*Phytochemistry*, 1976, Vol. 15, p. 435. Pergamon Press. Printed in England.

# STERINE AUS *UMBILICARIA CYLINDRICA*

HELMUT RIPPERGER und SIEGFRIED HUNECK
Institut für Biochemie der Pflanzen des Forschungszentrums für Molekularbiologie und Medizin der Akademie der Wissenschaften der DDR, DDR-401 Halle (Saale), Weinberg

(*Received* 13 *August* 1975)

**Key Word Index**—*Umbilicaria cylindrica*; Umbilicariaceae; lichesterol; ergosterol.

*Pflanze. Umbilicaria cylindrica* (L.) Del. *Herkunft.* Leg. H. Ripperger, ČSSR, Vysoké Tatry, Slavkovský Štít, 1300–1600 m ü. M., Juni 1974, det. S. Huneck, Juli 1974. *Bisherige Arbeit.* Über Zucker [1]. *Jetzige Arbeit.* Aus *U. cylindrica* wurden neben einer nicht identifizierten Verbindung $C_{29}H_{48}O$ Lichesterin [2,3] und Ergosterin isoliert. Beide isomeren Sterine zeigen charakteristische Intensitätsunterschiede der Peaks in den Massenspektren [3]. Während Ergosterin häufig in Pilzen und Flechten vorkommt, ist Lichesterin bisher nur aus *Xanthoria parietina* [2], *Pseudevernia furfuracea* [4], *Leptosphaeria typhae* [3], einer Mutante von *Saccharomyces cerevisiae* [5] und aus *Chlorella ellipsoidea* [6] bekannt.

## EXPERIMENTELLES

*U. cylindrica* (169 g lufttrockenes und gemahlenes Material) wurde 16 h mit $Et_2O$ extrahiert, der Extrakt eingedampft und der Rückstand mit 14 proz. MeOH-KOH 2 hr unter $N_2$ unter Rückfluß verseift. Das nach üblicher Aufarbeitung resultierende Rohsterin (0·25 g) wurde an 20 g Kieselgel chromatographiert: nach 60 ml Benzin und 70 ml Benzin–EtOAc–Benzol (90:5:5) eluierten 220 ml Benzin–EtOAc–Benzol (85:10:5) nacheinander 1 mg Substanz mit Schmp. 150–155° (aus EtOH Nadeln) und Summenformel $C_{29}H_{48}O$ [MS 70 eV *m/e* (rel. Int.): 412·3709, $M^+$ (39), 397·3462, M − Me (21), 328·2752, $C_{23}H_{36}O$ (48), 285·2227, $C_{20}H_{29}O$ (100), 269·2265, $C_{20}H_{29}$ (18)], 15 mg Lichesterin vom Schmp. 132–137° (EtOH) und $[\alpha]_D^{20}$ −32·7° ($CHCl_3$; *c* = 0·64) und 11 mg Ergosterin vom Schmp. 145–153° und $[\alpha]_D^{20}$ −124·8° ($CHCl_3$; *c* = 0·67). Das aus *U. cylindrica* isolierte Lichesterin ist nach MS [2,3] [70 eV *m/e* (rel. Int.): 396·3386, $M^+$ (79), 381·3136, M − Me (6), 363·3039, M − Me − $H_2O$ (100), 353·2844, M − $CH(Me)_2$ (2), 337·2891, $C_{25}H_{37}$ (8), 271·2065, M − Seitenkette (21), 253·1958, M − Seitenkette − $H_2O$ (16), 217·1584, $C_{15}H_{21}O$ (12), 211·1484, M − Seitenkette − Ring D − $H_2O$ − H[7] (12)], $^1$H-NMR [2] [100 MHz, $CDCl_3$, TMS, $\delta$ 0·67 (*s*, C-18), 0·82 (*d*, *J* 7 Hz, C-26), 0·84 (*d*, *J* 7 Hz, C-27), 0·92 (*d*, *J* 7 Hz, C-28), 1·03 (*d*, *J* 5 Hz, C-21), 1·18 (*s*, C-19), 2·27 (*m*, 4$\beta$-H), 2·35 (*m*, 4$\alpha$-H), 2·53 (*m*, C-7), 3·55 (*m*, 3$\alpha$-H), 5·21 (*m*, C-22, C-23), 5·45 ppm (*m*, C-6)] und GLC (1% SE-30, Gaschrom Q, 1·5 m × 6 mm, 225°, 60 ml $N_2$/min) identisch mit authentischem Material [2].

