cation, crystallisation first from methanol and then from *n*-butanol saturated with H_2O gave light yellow microneedles of kaempferol 3-gentiotrioside which transformed at 198–200° to a viscous melt becoming clear and liquid at 230°. $[\alpha]_D^{21}$ −27° (*c* 0.13, dimethylformamide). *Anal.* Calc. for $C_{38}H_{40}O_{21}.4H_2O$: C, 46.93; H, 5.73; H_2O 8.53. Found: C, 47.11; H, 6.00; H_2O 9.5.

Comparison of natural Primula 3-*triglucoside and synthetic* 3-*gentiotrioside of kaempferol.* The natural and synthetic glycosides had identical R_f values in *n*-BUOH–HOAc–H_2O (4:1:5) (0.24, 0.24) in *n*-BuOH–EtOH–H_2O (4:1:2.2) (0.22, 0.22), in PhOH–H_2. (0.28, 0.30), and in H_2O (0.41, 0.42) but clearly separated in 5% HOAc (0.35, 0.47) and in 15% HOAc (0.51, 0.57). They had identical mobilities when electrophorized in borate buffer pH 8.8 for 3 hr at 400 V/un, H_2O_2 oxidation of the 2 glycosides gave trisaccharides with different R_G values in some solvents. R_G values for gentiobiose, the sugar from the *Primula* triglucoside and the sugar from the synthetic 3-gentiotrioside were as follows: 0.32, 0.18 and 0.16 in BAW; 0.24, 0.17 and 0.17 in BEW; 0.46, 0.24 and 0.21 in BBPW; and 0.58, 0.44 and 0.27 in PhOH–H_2O.

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REFERENCES

1. Wagner, H. (1974) *Progress in the Chemistry of Organic Natural Products* **31**, 153.
2. E.g. Schmidt, R. D., Varenne, P. and Paris, R. (1972) *Tetrahedron* **28**, 5037; Sosa F. and Percheron F. (1970) *Phytochemistry* **9**, 441; Wagner, H., Ertan, M. and Seligmann, O. (1974) *Phytochemistry* **13**, 857.
3. Harborne, J. B. and Sherratt, H. S. A. (1961) *Biochem. J.* **78**, 298.
4. Jurd, L. (1962) *J. Org. Chem.* **27**, 1294.
5. Takiura, K, Honda, S., Endo, T. and Kakehi, K. (1972) *Chem. Pharm. Bull.* **20**, 438.
6. Hörhammer, L., Wagner, H., Arndt, H. G. and Farkas, L. (1966) *Tetrahedron Letters* 567.
7. Wagner, H., Danninger, H., Seligmann, O., Nógrádi, M., Farkas, L. and Farnsworth, N. (1970) *Chem. Ber.* **103**, 3678.

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A NEW FLAVAN GLYCOSIDE FROM *BUCKLEYA LANCEOLATA* LEAVES*

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Key Word Index—*Buckleya lanceolata*; Santalaceae; structural determination; flavan; 5,7,4′-trihydroxyflavan 5-xyloside.

Previously, Hopkins *et al.* [1] isolated acetylenic fatty acids from seeds of *Buckleya distichophylla* Torr. which grows in the eastern United States. We now report the structure of new flavan glycoside isolated from the leaves of *B. lanceolata* Miq., a species endemic to Japan.

Colour tests and UV spectrum indicated that the new glycoside (**1**) was a *para*-substituted, unconjugated phenol. MS exhibited M^+ and an aglycone peak formed by elimination of a five carbon sugar. PMR spectrum indicated the presence of four protons on a *para*-substituted benzene ring, two aromatic hydrogens giving a *meta* coupling constant, a $-CH_2CH_2-$, a CH, six –O–CH protons probably of the sugar moiety and five –OH protons. Two of the hydroxyls were phenolic and others were aliphatic, because **1** afforded the dimethyl ether **2** by reaction with CH_2N_2 and a pentaacetate **3**, containing two aromatic acetyl and three aliphatic acetyl groups. **2** was converted to a triacetate **4** by acetylation. On hydrolysis with acid or emulsin, **1** produced xylose and an aglycone **5** which gave a positive Gibbs test. On the basis of these data, **1** was presumed to be the 5-*O*-D-xyloside of 5,7,4′-trihydroxyflavan and this was confirmed by the following experiments.

Identity of the product **6** obtained from **2** by hydrolysis and authentic (2S)-7,4′-dimethoxy-5-hydroxyflavan was proved by mmp and IR comparison. The CD spectra of **5** and **6** supported the S-configuration of 2-position, because these spectra showed negative Cotton effects[2]. The coupling constant of the anomeric proton of TMSiate **7** of **1** (*J* 7.5 Hz)[3] and the result of hydrolysis of **1** using emulsin[4] indicated that xylose was bound by a β-D-glycosidic bond. **1** is thus (2S)-5,7,4′- trihydroxyflavan 5-*O*-β-D-xyloside.

