%; 10 ml) was added to a warm (70°C) solution of the chalcone **2** (0.87 g) in EtOH (10 ml). The mixture was allowed to cool and, after 24 h, it was diluted with water (20 ml). The precipitate gave *N*-benzenesulphonyl-1,2,3,4-tetrahydro-2-(4-methoxyphenyl)-4-quinolone **5**, yellow crystals (0.57 g), m.p. 132-133°C (MeOH). Hmr δ 2.59 (q, 3-H, J -18.0 and 6.0 Hz), 3.09 (q, 3-H, J -18.0 and 2.5 Hz), 3.77 (s, Me), 6.04 (q, 2-H, J 6.0 and 2.5 Hz), 6.70-8.17 (m, 13 H). Found: C, 67.2; H, 4.9; N, 3.8; S, 8.3. $C_{22}H_{19}NO_4S$ requires: C, 67.2; H, 4.9; N, 3.6; S, 8.1%.

Br_2 (2.04 g) in CCl_4 (50 ml) was added dropwise with stirring to a warm (40°C) suspension of the chalcone **2** (5.00 g) in CCl_4 (150 ml). After 4 h, the solvent was removed and the residue gave the chalcone dibromide **8**, colourless crystals (5.05 g), m.p. 134-135°C (toluene). Hmr δ 3.91 (s, Me), 5.66 (d , β-H, J 12.0 Hz), 5.95 (d, α-H, J 12.0 Hz), 6.90-8.22 (m, 13 H), 11.10 (bs, NH). Found: C, 48.1; H, 3.3; Br, 28.9; N, 2.7; S, 6.0. $C_{22}H_{19}Br_2NO_4S$ requires: C, 47.8; H, 3.5; Br, 28.9; N, 2.5; S, 5.8.%.

The dibromide **8** (0.50 g) was added to a suspension of anhydrous KOAc (0.089 g) in dry acetone (10 ml). After 2 h, the mixture was diluted with water (20 ml). Hmr spectroscopy showed the yellow precipitate to be a mixture of (E) **16** and (Z) **18** α-bromochalcones, 25:75 respectively. After crystallisation, it gave a mixture (17:83) of the (E) **16** and (Z) **18** isomers, colourless crystals (0.19 g), m.p. 132-135°C (EtOH). Hmr δ 3.78 (s, (Z)-OMe, 83%), 3.95 (s, (E)-OMe, 17%), 6.64-8.17 (m, 14 H), 9.38 (bs, (E)-NH), 11.05 (bs, (Z)-NH). Found C, 56.0; H, 4.0; Br, 16.8; N, 2.9; S, 6.5. $C_{22}H_{18}BrNO_4S$ requires: C, 55.9; H, 3.8; Br, 16.9; N, 3.0; S, 6.8.%.

Aqueous KOH (4.0 M; 3 ml) was added to a solution of the mixture (17:83; 300 mg) of (E) **16** and (Z) **18** isomers in EtOH (15 ml), stirred for 1 h, diluted with water (20 ml), and extracted with $CHCl_3$ (3 x 50 ml). The extract was washed, dried, and evaporated to dryness. The residual oil was purified by PLC and gave an inseparable mixture of *cis* **14** and *trans* **15** *N*-benzenesulphonyl-3-bromo-1,2,3,4-tetrahydro-2-(4-methoxyphenyl)-4-quinolone, orange oil (211 mg). Hmr δ 3.71 (s, OMe), 4.98 (d, 3-H, J 3.0 Hz), 5.04 (d, 3-H, J 6.0 Hz), 6.21 (d, 2-H, J 6.0 Hz), 6.48 (d, 2-H, J 3.0 Hz), 6.66-8.29 (m, 13 H). M/z 471, 473. Found: C, 56.1; H, 3.9; Br, 17.3; N, 3.0; S, 6.6. $C_{22}H_{18}BrNO_4S$ requires: C, 55.9; H, 3.8; Br, 16.9; N, 3.0; S, 6.8.%.

