

Die IR-Überlagerungsspektren von DF-F₂ mit auth. Hispidulin (5,7,4'-Trihydroxy-6-methoxyflavon) sind deckungsgleich und im Mischschmp. keine Depression.

DF-F₃. Hellgelbe Nadeln aus MeOH. Trotz mehrmaliger Polyamid-SC nicht in ganz reiner Form, Schmp.-Bereich 242–250°. UV: (MeOH) $\lambda_{\max}$ 276, 335; (NaOAc) $\lambda_{\max}$ 278, 353; (NaOAc-H₃BO₃) $\lambda_{\max}$ 276, 335. IR: (KBr) Hydroxyl 2750–3600 cm⁻¹, Carbonyl 1650 cm⁻¹. NMR: (DMSO) δ = 3,78 (3H, s, -OCH₃), δ = 3,86 (3H, s, -OCH₃), δ = 6,59 (1H, s, H-8), δ = 6,82 (1H, s, H-3), δ = 7,08 (2H, d, H-3' u. H-5', J 9), δ = 8,00 (2H, d, H-2' u. H-6', J 9), δ = 12,80 (1H, s, C₅-OH). Nach NMR-Daten handelt es sich bei DF-F₃ um einen Dimethyläther des Scutellareins (5,6,7,4'-Tetrahydroxyflavon) und UV-Verschiebungen deuten auf die Struktur 6,7-Dimethoxyscutellarein (*Cirsimaritin*, Schmp. 258–259°)³ hin.

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³ FARKAS, L., STRELISKY, J. und MAJOR, A. (1967) *Acta Chim. Acad. Sci. Hung.* **53**, 211.

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NEW ISOFLAVONE GLYCOSIDES FROM *IRIS FLORENTINA*

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Recently the presence of irilone (5,4'-dihydroxy-6,7-methylenedioxy-isoflavone)¹ has been described from *Iris germanica* L. We wish to report the isolation and structure determination of two new isoflavone glycosides, irilone-4'-glucoside (I) and irisolone-4'-bioside (II), from the rhizomes of *I. florentina* L. (white flowered variety, cultivated in Kobe City). Isoflavones previously reported from the rhizomes of the species include irigenin, iristectorigenin-B, irisolone, irisflorentin² and irifloside.³ Isolation of the acetates of the new glycosides from the EtOH extract was accomplished by a conventional acetylation, followed by column chromatography on silica gel. GLC estimation on the content ratio of I or II to iridin, the major isoflavone, was ca. 0.1 or 0.3, respectively.

Irilone-4'-glucoside (I). Penta-acetate: colorless needles from CHCl₃-MeOH, m.p. 233–235°; MS *m/e* 670 (M⁺), 340.0576 (Calc. for C₁₈H₁₂O₇: 340.0583; aglycone mono-acetate), 331.1033 (Calc. for C₁₄H₁₀O₉: 331.1029; tetraacetyl pyronium ion), 271 (331-HOAc), 211 (331-2HOAc), 169 (211-CH₂CO); UV (EtOH) nm 260, 320 (infl.), unshifted by NaOAc, AlCl₃ or NaOH; IR (CHCl₃) cm⁻¹ 1750, 1234 and 1040 (acetate), 1646 (C=O), 923 (OCH₂O); NMR (CDCl₃) δ ppm 2.03s and 2.06s (12H, 4OAc), 2.40s (3H,

¹ DHAR, K. L. and KALLA, A. K. (1973) *Phytochemistry* **12**, 734.

² MORITA, N., ARISAWA, M., KONDO, Y. and TAKEMOTO, T. (1973) *Chem. Pharm. Bull.* **21**, 600.

³ MORITA, N., ARISAWA, M., KONDO, Y. and TAKEMOTO, T. (1973) presented at the 93th Annual Meeting of Pharmaceutical Society of Japan (April 1973).

arom. OAc), 3·7–5·4 (7H, glucose), 6·12s (2H, OCH₂O), 6·80s (1H, C₈-H; a typical down-field shift in the 5-acetoxy flavonoids),^{2,4} 6·9–7·6 *AA'BB'* type ($J_{AB} \simeq J_{A'B'} \simeq 8\cdot8$ Hz; 4H, C_{2',3',5',6'}-H), 7·80s (1H, C₂-H); acid hydrolysis produced glucose (GLC and Glucostat reagent) and the aglycone irilone (m.p., UV, IR, NMR, MS; TMSi ether, NMR, GLC).

Irisolone-4'-bioside (II). Hepta-acetate: colorless crystals from MeOH, m.p. 173–175°; MS *m/e* 930 (M⁺), 629 (M⁺-301),⁵ 619·1843 (Calc. for C₂₆H₃₅O₁₇: 619·1874; hepta-acetyl glucosyl pyronium ion), 331·1020 (Calc. for C₁₄H₁₉O₉: 331·1029; tetraacetyl pyronium ion), 312·0620 (Calc. for C₁₇H₁₂O₆: 312·0634; aglycone), 284 (312-CO), 271 (331-HOAc), 211 (331-2HOAc), 169 (211-CH₂CO); UV (EtOH) nm 263, 322 (infl.), unshifted by NaOAc, AlCl₃ or NaOH; IR (CHCl₃) cm⁻¹ 1750, 1234 and 1040 (acetate), 1644 (C=O), 926 (OCH₂O); NMR (CDCl₃) δ ppm 1·89s, 1·99s, 2·02s, 2·05s and 2·07s (21H, 7OAc), 4·08s (3H, OMe), 3·7–5·4 (14H, biglucose), 6·08s (2H, OCH₂O), 6·66s (1H, C₈-H), 6·95–7·7 *AA'BB'* type ($J_{AB} \simeq J_{A'B'} \simeq 8\cdot6$ Hz; 4H, C_{2',3',5',6'}-H), 7·92s (1H, C₂-H); acid hydrolysis produced glucose (GLC and Glucostat reagent, no indication of any other sugar) and the aglycone irisolone (m.p., UV, IR, NMR, MS; TMSi ether, NMR, GLC).

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⁴ HILLIS, W. E. and HORN, D. H. S. (1965) *Australian J. Chem.* **18**, 531; (1966) **19**, 705; PACHLER, K. G. R. and ROUX, D. G. (1967) *J. Chem. Soc. C*, 604.

⁵ JOHNSON, G. S., RULIFFSON, W. S. and COOKS, R. G. (1970) *Chem. Commun.* 587.