*Part 1 in the series "The Chemical Components of Santalaceae".

EXPERIMENTAL

All mp's are uncorr. PMR were measured on a 100 MHz apparatus and chemical shifts are given in ppm relative to TMS as internal standard. MS were measured at 70 eV. For solvent of PC, *n*-BuOH–AcOH–H_2O (4:1:5) was used.

Plant. Plants were collected in Oume city, Tokyo in May, 1973. A voucher specimen (coll. Y. Sashida) is deposited in the Herbarium of the National Science Museum of Japan.

Extraction and isolation. Air-dried leaves (1.66 kg) were extracted with 10 l. hot MeOH for 100 hr, and the extract, after removal of solvent was extracted with *n*-hexane and subsequently with EtOAc. EtOAc extract (180 g) was fractionated by column chromatography over Si gel with CH_2Cl_2–MeOH. Fractions which were eluted with CH_2Cl_2–MeOH (9:1) gave *ca* 2.0 g colourless needles **1** after purification by re-chromatography, decolorization with active carbon and recrystallization from H_2O.

(2*S*)-5,7,4′-*trihydroxyflavan*-5-O-β-D-*xyloside* **1**. $C_{20}H_{22}O_8$ (Found: C, 61.41; H, 5.57. $C_{20}H_{22}O_8$ requires: C, 61.53; H, 5.68), mp 243°. Colour tests: benzidine, +; $FeCl_3$–K_3 $Fe(CN)_6$, +; Gibbs reag., −. $(\alpha)_D^{25°}$ −31.8°(*c* 0.40, EtOH). UV λ_{max} nm(log ε): 208(4.70), 227(shoulder, 4.38), 275(3.21), IR ν_{max}^{KBr} cm^{-1}: 3415, 1622, 1600, 1500, 1050, 834. PMR

(Me_2CO-d_6): δ 2.07(*m*, C-3 and impurities of solvent), 2.70(2H, *m*, C-4), *ca* 4.9(2H, *m*, C-2 and anomeric H of sugar), 6.02 and 6.23(2H, *d*, J=2Hz respectively, C-6 and 8), 6.84 and 7.26(4H, *d*, J=9Hz respectively, C-2',3',5' and 6'), 3.20–4.04(*ca* 5H, m, –O–CH of sugar), 4.24 and 4.55(3H, OH of sugar), 8.07 and 8.26(2H, *s* respectively, aromatic OH). MS *m/e*: 390(M^+), 258(M^+-sugar). Dimethyl ether **2**. CH_2N_2, mp 159°(MeOH-H_2O), IR ν_{max}^{KBr} cm^{-1}: 3370, 1620, 1595, 1500, 1142, 1052, 821; PMR($CDCl_3$). δ 3.61 and 3.76(6H, *s*, respectively, 2 × phenolic OMe). MS *m/e*: 418(M^+), 286(M^+-sugar). Penta-acetate **3**, C_5H_5N–Ac_2O, mp 183°(MeOH), IR ν_{max}^{KBr} cm^{-1}: 1768, 1750, 1615, 1602, 1495, 1375, 1220, 1197, 1130, 1076; PMR($CDCl_3$): δ *ca* 2.05(9H, 3 × MeCOO– of sugar moiety), 2.25 and 2.27(6H, 2 × phenolic CH_3COO–); MS *m/e*: 600(M^+), 342(M^+-sugar moiety) 300(342-CH_2CO). Dimethyl ether triacetate **4**, mp 183° (MeOH–H_2O), IR ν_{max}^{KBr} cm^{-1}: 1755, 1623, 1595, 1380, 1513, 1220, 1140, 1060; MS *m/e*: 544(M^+), 286(M^+-sugar moiety), 259. TMSiate **7** of **1**, HMDS-TMCS in C_5H_5N, PMR(CCl_4): δ 4.78(1H, *d*, J=7.5 Hz, anomeric H of sugar).

