

Phytochemistry, 1974, Vol. 13, pp. 757 to 758. Pergamon Press. Printed in England.

## NEW ISOFLAVONE GLUCOSIDES FROM THE BARK OF *CLADRASTIS PLATYCARPA*

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(Received 2 October 1973. Accepted 14 October 1973)

**Key Word Index**—*Cladrastis platycarpa*; Leguminosae; isoflavone glucosides; platycarpanetin-7-*O*- $\beta$ -monoglucoside; 8-methoxyretusin-7-*O*- $\beta$ -glucosylglucoside; formononetin-7-*O*- $\beta$ -glucosylglucoside.

*Plant.* *Cladrastis platycarpa* Makino (Japanese name: fujiki), tree, Leguminosae (subfamily Lotoideae). *Source.* Yamato-mura, Gifu Pref., Japan. *Previous work.* On barks<sup>1,2</sup> and wood<sup>3</sup> of *C. platycarpa*, woods of *C. lutea*<sup>4</sup> and *C. amurensis*.<sup>5</sup>

*Trunk bark.* The powdered barks (7 kg) were percolated with hot MeOH, and then the concentrated extract was successively treated with *n*-hexane, Et<sub>2</sub>O, EtOAc and *n*-BuOH. The Et<sub>2</sub>O soluble portion of the extract was chromatographed on silica followed by fractional recrystallization, affording fujikinetin (7-hydroxy-6-methoxy-3',4'-methylenedioxyisoflavone), 5-methoxy-afrormosin, platycarpanetin (7-hydroxy-5,8-dimethoxy-3',4'-methylenedioxyisoflavone), cladrastin (7-hydroxy-6,3',4'-trimethoxyisoflavone), afrormosin and formononetin. The ethyl acetate soluble fraction of the extract was chromatographed on silica and then fractionally recrystallized from MeOH, giving fujikinin (fujikinetin-7-*O*- $\beta$ -monoglucoside), wistin (afrormosin-7-*O*- $\beta$ -monoglucoside) and a new compound, platycarpanetin-7-*O*- $\beta$ -monoglucoside (**1**). The *n*-butanol soluble part of the extract was chromatographed on silica, yielding two new compounds, 8-methoxyretusin<sup>6</sup> (7-hydroxy-8,4'-dimethoxyisoflavone)-7-*O*- $\beta$ -glucosylglucoside (**2**) and formononetin-7-*O*- $\beta$ -glucosylglucoside (**3**) and one known compound (**4**), ononin (formononetin-7-*O*- $\beta$ -monoglucoside).

The identification of the known compound (**4**) was confirmed by direct comparison with the authentic ononin isolated from the woody portions of this plant. The structures of the three unknown constituents (**1**, **2** and **3**) were deduced from spectral data. The first compound (**1**) afforded an aglycone and sugar in equimolar ratio on acid hydrolysis. The IR spectrum of the aglycone was superimposable on that of authentic platycarpanetin isolated from the woody portions of this species. The sugar moiety was shown to be D-glucose by PC and the  $\beta$ -linkage was revealed both by the coupling constant (7 Hz) in the NMR spectrum and by the enzymatic hydrolysis with emulsin. The structure of this compound (**1**) was, therefore, established to be platycarpanetin-7-*O*- $\beta$ -monoglucoside. The second compound (**2**) gave a 1:2 ratio of aglycone to sugar on quantitative acid hydrolysis. The structure of the aglycone was confirmed by direct comparisons with authentic 8-methoxyretusin<sup>6</sup> and its acetate,<sup>6</sup> kindly provided by Dr. L. Jurd. The sugar moiety was shown to be

<sup>1</sup> IMAMURA, H., HIBINO, Y. and OHASHI, H. (1972) *Mokuzai Gakkaishi* **18**, 325.

<sup>2</sup> IMAMURA, H., HIBINO, Y. and OHASHI, H. (1973) *Mokuzai Gakkaishi* **19**, 293.

<sup>3</sup> OHASHI, H., NOZAKI, K., HIBINO, Y. and IMAMURA, H. (1974) *Mokuzai Gakkaishi* in press.

<sup>4</sup> SHAMMA, M. and STIVER, L. D. (1969) *Tetrahedron* **25**, 3887.

<sup>5</sup> NIKONOV, G. K. (1956) *Aptechnoe Delo* **5** (31), 30; (1957) *Chem. Abstr.*, **51**, 5369c.

