Phytochemistry, Vol. 26, No. 11, pp. 3090–3091, 1987.
Printed in Great Britain.

0031-9422/87 $3.00 + 0.00

(−)FLACOURTIN, A PHENOLIC GLUCOSIDE ESTER FROM *FLACOURTIA INDICA*

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(*Received* 17 *February* 1987)

Key Word Index—*Flacourtia indica*; Flacourtiaceae; new glucoside ester; flacourtin.

Abstract—The bark of an Indian medicinal plant, *Flacourtia indica*, yielded a new phenolic glucoside ester, flacourtin, identified as 3-hydroxy-4-hydroxymethylphenyl-6-*O*-benzoyl-β-D-glucopyranoside.

INTRODUCTION

The medicinal plant *Flacourtia indica* [1] has yielded a new phenolic glucoside ester, flacourtin. The identification of the latter compound is described here.

RESULTS AND DISCUSSIONS

Flacourtin, $C_{20}H_{22}O_9$ ($[M]^+$ 406), was isolated from *Flacourtia indica* Merr. by solvent extraction and crystallization. It formed a pentaacetate and produced benzoic acid on alkaline hydrolysis and glucose and benzoic acid on acid hydrolysis, indicating it to be a benzoate ester of a glucoside, this was corroborated by UV [λ_{max}^{EtOH} 228 (log ε 4.24), 282 nm (log ε 3.49)] and IR [ν_{max}^{KBr} 3440 *br s* (O–H str.), 1710 *s* (C=O str., aryl ester), 1605 *s* and 1500 *s* (arom C–C str.), 1285 *s*, 1120 *s*, 1060 *s* (C–O str.), 700 *s* (C_6H_5) cm^{-1}] spectra [2, 3].

Structure **1** was established for flacourtin from detailed analysis of its 360 MHz ^{1}H NMR spectrum with NOE experiments (Table 1). Assignments were made by decoupling; the hydroxyl protons (OH–8, OH-9 and OH-10) were all D_2O exchangeable. The substitution pattern of ring 2 was determined by NOE difference. When H-3 and H-4 were irradiated 3.5% NOE to aromatic H-F was observed and this proved the ring substitution pattern as indicated. Mass spectral analysis of **1** and its penta-acetate confirmed this structural assignment. Flacourtin gave a strong ion at *m/z* 267, due to a benzoylated glucose moiety, but there was no ion at *m/z* 163, showing that the benzoyl substituent is on the sugar [4, 5].

The configuration of H-1 of glucose was confirmed from the ^{1}H NMR spectrum. The appearance of one proton doublet centered at δ4.62 (J = 7.4 Hz) ppm was assigned to the anomeric proton of glucose and this is axial to the pyranose ring [6, 7]. As flacourtin forms a pentaacetate, and three OH groups (δ5.20, 5.30, 5.42 ppm) were present in the glucose moiety as already evident from the formation of benzoylated glucose fragment ion in the mass spectrum, the other two –OH groups (δ4.93, 8.98 ppm), one of which might be phenolic, are attached to the aglycone. Two singlet protons around δ5.05 ppm in ^{1}H NMR spectrum of flacourtin pentaacetate [8] are due to the benzylic hydrogens.

In the ^{1}H NMR spectrum, the aromatic region showed the presence of eight protons. The five protons appearing between δ7.0 to 8.0 ppm were located on the benzoic acid residue of flacourtin. The other three aromatic protons appeared between δ6 to 7 ppm showing coupling constants characteristic of a 1,2,4-trisubstituted aromatic nucleus. Flacourtin (**1**) differs in its location of substituents from related phenolic esters such as lacticolorin [8], nigracin [9] and xylosmacin [10].

EXPERIMENTAL

Mps are uncorr. IR, UV, ^{1}H NMR spectra were recorded in KBr, EtOH, and $CDCl_3$/DMSO-d_6 with TMS as int. standard respectively. Non aq. solvents were routinely dried over anhydrous Na_2SO_4 before use. Finely ground air dried bark (800 g) of *Flacourtia indica* (kindly identified and specimen preserved by Dr. S. R. Das, Plant Survery Officer, Regional Research Institute, CCRAS, Calcutta 700009), collected from Hoogly district, West Bengal, in the summer, was first extracted with $CHCl_3$ (18 hr) and then with 90% EtOH in a Soxhlet. The alcohol extract was concd (250 ml) by distillation under red. pres., H_2O was added and

