Phytochemistry, 1979, Vol. 18, pp. 175–176. © Pergamon Press Ltd. Printed in England.

0031-9422/79/0101-0175 $02.00/0

SHORT REPORTS

ORUWACIN, A NEW IRIDOID FERULATE FROM *MORINDA LUCIDA*

E. KAYODE ADESOGAN

Department of Chemistry, University of Ibadan, Ibadan, Nigeria

(*Revised received* 12 *June* 1978)

Key Word Index—*Morinda lucida*; Rubiaceae; oruwacin; iridoid ferulate.

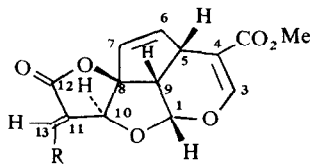
The isolation of oruwal and oruwalol together with many anthraquinones from the stem of *Morinda lucida* [1] aroused our curiosity as to whether other extracts from the plant would throw more light on the biosynthesis of anthraquinones in higher plants. We have therefore been looking at other parts of this plant collected in Benue Road, University of Ibadan and identified by the Federal Department of Forestry Research, Ibadan, with whom a herbarium specimen No. FHI 84187 is filed. The petrol extract of the leaves afforded a new colourless solid (*ca* 0.5 g/kg) named oruwacin. Oruwacin is produced in extractable amounts for only *ca* 3 weeks in the year, at the end of the rainy season (November).

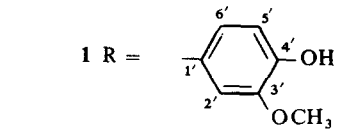
Oruwacin (**1**) was eluted with ether from a Si gel column and crystallized from MeOH as colourless needles mp 223°, $[\alpha]_D^{25}$ $CHCl_3$ +193°, and its molecular formula was shown to be $C_{21}H_{18}O_8$ by MS and elemental analysis. It had IR absorptions at ν_{max}^{Nujol} cm^{-1}: 3550 (OH), 1755 ($\alpha\beta$-unsaturated-γ-lactone), 1710 (C=C—CO_2CH_3), 1660 (C=C—O) and 1602 (C=C).

Oruwacin formed a colourless monoacetate mp 168–169° and a monomethyl ether with CH_2N_2, mp 216°. The OH was shown to be enolic by $FeCl_3$, consistent with its UV spectrum, λ_{max}^{EtOH} nm (log ε) 205 (4.05), 241 (4.08), sh 317 (3.84), 348 (4.13), that underwent a pronounced bathochromic shift from 348 to 423 nm on addition of NaOH. With the exception of the absorption at 241 nm assigned to the O—C=C—CO_2CH_3 chromophore [2] all the UV absorptions were assigned to a ferulate chromophore [3].

The signals in the ^1H NMR spectrum (100 MHz, TMS, $CDCl_3$) were assigned (with the aid of double resonance experiments where appropriate) as: δ 3.55 (*dd*; J = 9, 6 Hz; H-9), 4.06 (*ddd*; J = 9, 2, 2 Hz; H-5), 3.78 (*s*, CO_2CH_3), 5.21 (*brs*, H-10), 5.61 (*dd*; J = 2, 6 Hz; H-6 or H-7), 6.02 (*dd*; J = 2, 6 Hz; H-6 or H-7), 5.63 (*d*, J = 6 Hz; H-1), 7.45 (*s*, H-3), 7.75 (*brs*; H-13), 3.92 (*s*, ArO CH_3), 6.1 (*brs*, exchange with D_2O; OH), 6.97 (*d*; J = 2.5 Hz; H-2′). Signals corresponding to 21 carbon atoms were seen in the ^{13}C NMR spectrum (25.2 MHz. TMS, $CDCl_3$). The tentative assignments for the carbon atoms were based essentially on those reported for gardenoside [4]; δ 38.69 (C-5), 51.73 (C-9), 54.30 ($CO_2\underline{C}H_3$), 56.14 (ArO $\underline{C}H_3$), 82.31 (C-10), 102.39 (C-8) 104.36 (C-1), 112.70 (C-4), 147.16 (C-3), 149.24 (C-4′), 152.86 (C-3) 166.64 ($\underline{C}O_2Me$), 169.87 (C-12).

The remaining eight signals at 115.21, 120.27, 125.99, 126.37, 126.54, 126.99, 140.97 and 144.77 were due to the remaining aromatic and olefinic carbon atoms. The ^1H NMR data, particularly the coupling pattern of the non-ferulate portion of the molecule, were remarkably similar to those reported [5, 6] for plumericin (**2**). Like **2**, compound **1** absorbed 3 mol equivalents of hydrogen in 30 min on hydrogenation in EtOH with 10% Pd/C at NTP to give the hexahydro derivative, mp 184–185°, in which the γ-lactone and —CO_2Me remained intact. Furthermore, the significant fragments observed at *m/e* 369, 367, 366, 338, 337, 310, 309 in the MS of oruwacin have exact parallels in that of plumericin [7, but compare 8].





1 R =

2 R = CH_3

All the data suggest a very close relationship between oruwacin (**1**) and plumericin (**2**). Furthermore, the near identity of the specific rotation of oruwacin with that for plumericin ($[\alpha]_D^{25}$ +197°) is taken as being indicative of the same absolute stereochemistry in the two compounds. Structure **1** is therefore proposed for oruwacin.

