TABLE 1. τ-VALUES IN $CDCl_3$ (AT 100 MHz)

Compound	H_4	H_5	H_8	OMe	$-CH_2OH$	$-CH_2O\underline{H}$	Me_2C	$CH_2=CH-$	$CH_2=C\underline{H}-$
I	2·44 s	2·58 s	3·18 s	6·03 s	5·25 s	6 29 s	8 50 s	4·80 m 4·93 m	3 78 q
II	2·45 s	2·55 s	3·18 s	6 06 s	4·78 s*	7·85 s†	8 46 s	4·80 m 4·94 m	3·78 q

* $-CH_2OAc$
† $-CH_2O-COCH_3$.

Mass spectrum of I: molecular ion at *m/e* 274 ($C_{16}H_{18}O_4$ required 274); prominent ions at *m/e* 259 (M^+-Me), 246 (M^+-CO), 231 (M^+-Me,-CO), 215 (M^+-CH_2OH, -CO), 205 (M^+-$Me_2C-CH=CH_2$), 201 (M^+-3Me,-CO), 115 (M^+-$Me_2C-CH=CH_2$, -OMe,-CO, -CH_2OH; 100%), 69 ($Me_2\overset{+}{C}-CH=CH_2$), 41 ($CH_2=\overset{+}{C}-Me$; 98%).

Mass spectrum of II: molecular ion at *m/e* 316 ($C_{18}H_{20}O_5$ required 316); prominent ions at *m/e* 301 (M^+-Me; 100%), 289 (M^+-$CH_2=CH-$; 91%), 273 (M^+-Me,-CO), 257 (M^+-OCOMe), 247 (M^+-$Me_2C-CH=CH_2$), 243 (M^+-CH_2OCOMe), 219 (M^+-$Me_2C-CH=CH_2$, -CO), 215 (M^+-CH_2OCOMe,-CO), 69 ($Me_2C^+-CH=CH_2$).

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SALICACEAE

7-*O*-METHYLAROMADENDRIN FROM *POPULUS ALBA*

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Abstract—The 7-*O*-methylether of 4',5,7-trihydroxyflavanon-3-ol has been isolated from *Populus alba* L.

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7-*O*-METHYLAROMADENDRIN was obtained in the course of an investigation into the antifungal compounds produced by several species of *Populus*.[1] It lacked antifungal activity but is one of the rarer flavonoids and appears to have been found previously only in *Prunus avium*[2] and in *Eucalyptus* species.[3] The substance crystallized from an extract of the roots of *Populus alba* L. and identified by analytical, spectroscopic, and physical data (see Experimental). The identity was confirmed by a direct comparison with authentic 7-*O*-methylaromadendrin[3] by melting point, mixed melting point, mass spectrum, and chromatographic behaviour. The triacetyl derivative of the poplar metabolite was also indistinguishable in its mass spectrum and chromatographic behaviour from authentic but racemic 7-*O*-methylaromadendrin triacetate[2] but differed, as expected, in its melting point.

EXPERIMENTAL

Isolation. Chiefly 8-yr-old aspens (*Populus alba* L.) were taken from the field in September–October 1966. The bark (2 kg) of the carefully cleaned roots was cut into small pieces and soaked in CH_2Cl_2 at room temp. for 3·5 months. The extract was decanted, separated from the upper aqueous layer, filtered, and concentrated under reduced pressure to small volume. It was then chromatographed on a column of silica gel (Stahl; 800 g) with benzene–EtOH (10:1; 500 ml fractions) as eluant. During spontaneous evaporation, fractions 11–16 slowly deposited crystalline material (150 mg) which consisted of practically pure 7-*O*-methylaromadendrin. The mother liquors contained more of the substance, together with saligenin which could be isolated by sublimation. A preliminary examination showed that the flavanonal was also present in the aerial parts of the plant.

Characterization. Recrystallized from MeOH–$CHCl_3$, the substance had m.p. 187–188° dec.; $[\alpha]_{589}^{22.5}$ +29·7°, $[\alpha]_{578}^{22.5}$ +30·4° (*c*, 3·0 in MeOH; Perkin–Elmer 141 photoelectric polarimeter); λ_{max} (EtOH) 220, 226 (sh), 289, and 325 (sh) nm (ϵ 24,700, 24,000, 16,000, and 3600); ν_{max} KBr) 3475, 3460, and 1630 cm^{-1}. The NMR spectrum (in DMSO-d_6 with TMS as internal reference; varian A60A): δ 11·70 (1H, s, exchangeable, C-5-OH), 8·57 (1H, s, exchangeable, C-4′-OH), 7·33–6·64 (4 H, A_2B_2 system, ring B protons), 6·03 (2H, s, H-6 and H-8), 5·62 (1H, d, spacing ~6 Hz, exchangeable, C-3-OH), 5·07 (1H, d, spacing ~11·5 Hz, H-2), 4·56 (1H, dxd, spacings ~6 Hz and ~11·5 Hz, collapsing to d, spacing ~11·5 Hz, on addition of D_2O, H-3), and 3·76 (3H, s, C-7-OCH_3). (Found: C, 63·3; H, 4·7; mol. wt. 302 (Hitachi Perkin–Elmer RMV-D6 mass spectrometer). Calc. for $C_{16}H_{14}O_6$; C, 63·6; M, 4·7; mol. wt. 302.)

On acetylation,[2] the substance gave the triacetyl derivative, m.p. 136–136·5°. NMR spectrum ($CDCl_3$): δ 7·58–7·08 (4H, A_2B_2 system, ring B protons), 6·44 and 6·35 (2H, pair of doublets, spacings ~2·5 Hz, H-6 and H-8, relative assignment not implied), 5·73 (1H, d, spacing 12 Hz, H-3), 5·38 [1H, d (broadened by long-range coupling), spacing 12 Hz, H-2], 3·89 (3H, s, C-7-OCH_3), 2·38 and 2·32 (3H each, s, phenolic acetates), and 2·02 (3H, s, C-3-acetate). (Found: mol. wt. 428 (mass spectrometer). Calc. for $C_{22}H_{20}O_9$: 428.)

Chromatography was done on thin layers of silica (Merck) with MeOH–$CHCl_3$–HOAc (2:100:1) as irrigant and H_2SO_4 120° as developer.

[1] R. KREIENBÜHL, Thesis, Swiss Federal Institute of Technology (1967).
[2] J. CHOPIN and H. PACHECO, *Bull. Soc. Chim. Biol.* **40**, 1593 (1958). We thank Prof. J. Chopin for a sample of 7-*O*-methylaromadendrin.
[3] R. J. GELL, J. T. PINHEY and E. RITCHIE, *Australian J. Chem.* **11**, 372 (1958); S. S. SATWALEKAR, T. R. GUPTA and P. L. NARASIMHA RAO, *Chem. Abstr.* **51**, 1548 (1957).