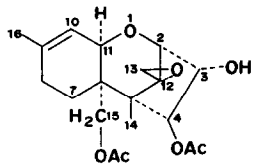

(1)

EXPERIMENTELLES

Der Pilz wurde in einem Nährmedium angezogen, das im l. 50 g D-Glucose, 5 g KH_2PO_4, 1·2 g NH_4NO_3, 1·0 g $MgSO_4.7H_2O$ und 2·0 ml Spurenstofflösung enthielt. Für die Spurenstofflösung wurden 2·2 g $ZnSO_4.7H_2O$, 1·0 g $FeSO_4.7H_2O$, 392 mg $CuSO_4.5H_2O$, 88 mg $Na_2B_4O_7.10H_2O$, 72 mg $MnCl_2.2H_2O$ und 37 mg $(NH_4)_6Mo_7O_{24}.4H_2O$ in 1 l. H_2O gelöst. Die Dauer der Kultivierung war 2–5 Tage. Nach Abfiltrieren des Mycels wurde bei pH 1·3–1·4 mit Essigester ausgeschüttelt. Aus 45 l. erhielt man nach Abdestillieren des Essigesters i. Vak. 9·9 g Rückstand, der an Kieselgel (Merck, 0·05–0·2 mm) chromatographiert wurde. Eluiert wurde mit $CHCl_3$; Kristallisation aus EtOH/Et_2O ergab 286 mg 1 vom Schmp. 163–165°, $[\alpha]_D^{20}$ −19·3° (c = 0·76 in $CHCl_3$) und R_f = 0·32 [$CHCl_3$/EtOAc/HOAc (90:10:5), Nachweis mit einer gesätt. Lösung von $Ce(SO_4)_2$ in 50 proz. H_2SO_4] [Lit. [2]: Schmp. 162–164°, $[\alpha]_D$ −27° in $CHCl_3$]. IR (KBr): 1738 (OAc), 1643 (C=C) und 1248 cm^{-1} (OAc); ^{1}H-NMR-Spektrum (100 MHz, $CDCl_3$, TMS): δ = 0·84 (*s*, 14-H_3), 1·74 (*s*, breit 16-H_3), 2.05 (*s*, OAc), 2·14 (*s*, OAc), 2·77 (*d*, *J* 4 Hz, 13-H), 3·05 (*d*, *J* 4 Hz, 13-H), 3·27 (*d*, *J* 3 Hz, OH, gegen D austauschbar), 3·69 (*d*, *J* 5 Hz, 2-H), 3·98 (*d*, *J* 13 Hz, 15-H), 4·18 (*d*, breit, 5 Hz, 11-H), 4·26 (*d*, 13 Hz, 15-H und *m*, 3-H), 5·16 (*d*, *J* 3 Hz, 4-H) und 5·52 ppm (*d*, breit, *J* 5 Hz, 10-H); Entkopplung: 13-H → 13-H, 11-H → 10-H und 16-H_3, 3-H → OH, 2-H und 4-H, 4-H → 3-H, 10-H → 16-H und 11-H; die Zuordnung stimmt mit der in Lit. [2] überein; ^{1}H-NMR-Spektrum mit Verschiebungsreagens [Eu(fod)$_3$]: Die gefundenen Werte befinden sich in Übereinstimmung mit der sterischen Anordnung der Wasserstoffatome in 1. ^{13}C-NMR-Spektrum ($CDCl_3$, TMS): praktisch identisch mit dem in Lit. [4] publizierten Spektrum; Massenspektren: Felddesorption m/e = 366 (M^+); Elektronenstoßionisation kein M^+, m/e = 348 (M-H_2O), 306 (M-AcOH, gef. 306·1468, ber. für $C_{17}H_{22}O_5$ 306·1467).

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DITERPENES FROM *ARAUCARIA ANGUSTIFOLIA*

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Key Word Index—*Araucaria angustifolia*; Araucariaceae; sitosterol; pinoresinol dimethylether; sugiol; agathic, agatholic and imbricatolic acids; diterpenes.

Plant. Araucaria angustifolia O. Ktze. (*Araucaria brasiliana* A. Rich, pinheiro do Paraná) [1]. *Source.* Widespread throughout southern Brazil, specially in the state of Paraná. *Uses.* Furniture, crates and paper pulp. *Previous work.* On roots [2] and wood [3].

