Phytochemistry, Vol. 23, No 9, pp 2098–2099, 1984
Printed in Great Britain

0031–9422/84 $3.00 + 0 00

A PYRANOCOUMARIN FROM *ATALANTIA CEYLANICA*

JAMAL AHMAD, K. M. SHAMSUDDIN and ASIF ZAMAN

Department of Research in Unani Medicine and Department of Chemistry, Aligarh Muslim University, Aligarh 202001, India

(*Received* 11 *November* 1983)

Key Word Index—*Atalantia ceylanica*; Rutaceae; 7,8-dimethoxy-5,6-pyranocoumarin; 8-methoxy-6,7-furanocoumarin.

Abstract—Ceylantin, assigned the structure 7,8-dimethoxy-5,6-pyranocoumarin, and xanthotoxin have been isolated from the heartwood of *Atalantia ceylanica*.

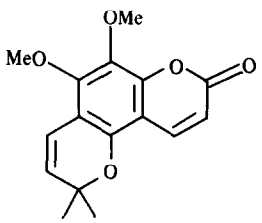
The requirement of large quantities of xanthotoxin by indigenous (Unani) medical centres for the treatment of leucoderma made it necessary to look for new sources of this compound. *Atalantia ceylanica* was collected from Western Ghat and its air-dried heartwood cut into small pieces and percolated with benzene. Chromatographic separation of the extracted constituents afforded xanthotoxin and a solid. The NMR spectrum of the solid revealed it to be a mixture of xanthotoxin and a new compound, ceylantin. Separation proved tedious but was ultimately achieved through repeated fractional crystallization from chloroform, and supplied xanthotoxin (combined yield 0.56%) and ceylantin (0.15%).

Ceylantin, mp 126–127° ($[M]^{+\cdot}$ at 288.1007; $C_{16}H_{16}O_5$ requires: 288.0998) is assigned a coumarin structure on the basis of IR absorption at 1720 cm^{-1} and bands at 249 and 301 nm in the UV spectrum. AB quartets at δ5.77, 6.65 and 6.26, 7.85 (J = 10 Hz) and singlets at δ1.57 (6H) and 3.84, 3.94 (3H) in the ^{1}H NMR spectrum establish the presence of the pyranocoumarin ring system with two methoxyls but do not distinguish between linear and angular isomers.

Since a 7-hydroxycoumarin may carry the C-5 side chain at the 5-, 6- or 8-positions, four structures are possible for the derived dimethoxycoumarin, three angular and one linear. A nuclear Overhauser effect (NOE) between the methyl and C-4 hydrogen is possible only in two cases and in one of these must be accompanied with an NOE between the methyl and the chromene α-hydrogen as well (Table 1). An NOE with just the chromene hydrogen is possible in only one structure. Irradiation of the C-4 H signal had no effect on the intensity of the methoxyl signals, excluding the presence of one at C-5. Additionally, irradiation of the C-4′ hydrogen or the methoxyl hydrogens at δ3.94 demonstrated the existence of an NOE between these. This establishes the structure of ceylantin as the angular pyranocoumarin (**1**).

Trioxygenated coumarins are rare in the Rutaceae and when present the oxygenation is specifically 5,7,8 in *Ruta* and 6,7,8 in *Zanthoxylum* [1]. *Atalantia* appears to be taxonomically related to *Ruta* because of the four species examined so far [2–5], two have yielded 5,7,8-trioxygenated coumarins.

Acknowledgements—We are grateful to Dr Peerzada, S. H. Khan, Scientist, National Botanical Research Institute, Lucknow, for his help in the collection and identification of plant material, and to the CCRUM, New Delhi, for financial assistance.



1

Table 1. Nuclear Overhauser effect (%) observed (δ ppm) for ceylantin (**1**) in $CDCl_3$

	Observed signals					
Saturated signals	3′-H 5.77	4′-H 6.65	3-H 6.26	4-H 7.85	OMe 3.84	OMe 3.94
3.84 (OMe)	0	+26.08	0	0	N.O.	N.O.
3.94 (OMe)	0	+27.3	0	0	N.O.	N.O.
6.65 (4′-H)	0	0	−10	0	0	+20.3
7.85 (4-H)	0	0	0	0	0	0

N.O. = Not observed.

REFERENCES

1. Gray, A. I. and Waterman, P. G. (1978) *Phytochemistry* **17**, 845.
2. Barua, A. K., Banerjee, S. K., Basak, A., Chakravartis, S., Ghosh, S., Sethi, K. and Bose, P. K. (1974) *Phytochemistry* **13**, 2017.
3. Desai, H. K., Gawad, D. H., Govindachari, T. R., Joshi, B. S., Kamat, V N., Modi, J. D., Mohamed, P. A., Parthasarthy,

P. C., Patankar, S. J., Sidhaye, A. R. and Viswanathan, N. (1970) *Indian J. Chem.* **8**, 851.
4. Talapatra, S. K., Bhattacharya, S. and Talapatra, B. (1970) *J. Indian Chem. Soc.* **47**, 600.
5. Desai, P. D., Ganguly, A. K., Govindachari, T. R., Joshi, B S., Kamat, V. N., Manmade, A. H., Mohamed, P. A., Nagle, S. K., Nayak, S. K., Saksena, A. K., Sothe, S. S. and Viswanathan, N. (1966) *Indian J. Chem.* **4** 457.

