formed could not be separated from synthetic **2** by chromatography. Its visible and IR absorption spectra were very similar to synthetic **2**. Red Band I was therefore identified as β-apo-4'-carotenoic acid methyl ester.

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REFERENCES

1. Valadon, L. R. G. and Mummery, R. S. (1974) *Microbios* **10A**, 97.
2. Aasen, A. J. and Liaaen Jensen, S. (1965) *Acta Chem. Scand.* **19**, 1843.
3. Valadon, L. R. G. and Mummery, R. S. (1969) *Microbios* **1A**, 3.
4. Fiasson, J. L. and Bouchez, M. P. (1970) *Phytochemistry* **9**, 1133.
5. Valadon, L. R. G. and Mummery, R. S. (1972) *Phytochemistry* **11**, 413.

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PHLORACETOPHENONE DERIVATIVES IN *PRUNUS DOMESTICA*

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Key Word Index—*Prunus domestica*; Rosaceae; plum; ketones; domesticoside; phloracetophenone-4-methyl ether; phloracetophenone; coumarin; fraxinol.

Prunus domestica, the tree of plum fruit, grows in India on Western temperate Himalayas. The sample under investigation was collected from Srinagar (Kashmir). A number of flavonoids were earlier isolated from the heartwood and studied [1]. The present communication reports the compounds isolated from an ether extract of the bark. The extract yielded four compounds, A–D, which were separated from one another and purified as described in the Experimental.

Compound A. $C_{15}H_{20}O_9$, mp 193–94°, was optically active. It gave a violet colour with alcoholic $FeCl_3$ (chelated phenolic —OH) and on acid hydrolysis, it yielded glucose and an aglucone. The IR spectrum of the glucoside showed the presence of hydroxyl groups, chelated carbonyl and phenyl ring. The UV maximum at 283 nm (log ε: 4.172) (in MeOH) was shifted to 337 nm with NaOMe (phenolic OH) and to 302 nm with $AlCl_3$–HCl (chelated carbonyl group). The NMR spectrum (TFA, δ) showed signals for a —COMe group attached to a benzene ring (2.90, *s*), one aromatic —OMe (3.95, *s*), sugar protons [5.4 (C-1') and 4.15–4.4] and two aromatic protons (6.3, *s*). The NMR spectrum of its pentaacetate ($CDCl_3$, δ) had peaks at 2.06 (12 H, *br. s*, four alcoholic acetate groups), 2.22 (3H, *s*, one phenolic acetate), 2.45 (3 H, *s*, —COMe group), 3.80 (3 H, *s*, —OMe), 4.25–5.30 (7 H, sugar protons) and 6.35 and 6.55 (ill-resolved doublets, $J = 3$ Hz, each integrating for one aromatic H). The above data indicate A to be a trisubstituted acetophenone with two free *meta* positions, the substituents being a hydroxy, a methoxy and a glucosyloxy group. Thus, A is a mono-*O*-glucoside of phloracetophenone monomethyl ether. The aglucone was conclusively identified as phloracetophenone 4-methyl ether by a direct comparison with an authentic sample. The following observations further showed that A is the hitherto unknown 6-*O*-glucoside. Thus, on ethylation and subsequent hydrolysis A yielded 2-*O*-ethyl-4-*O*-methylphloracetophenone (mp 134–35°) [Lit. mp 133–34°, [2]]. The glucoside could be hydrolysed with emulsin and on permethylation followed by Kiliani hydrolysis it gave 2,4-di-*O*-methylphloracetophenone and 2,3,4,6-tetra-*O*-methyl-D-glucose. It may be mentioned here that the 2-*O*-diglucoside of 4-*O*-methylphloracetophenone has been recently isolated from *Dorema hyrcanum* [3].

Compound B. mp 141–42°, was identified as 4-*O*-methylphloracetophenone by spectral data and direct comparison with an authentic sample. This is the first reported isolation of this compound from a natural source; the 2,4-dimethyl and trimethyl ethers of phloracetophenone are known to be naturally occurring [4, 5].

Compound D. Mp 169–71°, gave a brown colour with $FeCl_3$ and dissolved in aq. NaOH to give a deep yellow C_5H_5N) showing NMR peaks ($CDCl_3$, δ) at 2.30 (9 H, *s*, phenolic acetate), 2.48 (3 H, *s*, —COMe) and 6.9 (2 H, *s*, aromatic). These data indicated C to be phloracetophenone itself and this was confirmed by a direct comparison with an authentic sample. This is the first reported isolation of this parent compound from a natural source.

