and 4-epiimbricataloic acid was isolated (as the methyl ester) from *P. nigra* (Zinkel, D. F. unpublished results.)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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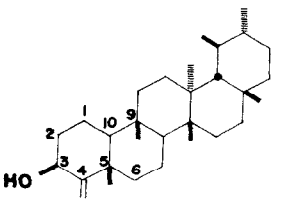
Key Word Index—*Cymbopogon citratus*; Gramineae; lemongrass; triterpenoids; cymbopogonol (D:A-friedours-4(23)-en-3β-ol).

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.

pound is only the second D:A-friedoursane type of triterpenoid to be isolated and the first triterpenoid with a 4(23) double bond.

The structural relationship between cymbopogonol and cymbopogone raises the possibility that cymbopogone is not a natural product but an artefact formed during the isolation of cymbopogonol. However, our attempts to demonstrate such a conversion have proved unsuccessful. Work is now in progress on the direct chemical correlation of cymbopogonol with α-amyrin.

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NEUE EUDESMAN-DERIVATE AUS *ISOCOMA WRIGHTII**

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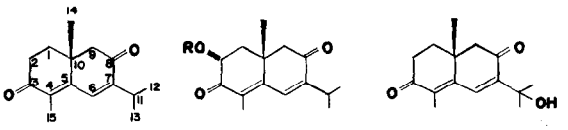
Key Word Index—*Isocoma* species; Compositae; new eudesmane type-sesquiterpenes.

Pflanze und Herkunft. Wurzeln von *Isocoma wrightii*, Prof. B. Turner, Department of Botany, University of Texas at Austin, Herbar 75–11.

Die zur Tribus Astereae gehörende Gattung *Isocoma* ist bisher noch nicht auf ihre Inhaltsstoffe untersucht worden. Der Extrakt der Wurzeln von *I. wrightii* liefert keine Acetylenverbindungen, dafür jedoch drei neue Sesquiterpene, deren Strukturen geklärt werden. Der Hauptinhaltsstoff ist das 8-Oxo-β-cyperon (**1**), während den beiden nicht trennbaren Alkoholen die Konstitutionen **2** und **4** zukommen dürften. Erst nach Acetylierung von **2** ist eine Trennung durch PLC möglich. Die absolute Konfiguration entspricht wahrscheinlich der des ß-Cyperons [1].



(1) (2) R = H (3) R = Ac (4)

In der Gattung *Haplopappus*, die der Gattung *Isocoma* nahe steht, sind derartige Sesquiterpene bisher nicht beobachtet worden. Dort findet man jedoch die für die Tribus Astereae typischen C_{10}-Acetylenderivate [2].

* 68 Mitt. in der Serie "Natürlich vorkommende Terpen-Derivate". 67 Mitt.: Bohlmann, F. und Zdero, C., vorstehend.

Table 1.

^{1}H-NMR-Daten für 1–4 (TMS als innerer Standard, δ-Werte)

	1			2	3	4
	C_6D_6	+Eu(fod)$_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$
1α–H 1β–H	*m* 1.30	*ddd* 1.57	*ddd* 1.81 *dd* 2.04	2.0	2.10	*ddd* 1.85
2α–H	*dd* 2.17	*dd* 2.74	*m* 2.60	—	—	*m* 2.60
2β–H	*ddd* 2.26	*ddd* 2.85		*dd* 4.39	*dd* 5.58	
6 –H	*s*(*br*) 6.84	7.04	7.17	*s*(*br*) 7.14	*s*(*br*) 7.15	*s*(*br*) 7.43
9α–H	*d* 2.11	2.35	2.43	*d* 2.47	*d* 2.47	*d* 2.44
9β–H	*d*(*br*) 1.94	2.20	2.52	*d*(*br*) 2.55	*d*(*br*) 2.56	*d*(*br*) 2.57
11 –H	*qq*(*br*) 3.07	3.26	3.03	*qq*(*br*) 3.02	*qq*(*br*) 3.04	—
12 –H	*d* 1.05	1.13	1.12	*d* 1.15	*d* 1.16	1.52
13 –H	*d* 1.01	1.09	1.08	*d* 1.11	*d* 1.12	
14 –H	*s* 1.86	2.23	1.96	*s* 1.98	*s* 1.99	*s* 1.98
15 –H	*s* 0.79	0.97	1.23	*s* 1.51	*s* 1.40	*s* 1.29

* 0.1 mol bezogen auf **1**. Kopplungen in Hz: **1**: $J_{1\alpha,1\beta} = 14$; $J_{1\alpha,2\alpha} = J_{1\alpha,2\beta} = 6$; $J_{1\beta,2\beta} = 3$; $J_{2\alpha,2\beta} = J_{9\alpha,9\beta} = 15$; $J_{11,12} = J_{11,13} = 7$; Einstrahlung auf 11–H → 12–H und 13–H s; 6–H scharf. **2** und **3**: 1α,2α = 6.5; 1β,2α = 12; $J_{9\alpha,9\beta} = 15$; $J_{11,12} = J_{11,13} = 7$. **4**: $J_{1\alpha,1\beta} = 14$; $J_{1\alpha,2\alpha} = 6$; $J_{1\beta,2\beta} = 3$; $J_{9\alpha,9\beta} = 15$.