Acknowledgements—We thank Messrs. B. B. P. Srivastava, R. K. Singh and Mrs. K. Kapoor for spectral data and Prof. Dr. F. Bohlmann, Berlin, for high resolution MS.

REFERENCES

1. Pant, P. and Rastogi, R. P. (1980) *Phytochemistry* **19**, 1869.
2. Zoghbi, M. D. G. B., Roque, N. F. and Gottlieb, O. R. (1981) *Phytochemistry* **20**, 180.
3. Ray, A. B., Chattopadhyay, K., Konno, C. and Hikino, H. (1980) *Tetrahedron Letters* 4477.
4. Gottlieb, O. R., Maia, J. G. S. and Mourao, J. C. (1976) *Phytochemistry* **15**, 1289.
5. Wenkert, E., Gottlieb, H. E., Gottlieb, O. R., Pereira, M. O. Da S. and Formiga, M. D. (1976) *Phytochemistry* **15**, 1547.
6. Pelter, A. and Ward, R. S. (1978) *Chemistry of Lignans* (Rao, C. B. S., ed.) Chap. 7. Andhra University Press, Waltair.

Phytochemistry, Vol. 21, No. 8, pp. 2149–2151, 1982.
Printed in Great Britain.
0031-9422/82/082149-03$03.00/0

BAKUCHALCONE, A DIHYDROFURANOCHALCONE FROM THE SEEDS OF *PSORALEA CORYLIFOLIA**

G. K. GUPTA, J. L. SURI, B. K. GUPTA and K. L. DHAR*

Regional Research Laboratory, Jammu Tawi 180001, India

(*Received* 17 *November* 1981)

Key Word Index—*Psoralea corylifolia*; Leguminosae; 4, 2′-dihydroxy-2″-(1-hydroxy-1-methylethyl)-2″, 3″-dihydrofurano(4″, 5″:3′, 4′)chalcone; (±)-6-acetyl-3, 5-dihydroxy-2, 2-dimethylchroman; (±)-8-acetyl-3, 5-dihydroxy-2, 2-dimethylchroman; (±)-5-acetyl-2, 3-dihydro-2(1-hydroxy-1-methylethyl)-4-hydroxybenzofuran.

Abstract—A new dihydrofuranochalcone has been identified in seeds of *Psoralea corylifolia* and its structure confirmed by synthesis.

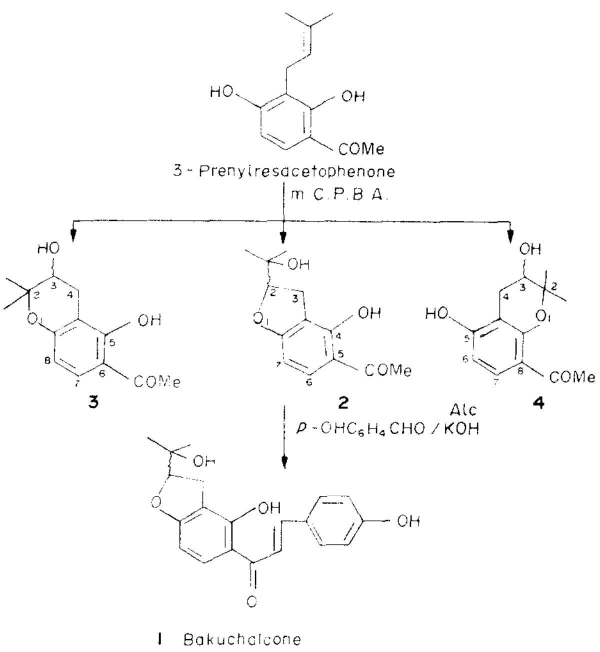
In continuation of our earlier investigations [1–7] on the phytochemistry of the seeds of *Psoralea corylifolia*, we now report the isolation of a minor constituent, bakuchalcone. It was obtained by repeated CC of the ether extract of the defatted seeds over Si gel.

Bakuchalcone (**1**) crystallized from acetone–*n*-hexane as pale-yellow needles mp 204–205°. The molecular ion at 340.1262 gave its molecular formula as $C_{20}H_{20}O_5$. Its chalcone structure was indicated by the UV bands at 366, 308, and 240 nm, which showed a bathochromic shift of 64 nm in the longer wavelength band with an increase in the intensity with sodium methoxide, indicative of the presence of a OH-4 group. A bathochromic shift of 54 nm with aluminium chloride–hydrochloric acid showed the presence of a chelated hydroxyl group. Its IR (KBr) showed characteristic absorption at 1637 cm^{-1} due to a chalcone carbonyl, at 1372 and 1360 cm^{-1} due to a gem dimethyl and at 838 cm^{-1} due to a *para*-substituted benzene ring. The compound formed a diacetate indicating the presence of two hydroxyl groups.

