Phytochemistry, 1973, Vol. 12, pp. 2501 to 2503. Pergamon Press. Printed in England.

A NEW CINNAMALDEHYDE FROM *PATAGONULA AMERICANA*

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(*Received* 24 *March* 1973. *Accepted* 17 *April* 1973)

Key Word Index—*Patagonula americana*; *Boraginaceae*; patagonaldehyde.

Abstract—The heartwood of *Patagonula americana* contains 3-hydroxy-2,4,5,6-tetramethoxy-*trans*-cinnamaldehyde (patagonaldehyde).

THREE yellow pigments have been isolated from the heartwood of *Patagonula americana* L. (Boraginaceae). Two of these are cordiachrome G (I)[1] and leucocordiachrome H (II),[1] and we now describe the third compound which is a phenolic aldehyde (patagonaldehyde). The NMR spectrum shows signals from four methoxyl groups at τ 5·95 (3H), 6·10 (3H) and 6·14 (6H), a hydroxyl at τ 4·28 (exchangeable with D_2O), and a low-field doublet at τ 0·33 (1H) from an aldehyde proton. The latter is part of an eight-line *ABX* system ($J_{AX} = 0$ Hz), the other centres being at τ 2·31 and 2·86, suggesting the presence of a *trans*-α,β-unsaturated aldehyde function. The resonance pattern is very similar to that of the side chain of cinnamaldehyde, and when patagonaldehyde methyl ether was oxidised with silver oxide it gave pentamethoxycinnamic acid.[2]

The natural compound is thus a hydroxytetramethoxycinnamaldehyde and it remains to locate the position of the hydroxyl group. The presence of three magnetically distinguishable types of methoxyl group, revealed by the NMR spectra of patagonaldehyde and its acetate, eliminates the *p*-hydroxy isomer as does the relatively small alkali shift[3] in the UV spectrum (λ_{max} 315 $\xrightarrow{HO^-}$ 335 nm). The position of the long-wave band relative to those of *p*-coumaraldehyde (λ_{max} 315 nm)[4] and coniferaldehyde (λ_{max} 341 nm)[5] also supports this view, but if coplanarity of the side chain and ring is prevented by the flanking methoxyl groups these arguments are less convincing. Oxidation of the aldehyde with silver oxide gave the *trans*-cinnamic acid but all attempts to convert this into a coumarin by irradiation[6] in ethanol or aqueous sodium hydroxide, or by treatment with aqueous alcoholic mercuric chloride,[7] failed. Thus the compound is not the *o*-hydroxy isomer.

It follows that patagonaldehyde is 3-hydroxy-2,4,5,6-tetramethoxycinnamaldehyde (III), and this was confirmed by hydrogenation over platinum in acidified ethanol. Two compounds were obtained. The first showed hydroxyl but no carbonyl absorption in the IR. The NMR spectrum showed *four* separate methoxyl signals at τ 6·05, 6·10, 6·15 and 6·19,

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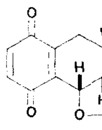
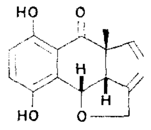
[1] MOIR, M. and THOMSON, R. H. (1973) *J. Chem. Soc. Perkin I* in press.
[2] DALLACKER, F. (1963) *Annalen* **665**, 78.
[3] SCOTT, A. I. (1964) *Interpretation of the Ultraviolet Spectra of Natural Products*, Pergamon Press, Oxford.
[4] FREUDENBERG, K. and GEHRKE, G. (1951) *Chem. Ber*, **84**, 443.
[5] PEW, J. C. (1963) *J. Org. Chem.* **28**, 1048.
[6] STOERMER, R. (1911) *Ber.* **44**, 637.
[7] SESHADRI, T. R. (1954) *Chem. Ind.* (*London*) 308.

and hydroxyl at τ 4·60, while the side chain was represented by a benzylic triplet (2H) at τ 7·42, a multiplet (2H) at τ 8·45, and a methyl triplet at τ 9·01. The side chain signals from dihydro-eugenol were very similar. This hydrogenation product is clearly the *m*-hydroxypropylbenzene (IV). The MS showed a strong peak at M-29 and subsequent fragmentation of methoxy groups.


