8′-apo-β-caroten-8′-ol acetate 7. Made by reduction of synthetic 8′-apo-β-caroten-8′-al (**2**) with $LiAlH_4$ [15,16], followed by acetylation with Ac_2O in Py [15,17]. Orange–reddish plates. λ_{max} (*n*-hexane): 402, 425 ($E^{1\%}_{1cm} = 2665$ as found by Rüegg *et al.* [18]) and 450 nm; ν_{max} (KBr): 2985–2860 (CH), 1745 (C=0), 1460 (CH_2, Me), 1365 (Me), 1240 (C–0), 1040, 980 and 965 cm^{-1} (*trans*-CH=CH-); NMR (100 MHz, $CDCl_3$, TMS) δ 6·8–6·11 (12 H olefinic), 4·58 *s* (CH_2, C–8′), 2·10 *s* (Me of acetate), 2·04 (CH_2, C–2), 1·99 *s* (3 × Me, C–9, 13, 13′), 1·86 *s* (Me, C–9′), 1·73 *s* (Me, C–5), *ca* 1·6 and 1·45 (protons of C–2 and C–3), 1·53 *s* (impurity: H_2O), 1·04 (2 × Me, C–1); similar NMR-values are given in [19].

Oxidation with p-*chloranil* [8]. A mixture of *ca* 1 mg of **4** or **6** in 0·5 ml C_6H_6 and 1 mg *p*-chloranil were let stand for 15 hr under N_2 in the dark at room temp. Synthetic alcohol (**6**) was converted to the corresponding aldehyde, whereas β-citraurinene (**4**) yielded mainly the starting compound with only traces of other products.

Treatment with acidified chloroform [20,21]. To *ca* 1 mg of β-citraurinene (**4**) was added 2 ml of *ca* 0·05 N HCl in $CHCl_3$. No color change was observed during 30 min. reaction time in the dark. Pigments were transferred to Et_2O upon admixture of aq bicarbonate soln. Only polar decomposition products (*ca* 10%), traces of a non-polar compound (λ_{max}: 401 (*sh*), 423 and 446 nm in *n*-hexane) and mainly unchanged β-citraurinene (**4**) (*ca* 85%) were detected in the reaction mixture by TLC examination. 8′-apo-β-caroten-8′-ol (**6**) yielded in a similar reaction mainly a non-polar product with λ_{max} 430 nm in *n*-hexane, without fine structure.

Acknowledgements—We are grateful to Dr. W. Brey, Gainesville, and Dr. G. Levy, Tallahassee, for the NMR spectra, and to Mr. G. Edwards, Lake Alfred, for the IR spectra. We are also indebted to Hoffman-La Roche, Basle for a sample of 8′-apo-β-caroten-8′-al.