^1H NMR (Me_2CO-d_6) of the compound gave a singlet at δ 1.25 for gem dimethyl protons. A doublet at δ 3.1 showed the presence of two benzylic protons. A triplet for a methine proton appearing at δ 4.75 was characteristic of a dihydrobenzofuran ring substituted at the 2-position. The two *ortho*-coupled doublets centred at δ 6.89 and 7.65, each integrating for two protons, were due to two sets of protons at C-3, C-5 and C-2, C-6 (A_2B_2 system of a *para*-substituted B-ring). An *ortho*-coupled doublet at δ 6.33 integrating for one proton could be assigned to the C-5′ proton indicating that the 5′- and 6′-positions of the A-ring are free. The corresponding downfield doublet for C-6′ proton appeared at δ 7.98 while the α- and β-protons of the chalcone molecule appeared as a singlet at δ 7.73. ^1H NMR ($CDCl_3$) of the diacetate showed the presence of only two hydroxyl groups. That one of these is present in the 4-position was confirmed by subjecting bakuchalcone to alkali hydrolysis; *p*-hydroxybenzoic acid was identified as one of the products. The bathochromic shift in the longer wavelength UV band with aluminium chloride confirmed the presence of a OH-2′ group and ruled out the possibility of a dihydrofuran ring attachment to ring A at C-2′ and C-3′. The above data accounted

---

*Communication no. RRL/81-011.



for all the oxygen functions except for one which could be in the form of a tertiary hydroxyl group which is also supported by mass spectrometry. Thus, based on the above data, bakuchalcone can be assigned the structure 4, 2′-dihydroxy-2″(1-hydroxy-1-methylethyl)-2″, 3″-dihydrofurano(4″, 5″: 3′, 4′)chalcone (**1**).

The above structure was also supported by mass spectrometry, the major fragmentation pathways being those characteristic of chalcones [8] and compounds containing a 2-(1-hydroxy-1-methylethyl)-2, 3-dihydrobenzofuran ring [9].

The proposed structure was confirmed by its total synthesis which involves first the synthesis of **2** from 3-prenylresacetophenone by treatment with *m*-chloroperbenzoic acid. This reaction where epoxidation and cyclization takes place simultaneously has recently been used by us in the synthesis of bavachromanol [10]. 3-Prenylresacetophenone, prepared by nuclear prenylation of resacetophenone, on treatment with *m*-chloroperbenzoic acid yielded three racemic products, chroman **3** (70%), **2** (15%) and chroman **4** (15%) which were separated by PLC. **2** on condensation with *p*-hydroxybenzaldehyde in alcoholic potassium hydroxide yielded (±)-bakuchalcone.

EXPERIMENTAL

Isolation of bakuchalcone. Whole seeds of *Psoralea corylifolia* (3 kg) were defatted and extracted with Et_2O. The viscous mass (350 g), obtained after the removal of the solvent, was chromatographed over Si gel. The column was successively eluted with petrol (bp 40–60°), petrol–C_6H_6 (1:1; 1:3), C_6H_6, C_6H_6–Et_2O (1:1), Et_2O, Et_2O–$CHCl_3$ (1:1), $CHCl_3$ and finally with MeOH. The residue from the Et_2O–$CHCl_3$ (1:1) eluate was rechromatographed over Si gel, elution being carried out with C_6H_6 and C_6H_6–EtOAc mixtures of increasing polarity. The residue obtained from C_6H_6–EtOAc (1:1) was subjected to repeated CC. Initial fractions of C_6H_6–EtOAc (3:1) gave bakuchalcone as yellow crystalline needles further crystallized from Me_2CO–petrol mixture mp 204–205° (25 mg). The compound gave a yellow colour with NaOH, orange-red with conc. H_2SO_4 and a positive reaction with 2:4-DNPH and $FeCl_3$. The compound analysed for $C_{20}H_{20}O_5$. M^+, 340.1262 ($C_{20}H_{20}O_5$ requires: M^+, 340.1309). UV λ_{max}^{MeOH} nm ($\log \epsilon$): 366 (4.3), 308 (3.7) and 240 (3.8); +$AlCl_3$, 420, 368, 318, 237; +$AlCl_3$ + HCl, 420, 370, 322 and 237. +NaOMe, 430, 318 inf., 302 inf., 260. IR ν_{max}^{KBr} cm^{-1}: 3240, 1637, 1600, 1372, 1360 and 838. ^1H NMR (Me_2CO-d_6). δ 1.25 (6H, *s*, Me_2C–), 3.1 (2H, *d*, ϕ –CH_2–), 4.75 (1H, *t*, $-\overset{|}{C}H-O$), 6.33 (1H, *d*, $J = 8$ Hz, C-5′), 6.89 (2H, *d*, $J = 7.5$ Hz, C-3, C-5), 7.65 (2H, *d*, $J = 7.5$ Hz, C-2, C-6), 7.73 (2H, *s*, α- and β-H of chalcone), 7.98 (1H, *d*, $J = 8$ Hz, C-6′), MS *m/z* (%): 340 $[M]^+$ (10), 325(19), 322(13), 307(100), 282(10), 281(38), 264(12), 221(90), 148(20), 147(10), 120(42) and 19(18).

