

THE LIGNANS OF *Gmelina asiatica*A. S. R. ANJANEYULU, A. MADHUSUDHANA RAO,
V. KAMESWARA RAO and L. RAMACHANDRA ROW

Department of Chemistry, Andhra University, Waltair 530003, India

(Received 23 September 1974)

Key Word Index — *Gmelina asiatica*; Verbenaceae; lignans: gmelinol; paulownin; cyclooolivil; lignan precursors: methyl *p*-methoxy- and *p*-hydroxy-cinnamates.

Our recent examination of *Gmelina arborea* L., revealed a series of novel lignans [1, 2] closely related to paulownin. It is now extended to *G. asiatica* L., a large and much branched shrub with a light pinkish red heartwood. This plant has apparently not been examined chemically except for its seed oil [3].

After exhausting the powdered heartwood with *n*-hexane, the methanolic extract was prepared and separated into crystalline components on silica gel as indicated in Table 1.

Table 1. Compounds isolated from *G. asiatica*

Fraction and compound	Eluent	R_f	Physical characteristics
Neutral fraction			
Methyl <i>p</i> -methoxy-cinnamate	Hexane	0.77*	Colourless needles from hexane mp 90
Sitosterol	Hexane	0.62*	Not pursued further
Paulownin	Hexane: C_6H_6 (4:1)	0.53*	Colourless needles from MeOH mp 105 $[\alpha]_D + 34$ (c 1.0 in $CHCl_3$)
Gmelinol	Hexane: C_6H_6 (1:1)	0.17*	Colourless hexagonal plates from EtOAc-Et ₂ O mp 124 $[\alpha]_D + 129$ (c 1.0 in $CHCl_3$)
Phenolic fraction			
Methyl- <i>p</i> -hydroxy-cinnamate	C_6H_6	0.68†	Needles from C_6H_6 , mp 137
Cyclooolivil	EtOAc	0.56‡	Colourless needles from ethyl acetate mp 167 $[\alpha]_D + 65^\circ$ (ethanol)

* C_6H_6 -EtOAc, 9:1.† C_6H_6 .

‡ EtOAc.

All the above compounds were confirmed by comparison with authentic compounds by mmp, IR and in a few cases by NMR also. The tetraacetate of cyclooolivil is now described for the first time. mp 150°, $[\alpha]_D + 3.8^\circ$ (c 1.0 in $CHCl_3$), R_f 0.78 (EtOAc). Found: C, 61.7; H, 5.85; $C_{28}H_{32}O_{11}$ requires C, 61.76 and H, 5.88%. NMR ($CDCl_3$): δ 1.16 to 1.42 *m* (2-H), 2.03s (2- CH_2OAc), 2.11s (3- CH_2OAc), 2.23s (7- $OCOCH_3$), 2.31s (4'- $OCOCH_3$), 2.73s (3-OH), exchanged by D_2O , 2.86d, 3.26d *J* 17.5 Hz (4- CH_3), 3.81s, 3.86s (3':6-OMe), and 4.09 *d* *J* 13 Hz (1-H).

The *Gmelina* species abound with the lignans of the furofuran series. Gmelinol is the major component in all and may be significant for taxonomic purposes. In *Gmelina asiatica*, it occurs along with the corresponding tetralin, cyclooolivil. This is the first instance of a tetralin co-occurring with a furofuran and may possess considerable biogenic significance. Although paulownin has been noted in *G. arborea* and *G. asiatica*, its presence in *G. leichhardtii* requires to be established.

Acknowledgements—Two of us (AMR and VKR) wish to express their thanks to CSIR (India) for fellowships. Our thanks are also due to Dr. Hasegawa, Tokyo Metropolitan University, for a sample of cyclooolivil.

REFERENCES

1. Anjaneyulu, A. S. R., Row, L. Ramachandra and Subrahmanyam, C. (1972) *Tetrahedron Letters* **22**, 2179.
2. Row, L. Ramachandra, Rao, V. Kameswara, Rao, K. Jaganmohan, Pelter, A. and Ward, R. S. (1974) *Chem. Commun.* 476.
3. Aggarwall, J. S. and Soni, Padmini (1949) *J. Sci. Ind. Res. (India)* **8B**, 49.