Compound D. mp 169–71°, gave a brown colour with $FeCl_3$ and dissolved in aq NaOH to give a deep yellow colour, which disappeared on acidification. The UV spectrum was typical of a coumarin and the IR spectrum showed appropriate bands for hydroxyl, lactone carbonyl and phenyl groups. The NMR spectrum ($CDCl_3$, δ) showed a singlet at 3.9 (6 H, two aromatic —OMe), a pair of characteristic doublets at 6.2 and 8.0 ($J = 11$ Hz) attributable to the C_3 and C_4 protons respectively and a singlet at 6.5 (1 H, aromatic). The above data showed D to be a dimethoxy-monohydroxycoumarin. The mp is in agreement with that of fraxinol (5,7-dimethoxy-6-hydroxycoumarin) [6] and the spectral data are fully compatible with this structure.

EXPERIMENTAL

Mps are uncorrected; comparisons with authentic samples were made by co-TLC, co-PC, co-IR and mmp.

Extraction. Air-dried bark (700 g, from a 8–10-year-old, 7-ft-tall tree) was extracted with hot petrol, Et_2O and EtOH respectively. The petrol extract contained mainly waxy matter. From the Et_2O extract was obtained a light pink-coloured solid (1.1 g).

Treatment of this solid with petrol and then with Et_2O left a colourless residue which on purification by preparative TLC on Si gel G (EtOAc–MeOH–H_2O, 100:16.5:13.5; R_f 0.62) gave compound A (0.3 g). The petrol-soluble portion was similar to the petrol extract of the bark. A TLC examination of the ether solubles showed the presence of 5 compounds; only compounds B, C and D, however, could be obtained in sufficient amounts by preparative TLC on Si gel G (C_6H_6–EtOAc; 4:1, R_f 0.76, 0.51 and 0.58 respectively).

Compound A. Crystallized from MeOH as colourless needles, mp 193–94°: $[\alpha]_D^{25}$ – 112° (*c*, 0.375, MeOH); ν_{max}^{KBr} 3440, 2920, 1625, 1585, 1500 and 1450 cm^{-1} (Found: C, 48.51; H, 6.69; $C_{15}H_{20}O_9.1\frac{1}{2}H_2O$ requires C, 48.51; H, 6.2%). The acetate crystallized from $CHCl_3$–petrol as colourless needles (0.025 g), mp 120–21° (Found: C, 54.5; H, 5.8; $C_{25}H_{30}O_{14}$ requires C, 54.15; H, 5.4%).

Acid hydrolysis of A. 0.060 g A was refluxed for 4 hr with MeOH (20 ml), H_2O (5 ml) and H_2SO_4 (sp. gr. 1.83; 1.8 ml). 20 ml of H_2O were then added and MeOH removed when a light yellow solid, identical with an authentic sample of 4-*O*-methylphloracetophenone, separated; mp 140–41° (light yellow plates from C_6H_6–EtOAc; Found: C, 59.2; H, 5.8; $C_9H_{10}O_4$ requires C, 59.3; H, 5.5%); ν_{max}^{KBr} 3080, 1640, 1580, 1510 and 1470 cm^{-1}. NMR (C_5H_5N, δ): 2.8 (3H, *s*, —COMe), 3.63 (3H, *s*, —OMe) and 6.25 (2H, *s*, aromatic); NMR (Me_2CO, δ) 11.5 (chelated phenolic —OH). The aq. filtrate was neutralized and concentrated to a syrup, which on PC examination was found to contain glucose.

Ethylation of A. 0.050 g A was refluxed with 0.020 ml Et_2SO_4, 0.700 g K_2CO_3 and 10 ml Me_2CO for 6 hr. The reaction mixture was then filtered and solvent removed when a colourless solid was obtained which on hydrolysis with 7% methanolic H_2SO_4 (25 ml) and working up yielded 2-*O*-ethyl-4-*O*-methylphloracetophenone as colourless needles, mp 134–35°. Its identity was confirmed by comparison with an authentic sample.

