This was identified as 7,8-dimethoxycoumarin by mmp with an authentic sample.

7,8-*Methylenedioxycoumarin* (*daphnetin methylene ether*) **2**. Colourless needles, mp 180–183° (EtOH, lit. 187–189° [2]), $C_{10}H_6O_4$ (Found: C, 63.4; H, 3.3. Calc. for $C_{10}H_6O_4$ C, 63.2; H, 3.2%). MS (*m/e*): 190 (M^+, base peak); UV λ_{max} nm (95% EtOH): 257, 264, 320. NMR: δ 6.12 (*s*, —O—CH_2—O—), 6.22 and 7.58 (*d*, 3-H and 4-H), 6.76 and 6.98 (*d*, 5-H and 6-H); IR ν_{max}^{KBr} cm^{-1}: 1730, 1715, 1640, 1580, 1500, 1460, 1285, 1050, 930, 840. The mp was not depressed on admixture with authentic 7,8-methylenedioxycoumarin.

7-*Methoxycoumarin* (*herniarin*) **3**. Colourless needles, mp 113–116° (MeOH), $C_{10}H_8O_3$ (Found: C, 67.5; H, 4.3. Calc. for $C_{10}H_8O_3$ C; 68.2; H, 4.6%). MS (*m/e*): 176 (M^+, base peak); UV λ_{max} nm (95% EtOH): 243, 253, 323. NMR: δ 3.88 (*s*, OMe), 6.24 and 7.60 (*d*, 3-H and 4-H), 6.80, 7.32. IR ν_{max}^{KBr} cm^{-1}: 1700, 1620, 1500, 1400, 1350, 1284, 1125. The mp was not depressed on admixture with an authentic 7-methoxycoumarin.

Phytosterols. Colourless needles, mp 136–140° (MeOH). MS (*m/e*): 414 (M^+), 412 (M^+), 400 (M^+). The result of comparison with authentic samples by GLC indicated the presence of campesterol (4.8%), stigmasterol (65.0%) and sitosterol (30.2%).

REFERENCES

1. Yano, K. (1969) 13th Symposium on the Chemistry of Terpenes, Essential Oils and Aromatics. Japan, p. 4.
2. Herz, W., Bhat, S. V. and Santhanam, P. S. (1970) *Phytochemistry* **19**, 891.
3. Pechmann, H. V. (1884) *Ber.* **17**, 929.

Phytochemistry, 1979, Vol. 18, pp. 1762–1763. Pergamon Press Ltd. Printed in England.

A NEW COUMARIN GLUCOSIDE FROM *PRANGOS PABULARIA*

S. K. KOUL, K. L. DHAR and R. S. THAKUR
Regional Research Laboratory, Jammu 180001, India

(*Revised received* 1 *February* 1979)

Key Word Index—*Prangos pabularia*; Umbelliferae; 4-[3-(β-D-glucopyranosyloxy)-2 hydroxy-3-methyl butoxy]-7H Furo [3,2-g] [1] benzopyran-7-one; 9-[3-(β-D-glucopyranosyloxy)-2 hydroxy-3-methyl butoxy]-7H Furo [3,2-g] [1] benzopyran-7-one; alloimperatorin methyl ether.

Prangos pabularia Lindl is the only species of the genus found in India in the N.W. Himalayas Range [1]. Earlier workers have shown the presence of some coumarins [2–4]. The residue left after solvent fractionation of the MeOH extract on repeated column chromatography gave a mixture of two compounds BB_1 and BB_2 which could not be separated even by prep. TLC. The mixture was, therefore, subjected to acetylation and on subsequent column chromatography gave BB_1-Ac and BB_2-Ac. Deacetylation of the two gave two compounds, BB_1 and BB_2, mp 250–253° and 196–197°, respectively.

