

Die Elution erfolgte mit Petroläther, Petroläther–Dichlormethan, Dichlormethan und schließlich mit Dichlormethan–Aceton–Gemischen. *Aurapten*—mit CH_2Cl_2 eluiert, Schmp. 66–68° (MeOH). In DC, UV- und IR-Spektren identisch mit auth. *Aurapten*. *Imperatorin*—mit CH_2Cl_2 eluiert, Schmp. 101–102° (n-Hexan). In DC, UV- und IR-Spektren identisch mit auth. *Imperatorin*. *Phellopterin*—mit CH_2Cl_2 eluiert, Schmp. 101–103° (MeOH). In DC, UV- und IR-Spektren identisch mit auth. *Phellopterin*. *N-Methylflindersin* (Pt/42)—mit CH_2Cl_2 –Aceton (9:1) eluiert. Schmp. 83–85° (n-Hexan). In DC, UV-, IR- und KMR-Spektren identisch mit auth. *N-Methylflindersin* (hergestellt nach [10]). 4,6,8-Trimethoxy-3-(3',3'-dimethylallyl)-*N-methylchinolon*-(2) (1) (Pt/46) mit CH_2Cl_2 –Aceton (95:5) eluiert. Schmp. 69–71° (Petroläther). UV: $\lambda_{\text{max}}^{\text{MeOH}}$: 348, 295 nm ; 283, 257, 237 nm ; $\log \epsilon$: 3,76; 3,98; 4,07; 4,46; 4,60. IR: $\nu_{\text{max}}^{\text{KBr}}$: 2960, 2850, 1640, 1620, 1580, 1480, 1465, 1450, 1370, 1270, 1200, 1060, 860 cm^{-1} . KMR: δ (CDCl_3 , TMS innerer Standard): 1,7; 1,9 (J 3 H *br.s.* = $\text{C}(\text{CH}_3)_2$); 3,4 (2 H *d* – CH_2 – $\text{CH}=\text{}$); 3,95 (9 H *s* 3OMe); 3,97 (3 H *s* NCH_3); 5,3 (1 H *tr* – CH_2 – $\text{CH}=\text{}$); 6,7 (1 H *d* H7); 6,9 (1 H *d* H5) ppm. MS: 317 (M^+ , 77%); 302 ($\text{M}^+ - \text{CH}_3$, 100%); 275 ($\text{M}^+ - \text{C}_3\text{H}_6$, 92%) (vgl. 8). *Ptelecortin* (2) (Pt/45)—mit Dichlormethan–Aceton (9:1) eluiert. Schmp. 122–124° (n-Hexan). In DC, UV und IR-Spektren identisch mit auth. *Ptelecortin*.

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NORCARPESTEROL AND A RELATED STEROL FROM *SOLANUM XANTHOCARPUM**

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Key Word Index—*Solanum xanthocarpum*; Solanaceae; steroids; norcarpesterol; 4 α -methyl-24 ζ -methylcholest-7-ene-3 β ,22 ζ -diol.

Plant and source. *Solanum xanthocarpum*. The plant material was supplied by Dr. Quentin Johnes, New Crops Research Branch, U.S. Department of Agriculture, Beltsville, Md, U.S.A. **Previous work.** carpesterol [1, 2], cycloartenol, cycloartanol, 4 α -methyl-24 ζ -ethylcholest-7-en-3 β -ol [3], 4 α -methyl-24 ζ -ethylcholest-7-ene-3 β ,22 ζ -diol, 4 α -methyl-24 ζ -ethylcholest-7-en-6-one-3 β ,22 ζ -diol, 22 ζ -hydroxy-6-oxo-4 α -methyl-24 ζ -ethylcholest-7-en-3 β -yl *p*-(hydroxy)benzoate,

14 α ,22 ζ -dihydroxy-6-oxo-4 α -methyl-24 ζ -ethylcholest-7-en-3 β -yl benzoate, 14 β ,22 ζ -dihydroxy-6-oxo-4 α -methyl-24 ζ -ethylcholest-7-en-3 β -yl benzoate [4], phytosterols, β -solamargin, solamargin, solasonine [3].

