a dimer of D-glucose on PC and the β-linkage of the biose to the aglycon was revealed by hydrolysis with emulsin and by the coupling constant (7 Hz) in the NMR spectrum. This compound (**2**) was consequently identified to be 8-methoxyretusin-7-*O*-β-glucosylglucoside. The third compound (**3**) also afforded a 1:2 ratio of aglycone and sugar on acid hydrolysis. The resulting aglycone was identical with the authentic formononetin[2] by IR. The form of the sugar–aglycon bonding was found to be β-linkage and the sugar moiety was confirmed to be a dimer of D-glucose by the same methods as those described above. Therefore, the structure of this compound (**3**) must be formononetin-7-*O*-β-glucosylglucoside.

Platycarpanetin-7-O-β-monoglucoside (**1**). Colorless needles, m.p. 142–144° (MeOH). IR (KBr) cm^{-1} 3400, 1640, 1620, 1600, 1510, 1040, 916. UV (MeOH) nm 258, 300 (sh.). NMR (as TMS ether in CCl_4) δ ppm 7·67 (*s*, H-2), 7·00, 6·90, 6·83, 6·77 (*m*, H-2′, H-5′, H-6′), 6·70 (*s*, H-6), 5·94 (*s*, $O_2C\underline{H}_2$), 4·93 (*d*, H-1″, *J* 7·0 Hz), 3·90 (*s*, $OC\underline{H}_3$), 3·83 (*s*, $OC\underline{H}_3$), 3·90 – 3·20 (*m*, 6 H).

8-Methoxyretusin-7-O-β-glucosylglucoside (**2**). Colorless needles, m.p. 194–195° (MeOH). IR (KBr) cm^{-1} 3400, 2930, 1615, 1590, 1560, 1515, 1065, 1000. UV (MeOH) nm 253, 300 (sh.). NMR (as TMS ether in CCl_4) δ ppm 7·90 (*s*, H-2), 7·87 (*d*, H-5, *J* 9·0 Hz), 7·43 (*d*, H-2′,6′, *J* 9·0 Hz), 7·10 (*d*, H-6, J 9·0 Hz), 6·85 (*d*, H-3′,5′, *J* 9·0 Hz), 5·03 (*d*, H-1″, *J* 7·0 Hz), 4·70 (*d*, H-1‴, *J* 3·6 Hz), 3·93 (*s*, $OC\underline{H}_3$), 3·79 (*s*, $OC\underline{H}_3$), 3·20 – 3·60 (*m*, 12 H).

Formononetin-7-O-β-glucosylglucoside (**3**). Colorless needles, m.p. 175–176° (MeOH). IR (KBr) cm^{-1} 3400, 2930, 1620, 1590, 1510, 1070, 1000. UV (MeOH) nm 258, 300 (sh.).

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A NEW COUMARIN IN *AMYRIS SIMPLICIFOLIA*

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Key Word Index—*Amyris simplicifolia*; Rutaceae; 3-(3,3-dimethylallyl)-xanthyletin.

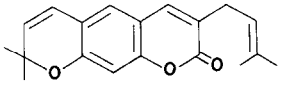
Amyris simplicifolia Karst (Rutaceae) is a perennial tree found in the Northern part of South America, where it grows in temperate climate near the sea.[1] *Source.* Chamariapa, East of Cumaná (Voucher specimen No. Bhat 0598 deposited in the University). *Previous work.* None.

Present work. The concentrated light pretrol. extract of the leaves of the plant on standing for 2 days at 0° deposited yellow plates of an optically inactive substance which after recrystalization from $CHCl_3$–MeOH had a sharp m.p. (103–104°). It gave a blue single UV

[1] SCHNEL, L. (1960) *Revista de la Facultad de Agronomía, Alcance* (3), 1311.

fluorescent spot on TLC (silica gel G). The yellow compound analysed for $C_{19}H_{20}O_3$ (Found: C, 76·99; H, 6·57. Calc. for $C_{19}H_{20}O_3$: C, 77·02; H, 6·75%).

Its UV max in EtOH were at 226 (log ϵ 4·45), 268 (log ϵ 4·31) and 347 nm (log ϵ 4·20). This spectrum was similar to that of xanthyletin. The IR spectrum in KBr showed peaks at 1715 cm^{-1} (conjugated δ-lactone), 1630 cm^{-1} (conjugated double bond of α-pyrone), 1650 cm^{-1}, 1575 cm^{-1} and 1495 cm^{-1} (aromatic), 1386 cm^{-1} and 1366 cm^{-1} (gem-dimethyl), 1270 cm^{-1} (C=C–O– antisymm. stretching), 1260 cm^{-1} (C=C–O– symm. stretching), 1140 cm^{-1} (Ar–O–CR_3), 835 cm^{-1} (trisubstituted double bond) and 680 cm^{-1} (disubstituted double bond). These data indicate that the compound is a coumarin of the xanthyletin type, with a C_5H_9 unit attached, whose structure (**1**) was elucidated from the NMR spectrum.



(1)

The NMR spectrum* showed a singlet at δ 7·30 (1H) which is assigned to the C–4 hydrogen, the absorption of this proton appears between 7·65 and 8·03 ppm.[2,3] The lack of coupling of the above signal shows that the C–3 position must be occupied by the C_5H_9 chain. In the aromatic region there are two other singlets at 7·02 (1H) and 6·71 (1H) which are assigned to the C–5 and C–8 protons respectively.[4] The absence of coupling between these aromatic signals revealed that the fusion of the 2,2-dimethylpyran nucleus to the coumarin must be linear and not angular.