BB_1 analysed for $C_{22}H_{26}O_{11}$, M^+ 466, λ_{max}^{MeOH} 238, 245, 275 and 316 nm. The IR showed bands at 1570, 1600, 1620, 1730 and 3315 cm^{-1}; $[\alpha]_D^{30}$ −30° (H_2O, *c* 0.5). The MS of the compound showed an aglycone fragment ion *m/e* 304 attributable to the loss of a C-3″ *O*-glycosyl moiety. The other prominent fragments were at *m/e* 292, 287, 245, 216, 194 and 145. The compound, on acetylation, formed a pentaacetate indicating the presence of five —OH groups. The IR showed bands at 1725, 1250 and 1550 cm^{-1}. The ^1H NMR ($CDCl_3$) showed signals at δ 1.43 (6H, *s*, side chain *gem* diMe), 2.13 (15H, *m*, 4 acetoxyl groups of sugar moiety and one acetoxyl of the side chain). All the methine and methylene groups of the side chain and the sugar moiety appear as an overlapped complex multiplet between 3.73 and 5.4, 6.31 (1H, *d*, $J_{3,4}$ = 9 Hz, C_3-H), 7.1 (1H, *d*, $J_{3',2'}$ = 2.2 Hz, $C_{3'}$-H), 7.15 (1H, *s*, C_8-H), 7.6 (1H, *d*, $J_{2',3'}$ = 2.2 Hz, $C_{2'}$-H) and 8.15 (1H, *d*, $J_{4,3}$ = 9 Hz, C_4-H).

The sugar obtained by alcoholic HCl hydrolysis of the glucoside was identified by PC as glucose. Emulsin hydrolysis showed the β-linkage of the sugar moiety and the aglycone. The aglycone which analysed for $C_{16}H_{16}O_6$, mp 134–135° ((±)-oxypeucedanin hydrate, lit. [2, 5] mp 135–135.5°) showed UV fluorescence, λ_{max}^{MeOH} 224, 260, 266 and 310 nm; and IR bands at 3380, 1715, 1580 cm^{-1}, $[\alpha]_D^{30}$ ±0° (MeOH, *c* 1) (lit. [2, 6] $[\alpha]_D^{30}$ ±0° ($CHCl_3$, *c* 2.05). The ^1H NMR ($CDCl_3$) showed signals at δ 1.43 (6H, *s*, C_5-side chain *gem* diMe), 2.53 and 3.2 (2H, *br s*, C_5-sidechain *sec* and *tert* OH, exchangeable with D_2O), 4.03 (1H, *m*, C_5-side chain methine), 4.06 (2H, *m*, C_5-side chain OCH_2), 6.3 (1H, *d*, $J_{3,4}$ = 9 Hz, C_3-H), 7.08 (1H, *d*, $J_{3',2'}$ = 2.2 Hz, $C_{3'}$-H), 7.2 (1H, *s*, C_8-H), 7.7 (1H, *d*, $J_{2',3'}$ = 2.2 Hz, $C_{2'}$-H) and 8.35 (1H, *d*, $J_{4,3}$ = 9 Hz, C_4-H).

^1H NMR ($CDCl_3$) of the monoacetate of the aglycone showed signals at δ 1.36 (6H, *s*, C_5 *gem* diMe), 2.03 (1H, *br s*, C_5-*tert* OH), 2.1 (3H, *s*, OCOMe of C_5-side chain), 4.65 (2H, *m*, C_5-OCH_2), 5.3 (1H, *m*, C_5-side chain methine), 6.2 (1H, *d*, $J_{3,4}$ = 9 Hz, C_3-H), 6.93 (1H, *d*, $J_{3',2'}$ = 2.2 Hz, $C_{3'}$-H), 7.56 (1H, *d*, $J_{2',3'}$ = 2.2 Hz, $C_{2'}$-H), 7.06 (1H, *s*, C_8-H) and 8 (1H, *d*, $J_{4,3}$ = 9 Hz, C_4-H).

