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A NEW TYPE OF SESQUITERPENE AND ACORANE DERIVATIVE FROM *CALEA PRUNIFOLIA*

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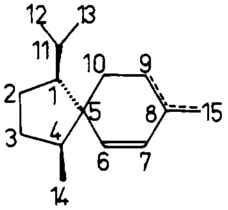
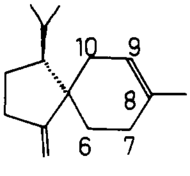
ABSTRACT.—Isolation from *Calea prunifolia* of sesquiterpenes derived from acorane, daucane, and a new type of alicyclic sesquiterpene carbon skeleton, caleprunane, is described. Furthermore, two benzofurans were isolated. The structures were elucidated by spectroscopic methods.

From the large genus *Calea* (Compositae, tribe Heliantheae, subtribe Neurolaeninae) several species have already been investigated chemically. Most species contain highly oxygenated sesquiterpene lactones (1). Having studied the constituents of a species from Costa Rica, *Calea prunifolia* H.B.K., we now report the results in this paper.

The aerial parts afforded a complex mixture of hydrocarbons that could be separated by $AgNO_3$-coated silica columns and plates. In addition to α- and β-farnesene, germacrene D, caryophyllene, and dauca-2,11-diene (2), three other hydrocarbons, the



1 Δ 8 9
2 Δ 8 15



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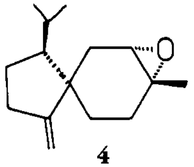

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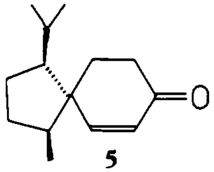

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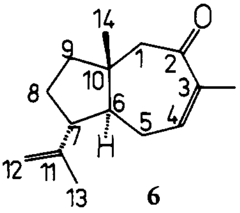

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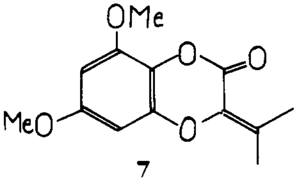

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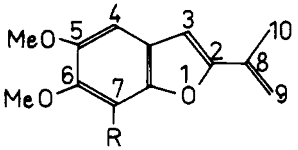
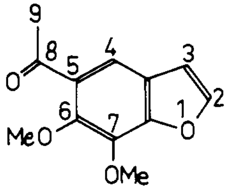


8 R=H
9 R=OMe



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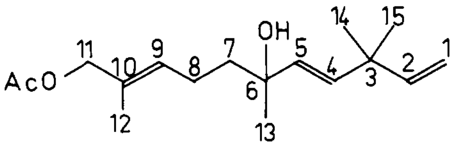
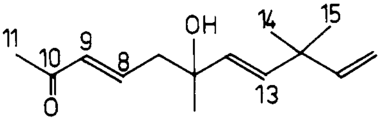
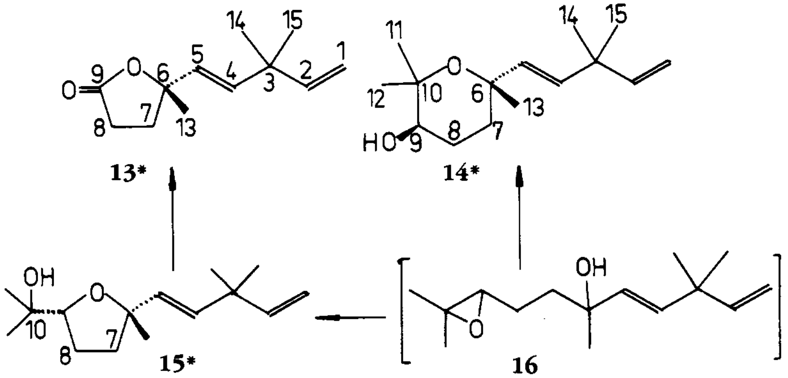


11



12*



13* **14*** **15*** **16**

*same numbering as in **11** for comparison of the pmr

acorane derivatives **1**, **2** and **3**, were obtained. Besides several compounds of known structural types such as the lactone **7** (3), a norsesquiterpene ketone (**5**) derived from **2**, dauca-3,11-dien-2-one (**6**), and the benzofurans **8** (4), **9**, and **10**; the acetate **11**, the norsesquiterpenes **12** and **13**, as well as the cyclic ethers **14** and **15**—all derivatives of a hitherto unknown sesquiterpene type—were present.