The chalcone dibromide **8** (300 mg) in EtOH (15 ml) when similarly treated with aqueous KOH (4.0 M; 3 ml), gave an oil (251 mg) which was fractionated into two components by PLC. The product with the larger

R_F value was 4-methoxybenzaldehyde, a yellow oil (11 mg). The other, an oil (174 mg), was an inseparable mixture of the *cis* **14** and *trans* **15** 3-bromo-4-quinolones and (E)-α-bromochalcone **16**; its Hmr spectrum contained all signals expected of these products and, in addition, δ 1.33 (t, J 7.0 Hz), 3.49 (q, J 7.0 Hz).

A suspension of the chalcone dibromide **8** (1.00 g) in aqueous acetone (75%; 40 ml) was stirred for 2 days, diluted with water (30 ml), and extracted with $CHCl_3$ (3 x 75 ml). The extract was dried and evaporated to dryness. The yellow solid (0.81 g) gave the bromohydrin **10**, colourless crystals (0.31 g), m.p. 149-150°C (EtOH). Hmr δ 3.34 (bs, OH); 3.79 (s, OMe), 5.25 (s, α-H, β-H), 6.84-8.12 (m, 13 H). Found: C, 54.0; H, 4.2; Br, 15.8; N, 2.7; S, 6.9. $C_{22}H_{20}BrNO_5S$ requires: C, 53.9; H, 4.1; Br, 16.3; N, 2.9; S, 6.5.%. Fractional crystallisation of the mother liquor gave additional bromohydrin **10** (0.15 g) and 2'-benzenesulphonamido-4-methoxychalcone **2**, yellow crystals (70 mg), m.p. 124-125°C.

A suspension of the chalcone dibromide **8** (300 mg) and anhydrous NaOAc (44 mg), in dry MeOH (10 ml), was heated until it dissolved, allowed to cool, and diluted with water (10 ml). The precipitate gave the α-bromo-β-methoxydihydrochalcone **11**, colourless crystals (161 mg), m.p. 108-109°C (MeOH). Hmr δ 3.21 (s, β-OMe), 3.91 (s, Ar-OMe), 4.83 (d, β-H, J 10.0 Hz), 5.19 (d, α-H, J 10.0 Hz), 6.91-8.16 (m, 13 H), 11.25 (bs, NH). Found: C, 54.8; H, 4.3; Br, 15.8; N, 2.7; S, 6.7. $C_{23}H_{22}BrNO_5S$ requires: C, 54.8; H, 4.4; Br, 15.8; N, 2.8; S, 6.4%.

Aqueous KOH (4.0 M; 3 ml) was added to a solution of the α-bromo-β-methoxydihydrochalcone **11** (290 mg) in EtOH (15 ml), stirred for 1 h, diluted with water (20 ml), and extracted with $CHCl_3$ (3 x 50 ml). The extract was washed, dried , and evaporated to dryness. The residual oil (167 mg) was fractionated into two components by PLC. The product with the larger R_F value was 4-methoxybenzaldehyde, a yellow oil (26 mg). The other, an oil (101 mg), showed, in its Hmr spectrum, all signals expected of the *cis* **14** and *trans* **15** 3-bromo-4-quinolones and, in addition, δ 1.31 (t, J 7.0 Hz), 3.49 (q, J 7.0 Hz).

2'-Acetamido-4-methoxydihydrochalcones

Pyridine (0.5 ml) was added to a solution of 2'-amino-4-methoxychalcone **1** (6.00 g) in Ac_2O (35 ml). After 40 min, the mixture was poured into iced water (60 ml). The precipitate gave 2'-acetamido-4-methoxychalcone **3**, yellow plates (6.11 g), m.p. 129-130°C (EtOH). Hmr δ 2.27 (s, Ac), 3.91

(s, OMe), 6.84-8.17 (m, 9 H), 8.79 (q, 3'-H, J 7.0 and 1.3 Hz), 11.55 (bs, NH). Found: C, 73.4; H, 5.8; N, 4.8. $C_{18}H_{17}NO_3$ requires: C, 73.2; H, 5.8; N, 4.7%.

