dem Massenspektrum von **3** die 9, 11 (15) Stellung der Doppelbindung sichern. Mit Alanat liefert **3** den Alkohol **5** der auch aus den Wurzeln von *O. floribunda* isoliert wird. Die oberirdischen Teile enthalten ebenfalls **2** und **4**.

Die axiale Stellung der Carboxylgruppen ergibt sich aus den beobachteten Verschiebungen im NMR-Spektrum von **3** in C_6D_5N (vgl [4]). Das Fehlen von Furanoeremophilanen in diesen *Othonna*-Arten ist bemerkenswert, da alle übrigen elf Arten, die bisher untersucht wurden, derartige Verbindungen enthalten.

EXPERIMENTELLES

NMR. Varian XL 100, in CCl_4, TMS als innerer Standard, δ-Werte; *IR*. Beckman IR 9, in CCl_4; *MS*. Varian MAT 711 mit Datenverarbeitung, 70 eV. 10 kg frisch zerkleinerte oberirdische Teile von *O. cylindrica* wurden mit Äther extrahiert und der erhaltene Extrakt an Si gel (Akt.-St. II) chromatographiert. Die mit Et_2O-Petroläther (= PÄ) eluierten Anteile (47 g) ergaben nach Veresterung mit Diazomethan nach mehrfacher Dünnschichtchromatographie (Si gel GF 254,1 mm) (Et_2O–PÄ 1:20) etwa im Verh. 1:1 **1** und **3**. 1.5 kg Wurzeln lieferten ebenfalls ein 1:1-Gemisch von **2** und **4** (20 g). Der Extrakt von 100 g Wurzeln von *O. floribunda* ergab 50 mg **5** und der von 500 g oberirdischen Teilen 800 mg **2** and **4** (*ca* 1:1).

(−)-*Pimar*-9,11(15)-*dien*-19-*säuremethylester* (**3**). Farbloses Öl. *IR*. 1729, 1155 (axiale CO_2R-Gruppe); 3090, 1640, 914, 830 (C = C) cm^{-1}. MS. M^+ *m/e* 316.239 (32%) (ber. für $C_{21}H_{32}O_2$ 316.240); $-{}^{\cdot}Me$ 301 (56); $-{}^{\cdot}CO_2Me$ 257 (50); –Isopren 248 (27); 301–MeOH und CO 241 (100); 241–Isopren 173 (49).

$$[\alpha]_{24}^{\lambda} = \begin{array}{ccccc} 589 & 578 & 546 & 436 & 365\ nm \\ \hline -59.6 & -62.0 & -71.2 & -123.0 & -195.2 \end{array}$$

(c = 1.0, $CHCl_3$)

40 mg **3** ergeben nach Reduktion mit $LiAlH_4$ 28 mg **5**, farbloses Öl. *IR*. 3640 (OH); 915, 880 (C = C) cm^{-1}. *MS*. M^+ *m/e* 288.246 (6%) (ber. für $C_{20}H_{32}O$ 288.245); $-{}^{\cdot}CH_2OH$ 257 (15); 257 –Isopren 189 (100). 70 mg **3** in 1.5 ml Dioxan und 0.5 ml H_2O gaben nach 10 hr Rühren mit 180 mg $NaJO_4$ und 2 mg OsO_4 nach PLC (Et_2O–PÄ 1:3) 15 mg **6**. 50 mg **3** ergaben nach partieller Hydrierung mit Pd–$BaSO_4$, Ozonisierung in CH_2Cl_2 bei −70° und Spaltung mit Wasser und Zinkstaub nach PLC (Et_2O–PÄ 1:3) 40 mg **7**, farbloses Öl. *MS*. M^+ *m/e* 350.245 (12%) (ber. für $C_{21}H_{34}O_4$ 350.246. 14 mg **7** lieferten nach Reduktion mit $LiAlH_4$ und PLC (Et_2O–PÄ 3:2) 6 mg **8**, farbloses Öl. *MS* M^+ *m/e* 354.275 (3%) (ber. für $C_{21}H_{38}O_4$ 354.277).