(I)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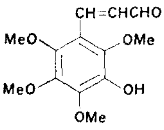
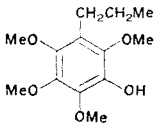
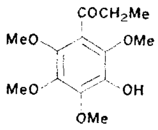

(III)


(IV)


(V)

The second hydrogenation product absorbed in the IR at 3350 and 1722 cm^{-1}, its NMR spectrum was similar to that of (IV) except that the high-field signals consisted of a quartet (2H) at τ 7·20 coupled to a methyl triplet at τ 8·78, and the MS included peaks at M–Et (70%) and M–Et–CO (12%). These data are consistent wiith the *m*-hydroxypropiophenone structure (V) and the high carbonyl stretching frequency can be explained by twisting of the side chain out of the ring plane by the two *o*-methoxy groups and the buttressing effect of the other substituents [*cf.* ν_{CO} 1712 cm^{-1} (C_6H_{12}) for 2,4,6-trimethoxyacetophenone[8]]. The formation of (IV) and (V) indicates that the aldehyde group is first reduced to the allylic alcohol (a), $ArCH{=}CHCH_2OH$, which in the presence of acid could isomerise to (b), $ArCH(OH)CH{=}CH_2$; either of these on further hydrogenation could give (IV) but evidently under the conditions of the experiment some of (b) undergoes double-bond rearrangement[9] to give (c), $ArC(OH){=}CHCH_3$, the enol of (V), which is not reduced further.

EXPERIMENTAL

Isolation of patagonaldehyde. The extraction of *P. americana* heartwood has been described.[1] The product from band (iii) was a brown solid which crystallized from petrol.–$CHCl_3$ to give *patagonaldehyde* (II) as greenish yellow needles, m.p. 108–109° (Found: C, 58·4; H, 6·1%, M$^+$ 268. $C_{13}H_{16}O_6$ requires: C, 58·2; H, 6·0%, M 268), λ_{max} (EtOH) 227 and 315 nm (log ϵ 4·12 and 4·36), ν_{max} (KBr) 3200, 1655 and 1613 cm^{-1}, τ ($CDCl_3$) 0·33 (1H, *d*, *J* 8 Hz, –CHO), 2·31 (1H, *d*, *J* 16 Hz, ArC*H*=CH–), 2·86 (1*H*, *dd*, *J* 8 and 16 Hz, ArCH=C*H*–CHO), 4·28 (1H, *s*, OH), 5·95 and 6·10 (each 3H, *s*, OMe), and 6·14 (6H, *s*, OMe), *m/e* (%) 268(32), 238(12), 237(100) and 193(8). The *acetate* was an oil (Found: C, 58·4; H, 5·9. $C_{15}H_{18}O_7$ requires: C, 58·1; H, 5·8%), ν_{max} (film) 1780, 1675, 1619, 1598 cm^{-1}, τ (CCl_4) 0·40 (1H, *d*, *J* 7·5 Hz, –CHO), 2·48 (1H,′ *d*, *J* 16 Hz, ArC*H*=CH–), 3·05 (1H, *dd*, *J* 7·5 and 16 Hz, ArCH=C*H*–CHO), 6·10 (6H, *s*, OMe), 6·15 and 6·28 (each 3H, *s*, OMe), and 7·70 (3H, *s*, OAc). The *methyl ether* crystallized from petrol. in needles, m.p. 67–69° (Found: C, 59·6; H, 6·3. $C_{14}H_{18}O_6$ requires: C, 59·6; H, 6·4%), ν_{max} (KBr) 1686 and 1628 cm^{-1}, τ (CCl_4) 0·40 (1H, *d*, *J* 7·5 Hz, CHO), 2·46 (1H, *d*, *J* 16 Hz, ArC*H*=CH), 3·04 (1H, *dd*, *J* 7·5 and 16 Hz, ArCH=C*H*–CHO), 6·06 (3H, *s*, OMe), 6·14 (6H, *s*, OMe) and 6·17 (3H, *s*, OMe).