Bakuchalcone diacetate (Ac_2O–*pyridine*). Colourless needles, mp 144–146° (Me_2CO–petrol mixture). It analysed for $C_{24}H_{24}O_7$, M^+, 424.1504 ($C_{24}H_{24}O_7$ requires: M^+, 424.1520) UV λ_{max}^{MeOH} nm: 222 and 306. IR ν_{max}^{KBr} cm^{-1}: 3400, 1760, 1610, 1362. ^1H NMR (60 MHz, $CDCl_3$): δ 1.26 and 1.37 (6H, 2*s*, Me_2C–O), 2.30 and 2.33 (6H, 2*s*, 2 × O–COMe), 3.13 (2H, *d*, C-3″), 4.76 (1H, *t*, C-2″) and signals for six aromatic protons. MS *m/z* (%): 422 $[M]^+$ (36), 382(24), 340(20), 322(70), 312(4), 307(8), 282(100), 281(40), 264(64), 221(8), 162(64), 161(56), 147(36), 134(36), 120(36) and 119(16).

Alkaline hydrolysis of bakuchalcone. 5.0 mg **1** was refluxed with aq. KOH (50%, 5 ml) for 3 hr. The soln was cooled, acidified with HCl and extracted with 5% aq. $NaHCO_3$, the alkaline soln. was neutralized and then re-extracted with Et_2O. The concd Et_2O extract, on examination by PC (*n*-BuOH–5% HOAc, 1 : 1) was found to contain *p*-hydroxybenzoic acid (R_f 0.87 identical with an authentic sample).

Synthesis of (±) *bakuchalcone.* To an ice-cold soln of 3-prenylresacetophenone (0.6 g) in $CHCl_3$ (10 ml) was added slowly with constant shaking an ice-cold soln of *m*-chloroperbenzoic acid (0.45 g) in $CHCl_3$ (10 ml). The reaction mixture was left at room temp. for 48 hr and then successively washed with 5% aq. $NaHCO_3$, H_2O and the $CHCl_3$ layer dried. TLC (C_6H_6–EtOAc, 17 : 3) of the $CHCl_3$ soln showed two spots of R_f 0.56 and 0.47 in addition to some unreacted 3-prenylresacetophenone. These were separated by subjecting the concd $CHCl_3$ soln to prep. TLC (Si gel, 0.75 mm) and identified as follows.

(±)-6-*Acetyl*-3, 5-*dihydroxy*-2, 2-*dimethylchroman* (**3**). A white amorphous solid (200 mg) mp 82–84° (petrol), R_f 0.56. IR ν_{max}^{neat} cm^{-1}: 3400, 3160, 1615; ^1H NMR (60 MHz, CCl_4): δ 1.33 (6H, *s*, Me_2C–), 2.51 (3H, *s*, –COMe), 2.6–2.86 (2H, *m*, –CH_2–), 3.71 (1H, *t*, C-3), 6.26 (1H, *d*, $J = 8$ Hz, C-8), 7.43 (1H, *d*, $J = 8$ Hz, C-7) and 13.44 (1H, *s*, D_2O exchanged –OH).

(±)-5-*Acetyl*-2,3*dihydro*-2(1-*hydroxy*-1-*methylethyl*)-4-*hydroxy-benzofuran* (**2**). A semi-solid mass (45 mg), R_f 0.46. IR ν_{max}^{neat} cm^{-1}: 3400, 3160, and 1610; ^1H NMR, (60 MHz, CCl_4): δ 1.57 and 1.63 (3H each, 2*s*, Me_2C–), 2.5 (3H, *s*, –COMe), 3.07 (2H, *d*, –CH_2–), 4.67 (1H, *t*, C-2), 6.27 (1H, *d*, $J = 8$ Hz, C-7), 7.5 (1H, *d*, $J = 8$ Hz, C-6) and 12.4 (1H, *s*, D_2O exchanged, –OH).

(±)-8-*Acetyl*-3,5-*dihydroxy*-2,2-*dimethylchroman* (**4**). The alkaline soln was neutralized with dil. HCl and then re-extracted with $CHCl_3$. Excess of the acid crystallized by concentrating and chilling this soln. The mother liquor left after the removal of excess acid, on examination by TLC (C_6H_6–EtOAc, 17:3), was found to contain one ferric-positive spot (R_f 0.12). This was isolated by prep. TLC as before. Crystallization from Me_2CO yielded colourless needles, mp 176–178° (45 mg).