The molecular formula of **5** indicated that it was a norsesquiterpene, while the presence of a conjugated ketone could be deduced from the ir and pmr data (δ=6.00 d and 6.54 dd) (Table 1). Irradiation of the signal at δ=6.54 changed the signals at δ=6.00 and 1.80, indicating a W-coupling in addition to a vicinal coupling. Further spin decoupling allowed the assignment of all signals which led to the structure **5**, a ketone already prepared by synthesis (5). The cmr data and all other data agree well with those which are reported (5) and the sign of the optical rotation indicated the same absolute configuration.

The structures of **1** and **2** followed from the pmr data (Table 1) and could be established by partial synthesis. Reaction of **5** with methyl lithium afforded the corresponding carbinol (6) which was transformed to **1** and **2** by elimination of H_2O. The hydrocarbons obtained were identical with the natural products, thus indicating that **1** differed from (−)-acora-6,8-diene (6) as also followed from comparison of the pmr spectra.

The relative position of the trisubstituted double bond of the third diene **3** could not be deduced directly from the pmr data (Table 1). However, partial epoxidation afforded a single epoxide, and its structure clearly could be established from the pmr data (Table 1) and especially by nOe difference spectroscopy. While the conformation of the six membered ring followed from the couplings of the epoxide proton and from the presence of a W-coupling between H-6β and H-10β, the relative position of the epoxide group could be deduced from the results of the nOe experiment. Irradiation of H-13 gave a clear nOe with H-10α, while saturation of H-14 showed a nOe with H-9 and H-10β. Thus, **3** was derived from **1** by transferring the Δ^{6}- to a $\Delta^{4(14)}$-double

TABLE 1. Pmr Spectral Data of **1-5** (400 MHz, $CDCl_3$, TMS as Internal Standard)[a]

	1	**2**	**3**	**4**	**5**
1-H	1.63 m		1.45 m	1.27 ddd	1.48 m
2-H	1.80 m	1.25-1.37 and 1.45-1.90 m	1.75 m	1.75 m	1.95
2′-H	1.17 m		1.45 m	1.39 ddd	
3-H	1.33 m		2.40 ddddd	2.36 dddd	1.90 m
3′-H	1.28 m		2.29 m	2.19 ddddd	1.36 m
4-H	1.52 m	1.65 m	—	—	1.85 m
6-H	5.23 d br	5.36 d br	1.50 m 1.42 ddd br	1.47 ddd 1.00 dddd	6.54 dd
7-H	5.62 dd	6.15 d br	1.98 ddd 1.88 ddd br	1.75 m	6.00 d
9-H	5.27 s br	2.44 ddddd	5.36 s br	3.05 d	2.54 ddd
9′-H		2.32 ddd br			2.41 ddd
10-H	2.22 d br	1.50 ABX_2	2.31 d br 1.73 d br	2.21 d 1.70 ddd	1.90 ddd
10′-H	1.87 dd br				1.80 dddd
11-H	1.49 m	1.55 m	1.75 m	1.66 dqq	1.58 dqq
12-H	0.85 d	0.83 d	0.94 d	0.98 d	0.88 d
13-H	0.82 d	0.85 d	0.84 d	0.85 d	0.85 d
14-H	0.96 d	0.86 d	4.76 ddd 4.71 ddd	4.83 dd br 4.63 dd br	0.96 d
15-H	1.65 ddd	4.77 s br	1.64 s br	1.27 s	—
15′-H		4.73 s br			—

[a] Coupling constants [Hz]: Compound **1**: 1,11=4,14=13,12=11,13=7; 6,7=11; 7,9=9,10=9,15=10,15~1.5; 9,10′=6; 10,10′=18.5; compound **2**: 1,11=4,14=11,12=11,13=7; 6,7=11; 9,9′=15; 9,10=8; 9,10′=7; 9,15~1; 9′,10=9′,10′=5.5; 9′,15~1; compound **3** and **4**: 2,3=9.5; 2′,3=2; 2,3′=5; 2′,3′=2.5; 3,3′=17; 3,14=3′,14=3,14′=3′,14′=5,14~1.5; 6,6′=12.5; 6,7=6.5; 6,7′=11; 6,7′=3; 6′,7′=5; 7,7′=17; (compound **3**: 7,9=7′,9=9,15~2; 9,10~3; 9,10′~5; 10,10′=17; compound **4**: 6,10′=2; 9,10′=5; 10,10′=16); compound **5**: 1,11=4,14=11,12=11,13=7; 6,7=11; 6,10′=1.3; 9,9′=18; 9,10=11; 9′,10=11; 9,10=4.5; 9,10′=7; 9′10′=6.5; 10,10′=15.

bond. The nOe between H-14 and H-7β is weak indicating that the five membered ring is in a conformation where the exomethylene group is nearer to C-9, probably a result of steric effects between C-14 and H-7β and H-10α and the isopropyl group.

