vor,[1] während die Wurzel nur selten untersucht wurde. Wir haben nachgeweisen, daß das Wurzelöl überwiegend aus Kohlenwasserstoffen besteht, die z.T. thermolabil sind;[2] kürzlich wurde daraus Geijeren (**1**) isoliert.[3] Durch GLC bei 100° läßt sich jedoch zeigen, daß **1** nur in sehr geringen Mengen im Wurzelöl enthalten ist und ein anderer Kohlenwasserstoff (**2**) mit dem gleichen MG wie **1** (MS *m/e* 162) vorherrscht. Oberhalb 120° lagert sich **2** vorweigend zu **1** um, das weitgehend als Thermoartefakt anzusehen ist und im genuinen Öl frischer Pflanzen höchstens bis zu 1% enthalten ist. **2** wurde aus dem durch Wasserdampfdestillation gewonnenen ätherischen Öl frischer Wurzeln über das entsprechende $AgNO_3$-Addukt isoliert und nach SC an Al_2O_3 mit *n*-Pentan in reiner Form erhalten. MG 162 (MS). UV (EtOH) λ_{max} 251 nm; λ_{min} 228 nm. IR (NaCl) ν_{max} 2925, 2858, 1455, 1379, 1177, 980, 888, 860, 720 cm^{-1}. GLC: $I^{100}_{Carbowax\ 20M} = 1526$. Aufgrund der Übereinstimmung von MG, UV- bzw. IR-Spektrum sowie des gc-Verhaltens mit entsprechenden Werten der Literatur[4] konnte **2** als 1,5-D methylcyclodeca-1,5,7-trien (Pregeijeren) identifiziert werden. Oberhalb 120° wandelt sich **2** unter Cope-Umlagerung in **1** um.

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CHRYSOPHANIC ACID, CHRYSOPHANEIN AND CHAPARRIN FROM

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Key Word Index—*Alvaradoa*; Simaroubaceae; chrysophanic acid; chrysophanein; chaparrin; anthraquinones; quassinoid.

Plant. Alvaradoa amorphoides Liebm. is a small tree belonging to the Simaroubaceous family which grows in the southern part of Mexico and is named "camaron" or "canelillo" by the local population.

Present work. Column chromatography of the methanolic extract of the dried defatted rods yielded three compounds, *A*, *B* and *C*.

Compound A was identified as chrysophanic acid. Yellow plates from benzene or methanol m.p. 194–196°. Empirical formula: $C_{15}H_{10}O_4$ (SM: $M^+ = 254$) (found: C 70·90%; H 3·89%. Calculated: C 70·86%; H 3·96%). λ_{max}: 226 nm ($\log \epsilon = 4{\cdot}55$), 257 nm ($\log \epsilon = 4{\cdot}35$) and 430 nm (4·05). Its NMR spectrum ($CDCl_3$) displays the following signals: 1

singlet (3 H) at 2·42 ppm (→C–CH_3); two signals (1 H each one) at 11·8 and 11·93 ppm, disappearing after deuteration and which can be attributed to the two phenolic OH. Aromatic protons: multiplet centered at 7·0 ppm (H_2), quadruplet centered at 7·22 ppm (H_7) ($J_{6,7}$ 7·5 Hz; $J_{5,7}$ 2·5 Hz), multiplet at 7·56 (H_4), triplet at 7·6 ppm (H_6), and quadruplet centered at 7·75 ppm (H_5).

Diacetate $C_{19}H_{14}O_6$, m.p. 205–207° (M^+ at m/e 338). Its NMR spectrum shows a singlet (6H) at 2·41 ppm (2$\underline{CH_3}$COO–) and a singlet (3H) at 2·47 ppm (→C–CH_3). The signals due to the aromatic protons are found more downfield than in the non-acetylated compound, especially H_4 et H_5; H_2 (multiplet at 7·2 ppm), H_7 (quadruplet at 8·2 ppm).

Finally, the identification of compound A was achieved by direct comparison with an authentic sample of chrysophanic acid.

Compound B was identified as the glucoside of chrysophanic acid, chrysophanein. Yellow needles from ethyl acetate or alcohol, m.p. 245–248°. It gives a red brown color with $FeCl_3$; λ_{max}: 256 nm (log ϵ = 4·04) and 410 nm (3·53). Pentaacetate m.p. 188–192°, $[\alpha]_D$ = −35°.4 (c = 0·79; $CHCl_3$) which does not give any more a color with Cl_3Fe.SM (M^+ = 416). Its NMR spectrum reveals one methyl grouping (singlet, 3H at 2·47 ppm), 5 acetoxy groupings 3 singlets (3H each one) at 2·51; 2·12 and 2·07 ppm and 1 singlet (6H) at 2·03 ppm. Study of the pattern given by the aromatic protons shows clearly that the isolated pentaacetate consists of a mixture of 1-acetyl- and 8-acetyl-chrysophanol-monoglycosid-tetraacetate in the ratio of (1:3).[1,2] Consequently, chrysophanein isolated from *Alvaradoa* is a mixture of 1- and 8-glucosyl chrysophanol. It behaves on TLC as the sample of chrysophanein we were kindly sent by Dr. C. Bellaart and Prof. L. Horhammer.

Compound C has been identified as the quassinoid, chaparrin[3] m.p. 298–300° Tetraacetate, m.p. 230°. The identification has been performed by direct comparison with authentic materials by TLC, IR and NMR analysis.

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