^1H NMR ($CDCl_3$) of the dehydrated product of the monoacetate showed signals at δ 1.9 (3H, *s*, C_5-side chain Me), 2.08 (3H, *s*, C_5-side chain OCOMe), 4.46 (2H, *d*, *J* = 5 Hz, C_5-side chain methylene), 5.1 (2H, *d*, *J* = 5 Hz, C_5-OCH_2), 5.56 (1H, *t*, C_5-side chain methine),

6.23 (1H, *d*, $J_{3,4}$ = 9 Hz, C_3-H), 6.93 (1H, *d*, $J_{3',2'}$ = 2.2 Hz, $C_{3'}$-H), 7.13 (1H, *s*, C_8-H), 7.6 (1H, *d*, $J_{2',3'}$ = 2.2 Hz, $C_{2'}$-H) and 8.06 (1H, *d*, $J_{4,3}$ = 9 Hz, C_4-H). On the basis of above data, the aglycone was identified as (±)-oxypeucedanin hydrate. This was also confirmed by co-TLC, mmp and ^{1}H NMR of the authentic sample of oxypeucedanin hydrate (isolated from *P. pabularia*). Hence the aglycone has two OH groups, one of which is involved in the linkage with the sugar moiety. To establish which one is involved in the linkage, dehydration of BB_1 with $POCl_3/C_5H_5N$ was tried without success. However, the dehydrated product of the aglycone monoacetate was obtained and identified by ^{1}H NMR. This further indicated that the free OH of the side chain in BB_1 is secondary in nature. This was finally confirmed by partial synthesis of BB_1 from aglycone monoacetate and tetraacetoxy α-glucosidyl bromide in EtOH-free $CHCl_3$ and $AgCO_3$ [7].

The natural product BB_1 is therefore (−)4-[3-β-D-glucopyranosyloxy)-2 hydroxy-3-methyl butoxy]-7H Furo [3,2-g] [1]benzopyran-7-one.

BB_2, mp 196–197° (lit. [8, 9], mp 197–198°), analysed for $C_{22}H_{26}O_{11}$ and was identified as (−)9-[3-(β-D-glucopyranosyloxy)-2 hydroxy-3-methyl butoxy]-7H Furo [3,2-g] [1]benzopyran-7-one, by UV, IR and ^{1}H NMR, mmp and co-TLC. Further confirmation was from hydrolysis which yielded heraclenol.

The third compound isolated (see Experimental) had mp 102° and analysed for $C_{17}H_{16}O_4$, λ_{max}^{MeOH} 312, 267, 252 and 247 nm, IR 1726, 1710, 1600 and 1560 cm^{-1}. ^{1}H NMR (CCl_4) showed signals at δ 1.7 and 1.83 (3H, each *s*, side chain *gem* diMe), 3.63 (2H, *d*, *J* = 7 Hz, side chain CH_2), 4.17 (3H, *s*, C_5-OMe), 5.1 (1H, *t*, side chain olefinic H), 6.16 (1H, *d*, $J_{3,4}$ = 9 Hz, C_3-H), 6.7 (1H, *d*, $J_{3',2'}$ = 2.2 Hz, $C_{3'}$-H), 7.6 (1H, *d*, $J_{2',3'}$ = 2.2 Hz, $C_{2'}$-H) and 7.76 (1H, *d*, $J_{4,3}$ = 9 Hz, C_4-H). From the above data, the compound was identified as the Me ether of alloimperatorin, mmp (undepressed), co-TLC, superimposable IR and ^{1}H NMR with the authentic compound [10].

EXPERIMENTAL

Air-dried rhizomes of *P. pabularia* (2 kg) were extracted exhaustively with MeOH. The extract was concd *in vacuo* and extracted with C_6H_6, $CHCl_3$ and EtOAc, respectively. The C_6H_6 extract, on repeated column chromatography over Si gel and elution with C_6H_6, gave a compound, mp 102°. (Analysed for $C_{17}H_{16}O_4$: C, 72.06; H, 5.77. $C_{17}H_{16}O_4$ requires: C, 71.83; H, 5.63%). The residue left after solvent extraction was repeatedly chromatographed (20 g) over Si gel. Elution with $CHCl_3$–MeOH (9:1) yielded a glycoside mixture (2.5 g) which could not be separated even on repeated chromatography and PLC. The mixture was acetylated (Ac_2O/C_5H_5N), refluxing for 6 hr. Chromatography of the crude acetate over Si gel and elution with $CHCl_3$–EtOAc (3:1) gave the acetate derivatives of compounds BB_1, mp 181–9° and BB_2, mp 131°. Recrystallization of BB_1-Ac (EtOAc–petrol, 9:1), mp 190–2°. (Found: C, 57.00; H, 5.49. $C_{32}H_{36}O_{16}$ requires: C, 56.80; H, 5.32%).