Oruwacin consists of a C_6-C_3 unit (the ferulate) and the C_{10} unit (the iridoid moiety). The iridoid moiety is probably biosynthesized as in plumeride, a glucoside closely related to **2** which has been shown to be biosynthesized from mevalonate and acetic acid in which the latter is solely incorporated into C-11, C-12, C-13 and C-14 [9]. The ferulate portion is assumed to be derived from shikimic acid [10]. It is not yet clear what role, if any, oruwacin plays in the biosynthetic pathway of anthraquinones which are proposed to proceed by the shikimate–mevalonate pathway in higher plants [1].

Acknowledgements—The author thanks Mr. G. A. Adesida and his group for providing *M. lucida* crude

extract, and Dr. Emsley and Mrs. J. Street, University of Southampton, England for the NMR spectra.

REFERENCES

1. Adesogan, E. K. (1973) *Tetrahedron* **29**, 4099.
2. Sheith, K., Ramstad, E. and Wolinsky, J. (1961) *Tetrahedron Letters* 394.
3. Aulin-Erdtman, G. and Sanden, R. (1968) *Acta Chem. Scand.* **22**, 1187.
4. Bailleul, F., Delaveau, P., Alain, R., Plat, M. and Koch, M. (1977) *Phytochemistry* **16**, 723.
5. Albers-Schonberg, G. and Schmid, H. (1961) *Helv. Chem. Acta.* **44**, 1447.
6. Kupchan, S. M., Dessertine, A. L., Blaylock, B. T. and Bryan, R. F. (1974) *J. Org. Chem.* **39**, 2477.
7. Pai, B. R., Subramaniam, P. S. and Rao, U. R. (1970) *Indian J. Chem.* **8**, 851.
8. Bentley, T. W., Johnstone, R. A. W. and Grinshaw, J. (1967) *J. Chem. Soc. (C)* 2234.
9. Yowell, D. A. and Schmid, H. (1964) *Experientia* **20**, 250.
10. Geissman, T. A. and Crout, D. H. G. (1969) in *Organic Chemistry of Secondary Plant Metabolism*. p. 143. Freeman, Cooper, San Francisco.

Phytochemistry, 1979, Vol. 18, p. 176. © Pergamon Press Ltd. Printed in England.

DITERPENES OF THE FERRUGINOL TYPE FROM *CHAMAECYPARIS PISIFERA*

MITSUYOSHI YATAGAI and TOSHIO TAKAHASHI
Forestry and Forest Products Research Institute, P.O. Box 02, Ushiku, Ibaraki 300-12, Japan

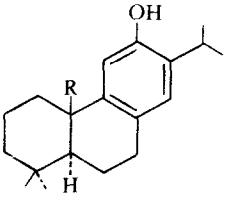
(*Received* 23 *June* 1978)

Key Word Index—*Chamaecyparis pisifera*; Cupressaceae; ferruginol type; methyl pisiferate; pisiferol.

In a previous paper [1], we reported the isolation of a new phenolic diterpene acid, pisiferic acid (**1**), from the leaves of *Chamaecyparis pisifera* (Cupressaceae). Further examination of the leaves has now led to the isolation of a phenolic diterpene alcohol (**2**), named pisiferol, and methyl pisiferate (**3**) [1].

On the basis of the spectral data (IR, NMR, UV spectra), pisiferol (**2**) was identified as 12-hydroxyabieta-8,11,13-trien-20-ol which had been synthesized previously by us from pisiferic acid (**1**) by treatment with sodium dihydro-bis(2-methoxyethoxy)aluminate [1]. It was for the first time that pisiferol (**2**) and methyl pisiferate (**3**) were isolated from natural sources.

Although the presence of ferruginol (**4**) [2] was estimated by co-chromatography (TLC, Si gel) of the methanol extract with an authentic sample, ferruginol could not be isolated because of its small content in the leaves.



1 R = CO_2H
2 R = CH_2OH
3 R = CO_2Me
4 R = CH_3

EXPERIMENTAL

Pisiferol (**2**). The fresh leaves of *Chamaecyparis pisifera* (200 g), collected in Tokyo in January 1978, were extracted with MeOH for 1 week. Evapn yielded an extract (5 g), which was partitioned between Et_2O and H_2O. The Et_2O-soluble fraction (2 g) was chromatographed on Si gel (Merck, Kieselgel 60, 70–230 mesh 80 g). Elution with C_6H_6 followed by Et_2O yielded an enriched pisiferol fraction (250 mg), and a portion (150 mg) of the enriched fraction was subjected to PLC on Si gel (Merck, Kieselgel $GF_{254+366}$, eluent $CHCl_3$–HOAc, 20:1) to give crude pisiferol. The crude pisiferol was recrystallized from C_6H_6–Et_2O to give pure needles of pisiferol (**2**) (95 mg).

Methyl pisiferate (**3**). A portion (1 g) of the above MeOH extract was chromatographed on Si gel. Elution with *n*-hexane followed by C_6H_6 yielded a crude phenolic diterpene alcohol fraction (140 mg). The fraction was rechromatographed on Si gel to give a pure compound (82 mg) which was identical (TLC, IR, NMR spectra) with the authentic sample of methyl pisiferate (**3**).

Chromatography of the C_6H_6 extract of the leaves on Si gel using C_6H_6 as eluent also gave methyl pisiferate (**3**).

REFERENCES

1. Yatagai, M., Shirato, T., Hayashi, Y., Fukuhara, N. and Takahashi, T. (1978) *Mokuzai Gakkaishi* **24**, 267.
2. Brandt, C. W. and Neubauer, L. G. (1939) *J. Chem. Soc.* 1031.