Anerkennung—Der Deutschen Forschungsgemeinschaft danken wir für die Förderung dieser Arbeit.

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DITERPENE RESIN ACIDS OF *PINUS DENSIFLORA* NEEDLES AND CORTEX

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Key Word Index—*Pinus densiflora*; Pinaceae; resin acids; 4-epicommunic acid; 8(17),*E*-12,14-labdatrien-18-oic acid.

Plant. Pinus densiflora Sieb. & Zucc. (Japanese Red Pine). Samples were obtained from the Morris, Olustee (Fla.), and University of Wisconsin arboreta.

Needles. The ether extracts were separated into neutral and acidic fractions by DEAE-Sephadex [1]. GLC analysis [2] of the methylated (CH_2N_2) acidic fractions on DEGS and SE-30/EGiP columns indicated the presence of a new pine resin acid at R_{pim} of 1.18 and 1.53, respectively, that comprised 50–70% of the total resin acids; the remainder consisted primarily of levopimaric/palustric acids with smaller amounts of abietic, neoabietic, sandaracopimaric, isopimaric, and dehydroabietic acids. The NMR and UV spectra for a small GLC isolate of the methyl ester suggested the identity of the resin to be the C-4 epimer of communic acid.

A 300-mg acid fraction was prepared via the DEAE-Sephadex procedure. Attempts to crystallize the sodium salt analogous to the isolation and purification of communic acid [3] were not successful. Purification was accomplished by chromatography of the methyl esters on successive 20% $AgNO_3$–Si gel columns using a stepwise gradient of 1–10% Et_2O in hexane. The methyl 4-epicommunate (methyl 8(17),*E*-12,14-labdatrien-18-oate)† was obtained as a colourless liquid of 99% purity by GLC. The contaminants, persistent during attempts at purification were probably isomers. The spectral data were in accord with data published recently for the same compound but called methyl *trans*-ozate; $[\alpha]_D^{21}$ +33.2° (c 1.0, $CHCl_3$) (lit. [4] +34.5°).

Cortex. The resin acids consisted primarily of neoabietic and levopimaric/palustric acids with the usual array of abietic, pimaric, and isopimaric type acids. In addition, very small amounts of 4-epicommunic and 4-epiimbricataloic acids were found, (Imbricataloic acid was found in slash pine [5].).

The 4-epicommunic acid was also found in the needles of *Pinus nigra* and *Pinus nigra* × *P. resinosa* hybrids

* Maintained at Madison, Wis. (U.S.A.), in cooperation with the University of Wisconsin. A preliminary account of this work was included in a paper by the author at the 9th International Symposium on Chemistry of Natural Products, Ottawa, Canada (1974).

† The systematic nomenclature follows the proposals of a committee chaired by Dr. J. W. Rowe, *The Common and Systematic Nomenclature of Cyclic Diterpenes* Forest Products Laboratory, USDA, Madison, Wis. (1968, with Addenda and Corrigenda, February 1969).

and 4-epiimbricataloic acid was isolated (as the methyl ester) from *P. nigra* (Zinkel, D. F. unpublished results.)

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CYMBOPOGONOL, A NEW TRITERPENOID FROM *CYMBOPOGON CITRATUS*

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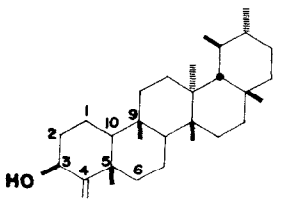
Key Word Index—*Cymbopogon citratus*; Gramineae; lemongrass; triterpenoids; cymbopogonol (D:A-friedours-4(23)-en-3β-ol).

During investigations into the constituents of the leaf wax of *Cymbopogon citratus* Stapf, lemongrass, two triterpenoids were isolated, a ketone, cymbopogone, and an alcohol, cymbopogonol. We have reported previously that cymbopogone is D:A-friedoursan-3-one [1]. The spectroscopic and analytical data for cymbopogonol, which we report here, are consistent with structure **1**.



