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Phytochemistry, 1975, Vol. 14, pp. 2309–2310. Pergamon Press. Printed in England.

ALKALOIDS AND COUMARINS FROM *ZANTHOXYLUM BELIZENSE*

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(*Received* 26 *March* 1975)

Key Word Index—*Zanthoxylum belizense*; Rutaceae; alkaloids; coumarins; skimmianine; dictamnine; platydesmine; canthine-6-one; citropten; marmesin; isopimpinellin.

Plant. Zanthoxylum belizense (Lundell). A herbarium specimen is deposited at the Herbarium of the National Arboretum, Agricultural Research Service, U.S. Department of Agriculture, Washington, D.C., Beltsville, MD. *Source.* Panama, Material collected in 1972. *Previous work.* No phytochemical or pharmacological work has been reported on this species.

Present work. Dried, ground twig and leaf material (5 kg) was extracted with petrol (bp 40–60°) and subsequently with MeOH. The MeOH extract (462 g) was partitioned between $CHCl_3$ (5 × 900 ml) and H_2O (1 × 1). The $CHCl_3$ soln was extracted with 5% HCl (600 ml), dried (Na_2SO_4) and evaporated to afford fraction A (87 g). The acid solution was basified (pH 9) and extracted with EtOAc (3 × 400 ml). Evaporation of the dried EtOAc soln afforded fraction B (14·6 g). *Fraction A.* The $CHCl_3$ extract (2 g) was dissolved in MeOH, charcoal added, and the mixture filtered hot through Celite. Cooling produced crystals of citropten (70 mg), mp 146° (lit. [1] 147°). Citropten has not previously been reported from any *Zanthoxylum* sp. Chromatography of fraction A (2 g) on Florisil (25 g), and elution with $CHCl_3$, afforded citropten (95 mg) and isopimpinellin (60 mg), mp 150° (lit. [1] 151°). Isopimpinellin was previously isolated from *Z. ovalifolium* [2] *Fraction B.* The total fraction (14·6 g) was chromatographed on Florisil (200 g), eluting with $CHCl_3$. Extensive preparative TLC of the resulting fractions afforded seven compounds. Citropten (57 mg) and isopimpinellin (60 mg) were again isolated. In addition, platydesmine (73 mg), mp 137° (lit. [3] 139°); marmesin (5 mg), mp 185° (lit. [4] 189°); dictamnine (10 mg), mp 131° (lit. [5] 134°); skimmianine (54 mg), mp 174° (lit. [5] 177°) and canthin-6-one (5 mg), mp 158° (lit. [6] 159°) were isolated. All compounds isolated were identified by their UV, IR, NMR, Mass spectral and TLC data, by comparison with those of authentic samples. Platydesmine has not previously been isolated from any *Zanthoxylum* sp. Marmesin was previously isolated from *Z. arnottianum.* [7, 8] Dictamnine was previously isolated from *Z. cuspidatum* [9] and *Z. decaryi.* [5] Skimmianine was previously obtained from *Z. decaryi*, [5] *Z. pluviatile*, [10] *Z. piperitum*, [11] *Z. cuspidatum* [9], and *Z. schinifolium* [12]. Canthin-6-one was previously isolated from *Z. ovalifolium*

[2], *Z. elephantiasis* [6, 13], and *Z. suberosum* [14, 15].

Acknowledgements—The authors are indebted to Dr. R. E. Purdue, Medical Plant Resources Laboratory, Plant Genetics and Germplasm Institute, Beltsville, M.D., for the supply and botanical identification of the plant material and to Prof. I. D. Spenser, J. L. Beal, H. G. Floss and Dr. W. Steck for authentic samples.

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Phytochemistry, 1975, Vol. 14, pp. 2310–2311. Pergamon Press. Printed in England.

ZWEI NEUE ANTHRACHINONE AUS DEN WURZELN VON *DIGITALIS ORIENTALIS**

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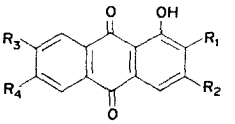
(*Received* 17 *March* 1975)

Key Word Index—*Digitalis orientalis*; Scrophulariaceae; anthraquinones.

Pflanze und Herkunft. Digitalis orientalis Lam.; gesammelt zusammen mit den Wurzeln im Juli 1972 in der Nähe von Kizilcahamam/Ankara, Türkei.

Isolierung und Identifizierung. Die getrockneten Wurzeln der Pflanze wurden mit 96% igem EtOH erschöpfend perkoliert. Nach Entfernung von EtOH wurde der wässrige Rückstand mit C_6H_6 extrahiert und dann chromatographierten wir den eingeengten C_6H_6-Extrakt an einer Kieselgelsäule mit C_6H_6. Aus den Fraktionen, die gruppenweise getrennten Anthrachinone enthielten, konnten wir mit Hilfe von präparativer Kieselgel-DC und Polyamid-SC zehn Farbstoffe in reiner und kristalliner Form isolieren. Sie wurden mit den Bezeichnungen von A_1 bis A_{10} gekenzeichnet.

Durch Vergleich mit authentischen Substanzen (Cochromatographie, Mischschmp., UV- und IR-Spektroskopie) stellten wir fest, dass acht von diesen Farbstoffen mit den folgenden Verbindungen identisch sind: A_1 = 1,5-Dihydroxy-3-methylanthrachinon (Ziganein) [1], A_2 = 1-Hydroxy-3-methylanthrachinon (Pachybasin) [2], A_3 = 1,8-Dihydroxy-2-methylanthrachinon (Isochrysophanol) [3], A_4 = 2,5-Dihydroxy-1-methoxy-3-methylanthrachinon (5-Hydroxydigitolutein) [4,5], A_5 = 2-Hydroxy-1-methoxy-3-methylanthrachinon (Digitolutein) [6], A_6 = 5-Hydroxy-1-methoxy-3-methylanthrachnion (Ziganein-1-methyläther) [1], A_7 = 4-Hydroxy-



(1) $R_1 = CH_2OH$, $R_2 = R_3 = R_4 = H$
(2) $R_2 = CH_2OH$, $R_1 = R_3 = R_4 = H$
(3) $R_3 = CH_2OH$, $R_1 = R_2 = R_4 = H$
(4) $R_4 = CH_2OH$, $R_1 = R_2 = R_3 = H$
(5) $R_2 = COOH$, $R_1 = R_3 = R_4 = H$

* Mitt. 9 über "Flavon und Anthrachinon-Farbstoffe der Digitalis-Arten". Mitt. 8. (1973) *Phytochemistry* **12**, 2317.