Present work. Crude preparations of carpesterol and 4 α -methyl-24 ζ -ethylcholest-7-ene-3 β ,22 ζ -diol from *S. xanthocarpum* were subjected to preparative TLC, and yielded two new sterols, norcarpesterol and 4 α -methyl-24 ζ -methylcholest-3 β ,22 ζ -diol, respectively. *Norcarpesterol*. Colourless plates after recrystallization from EtOAc, mp

* cf. Ref. [4] for the preceding paper.

236–237°, $[\alpha]_D^{20} + 67.1^\circ$, $C_{36}H_{52}O_4$. IR (KBr) $\nu_{\max}$ cm^{-1} : 3600, 3500 (OH), 1712 (ester C=O), 1670 (α,β -unsaturated ketone), 1625 (aromatic). NMR ($CDCl_3$) ppm: 4.70 (1H, *m*, C_{3x} – H), 5.57 (1H, *bs*, C_7 – H), 0.62 (3H, *s*, C_{18} – 3H), 0.93 (3H, *s*, C_{19} – 3H), 3.77 (1H, *d*, J 10 Hz; C_{22} – H), 1.16 (3H, *d*, J 6 Hz, C_{30} – 3H), 8.06 (2H, *q*, J_1 7, J_2 1.5 Hz), 7.57 (1H, *q*, J_1 7, J_2 1.5 Hz), 7.41 (2H, *t*, J 7 Hz). MS *m/e* (relative abundance): 548 (27), 426 (99), 312 (100), 297 (43), 283 (23), 257 (99), showing M^+ less than the parent peak of carpesterol by 14 mass units in spite of many same fragment ions recognized in the spectra of norcarpesterol and carpesterol. Because the same aldehyde, mp 177–180°, $C_{30}H_{38}O_4$, IR (KBr) $\nu_{\max}$ cm^{-1} : 1710 (ester, aldehyde), 1675 (α,β -unsaturated ketone), 1625 (aromatic), NMR ($CDCl_3$) ppm: 9.5 (1H, *d*, J 7, C_{22} – H), 7.3–8.1 ppm (5H, aromatic H), 5.75 (1H, unresolved, C_7 – H), was obtained through ozonolysis of carpesterol dehydrate [3] and norcarpesterol dehydrate, mp 181–183°, $C_{36}H_{50}O_3$, IR ($CHCl_3$) $\nu_{\max}$ cm^{-1} : 1710, 1275 (ester), 1670 (α,β -unsaturated ketone), 1625 (aromatic), NMR ($CDCl_3$) ppm: 7.3–8.1 ppm (5H, aromatic H), 5.72 (1H, unresolved, C_7 – H), 5.2 (2H, *m*, C_{22} – H and C_{23} – H), the structure, 22 ζ -hydroxy-6-oxo-4-methyl-24 ζ -methylcholest-7-en-3 β -yl benzoate is proposed for norcarpesterol. 4 α -

Methyl-24 ζ -methylcholest-7-ene-3 β ,22 ζ -diol. Colourless needles from AcOEt, mp 176–177°, $[\alpha]_D^{20} + 18.7^\circ$, $C_{29}H_{50}O_2$. IR (KBr) $\nu_{\max}$ cm^{-1} : 3600, 3400 (OH), NMR ($CDCl_3$) ppm: 3.18 (1H, *m*, C_{3x} – H), 5.18 (1H, *d*, J 6 Hz, C_7 – H), 0.57 (3H, *s*, C_{18} – 3H), 0.83 (3H, *s*, C_{19} – 3H), 3.77 (1H, *d*, J 10, C_{22} – H). MS *m/e* (relative abundance): 430 (17), 412 (17), 316 (6), 287 (28), 285 (17), 269 (19), 302 (100). The Wolf–Kishner reduction of norcarpesterol provided two products, one of which showed identical properties to those of the isolated compound, 4 α -methyl-24 ζ -methylcholest-7-ene-3 β ,22 ζ -diol [TLC, IR, NMR].

Comment. Norcarpesterol appears to be biosynthesized in a similar way as carpesterol, (22*R*)-22-hydroxy-6-oxo-4 α -methyl-5 α -stigmast-7-en-3 β -yl benzoate, a major sterol in *Solanum xanthocarpum*. Also, hydroxylation at C_{22} appears to be common in both the 4 α -methyl-24-methyl- and 4 α -methyl-24-ethyl-cholesteryl derivatives in this plant.

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