Two doublets (J 10 Hz) at 5·66 (1H) and 6·36 (1H) are attributed to the C–3′ and C–4′ protons. A singlet (6H) at 1·47 accounts for the gem–dimethyl group joined to C–2′. The remaining signals corresponding to the C–3 side chain. A doublet (J 7 Hz) at 3·29 coupled with a multiplet at 5·33 (1H) accounts for the methylenic and the olefinic protons of the side chain. Further evidence for this assignment is obtained by decoupling measurements. By irradiating the olefinic proton at +126 Hz the doublet at 3·29 ppm collapsed to a singlet and irradiation of the methylene at −126 Hz collapsed the multiplet at 5·33 ppm to a singlet. Finally, the two olefinic methyls appeared as singlets at 1·69 (3H) and 1·80 (3H).

Recently, a coumarin, 3-(1,1-dimethylallyl)-xanthyletin, has been reported;[5] it differs from the present compound in the C–3 side chain. Both compounds have similar UV and IR spectra and their NMR signals differ mainly in the absorption corresponding to the side chain. While the former compound shows signals at 1·43 (s)(12H) corresponding to the gem-dimethyl group of the side chain and the gem-dimethyl group of the C–2′ position and at 5·05 (s)(1H), 5·08 (s) (1H) and 6·18 (s) (1H) corresponding to the olefinic protons of the 1,1-dimethylallyl substituent, the latter shows signals at 3·29 (d) (2H), 5·35 (m) (1H), 1·69 (s) (3H) and 1·80 (s) (3H) corresponding to the 3,3-dimethylallyl chain, confirming our structure.

* 60 MHz spectrum in $CDCl_3$ with TMS as internal reference. Chemical shifts (δ).

[2] DHARMATTI, D. S., GOVIL, C., KENEKAR, C. R., KHETRAPAL, C. L. and VIRMANI, Y. P. (1961) *Proc. Indian Acad. Sci.* **A56,** 71.

[3] ARTHUR, H. R. and OILS, W. D. (1963) *J. Chem. Soc.* 8910.

[4] GONZÁLEZ, A. G., ESTÉVEZ, R. and JARAIZ, I. (1971) *Phytochemistry* **10,** 1621.

[5] NAYAN, M. N. S., BHAN, M. K. and GEORGE, V. (1973) *Phytochemistry* **12,** 2073.

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METHYLATED FLAVONOLS FROM BUDS OF SEVERAL SPECIES OF POPULUS

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Key Word Index—*Populus*; Salicaceae; flavonoids; quercetin and kaempferol methyl ethers.

Plants. Various species of *Populus*. *Source.* Forschungsinstitut für Pappelwirtschaft, Hann. Münden. *Previous work.* Flavones, flavonols and flavanones from bud oil of *P. nigra*;[1] chalkones from bud oil of some species of *Populus*;[2] pinobanksin 3-acetate from many species.[3]

Present work. Buds were extracted with acetone and the solution concentrated. Flavonoids were isolated by preparative TLC on polyamide (solvent *A*, C_6H_6–petrol./MeCOEt–MeOH, 60:26:7:7, *B*, C_6H_6–dioxane–MeOH, 8:1:1) and silica gel (C_6H_6–Me_2CO, 9:1) and identified by co-chromatography with authentic substances and UV-spectra.

Flavonols. Besides many of the flavonoids described earlier from *P. nigra*, we have now found the following: quercetin-3,3′-dimethyl ether. Dark spot on polyamide, R_f 0·1 (*A*), 0·31 (*B*), yellow with "Naturstoffreagenz A" (colours in UV). UV λ_{max} 366, 268 (shoulder) and 255 nm; with added $AlCl_3$ 396, 368, (300) and 270 nm; with NaOEt 408, 326 and 268 nm; with NaOAc 368, 321 and 272 nm; no shift with NaOAc–H_3BO_3. Quercetin 3,7-dimethyl ether. Dark reddish-brown spot on polyamide, R_f 0·18 (*A*), 0·45 (*B*), orange-yellow with Naturstoffreagenz. UV λ_{max} 363, 257 nm; with $AlCl_3$ 403, 365 and 270 nm; with NaOEt 400 and 270 nm; with NaOAc 364 and 257 nm; with NaOAc–H_3BO_3 382 and 258 nm. Kaempferol 7,4′-dimethyl ether. R_f 0·78 (*A*), 0·98 (*B*). Kaempferol 4′-methyl ether. R_f 0·18 (*A*), 0·45 (*B*). Apigenin 4′-methyl ether. R_f 0·24 (*A*), 0·54 (*B*).

The two rare dimethyl derivatives of quercetin have been also found recently together in *Larrea cuneifolia*.[4] *Distribution.* Qu 3,3′-dimethyl ether in *P. deltoides*, *P. sargentii* and one clone of *P. euramericana*. Qu 3,7-dimethyl ether in *P. wislicenii*, *P. euramericana*, *P. acuminata*, *P. cathayana*, *P. simonii*, *P. szechuanica*, *P. candicans*, *P. generosa*, *P. deltoides* × *P. simonii*. Km 7,4′-dimethyl ether in *P. androscoggin* (*P. maximowiczii* × *P. tricho-*

* β-Aminoaethyl ester of diphenyl boric acid.

[1] WOLLENWEBER, E. and EGGER, K. (1971) *Phytochemistry* **10**, 225.
[2] WOLLENWEBER, E. and WEBER, W. (1973) *Z. Pflanzenphys.* **66**, 125.
[3] WOLLENWEBER, E., CHADENSON, M. and HAUTEVILLE, M. (1974) *Z. Naturf.*, in press.
[4] VALESI, A. G., RODRIGUEZ, E., VANDER VELDE, G. and MABRY, T. J. (1972) *Phytochemistry* **11**, 2821.