Deacetylation. NH_4OH soln (25%) was added dropwise to BB_1 pentaacetate (200 mg) in 60 ml MeOH. After work-up, the product, on crystallization from dil. EtOH, gave a compound, mp 250–63°. (Found: C, 57.09; H, 6.00. $C_{22}H_{26}O_{11}$ requires: C, 56.86; H, 5.57%).

Hydrolysis of BB_1. BB_1 (500 mg) was treated with 5% HCl in MeOH. After work-up, the aglycone was isolated and recrystallized from petrol–EtOAc (1:3), mp 134–5°. It analysed for $C_{16}H_{16}O_6$ (C, 63.3; H, 5.31. $C_{16}H_{16}O_6$ requires: C, 63.15; H, 5.26%). The sugar was identified as glucose by PC (C_5H_5N–EtOAc–H_2O, 5:12:4 and *n*-BuOH–HOAc–H_2O, 4:1:5).

Acetylation of aglycone. The aglycone (70 mg) was treated with Ac_2O–C_5H_5N at room temp. After work-up, the product was recrystallized from petrol–EtOAc (1:9), mp 136–137°. It analysed for $C_{18}H_{18}O_7$ (C, 62.52; H, 5.29. $C_{18}H_{18}O_7$ requires: C, 62.42; H, 5.20%). $[\alpha]_D^{30}$ ±0° (MeOH, *c* 0.5).

Dehydration of aglycone monoacetate. $POCl_3$ (3 drops) was added to the aglycone monoacetate (50 mg) in 1 ml C_5H_5N and heated at 60° for 1 hr. Work-up gave a product, mp 89–90°. It analysed for $C_{18}H_{16}O_6$ (C, 66.02; H, 5.02. $C_{18}H_{16}O_6$ requires: C, 65.85; H, 4.87%).

Deacetylation of BB_2. BB_2 was deacetylated in the same way as BB_1 to give a compound, mp 196–197°. (Found: C, 57.1; H, 4.59. $C_{22}H_{26}O_{11}$ requires: C, 56.80; H, 5.57%).

Hydrolysis of BB_2. BB_2 was hydrolysed in the same way as BB_1. The aglycone analysed for $C_{16}H_{16}O_6$ (C, 64.00; H, 5.34. $C_{16}H_{16}O_6$ requires: C, 63.15; H, 5.26%). The sugar obtained was glucose and was identified by PC.

Acknowledgements—We thank the Director, Dr. C. K. Atal, for his fruitful suggestions and facilities. We also thank Dr. Baddley for MS, B. P. Jallali for ^{1}H NMR and the CSIR for financial assistance to one of us (S. K. K.).

REFERENCES

1. Sarin, Y. K. and Kapur, L. D. (1963) *Perfum. Essent. Oil Rec.* **54**, 437.
2. Gupta, B. K., Wali, B. K., Vishwapaul and Handa, K. L. (1964) *Indian J. Chem.* **2**, 464.
3. Basa, S. C., Chatterji, J. and Asima, C. (1970) *Chem. Ind.* **23**, 746.
4. Kuznetswa, G. A. (1961) *Zh. Obshch. Khim.* **31**, 3818 (from *CA* **47**, 128698A).
5. Hata, K., Kozawa, M., Yen, K. and Kimura, V. (1963) *J. Pharm. Soc. Jpn.* **83**, 611.
6. Nielson, Bent, E. and Lemmich, J. (1964) *Acta Chem. Scand.* **18**, 1379.
7. Murakami, S., Robertson, A. and Robinson, R. (1931) *J. Chem. Soc.* 2665.
8. Bandopadhyaya, M. and Seshadri, T. R. (1970) *Indian J. Chem.* **8**, 1146.
9. Bandopadhyaya, M. and Seshadri, T. R. (1973) *Indian J. Chem.* **11**, 410.
10. Dreyer, D. L. (1966) *Tetrahedron* **22**, 2923.