Present work. Bark. The C_6H_6 extract of dried and milled bark was separated into neutral (80·51 g) and acidic (75·23 g) fractions, which were chromatographed on alumina and Si gel columns, respectively. *Neutral.* Besides (a) *sitosterol* (1·07 g), the neutral fraction furnished (b) *pinoresinol dimethylether* [2] (0·37 g), mp 107–109°; $[\alpha]_D^{25}$ + 46° (c 1, $CHCl_3$). These substances were identified by direct comparison with authentic samples (IR, PMR, mp and mmp). *Acidic.* Four diterpenes were obtained. (c) *Sugiol* [4] (30 mg), mp 291–293°; $[\alpha]_D^{25}$ +32° (c 1, C_5H_5N), identical in all respects with an authentic sample. (d) *Agathic acid* [5] (2·75 g), mp 201–203°; $[\alpha]_D^{25}$ +64° (c 1,

EtOH). The IR spectrum showed strong absorption at 3400–2300, 3070, 1685, 1675, 1635, 1415, 1255 e 895 cm^{-1} suggesting the presence of carboxyl, conjugated double bond and terminal methylene groups; confirmed by the PMR spectrum which showed also signals of three methyl groups. Mono- and dimethyl esters were prepared. Dimethyl agathate [5–7], $[\alpha]_D^{25}$ +54° (*c* 1, $CHCl_3$); MS M^+ *m/e* 348·2293 ($C_{22}H_{34}O_4$), was reduced to agathadiol [5–7], mp 104–106°, $[\alpha]_D^{25}$ +32° (*c* 1, $CHCl_3$). (e) *Agatholic acid* [7] (350 mg), mp 183–184°; $[\alpha]_D^{25}$ +46° (*c* 1, EtOH). The IR spectrum had strong absorption at 3500–2400, 3280, 3075, 1680, 1655, 1250, 1240, 1165, 1040 and 905 cm^{-1}, indicating the presence of carboxyl, hydroxyl, conjugated double bond and terminal methylene groups. The PMR spectrum was similar to that of agathic acid, excepting the AB quartet due to $-C\underline{H}_2OH$. Methyl agatholate [7], mp 71–73°; $[\alpha]_D^{25}$ +43° (*c* 1, $CHCl_3$); MS M^+ *m/e* 334·2502 ($C_{21}H_{34}O_3$), was prepared and reduced to agathadiol. (f) *Imbricatolic acid* [8,9] (0·79 g), oily (mp 52–60°, after drying *in vacuo*); $[\alpha]_D^{25}$ +48° (*c* 1, $CHCl_3$); MS M^+ *m/e* 322. The absorption bands in the IR spectrum at 3400, 3200–2400, 3080, 1700, 1650, 1265 and 890 cm^{-1} suggested the presence of carboxyl, hydroxyl and terminal methylene groups; confirmed by the PMR spectrum δ ($CDCl_3$) 0·55 (*s*, Me at C−10); 0·90 (*br*, Me at C−13); 1·25 (*s*, Me at C−4); 3·60 (*t*, $J \sim 6$Hz, $-CH_2C\underline{H}_2OH$); 4·50 and 4·75 (both *br s*, $=CH_2$) and 7·75 (*br s*, COOH and OH). The acetate (acetyl-imbricatolic acid), $[\alpha]_D^{25}$ +45° (*c* 1, $CHCl_3$), showed in MS, M^+ *m/e* 364·2602 ($C_{22}H_{36}O_4$). The methyl ester of (f), $[\alpha]_D^{25}$ +47° (*c* 1, $CHCl_3$), MS M^+ *m/e* 336, was reduced to imbricatadiol [8,9], mp 111–113°; $[\alpha]_D^{25}$ +25° (*c* 1, $CHCl_3$). Authentic samples were not available but the spectral data were in accordance with those reported for the three diterpenic acids [5–9].

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TEREBENTHIFOLIC ACID AND BAUERENONE: NEW TRITERPENOID KETONES FROM *SCHINUS TEREBENTHIFOLIUS*

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Key Word Index—*Schinus terebenthifolius*; Anacardiaceae; amyrin; amyrenone; bauerenone; terebenthifolic acid.

Studies of the terpene constituents of *Schinus terebenthifolius* Radii, commonly known as Aroeira, have led to the isolation of schinol [1–4], masticadienonic acid [3], sitosterol, triacontane, and simiarenol [4]. This note describes the isolation of additional triterpenes and their characterization by chemical and spectral methods. The benzene extract of dried and finely ground bark,