(**1**)

Cymbopogonol crystallised from EtOH as needles (overall yield based on fresh leaves 0.02%), mp 191–193°, $[\alpha]_D$ + 15.9° ($CHCl_3$). The IR spectrum indicated the presence of an OH group (3400 cm^{-1}) and a double bond (1625 and 910 cm^{-1}) and C,H and MS analysis gave a molecular formula of $C_{30}H_{50}O$. The MS of cymbopogonol (*m/e* 426 (M^+, 87%), 411 (23%), 408 (11%), 393 (6%), 383 (7%), 341 (36%), 302 (3%), 286 (19%), 273 (30%), 218 (77%), 205 (72%), 123 (100%) and 109 (48%)) showed distinct similarities to those of friedelin and cymbopogone [1] (although with additional peaks corresponding to loss of H_2O) and clearly indicated a pentacyclic triterpenoid with a D:A-friedo structure having the hydroxyl group and the double bond in the A-ring. The NMR spectrum (in $CDCl_3$) showed two resonances in the olefinic region, δ 4.85 (1H, *d*, *J* 1.5 Hz) and 4.79 (1H, *d*, *J* 1.5 Hz), indicating an olefinic methylene group, $R^1R^2C{=}C\underline{H}_2$. A resonance at δ 4.32 (1H, *t*, *J* 3 Hz) can be assigned to an equatorial C<u>H</u>—OH proton coupling with two vicinal protons and a three proton singlet at δ 1.23 can be assigned to a methyl group that is 1,3-diaxial to a hydroxyl group [2].

Careful oxidation of cymbopogonol with chromium trioxide in pyridine gave an α,β-unsaturated ketone, mp 188–190°, $[\alpha]_D$ 0.0 ($CHCl_3$), molecular formula $C_{30}H_{48}O$ (C,H analysis and MS molecular ion at *m/e* 424). The IR spectrum showed absorptions at 1695 and 1600 cm^{-1} and the UV exhibited a maximum at 222 nm (ϵ 3800). The NMR spectrum (in $CDCl_3$) showed two resonances in the olefinic region, δ 5.57 (1H, *d*, *J* 1.5 Hz) and 5.02 (1H, *d*, *J* 1.5 Hz).

The above data can be explained if cymbopogonol is an allylic alcohol having a 3β-hydroxyl group (1,3-diaxial to a 5-methyl group) and an olefinic methylene group in the 4-position. In order to confirm this A-ring structure NMR shift reagents were employed. $Pr(fod)_3.d_{30}$ was found to give the clearest results. The observed $Pr(fod)_3.d_{30}$ induced shifts for some of the protons in cymbopogonol are given in Table 1 along with those calculated using the McConnell–Robertson equation [3]. Considering the errors that may arise due to a lack of knowledge of both the preferred conformation of cymbopogonol and the exact position of the Pr atom in the complex, the correlation is good and confirms the structure of the A-ring.

The overall structure of cymbopogonol follows from the fact that the α,β-unsaturated ketone obtained on oxidation of cymbopogonol can be hydrogenated (Pt–C catalyst) to give a saturated ketone that is identical (mp, mmp, IR and MS) with cymbopogone. Hence cymbopogonol is D:A-friedours-4(23)-en-3β-ol (**1**). This com-

Table 1. Observed and calculated* $Pr(fod)_3.d_{30}$ induced shifts for some of the protons in cymbopogonol. The values are relative to H-3α = 100

	H-2β	H-1β	H-2α	5β-Me	H–C=†	H-10α	H-1α	H–C=‡	H-6α	H-6β	9β-Me
Observed shift§	73	50	41	41	36	31	25	24	17	17	10
Calculated shift	65	55	40	40	33	26	29	24	16	16	12

* The induced shifts were calculated using the McConnell-Robertson equation [3], taking the O to Pr distance as 2.2 Å with the O-Pr axis in the H–C–O plane at an angle of 160° to the axis of the C–O bond [4]. †Olefinic proton cis to C-3. ‡ Olefinic proton trans to C-3. § Resonances were assigned according to their shapes and integrated areas.