REFERENCES

1. Stewart, I. and Wheaton, T. (1973) *Phytochemistry* **12,** 2947.
2. Stewart, I. and Wheaton, T. (1972) *J. Agr. Food Chem.* **20(2),** 448.
3. Wheaton, T. and Stewart, I. (1973) *J. Am. Soc. Hort Sci.* **98(4),** 337.
4. Stewart, I. and Wheaton, T. (1971) *J. Chromatog.* **55,** 325.
5. Leuenberger, F. J., Schocher, A. J., Britton, G. and Goodwin, T. W. (1973) *FEBS Letters* **33(2),** 205.
6. Nybraaten, G. and Liaaen-Jensen, S. (1974) *Acta Chem. Scand.* **B28,** 485.
7. Warren, C. K. and Weedon, B. C. L. (1958) *J. Chem. Soc.* 3972.
8. Liaaen-Jensen, S. (1965) *Acta Chem. Scand.* **19,** 1166.
9. Gross, J., Carmon, M., Lifshitz, A. and Sklarz, B. (1975) *Phytochemistry* **14,** 249.
10. Yokoyama, H. and White, M. J. (1966) *Phytochemistry* **5,** 1159.
11. Yokoyama, H. and White, M. J. (1967) *J. Agr. Food Chem.* **5(4),** 693.
12. Taylor, R. and Davies, B. (1974) *Biochem. J.* **139,** 751.
13. Taylor, R. and Davies, B. (1974) *Biochem. J.* **139,** 761.
14. Weedon B. C. L. (1971) in *Carotenoids* (Isler, O. Ed.) p. 48. Birkhaeuser-Verlag, Basle.
15. Aasen, A. J. and Liaaen-Jensen, S. (1966) *Acta Chem. Scand.* **20,** 1970.
16. Liaaen-Jensen, S. (1963) *Acta Chem. Scand.* **17,** 303.
17. Liaaen-Jensen, S., Hertzberg, S., Weeks, O. B. and Schwieter, U. (1968) *Acta Chem. Scand.* **22,** 1171.
18. Rüegg, R., Montavon, M., Ryser, G., Saucy, G., Schwieter, U. and Isler, O. (1959) *Helv. Chim. Acta.* **42,** 854.
19. Vetter, W. (1971) in *Carotenoids* (Isler, O. Ed.) p. 228. Birkhaeuser Verlag, Basle, Switzerland.
20. Leuenberger, U. (1973) Thesis, University of Berne, Switzerland.
21. Leuenberger, U. (1975) *Helv. Chim. Acta.* (in press).

Phytochemistry, 1976, Vol. 15, pp. 229–230. Pergamon Press. Printed in England.

AURENTIACIN, A NEW CHALCONE FROM *DIDYMOCARPUS AURENTIACA*

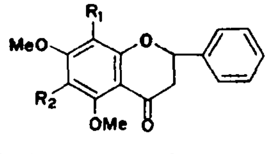
NARAYAN ADITYACHAUDHURY, ASIT K. DAS, ASHIM CHOUDHURY and PANNA L. DASKANUNGO
Department of Agricultural Chemistry & Soil Science, Faculty of Agriculture,
Bidhan Chandra Krishi Viswa Vidyalaya, West Bengal, India

(*Received* 31 *May* 1975)

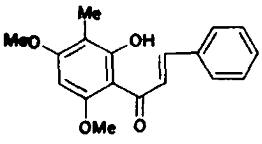
Key Word Index—*Didymocarpus aurentiaca*; Gesneriaceae; aurentiacin; 2′-hydroxy-4′,6′-dimethoxy-3′-methylchalcone.

Phytochemical investigation of *Didymocarpus pedicellata* has revealed the presence of a number of chalcones, quinochalcones and flavanones [1, 2]. These results prompted us to examine another species, *D. aurentiaca*, growing in the Darjeeling area, West Bengal. A new chalcone, aurentiacin, has been isolated from this plant and its structure-elucidation is described here.

It was obtained as an orange coloured crystalline compound, $[\alpha]_D \pm 0°$ ($CHCl_3$), $C_{18}H_{18}O_4$ (M^+ 298). Colour reactions indicated it to be chalcone. Functional group analysis revealed the presence of two OMe (two 3<u>H</u> singlets at 3·95δ and 4·0δ), one aromatic – Me (3<u>H</u> singlet at 2·06δ), a conjugated >C=O (ν_{max}^{KBr} 1620 cm^{-1}), a chelated –OH (ν_{max}^{KBr} 3200 cm^{-1}; 1<u>H</u> singlet 14·06δ, exchangeable with D_2O, brown colour with $FeCl_3$) and a complex aromatic substitution pattern (ν_{max}^{KBr} 1600, 1550, 1125, 790, 745 cm^{-1}) with an unsubstituted benzene ring [2] (ν_{max}^{KBr} 700 cm^{-1}). The presence of six aromatic protons was also discernible in the NMR spectrum. The NMR spectrum also showed 2 *trans*-olefinic protons at 7·7δ as a 2H—singlet providing evidence for a chalcone system [1,3]. The mass spectrum showed peaks characteristics of chalcones [4]. The unsubstituted nature of the B-ring of aurentiacin was readily apparent from the appearance of 2 prominent peaks at *m/e* 221 (M^+–77; $M^+ - C_6H_5$) and *m/e* 195 (M^+ – 103; $M^+ - C_6H_5 - CH$