Br_2 (3.06 g) in CCl_4 (55 ml) was added dropwise, with stirring, to a solution of the chalcone **3** (5.00 g) in CCl_4 (150 ml). Next day, the solvent was removed and the residue gave the chalcone dibromide **6**, yellow crystals (5.26 g), m.p. 109-119°C (decomp.) (toluene). Hmr δ 2.31 (s, Ac), 3.88 (s, OMe), 5.71 (d, β-H, J 11.0 Hz), 6.03 (d, α-H, J 11.0 Hz), 6.89-8.25 (m, 7 H), 8.92 (q, 3'-H, J 8.0 and 1.6 Hz), 11.28 (bs, NH). Found: C, 47.4; H, 3.8; Br, 35.2; N, 2.7. $C_{18}H_{17}NO_3$ requires: C, 47.5; H, 3.8; Br, 35.1; N, 3.1%.

A suspension of the dibromide **6** (100 mg) and anhydrous NaOAc (18 mg), in MeOH (2.5 ml), was heated until it dissolved. On cooling, pure 2'-acetamido-α-bromo-β-methoxydihydrochalcone **6a** crystallised, yellow needles (55 mg), m.p. 153-154°C. Hmr δ 2.28 (s, Ac), 3.21 (s, β-OMe), 3.86 (s, 4-OMe), 4.82 (d, β-H, J 10.0 Hz), 5.28 (d, α-H, J 10.0 Hz), 6.90-7.87 (m, 6 H), 8.05 (q, 6'-H, J 8.0 and 1.4 Hz), 8.86 (q, 3'-H, J 8.0 and 1.0 Hz), 11.38 (bs, NH). Found: C, 56.2; H, 4.8; Br, 20.0; N, 3.6. $C_{19}H_{20}BrNO_4$ requires: C, 56.2; H, 5.0; Br, 19.7; N, 3.4%.

A solution of the dibromide **6** (1.00 g) in MeOH (20 ml) was refluxed for 4 h and diluted with water (20 ml). The yellow precipitate gave the 2'-amino-α-bromo-β-methoxydihydrochalcone **12**, orange needles (0.39 g), m.p. 123-124°C (MeOH). Hmr δ 3.21 (s, β-OMe), 3.85 (s, OMe), 4.86 (d, β-H, J 10.0 Hz), 5.26 (d, α-H, J 10.0 Hz), 6.37 (bs, NH), 6.54-7.97 (m, 8 H). Found: C, 56.0; H, 4.8; Br, 22.0; N, 3.8. $C_{17}H_{18}BrNO_3$ requires: C, 56.1; H, 5.0; Br, 21.9; N, 3.8%.

KOAc (43 mg) was added to a solution of the dibromide **6** (200 mg) in aqueous THF (90%; 13 ml). After 2 h, the mixture was diluted with water (20 ml) and extracted with $CHCl_3$. The extract was washed, dried, and evaporated to dryness. The solid residue was purified by PLC and gave the bromohydrin **7**, colourless crystals (167 mg), m.p. 129-130°C (toluene). Hmr δ 2.16 (s, Ac), 3.51 (bs, OH), 3.79 (s, OMe), 5.29 (s, α-H, β-H), 6.65-8.06 (m, 7 H), 8.76 (q, 3'-H, J 8.0 and 1.0 Hz), 11.31 (bs, NH). Found: C, 54.9; H, 4.4; Br, 20.2; N, 3.5. $C_{18}H_{18}BrNO_4$ requires: C, 55.1; H, 4.6; Br, 20.4; N, 3.6%.

After 5 days, a solution of the dibromide **6** (150 mg) in dry acetone (5 ml) was evaporated to dryness. Purification of the solid residue gave 2'-acetamido-4-methoxychalcone **3**, yellow plates (90 mg), m.p. 129-130°C (EtOH). A solution of the dibromide **6** (300 mg) was refluxed in aqueous acetone (90%; 10 ml) for

2.5 h, concentrated by evaporation, taken-up in $CHCl_3$, washed with water, and dried. Removal of the solvent gave an oil which was fractionated by PLC into two components. The one with the larger R_F value was 2'-acetamido-4-methoxychalcone **3**, yellow plates (85 mg), m.p. 129-130°C (EtOH). The other was the bromohydrin **7**, colourless crystals (87 mg), m.p. 129-130°C (toluene).

A solution of the dibromide **6** (100 mg) in $CHCl_3$ (3 ml) was fractionated by PLC into three components. The one with the lowest R_F value gave the bromohydrin **7**, colourless crystals (71 mg), m.p. 129-130°C (toluene).

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