The molecular formula of **6** ($C_{15}H_{22}O$), together with the ir spectrum, which showed the presence of a conjugated ketone, indicated that a bicyclic sesquiterpene had to be assumed, since the pmr spectral data (see Experimental section) required two double bonds. Careful spin decoupling in C_6D_6 allowed the assignment of all signals, although a few were overlapped multiplets. A pair of doublets at δ=2.81 and 2.26 obviously were due to methylene protons next to a carbonyl group. One of these doublets (δ=2.26) was broadened by a W-coupling with a methyl singlet. The 12-H signals were coupled with a broadened threefold doublet at δ=2.64, which itself showed a 10 Hz coupling with a proton which formed a multiplet at δ= 1.88 m which was due to H-6 as further decouplings indicated the sequence of H-4 to H-6. Thus **6** obviously was a keto derivative of dauca-2,11-diene (2).

The structure of **9** could be easily deduced from the pmr data (see Experimental section) which were close to those of **8** (4). The structure of **10** could also be assigned from the pmr data, as the pmr spectrum (see Experimental section) was close to that of the corresponding euparine derivative (7). The 2-isopropenyl group of the euparine derivative was replaced by a proton in **10** as followed from an additional low field signal (δ=6.32 d). Irradiation of this signal collapsed a narrowly split doublet at δ=6.64 to a broadened singlet. The latter was further coupled with a broadened singlet at δ=7.52, obviously the proton at C-4.

The molecular formula of **13** was $C_{12}H_{18}O_2$ while the ir band at 1780 cm−1 indicated the presence of a γ-lactone. The pmr spectrum (Table 2) showed three methyl singlets, the signals of a vinyl group and of the protons of a *trans*-double bond. The remaining signals nicely agreed with those of a butyro lactone with two substituents in the γ-position (8). These elements can only be combined to **13** as the two olefinic double bonds must be separated by a quarternary carbon.

TABLE 2. Pmr Spectral Data of **11-15** (400 MHz, $CDCl_3$, TMS as Internal Standard)[a]

	11	**12**	**13**	**14**	**15**
1c-H	4.92 dd	4.93 dd	4.95 dd	4.92 dd	4.91 dd
1t-H	4.94 dd	4.94 dd	4.94 dd	4.93 dd	4.93 dd
2-H	5.81 dd	5.79 dd	5.78 dd	5.80 dd	5.80 dd
4-H	5.43 d	5.47 d	5.45 d	5.33 d	5.50 d
5-H	5.63 d	5.65 d	5.70 d	5.49 d	5.61 d
7-H	2.05 m	2.45 dd	2.18 dt	2.07 m	2.45-2.25 m
7′-H			2.07 dt	1.7-1.5 m	
8-H	1.55 m	6.77 dt	2.55 dd		
9-H	5.45 t br	6.07 dt	—	3.42 dd	3.85 t
11-H	4.44 s br	2.25 s	—	1.13 s	1.24 s
12-H	1.64 s br	—	—	1.14 s	1.13 s
13-H	1.28 s	1.33 s	1.49 s	1.25 s	1.31 s
14-H . . .	1.10 s	1.11 s	1.10 s	1.10 s	1.10 s
15-H . . .					

[a]Coupling constants [Hz]: Compound **11**: 1c,1t=1.5; 1c,2=10; 1t,2=17; 4,5=16; 8,9=6.5; compound **12**: 1c,1t=1.5; 1c,2=10; 1t,2=17; 4,5=16; 7,8=7.5; 7,9=1.5; 8,9=16; compound **13**: 1c,1t=1.5; 1c,2=10; 1t,2=17; 4,5=16; 7,7′=13; 7,8=7.5; 7′,8=8.5; compound **14**: 1c,1t=1.5; 1c,2=10; 1t,2=17; 4,5=16; 8,9=5; 8′,9=11; compound **15**: 1c,1t=1.5; 1c,2=10; 1t,2=17; 4,5=16; 8,9=7.

When the pmr data of **13** were compared with those of **11** and **12** (Table 2), it was obvious that these compounds were related to **13**. However, as indicated by the molecular formulas, that could be deduced from the cims spectra, **11** was an acetoxy derivative of a hydroxysesquiterpene and **12** was a norsesquiterpene ($C_{14}H_{22}O_2$). Accordingly, the pmr data showed clear differences. The signals of the molecular part representing C-1-C-6 and C-13-C-15 were nearly identical in all spectra. In the spectrum of **11** the position of the acetoxy group could be deduced from the typical pmr shifts of H-9, H-11 and H-12 (9). Furthermore H-9 showed a nOe with H-11. As the signals at $\delta=5.45$ (1H), 4.44 (2H), and 1.64 (3H) required a normal substituted prenyl group, the only structure possible, therefore, was **11**. In the case of **12** all signals could be assigned by spin decoupling. The two resulting sequences could only be combined to **12** as the chemical shift of one of the methyl signals required the presence of a methyl ketone.