3-*Hydroxy*-2,4,5,6-*tetramethoxycinnamic acid.* Finely powdered patagonaldehyde (100 mg) was oxidised by freshly prepared Ag_2O (from 130 mg $AgNO_3$) in H_2O and stirred for 1·5 hr. After acidification, the product was taken into Et_2O, transferred to aq. $NaHCO_3$, re-acidified and extracted with Et_2O which was washed, dried ($MgSO_4$), and evaporated. The residual gum crystallized from petrol. to give the *cinnamic acid* as needles, m.p. 159–161° (65 mg) (Found: C, 54·6; H, 5·5. $C_{13}H_{16}O_7$ requires: C, 54·9; H, 5·6%), λ_{max} (EtOH) 225 and 298 nm (log ϵ 4·04 and 4·15), ν_{max} 3440, 2800–2200, 1665, 1625 cm^{-1}, τ ($CDCl_3$–Me_2CO-d_6) 2·03 (1H, *d*, *J* 16 Hz, ArC*H*=CH–), 3·13 (1H, *d*, *J* 16 Hz, –CH=C*H*–CO_2H), 6·01 and 6·11 (each 3H, *s*, OMe), and 6·18 (6H, *s*, OMe).

Pentamethoxycinnamic acid. Patagonaldehyde methyl ether (28 mg) was oxidized with Ag_2O, as above, to give pentamethoxycinnamic acid, m.p. 138–139° (lit.[2] 134·5°) (from C_6H_{12}) (13 mg) identical (TLC, IR) with an authentic sample.

[8] HUISGEN, R., SEIDL, G. and WIMMER, I. (1964) *Annalen* **677**, 21.

[9] RYLANDER, P. N. (1967) *Catalytic Hydrogenation over Platinum Metals*, Academic Press, New York.

Hydrogenation of patagonaldehyde. The aldehyde (40 mg) was hydrogenated at atmospheric pressure over Pt (18 mg oxide) in EtOH (20 ml) containing a few drops of $HClO_4$, for 1 hr. After filtration and dilution with H_2O, the solution was extracted with Et_2O, washed, dried ($MgSO_4$), and evaporated leaving an oil (32 mg). This was separated on silica gel plates in $CHCl_3$–MeCOEt (10:1) into two components. Band (i) yielded 3-*hydroxy*-2,4,5,6-*tetramethoxy*-n-*propylbenzene* (V) as an oil (15 mg) (Found: M^+ 256·1299. $C_{13}H_{20}O_5$ requires 256·1310), ν_{max} (film) 3400, 1612 cm^{-1}, τ ($CDCl_3$) 4·60 (1H, *s*, OH), 6·05, 6·10, 6·15 and 6·19 (each 3H, *s*, OMe), 7·42 (2H, *t*, *J* 7 Hz, Ar–CH_2–CH_2–), 8·45 (2H, *m*, –CH_2–CH_2–Me), and 9·01 (3H, *t*, *J* 7 Hz, –CH_2–CH_3), *m*/*e* (%) 256(100), 241(38), 227(36), 212(11), 198(10), 197(10) and 169(14). Band (ii) afforded 3-*hydroxy*-2,4,5,6-*tetramethoxypropiophenone* (VI) (10 mg) as an oil (Found: M^+ 270·1086. $C_{13}H_{18}O_6$ requires 270·1103), ν_{max} (film) 3350, 1722 and 1610 cm^{-1}, τ ($CDCl_3$) 4·62 (1H, *s*, OH), 6·08, 6·14, 6·19 and 6·21 (each 3H, *s*, OMe), 7·20 (2H, *q*, *J* 7 Hz, –CO–CH_2–Me) and 8·78 (3H, *t*, *J* 7 Hz, –CH_2–CH_3), *m*/*e* (%) 270(100), 241(70), 213(12), 212(16), 211(11) and 183(16); peaks at *m*/*e* 256 and 227 (from V) were also present.

Acknowledgements—One of us (M.M.) is indebted to the Chemical Society for the award of a Briggs Scholarship. We also thank the Instituto De Pesquisas Technológicas and the Instituto Florestal, São Paulo, Brazil for *P. americana* wood, Professor F. Dallacker for a sample of pentamethoxycinnamic acid, and Mr. A. McGill for MS.