Phytochemistry, Vol. 23, No. 9, pp. 2099–2101, 1984
Printed in Great Britain.

0031-9422/84 $3 00+0 00

MINOR LIGNANS OF *PIPER CLUSII*

S. K. KOUL, S. C. TANEJA, K. L. DHAR* and C. K. ATAL

Regional Research Laboratory, Jammu Tawi 180001, India

(*Revised received* 30 *January* 1984)

Key Word Index—*Piper clusii*; Piperaceae; new lignans.

Abstract—Further investigations on the petrol extract of *Piper clusii* have afforded four more new lignans. These are 2*S*,3*R*,4*R*,2-ethoxy-3-(3,4,5-trimethoxyphenyl)methyl 4-(1,3-benzodioxol-5-yl) methyl tetrahydrofuranol; 3*R*,4*R*,*bis*-3,4-(3,4,5-trimethoxyphenyl) methyl tetrahydrofuran-2-one; 2*R*,3*R*,2-(7-methoxy-1,3-benzodioxol-5-yl) methyl 3-(3,4,5-trimethoxyphenyl) methyl butan-1,4-diol and 2*R*,3*R*,2-(1,3-benzodioxol-5-yl) methyl 3-(3,4,5-trimethoxyphenyl) methyl butan-1,4-diol. This is the first report of these compounds from a natural source.

INTRODUCTION

Recently we have reported the presence of a new lignan, (−)-clusin **1** from the petrol extract of *Piper clusii* [1]. It is the precursor of an active anti-cancer compound namely steganacin [2] and could also be one of the possible biogenetic precursors of the same. Further exhaustive chemical investigations on the petrol extract of this plant have resulted in the isolation and characterisation of four more new minor lignans, viz **2**–**5**. Two of these, **2** and **5**, belong to the same aromatic substitution class as clusin. The compounds characterized are 2*S*,3*R*,4*R*,2-ethoxy-3-(3,4,5-trimethoxyphenyl) methyl 4-(1,3 benzodioxol-5-yl) methyl tetrahydrofuranol (**2**), 3*R*,4*R-bis*-3,4-(3,4,5-trimethoxyphenyl) methyl tetrahydrofuran-2-one (**3**), 2*R*,3*R*,2-(7-methoxy 1,3-benzodioxol-5-yl) methyl 3-(3,4,5-trimethoxy phenyl) methyl butan-1,4-diol (**4**), and 2*R*,3*R*,2-(1,3-benzodioxol-5-yl) methyl 3-(3,4,5 trimethoxyphenyl) methyl butan-1,4-diol (**5**).

RESULTS AND DISCUSSION

Lignan **2** is a semi-solid which analysed for $C_{24}H_{30}O_7$ and is also corroborated by its mass spectrum ($[M]^+$ at *m/z* 430). It differs from clusin by an ethyl group in its molecular formula. In the IR of the compound no absorption was observed for carbonyl or alcoholic functions. In the ^{1}H NMR methylenedioxy protons were observed at δ 5.90 as a sharp singlet. Another broad singlet at δ 4.30 is assigned to an acetalic proton. The weak coupling of this proton with the vicinal methine proton is explained when both have the *cis* orientation. The signals for methine as well as four benzylic protons were located as an envelope between δ 2.0–2.8. A triplet at δ 1.20 (J = 7 Hz) for three protons shows the presence of a methyl group adjacent to a methylene. The presence of such a signal is indicative of an ethoxyl grouping. The signals for OCH_2 protons were however, submerged in the other proton signals for methoxyls and the tetrahydrofuran system observed between δ 3.4 and 4.2. This data clearly indicates that **2** is the ethyl ether of clusin—a hemiacetalic lignan which is also supported by its molecular formula.

The possibility of **1** being an artifact is ruled out from the fact that at no stage of the processing was ethanol used and its presence has also been confirmed by comparison with the original extract on TLC.

Paucity of this compound prevented us from doing any further chemical reaction on it. However, the proof for its final structure came when clusin was converted into **2** by reaction with ethanol and *p*-toluenesulphonic acid. One of the products obtained during this transformation was found to be same as **2** which was confirmed by its superimposable IR and co-TLC. As clusin and **2** both have the same sign of rotation, their configuration at C-2 and C-3 should also be same. The structure has also been supported by mass spectrometry.

Lignan **3** is a semi-solid which analysed for $C_{24}H_{30}O_8$. The mass spectrum showed $[M]^+$ at *m/z* 446. In the IR of the compound a strong absorption was observed at 1770 cm^{-1} which clearly indicated the presence of a five membered lactone system. No absorption was observed for a hydroxyl group. The ^{1}H NMR (CCl_4) showed a four proton envelope at δ 2.43 and a narrow two proton envelope at δ 2.76 assigned to benzylic and methine (β, β') protons, respectively. The presence of two such envelopes is indicative of the *trans* stereochemistry of the two methine protons [3]. Two sharp singlets each integrating for two protons at δ 6.10 and 6.23, respectively, were assigned to two symmetrical pairs of protons (2′ and 6′) on the aromatic ring. The signals for six methoxyls were observed at δ 3.78–3.85 and for OCH_2 protons in the form