(1) R_1 = Me, R_2 = H
(2) R_1 = H, R_2 = Me



(3)

=CH) in the MS and it further indicated that all the substituents were present in the A-ring. The UV spectrum favoured a phloroglucinol substitution [5] pattern in the A-ring. Location of the substitution [2–OMe, 1–OH (chelated), 1–Me] in ring-A of aurentiacin was secured by converting it into the isomeric flavanone isoaurentiacin, $C_{18}H_{18}O_4$. In its NMR spectrum, the protons of the γ-pyrone ring constituting an ABX system [4] appeared as a multiplet (AB-part, 2·90δ) and a double doublet (X-part, 5·41δ). Its UV spectrum was similar to that of 5,7-dimethoxy- and 5,7-dihydroxyflavanones [5]. Thus isoaurentiacin is either (**1**) or (**2**). The appearance of a sharp 1H-singlet at 6·11δ in its spectrum provided evidence [6,7] that an aromatic proton is situated either at C–6 or C–8 position. The physical properties of isoaurentiacin agreed well with those reported for 5,7-dimethoxy-8-methylflavanone [8] thereby settling the structure of aurentiacin.

The structure of aurentiacin was finally confirmed as (3) by synthesis. Nuclear methylation of phloroacetophenone furnished 2-hydroxy-4,6-dimethoxy-3-methylacetophenone [9], which on condensation with benzaldehyde afforded **3** as bright orange plates, identical with natural material in all respects. Aurentiacin is the first *C*-methylated chalcone to be found in *Didymocarpus*.

EXPERIMENTAL

Mp's are uncorrected. UV spectra were recorded in EtOH. For column chromatography Si gel (BDH, 60–120 mesh) was used. NMR spectra were determined in $CDCl_3$ with TMS as internal standard. Light petrol used had bp 60–80°. The whole plant of *D. aurentiaca* [10] was collected during the month of May–June, 1974.

Isolation of aurentiacin. The air dried and milled whole plant of *Didymocarpus aurentiaca* (1 kg) was exhaustively extracted (24 hr) with petrol. The extract was concentrated and chromatographed over Si gel (300 g). The chromatogram was eluted with solvents of increasing polarity. C_6H_6-eluates afforded a yellowish solid (1·25 g) which was further purified by rechromatography over Si gel (30 g). Elution of the chromatogram with petrol–C_6H_6 (1:1) furnished an orange–yellow solid which crystallised from petrol(C_6H_6 (19:1) as bright orange plates, mp 140–141° (yield 0·06%), R_f: 0·8 (C_6H_6–$CHCl_3$, 9:1) and 0·6 (C_6H_6–$CHCl_3$, 19:1), UV: λ_{max} 343 nm (log ϵ 6·8); $\lambda_{max}^{EtOH-NaoEt}$ 344 nm; *IR*: ν_{max}^{Nujol} cm^{-1}, 1615, 700, 1600, 1550, 1125, 790, 745, 3200; (Found: C, 71·9; H, 6·2, $C_{18}H_{18}O_4$ requires: C 72·4; H, 6·04%). *NMR*: (δ) 7·7 (*s*, 2H, *trans*-olefinic); 2·06 (*s*, 3H, 1–Me); 3·95 (*s*, 3H, 1–OMe); 4·0 (*s*, 3H, (1–OMc); 7·43 (*m*, 5–ArH), 6·03 (*s*, 1–ArH), 14·06 (*s*, chelated phenolic OH, disappeared on D_2O exchange); *MS*: 298 (M^+, base peak), 297 (M^+–1), 221, 195.