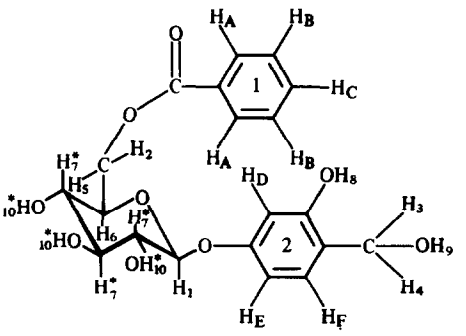

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Table 1. 360 MHz ^{1}H spectral analysis of flacourtin in DMSO-d_6 with NOE

Chemical shift (δ)	Appearance of signals and other observations (J Hz)	Assignment and other conclusions	
7–8	5H, *m*	Five protons of aromatic ring 1	
7.92, 7.51, 7.65		H_A, H_B, H_C	
6.31	1H, *dd*, J_o 8.8, J_m 3.0	H_E	An ABX pattern, J_{AB} 3.0 (*m*),
6.71	1H, *d*, J_m 3.0	H_D	J_{AX} 8.8 (*o*), J_{BX} 0.0 (*p*); A and B
6.83	1H, *d*, J_o 8.8	H_F	adjacent to O inferred because of their high field position.
	[exhibits 3.5% NOE enhancement when H_3 (4.50) and H_4 (4.34) are irradiated]		
4.62	1H, *d*, $J_{1,7}$ 7.4	H_1	J value indicated that H_1 was axial to the pyranose ring and the configuration of C_1 of flacourtin was therefore β.
4.55	1H, *dd*, J_{gem} 11.8, $J_{2,6}$ 2.1	H_2	
4.28	1H, *dd*, J_{gem} 11.8, $J_{5,6}$ 7.5	H_5	
4.50	1H, *d*, J_{gem} 14.3	H_3	
4.34	1H, *d*, J_{gem} 14.3	H_4	
3.64	1H, *m*	H_6	
3.29	3H, *m*	H_{7*}	(three methine protons)
8.98	1H, *s*	H_8	(phenolic OH)
4.93	1H	H_9	(benzylic OH)
5.42, 5.35, 5.20	3H	H_{10*}	(three glucose OH)

distillation continued. In this way most of the alcohol was distilled off and the vol. was kept to 250 ml. The liquid was filtered hot and the cold soln was basified with 5% aq. $NaHCO_3$. The alkaline solution was then extracted exhaustively with ether (250 ml × 20). The ether extract was washed with H_2O and dried. On concn a solid (390 mg), mp 198–200°, separated. The solid was first crystallized from EtOAc and then from EtOAc–Me_2CO when needles of flacourtin (275 mg, 0.034%), mp 212°, were obtained [R_f 0.30, silica gel G plate, $CHCl_3$–MeOH (17:1), iodine vapour]. Found in a dry sample: C, 58.7; H, 5.30. $C_{20}H_{22}O_9$ requires C, 59.1; H, 5.4%. $[\alpha]_D^{30°}$ −49.3° (MeOH; *c*0.77).

Alkaline hydrolysis of flacourtin with aq. $Ba(OH)_2$ furnished benzoic acid identified from MS, mp, mmp and superimposable IR spectra. Acidic hydrolysis furnished glucose (identified by co-chromatography and benzoic acid. Flacourtin pentaacetate was obtained as needles, mp 105–106° from ether–petrol. Found in a dry sample: C, 58.30; H, 5.10. $C_{30}H_{32}O_{14}$ requires C, 58.40; H, 5.20%. ^{1}H NMR (90 MHz): δ8.03–6.75 (8H, *m*, aromatic protons), 5.05 (2H, *s*, benzylic proton, Ar$\underline{CH}_2$OAc), 2.23, 2.10, 2.06, 2.03, 2.03 (15H, 4*s*, 15 protons for the 5 OCOMe) ppm. MS: *m/z* 393 (6%), 231 (44%), 169 (12%), 122 (46%), 109 (30%), 105 (100%), 77 (47%), 43 (95%).

Acknowledgements—Thanks to Dr B. C. Das, CNRS, France for the mass spectrum and to Professor Maurice Shamma and Mr Alan J. Freyer, the Pennsylvania State University, U.S.A. for 360 MHz ^{1}H NMR spectrum with NOE of flacourtin. Authentic samples or spectra of lacticolorin, nigracin or xylosmacin were kindly provided with by Professors G. W. Perold, Johanesburg; H. Thieme and R. Beneeke, Leipzig and G. A. Cordell, Chicago. This work was funded by International Foundation for Science, Sweden.

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