*Danksagung*—Herrn Professor Dr. H. Budzikiewicz, Köln, danken wir für das NMR-Spektrum, Herrn Dr. P. Franke, Berlin, für die Massenspektren, Herrn Dr. L. J. Goad, Liverpool, für den gaschromatographischen Vergleich von Lichesterin, Frau H. Ripperger für Hilfe beim Sammeln des Pflanzenmaterials und Frau E.-M. Schneider für Unterstützung bei der chemischen Arbeit.

## LITERATUR

1. Culberson, C. F. (1969) *Chemical and Botanical Guide to Lichen Products*, The University of North Carolina Press, Chapel Hill.
2. Lenton, J. R., Goad, L. J. und Goodwin, T. W. (1973) *Phytochemistry* **12**, 1135.
3. Alais, J., Lablache-Combier, A., Lacoste, L. und Vandewalle, B. (1974) *Phytochemistry* **13**, 2833.
4. Wojciechowski, Z. A., Goad, L. J. und Goodwin, T. W. (1973) *Phytochemistry* **12**, 1433.
5. Barton, D. H. R., Corrie, J. E. T., Widdowson, D. A., Bard, M. und Woods, R. A. (1974) *J. Chem. Soc., Perkin Trans.* **1**, 1326.
6. Patterson, G. W., Thompson, M. J. und Dutky, S. R. (1974) *Phytochemistry* **13**, 191.
7. Vgl. Budzikiewicz, H., Djerassi, C. und Williams, D. H. (1964) *Structure Elucidation of Natural Products by Mass Spectrometry*, Vol. II, S. 98, Holden-Day, San Francisco.

---

*Phytochemistry*, 1976, Vol. 15, pp. 435–436. Pergamon Press. Printed in England.

# SIMPLE ANTIBIOTICS FROM THE RED SEAWEED *DASYA PEDICELLATA* VAR. *STANFORDIANA*

WILLIAM FENICAL and OLIVER MCCONNELL
Institute of Marine Resources, Scripps Institution of Oceanography, La Jolla, CA 92093, U.S.A.

(*Received* 12 *August* 1975)

**Key Word Index**—*Dasya pedicellata* var. *stanfordiana*; Dasyaceae; Rhodophyceae; *p*-hydroxybenzaldehyde; *p*-hydroxybenzyl alcohol.

*Plant. Dasya pedicellata* var. *stanfordiana*, a mixed collection of ⊕, ♂ and + stages collected April, 1974, Isla Angel de la Guarda, Gulfo de California, Mexico. *Previous work.* none.

*Present work.* The $CH_2Cl_2$ extract of the air-dried and finely ground algae (0·50% dry wt) was chromatographed over silica gel (Davison grade 62). The $C_6H_6$–$Et_2O$ eluate (1:1) gave *p*-hydroxybenzaldehyde, mp 114–116°

($CCl_4$) (0·005%) which was identical to a commercial sample as determined by NMR, IR and MS comparison. Continued elution gave *p*-hydroxybenzyl alcohol, mp 115–116° (0·002%) also identical in all respects (NMR, IR, MS) to an authentic sample. *p*-Hydroxybenzaldehyde appears to be the active component of the extract, which shows moderate antimicrobial activity against *Vibrio anguillarium*, *Candida albicans*, and *Staphylococcus aureus*.

*Acknowledgements*—The authors express appreciation to Mr. Jim Norris, Marine Science Institute, University of California, Santa Barbara, for an accurate taxonomic assignment of this alga and thank the captain and crew of the R/V DOLPHIN for aid in collection.

*Phytochemistry*, 1976, Vol 15, p. 436. Pergamon Press. Printed in England.

# LIPID AND PHENOLIC CONSTITUENTS OF *TECOMA RADICANS*

TEMPLE U. OKARTER, PAUL L. SCHIFF, JR., JOSEPH E. KNAPP and DAVID J. SLATKIN
Department of Pharmacognosy, School of Pharmacy, University of Pittsburgh, Pittsburgh, PA 15261 U.S.A

(*Received* 25 *July* 1975)

**Key Word Index**—*Tecoma radicans*; Bignoniaceae; *n*-alkanes; squalene; *n*-alkanols; salicylic acid; 3,4,5-trimethoxycinnamic acid; ferulic acid; ursolic acid.

*Plant. Tecoma radicans* (L.) Juss; *Source.* Lafayette County, Mississippi, USA. *Previous work.* Carotenoid flower pigments [1], boschniakine [2]. *Present work.* The dried, ground leaves (3·6 kg) were extracted by percolation with EtOH. After removal of the solvent, *in vacuo*, at 40° the residue (235 g) was partitioned between 2% HCl and $CHCl_3$ to give basic (7·8 g) and non-basic (210 g) fractions. The non-basic fraction was fractionated by standard methods into neutral (98·2 g), acidic (4·8 g), and phenolic (57·0 g) fractions.

