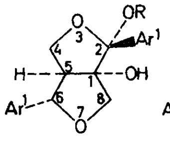
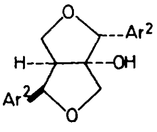
Structure of Gmelanone—A Novel Lignan with the 3,6-Dioxabicyclo[3,2,1]octane Skeleton

By L. Ramachandra Row, K. Jaganmohan Rao, and V. Kameswara Rao
(*Department of Chemistry, Andhra University, Waltair, India*)
and Andrew Pelter* and Robert S. Ward
(*Department of Chemistry, University College of Swansea, Singleton Park, Swansea* SA2 8PP)

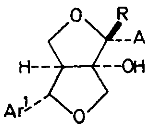
Summary Gmelanone, a lignan from *Gmelina arborea* is shown to have a rearranged carbon skeleton relative to other known lignans; it is the first reported example of a lignan derived from 3,6-dioxabicyclo[3,2,1]octane.



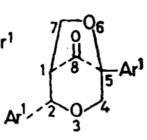
(1) a, R = H
b, R = Me
c; R = Et



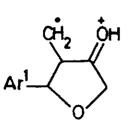
(2)



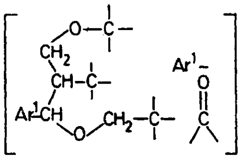
(3) a, R = H
b, R = OH



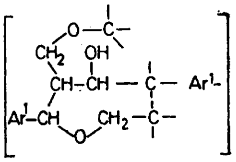
(4)



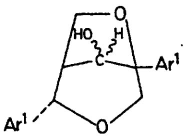
(5)



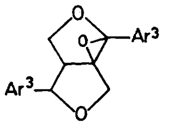
(6)



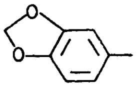
(7)



(8)



(9)

Ar1 =


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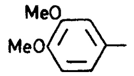
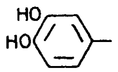


Ar3 =


The isolation of methyl arboreol† (**1b**) and gmelinol (**2**) from *Gmelina arborea* has been previously reported.[1,2] From the same source we have isolated in addition to paulownin (**3a**),[3] four new lignans, three of which, arboreol (**1a**), ethyl arboreol (**1c**), and isoarboreol (**3b**) have the same basic skeleton as methyl arboreol. (Details of the establishment of these structures will be published separately).

The fourth lignan, gmelanone, m.p. 190°, $[\alpha]_D$ −78°, $C_{20}H_{16}O_7$, had ν_{max} 1765 cm^{-1} suggesting it was a γ-lactone or an alicyclic ketone. It further differed from the other lignans isolated in that it had no hydroxy-groups. This compound has been assigned structure (**4**) and is the first example of a lignan derived from 3,6-dioxabicyclo[3,2,1]-octane. Indeed the two dilactones, sceleranecic and sceleratinic dilactones[4] are the only known natural products which formally are derived from this system.

The mass spectrum had the usual peaks at *m/e* 164 $(\overset{\bullet}{\mathrm{Ar}}\mathrm{CH{-}O{-}}\overset{+}{\mathrm{CH}_2})$ and 161 $(\mathrm{ArCH{=}CH{\cdot}CH_2^+})$ suggesting that the sequence of atoms from C-4 to C-8 in the arboreols, gmelinol, eudesmin, *etc.* was intact. However, the peak at *m/e* 220 found in arboreol and gmelinol and for which structure (**5**) has been proposed[5] is missing.

Table

^{1}H N.m.r. data (coupling constants in Hz, in parentheses)

Isoarboreol ($CDCl_3$–Me_2SO)		Gmelanone ($CDCl_3$–Me_2SO)		$LiAlH_4$ reduction product ($CDCl_3$)	$NaBH_4$ reduction product ($CDCl_3$)
4*a*-H	6·23 dd (2, 8)	7*a*-H	5·63 dd (8, 5)	5·88 d (2)	6·17 dd (8, 5)
4*e*-H	5·82 dd (7,8)	7*e*-H	5·39 d (8)		5·86 d (8)
5-H	7·4 m	1-H	6·60 dd (3, 5)	7·03 m	7·56 br.t (5)
6-H	5·53 d (6)	2-H	4·62 d (3)	5·14 d (2)	4·73 br. s
8*a*-H	6·90 d (10)	4*a*-H	6·17 d (11)	6·40 d (12)	6·37 d (11)
8*e*-H	6·65 d (10)	4*e*-H	5·95 d (11)	5·68 d (12)	5·60 d (11)
		8-H	—	5·94[b]	5·80 d (5)
OCH_2O	4·08, 4·09		4·07, 4·12	4·14, 4·20	4·16 (4H)
ArH	2·9—3·3		3·0—3·4	2·7—3·4	2·7—3·4
OH	3·54, 4·72[a]		—	7·78[a]	7·56[a]

[a] Signals disappear on shaking with D_2O. [b] Broad one-proton signal which becomes a sharp doublet (J = 4 Hz) after D_2O exchange.

The ^{1}H n.m.r. spectrum of gmelanone (Table) showed that the molecule contained two 3,4-methylenedioxy-groups and confirmed the part structure‡ (**6**). All the aliphatic protons were shifted downfield by up to 1 p.p.m. relative to the arboreol series, suggesting that the carbonyl group was occupying a central position in the gmelanone molecule.

Reduction with lithium aluminium hydride and sodium borohydride gave the epimeric alcohols (**8**), the ^{1}H n.m.r. spectra of which made it clear that they could be represented by part structure (**7**). This meant that gmelanone

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† This compound has been previously called arboreol but we now, more logically, reserve the name for the parent diol (**1a**).

‡ All ^{1}H n.m.r. assignments are backed by spin-decoupling experiments.

could not be a γ-lactone and that the reduction products could only be represented by (**8**), the tertiary carbon atoms in (**7**) being in fact the same carbon atom. In turn gmelanone itself has structure (**4**), in accord with all the data.

A ^{13}C n.m.r. study of these and other lignans fully supports this assignment of structure. For example, a signal at 204·7 p.p.m. in gmelanone confirms that the carbonyl group is that of a ketone whilst the C-5 quaternary carbon atom gives a signal at 81·37 p.p.m. This is in sharp contrast to the two quaternary carbon atoms in the arboreol series which appear at *ca.* 105 p.p.m. (C-2) and 95·5 p.p.m. (C-1).

Gmelanone (**4**) could formally arise from arboreol (**1**) by a pinacol–pinacolone type of rearrangement initiated by ionisation of the benzylic hydroxy-group and it is on this relationship that the assignment of stereochemistry shown in (**4**) has been made. However, a common precursor such as (**9**) could by suitable manipulation yield all the compounds isolated including the very unusual ethyl ether, ethyl arboreol (**1c**).

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[2] T. R. Govindachari, P. C. Parthasarathy, and H. K. Desai, *Indian J. Chem.*, 1972, **10**, 1120.

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[4] (a) R. Adams and M. Gianturco, *J. Amer. Chem. Soc.*, 1956, **78**, 4458; (b) H. L. de Waal and B. L. van Duuren, *ibid.*, p. 4464.

[5] A. Pelter, *J. Chem. Soc.* (*C*), 1967, 1376.