<sup>6</sup> JURD, L., STEVENS, K. and MANNERS, G. (1972) *Phytochemistry* **11**, 2535.

a dimer of D-glucose on PC and the  $\beta$ -linkage of the biose to the aglycon was revealed by hydrolysis with emulsin and by the coupling constant (7 Hz) in the NMR spectrum. This compound (2) was consequently identified to be 8-methoxyretusin-7-O- $\beta$ -glucosylglucoside. The third compound (3) also afforded a 1:2 ratio of aglycone and sugar on acid hydrolysis. The resulting aglycone was identical with the authentic formononetin<sup>2</sup> by IR. The form of the sugar-aglycon bonding was found to be  $\beta$ -linkage and the sugar moiety was confirmed to be a dimer of D-glucose by the same methods as those described above. Therefore, the structure of this compound (3) must be formononetin-7-O- $\beta$ -glucosylglucoside.

*Platycarpanetin-7-O- $\beta$ -monoglucoside (1).* Colorless needles, m.p. 142–144° (MeOH). IR (KBr)  $\text{cm}^{-1}$  3400, 1640, 1620, 1600, 1510, 1040, 916. UV (MeOH) nm 258, 300 (sh.). NMR (as TMS ether in  $\text{CCl}_4$ )  $\delta$  ppm 7.67 (s, H-2), 7.00, 6.90, 6.83, 6.77 (m, H-2', H-5', H-6'), 6.70 (s, H-6), 5.94 (s,  $\text{O}_2\text{CH}_2$ ), 4.93 (d, H-1'', J 7.0 Hz), 3.90 (s,  $\text{OCH}_3$ ), 3.83 (s,  $\text{OCH}_3$ ), 3.90 – 3.20 (m, 6 H).

*8-Methoxyretusin-7-O- $\beta$ -glucosylglucoside (2).* Colorless needles, m.p. 194–195° (MeOH). IR (KBr)  $\text{cm}^{-1}$  3400, 2930, 1615, 1590, 1560, 1515, 1065, 1000. UV (MeOH) nm 253, 300 (sh.). NMR (as TMS ether in  $\text{CCl}_4$ )  $\delta$  ppm 7.90 (s, H-2), 7.87 (d, H-5, J 9.0 Hz), 7.43 (d, H-2', 6', J 9.0 Hz), 7.10 (d, H-6, J 9.0 Hz), 6.85 (d, H-3', 5', J 9.0 Hz), 5.03 (d, H-1'', J 7.0 Hz), 4.70 (d, H-1''', J 3.6 Hz), 3.93 (s,  $\text{OCH}_3$ ), 3.79 (s,  $\text{OCH}_3$ ), 3.20 – 3.60 (m, 12 H).

*Formononetin-7-O- $\beta$ -glucosylglucoside (3).* Colorless needles, m.p. 175–176° (MeOH). IR (KBr)  $\text{cm}^{-1}$  3400, 2930, 1620, 1590, 1510, 1070, 1000. UV (MeOH) nm 258, 300 (sh.).

*Acknowledgements*—The authors thank Dr. L. Jurd, Western Regional Research Laboratory, Berkeley, U.S.A., for the supply of 8-methoxyretusin, its methyl ether and acetate.

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Phytochemistry, 1974, Vol. 13, pp. 758 to 760. Pergamon Press. Printed in England.

## A NEW COUMARIN IN *AMYRIS SIMPLICIFOLIA*

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(Received 29 September 1973. Accepted 22 October 1973)

**Key Word Index**—*Amyris simplicifolia*; Rutaceae; 3-(3,3-dimethylallyl)-xanthyletin.

*Amyris simplicifolia* Karst (Rutaceae) is a perennial tree found in the Northern part of South America, where it grows in temperate climate near the sea.<sup>1</sup> *Source*. Chamariapa, East of Cumaná (Voucher specimen No. Bhat 0598 deposited in the University). *Previous work*. None.

*Present work*. The concentrated light petrol. extract of the leaves of the plant on standing for 2 days at 0° deposited yellow plates of an optically inactive substance which after recrystallization from  $\text{CHCl}_3$ –MeOH had a sharp m.p. (103–104°). It gave a blue single UV

<sup>1</sup> SCHIEL, L. (1960) *Revista de la Facultad de Agronomía, Alcanje* (3), 1311.