Isomerisation of aurentiacin. To 0·1 g dissolved in EtOH (15 ml) was added conc. H_2SO_4 (1·2 ml) and the soln was refluxed on a water bath for 40 hr. The flavanone was eventually obtained as colourless needles, mp 141–142° from light petrol–C_6H_6 (1:1) (0·025 g); R_f: 0·9 (C_6H_6–EtOAc, 4:1), 0·7 ($CHCl_3$) and 0·2 (C_6H_6–$CHCl_3$, 1:1). UV: λ_{max} 288 (log ϵ 4·3), 320 (*sh*) nm (log ϵ 3·5). *IR*: ν_{max}^{KBr} cm^{-1}, 1670, 700, 1610, 1580, 1500, 900, 770, *NMR*: (δ), 2·90 (*m*, *J* 4·5 Hz, 2H); 5·41 (*dd*, *J* 6 Hz, 1H); 3·95 and 4·0 (*s*, 6H, 2–OMe); 2·06 (*s*, 3H, 1–Me); 6·11 (*s*, 1–Arh); 7·45 (*s*, 5–ArH); Found: C, 72·1, H, 6·1. $C_{18}H_{18}O_4$ requires: C, 72·4; H, 6·04%.

Synthesis of aurentiacin. Phloroacetophenone (1 g) with MeI (4 ml) and dry K_2CO_3 (3 g) in Me_2CO (20 ml) was refluxed for 5 hr. The product crystallised as pale yellow needles, mp 141–142° (0·3 g). An intimate mixture of this compound (0·1 g in EtOH 4 ml) and benzaldehyde (0·12 g) was treated with alkali (1 g NaOH in 1 ml of H_2O) dropwise with constant stirring in the cold (0–5°) and then kept at room temp. for 24 hr. The reaction mixture was acidified with 6(N) HCl and extracted with Et_2O. The Et_2O fraction after chromatography over Si gel and elution with petrol–C_6H_6 (1:1), afforded an orange solid, crystallising from petrol–C_6H_6 (19:1) as bright orange plates, mp 140–141°. The latter was found to be identical with aurentiacin in all respects (mp, mmp, CO-TLC and superimposable IR).

Acknowledgements—The authors thank C.S.I.R., India for fellowships to A.C. and P.D. and B.C.K.V.V., Kalyani, for a University scholarship to A.K.D. They are also grateful to Dr. B. C. Das, CNRS, Gif-sur-Yvette, France and Dr. D. N. Roy, University of Toronto, Canada, for spectral measurements and to Professor H. Erdtman, Stockholm, for kindly supplying a synthetic sample of 4′,6′-dimethoxy-3′-methyl-2′-hydroxychalcone.

REFERENCES

1. Agarwal, S. C., Bhaskar, A. and Seshadri, T. R. (1973) *Ind. J. Chem.*, **11**, 9; and references cited therein.
2. Bhaskar, A. and Seshadri, T. R. (1973) *Ind. J. Chem.* **11**, 404 and references cited therein.
3. Krishna, B. M. and Chaganty, R. B. (1973) *Phytochemistry* **12**, 238.
4. Adityachaudhury, N., Kirtaniya, C. L. and Mukherjee, B. (1971) *Tetrahedron* **27**, 2111.
5. Jurd, L. (1962) in *The Chemistry of Flavonoid Compounds* (Geissman, T. A., ed), p. 151–153, Pergamon Press, Oxford.
6. Kaufman, F. and Lam, J. (1967) *Acta. Chem. Scand.* **21**, 311.
7. Seshadri, T. R. and Sood, M. S. (1967) *Tetrahedron Letters* 853.
8. Lindsteadt, G. and Misiorny, A. (1951) *Acta. Chem. Scand.* **5**, 1.
9. Curd, H. F. and Robertson, A. (1933) *J. Chem. Soc.* 437.
10. The plant material used in this investigation was obtained from Mukherjee & Co., Kalimpong, West Bengal, where a voucher specimen has been preserved.