Permethylation of A. To a pre-heated (70°, 1 hr) mixture of NaH (0.060 g) and DMSO (0.8 ml) was added A (0.020 g) in DMSO (0.8 ml) and the mixture heated for 1.5 hr at 70°. This was cooled in ice, MeI (2 ml) added with stirring and the mixture left at room temp. for 16 hr. It was then diluted with H_2O, extracted with $CHCl_3$; the $CHCl_3$ layer washed, dried and evaporated. The syrupy mass (single spot on TLC in $CHCl_3$) was refluxed with Kiliani mixture for 4 hr. The hydrolysate was found to contain 2,3,4,6-tetra-*O*-methyl-D-glucose (by PC comparison with an authentic sample, *n*-BuOH:EtOH:H_2O::5:1:4) and 2,4-di-*O*-methylphloracetophenone (TLC comparison with an authentic sample, toluene–ethyl formate–formic acid, 5:4:1).

Compound B. This was obtained as light yellow plates (0.08 g) from EtOAc–C_6H_6, mp 141–42°; λ_{max}^{MeOH} nm (log ε): 285 (4.364); + NaOMe: 295, 360 nm; + $AlCl_3$ + HCl: 305 nm. The IR and NMR spectra of B were identical with those of the aglucone of A.

Compound C. This separated as light yellow plates (0.03 g) from Me_2CO, mp 216–18°; λ_{max}^{MeOH} nm (log ε): 286 (4.238); + NaOH: 315 nm; + $AlCl_3$ + HCl: 303 nm; ν_{max}^{KBr} 3540, 3470, 3100, 1625, 1560, 1520 and 1460 cm^{-1}; NMR (C_5H_5N, δ): 2.84 (3H, *s*, —COMe) and 6.37 (2H, *s*, aromatic).

Compound D. This was obtained as crystalline solid (0.015 g), mp 169–171°; λ_{max}^{MeOH} nm (log ε): 264 (3.297) and 321 (4.191): + NaOAc: 267 and 320 nm; + NaOH: 330 and 385 nm; ν_{max}^{KBr}: 3320, 1700, 1615, 1555, 1500 and 1465 cm^{-1}.

REFERENCES

1. Nagarajan, G. R. and Seshadri, T. R. (1964) *Phytochemistry* **3**, 477 (1966) *Curr. Sci.* **35**, 409.
   Nagarajan, G. R. and Parmar, V. S. (1977) *Planta Med.* In press.
2. Sonn, A. (1928) *Chem. Ber.* **61**, 2300.
3. Nurmukhamedova, N. R. and Nikonov, G. K. (1976) *Khim. Prir. Soedin* **1**, 101 [(1976) *Curr. Abstr. Chem. and Index Chemicus*, **62**, No. 1, issue 657, 244862].
4. Finleyson, H. H. (1926) *J. Chem. Soc.* 2763.
5. Kondo, H., Ishivata, S. and Okayama, S. (1933) *Chem. Zentr.* **II**, 3132.
6. Shimada, H. (1952) *J. Pharm. Soc. Japan* **72**, 65.

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4-METHOXY-2-(*TRANS*-1-PROPENYL)PHENYL (±)-2-METHYLBUTANOATE FROM ANISE PLANTS

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The constituents of anise plants, *Pimpinella anisum* L., have been extensively investigated since the early work of Dumas [1]. Recent work includes the quantitation of myristicin in the seeds [2], comparison of essential oil components of roots and seeds [3], and the identification of some sterols and coumarins in root tissue [4].

Steam distillation of the aerial portions of mature anise plants (grown from seeds on the University of Wisconsin Experimental Farm at Arlington), followed by ether extraction of the distillate, yielded an oil from which the title compound was isolated by column chromatography on silicic acid and preparative silica gel TLC. Column fractions 280–350 (200 g Mallinckrodt SilicAR CC-4, in a 3 × 55 cm column, eluted with Skellysolve B, 10.5 ml fractions) upon further purification on TLC (silica gel H and silica gel PF-254, developed with Skellysolve B) gave the title compound (R_f 0.4) in 1.5% yield (based on oil). This substance has not been reported previously as a natural product.

Structure **1** was deduced from spectral data and chemical transformations. The high resolution mass spectrum established the composition $C_{15}H_{20}O_3$ for the molecular ion (M^+ = 248) and exhibited peaks at *m/e* 164 (31%, M-C_5H_8O), 149 (27%, M-C_5H_8O-Me) and