Benzylation of **4** (C_6H_5Cl–K_2CO_3 in Me_2CO) yielded 8-acetyl-5-benzyloxy-3-hydroxy-2,2-dimethylchroman as colourless needles from *n*-hexane–M_2CO, mp 110°, identified by comparison with an authentic sample prepared earlier [10] (mmp, co-TLC and IR).

(±) *Bakuchalcone* (**1**). A mixture of **2** (30 mg) and *p*-hydroxybenzaldehyde (15 mg) in EtOH (2 ml) was treated with aq. KOH (0.5 ml, 80%) dropwise at *ca* 0° and the reaction kept at room temp. for 4 days. It was diluted with ice-cold H_2O to 15 ml, neutralized with dil. HCl and extracted with $CHCl_3$ (4 × 15 ml). Bakuchalcone was separated from the reaction mixture by prep. TLC (C_6H_6–EtOAc, 17:3, R_f 0.25). Crystallized from *n*-hexane–Me_2CO, as pale-yellow needles (5 mg) mp 201–202°. It was identical with the natural compound (mmp, IR, co-TLC).

Acknowledgements—We thank Dr. C. K. Atal, Director of this Laboratory, for his keen interest and to the Instrumentation Division for providing the spectral data.

REFERENCES

1. Jain, A. C., Gupta, G. K. and Rao, P. R. (1974) *Indian J. Chem.* **12**, 659.
2. Gupta, G. K., Dhar, K. L. and Atal, C. K. (1977) *Phytochemistry* **16**, 403.
3. Gupta, G. K., Dhar, K. L. and Atal, C. K. (1978) *Phytochemistry* **17**, 164.
4. Suri, J. L., Gupta, G. K., Dhar, K. L. and Atal, C. K. (1978) *Phytochemistry* **17**, 2046.
5. Suri, J. L., Gupta, G. K., Dhar, K. L. and Atal, C. K. (1980) *Phytochemistry* **19**, 336.
6. Gupta, B. K., Gupta, G. K., Dhar, K. L. and Atal, C. K. (1980) *Phytochemistry* **19**, 2034.
7. Gupta, B. K., Gupta, G. K., Dhar, K. L. and Atal, C. K. (1980) *Phytochemistry* **19**, 2232.
8. Harborne, J. B., Mabry, T. J. and Mabry, H. (1975) in *The Flavonoids* p. 106. Chapman & Hall, London.
9. Shipchandler, M. and Soine, T. O. (1968) *J. Pharm. Sci.* **57**, 741.
10. Suri, J. L., Gupta, G. K., Teneja, S. C., Dhar, K. L. and Atal, C. K. (1980) *Indian J. Chem.* **19**, 813.

Phytochemistry, Vol. 21, No. 8, pp. 2151–2154, 1982.
Printed in Great Britain.

0031-9422/82/082151-04$03.00/0
Pergamon Press Ltd.

^{13}C NMR SPECTRA OF 1, 3, 6 -TRIHYDROXY-7-METHOXY-8-(3, 7 -DIMETHYL-2,6-OCTADIENYL)XANTHONE AND ITS DIMETHYL DERIVATIVE

HIOK-HUANG LEE* and SOON NG†

*Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 0511; †Department of Chemistry, University of Malaya, Pantai Valley, Kuala Lumpur, Malaysia

(*Revised received* 3 *August* 1981)

Key Word Index—*Garcinia cowa*; Guttiferae; 1,3,6-trihydroxy-7-methoxy-8-(3,7-dimethyl-2,6-octadienyl)-xanthone; ^{13}C NMR spectra.

Abstract—The ^{13}C NMR spectra of 1, 3, 6-trihydroxy-7-methoxy-8-(3, 7-dimethyl-2, 6-octadienyl)xanthone and its dimethyl derivative are discussed. The data obtained confirmed the assigned structures. The geometrical configuration of the C_{10} dienyl side-chain has been deduced as *trans*.

A yellow pigment, $C_{24}H_{26}O_6$, isolated from the stem of *Garcinia cowa* (Guttiferae), has been assigned the xanthone structure, **1**, based on evidence from light absorption and ^1H NMR as well as from mass spectra [1]. The alternative structure, **2**, proposed for cowaxanthone [2], a pigment reported to have been isolated also from the same plant, was not rigorously excluded by the available data. In this paper, we describe a study of the ^{13}C NMR spectra of **1** and its dimethyl derivative, **3**, which unequivocally support the assigned structure.

Several papers on the ^{13}C NMR spectra of naturally