*Neutral fraction.* Chromatography over silicic acid and elution with light petrol gave an alkane fraction which crystallized from MeOH (23 mg); mp 61–63°; $\nu_{max}^{KBr}$ $cm^{-1}$: 2940, 2870, 1465, 1380, 730 and 720. GLC on 160 cm column of 3·0% OV-101 on Gas Chrom Q (80–100 mesh) showed the mixture to be composed primarily of $C_{23}$–$C_{31}$ *n*-alkanes; $C_{23}$ (6%), $C_{24}$ (13), $C_{25}$ (10), $C_{26}$ (4), $C_{27}$ (12), $C_{28}$ (9), $C_{29}$ (30), $C_{30}$ (10), $C_{31}$ (15). The identity was confirmed by GC–MS.

Elution with light petrol–$CHCl_3$ (4:1) afforded a fraction which was rechromatographed over silicic acid. Elution with light petrol gave squalene; $\nu_{max}^{KBr}$ $cm^{-1}$: 2990, 2940, 2870, 1670, 1440, 1375, 1105, 985, 890 and 830; MS: M+ *m/e* 410 (7%), 395 (10%), 367 (3), 341 (10), 149 (40) and 136 (100). Direct comparison (IR, MS, NMR) with an authentic sample confirmed the identity.

Elution with light petrol–$CHCl_3$ (2:1) gave a fraction which was rechromatographed over silicic acid. Elution with light petrol–$CHCl_3$ (7:3) afforded an *n*-alkanol fraction which crystallized from light petrol (14 mg); mp 82–83°; $\nu_{max}^{KBr}$ $cm^{-1}$: 3400 (broad), 2940, 2870, 1465, 1060, 730 and 720; GLC of the TMS ethers on 160 cm column of 3% OV-17 on Gas Chrom Q (80–100 mesh) showed the mixture to be composed of $C_{25}$-$C_{31}$ *n*-alkanols: $C_{25}$ (3%), $C_{26}$ (4), $C_{27}$ (21), $C_{28}$ (46), $C_{29}$ (14) $C_{30}$ (7), $C_{31}$ (3). The identity was confirmed by GC–MS of the TMS ethers.

*Acidic fraction.* Chromatography over silicic acid and elution with light-petrol–$CHCl_3$ (1:1) gave salicylic acid (45 mg), mp 155–156° (light petrol); $\nu_{max}^{KBr}$ $cm^{-1}$: 3000 (broad), 1655, 1612, 1580, 1485, 1440, 1295, 1250, 1210, 1160, 1030, 760, 695 and 660. Direct comparison (mp, mmp, IR, MS) with an authentic sample confirmed the identity. Elution with light petrol–$CHCl_3$ (3:7) afforded 3,4,5-trimethoxycinnamic acid (15 mg), mp 123·5–124·5° (light petrol–EtOAc); $\nu_{max}^{KBr}$ $cm^{-1}$: 3000 (broad), 1690, 1625, 1580, 1500, 1450, 1400, 1330, 1285, 1250, 1200, 1120, 1000, 980 and 830. Direct comparison (mp, mmp, IR, MS) with an authentic sample confirmed the identity. Elution with light petrol–$CHCl_3$ (1:4) yielded ferulic acid (65 mg), mp 167·5–169·5° (light petrol–EtOAc); $\nu_{max}^{KBr}$ $cm^{-1}$: 3460, 3000 (broad), 1680, 1620, 1590, 1510, 1435, 1275, 1205, 1040, 940, 855 and 805. Direct comparison (mp, mmp, IR. MS) with an authentic sample confirmed the identity.

Elution with MeOH–$CHCl_3$ (4:96) afforded ursolic acid (135 mg), mp 257° (EtOH); $\nu_{max}^{KBr}$ $cm^{-1}$: 3460 (broad), 2945, 2895, 1690, 1450, 1380, 1370, 1030 and 995. Direct comparison (mp, mmp, IR, MS) with an authentic sample confirmed the identity.

*Acknowledgements*—The authors are grateful to Mr. John Naworal, Graduate School of Public Health, University of Pittsburgh for determining the mass spectra. This investigation was supported in part by Research Grant 5SO1RR05455-10 from the National Institutes of Health Education and Welfare, Bethesda, Maryland 20014. The mass spectrometer facility was supported by Research Grant RR-00273 to the University of Pittsburgh from the National Institutes of Health.

## REFERENCES

1. Grangaud, R. and Garcia, I. (1952) *Compt. Rend. Soc. Biol.* **146**, 1577.
2. Gross, D., Berg, W. and Schütte, H. R. (1972) *Phytochemistry* **11**, 3082.