Hydrolysis of **1**. Enzymatic hydrolysis: **1**(140 mg) was suspended in H_2O(28 ml) and incubated at 30° for 4 days with emulsin (100 mg). The hydrolysate was extracted with Et_2O and extract evaporated and recrystallized with EtOH–H_2O to give **5**, mp 204°, Gibbs test, +. IR ν_{max}^{KBr} cm^{-1}: 3400, 1620, 1600, 1517, 1460, 1245, 1145, 1067, 827, 810.; MS *m/e*: 258(M^+), 139, 120; CD(in MeOH, *c* 0.001 g/ml): $(\theta)_{285}$O, $(\theta)_{269}$ − 732, $(\theta)_{250}$0, $(\theta)_{238}$ + 410. From aq layer, D-xylose was identified by PC(R_f 0.28). Hydrolysis using HCl: **1** was refluxed with 1% HCl in 90% MeOH in N_2 for 1 hr. **5** was isolated from Et_2O extract of the hydrolysate, and D-xylose in aqueous MeOH layer was identified by direct comparison of its osazone, mp 162°, with an authentic D-xylosazone.

Hydrolysis of **2**. **2** was refluxed with 1% HCl in 90% MeOH in N_2 for 2 hr. From the Et_2O extract, **6** was obtained. **6**, MS *m/e*: 286(M^+), mp 135° (*n*-hexane), undepressed on admixture with (2S)-7,4'-dimethoxy-5-hydroxyflavan prepared from naringenin, and IR spectra of both substances were identical. CD(in MeOH, *c* 0.001 g/ml): $(\theta)_{283}$O, $(\theta)_{271}$ −729, $(\theta)_{246}$O, $(\theta)_{240}$ +415.

Synthesis of (2*S*)-7,4'-*dimethoxy*-5-*hydroxyflavan*. By methylation using CH_2N_2, authentic naringenin ((2S)-5,7,4'-trihydroxyflavanone) afforded the dimethyl ether, mp 116°(MeOH), MS *m/e*: 300(M^+). This (60 mg) was dissolved in AcOH and was allowed to stand for 1 day with Zn Hg(5g) and conc HCl(5 ml). From Et_2O extract of reaction mixture, (2S)-7,4'-dimethoxy-5-hydroxyflavan was obtained. Its mp 134°(*n*-hexane), $C_{17}H_{18}O_4$ (Observed: *m/e* 286.12155, $C_{17}H_{18}O_4$ requires: 286.12051); IR ν_{max}^{KBr} cm^{-1}: 3365, 1620, 1605, 1515, 1246, 1140, 1080, 810.

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REFERENCES

1. Hopkins, C. Y. and Chisholm, M. J. (1966) *Chem. Ind.* 1533.
2. Cardillo, G., Merlini, L. and Nasini, G. (1971) *J. Chem. Soc.(C)*, 3967.
3. Kamerling, J. P., de Bie, M. J. A. and Vliegenthart, J. F. G. (1972) *Tetrahedron* **28**, 3037.
4. Arya, V. P., Erdtman, H., Krolikowska, M. and Norin, T. (1962) *Acta Chem. Scand.* **16**, 518.

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ONYCHINE, AN ALKALOID FROM *ONYCHOPETALUM AMAZONICUM**

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Key Word Index—*Onychopetalum amazonicum*; Annonaceae; onychine; 1-aza-4-methylfluorenone; phenylalanine-mevalonate alkaloid.

The trunk wood of *Onychopetalum amazonicum* (Annonaceae), trivial name "envira cajú", from the vicinity of Manaus, Amazonas, contains besides sitosterol and stigmasterol an alkaloid designated onychine. The hydrogens of onychine, $C_{13}H_9NO$, were assigned to an *ortho*-disubstituted benzene ring, in view of the IR (760 cm^{-1} band) and NMR evidence, and a γ-methylpyridine unit. The NMR doublets (J = 5.5 Hz) due to the α-(τ 1.61) and β-(τ 3.04) protons appeared at the expected frequencies (τ 1.50 and 2.94 resp.) [1] and the Hβ-signal showed secondary splitting which could be cancelled by double irradiation at the methyl frequency. The ring systems must be bridged by a carbonyl (ν_{max} 1703 cm^{-1}), a consideration which, in view of the preceding evidence, pointed to 1-(or 4)-aza-4(or 1)-methylfluorenone as the structure for onychine.

Indeed, onychine and fluorenone (ν_{max} 1705 cm^{-1} [2a]) gave strikingly similar UV spectra (see Experimental). Also, reduction of onychine led to a mixture of enantiomeric secondary alcohols with two aromatic substituents, as evidenced by the frequency (τ 4.43) and shift upon acetylation (Δ −1.43 ppm) of the NMR singlet due to the oxymethine proton. Hydrogenolysis of the carbinol produced a methylene group which, precisely as the CH_2-group of fluorene [2b], gave rise to a singlet at τ 6.24.

The structural alternative in which the CO and methyl groups are *ortho*-related cannot represent onychine, reduction of the carbonyl affected the methyl NMR fre-

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