The structures of **14** and **15** also followed from their pmr spectra (Table 2). Again, one part of the molecule (C-1 to C-6 and C-13 to C-15) displayed signals very similar to those of **11-13** indicating an identical part in the molecule. The remaining signals of **14** and **15** also were similar. However, in the spectrum of **14** a low field double doublet at $\delta=3.42$ showed couplings that are typical for protons on a carbon with an equatorial hydroxyl in a six-membered ring ($J=11$ and 5 Hz). A corresponding signal in the spectrum of **15** was a triplet with a 7 Hz coupling, typical for protons on a carbon that bears an oxygen function in a five-membered ring (10). All data, therefore, agreed nicely with the presence of the isomeric cyclic ethers **14** and **15**. The relative configuration at C-6 and C-9 of the latter followed from a nOe difference spectrum. Irradiation of 13-H caused a clear nOe of 9-H. The cmr spectrum (see Experimental section) also agrees with the structures. The absolute configuration of **11-13** could not be determined. Compounds **14** and **15** most likely are formed via the epoxide **16**. This epoxide presumably is derived from a hydroxy derivative which also is the precursor of **11**. The ketone **12** and the lactone **13** obviously are formed by oxidative degradation. The carbon skeleton of **11, 14** and **15** seems to be new, and we have named it caleprunane.

Thus, **11** is 11-acetoxycalepruna-1,4*E*,9-trien-6-ol; **12** is 6-hydroxy-norcalepruna-1,4*E*,8*E*-trien-10-one; **14** is 6,10-oxidocalepruna-1,4*E*,dien-9-ol; and **15** is 6,9-oxidocalepruna-1,4*E*-dien-6,9-olide.

Calea species usually contain sesquiterpene lactones, mainly furoheliangolides, but these could not be detected in the extract of this species. However, some species lack these lactones. Compounds like **7-10** derived from euparine by degradation, and also thymol derivatives, are widespread in this genus, while compounds derived from acorane, daucane, and caleprunane have not been reported so far.

EXPERIMENTAL

MATERIAL AND METHODS.—Plant material was collected in February 1983, Puriscal, Costa Rica (voucher specimen is deposited in the CIPRONA herbarium). Nmr spectra were recorded on a Bruker WM 400, ir spectra on a Beckman ir 9, and the mass spectra on a Varian MAT 711, 70 eV, direct inlet, or Varian MAT 44S. Optical rotations were determined on a Perkin-Elmer Polarimeter.

ISOLATION.—The air-dried aerial parts (500 g) were ground and extracted with Et_2O-MeOH, 1:1, at room temperature for 24 h. The extract obtained after evaporation was divided into three fractions by column chromatography (cc) on SiO_2: Fraction 1 (petrol), fraction 2 (Et_2O-petrol, 1:3) and fraction 3 (Et_2O). Fraction 1 was further separated by cc (SiO_2 5% $AgNO_3$ coated, Et_2-O petrol, 1:30) affording 24 mg α- and 200 mg β-farnesene, 40 mg germacrene D, 24 mg caryophyllene, 60 mg squalene, and a mixture of **1-3** and dauca-2,11-diene (500 mg ~ 1:2:2:2). Of this mixture 50 mg was separated by tlc (SiO_2 PF 254, $AgNO_3$ coated, 0.2 mm, petrol, developed three times) affording 4 mg **1**, 8 mg **2**, 8 mg **3**, and 8 mg dauca-2,11-diene (increasing polarity). Repeated tlc of fraction 2 (SiO_2 PF 254, C_6H_6-CH_2Cl_2-Et_2O, 9:9:1) gave 14 mg caryophyllene epoxide, 8 mg spathulenol, 20 mg stigmasterol, 20 mg sitosterol, 5 mg epi-friedelinol, 10 mg phytol, 20 mg lupeol and its Δ^{12}-isomer (~ 2:1), 3 mg 10-isobutyryloxy-8,9-epoxy thymol isobutyrate, 35 mg **5**, 12 mg **6**, 20 mg **7**, 20 mg **8**, 30 mg **9**, 15 mg **10**, 2 mg **11**, 1 mg **13**, 1 mg **14**, and 5 mg **15**. Tlc of fraction 3 (Et_2O) gave 1 mg **12**. Known compounds were identified by comparing the 400 MHz pmr spectra with those of auhentic materials. Due to the complexity of the mixtures, the numerous separations surely caused considerable losses of material. The new compounds were homogeneous by tlc in different solvent mixtures and showed no impurities in the 400 MHz pmr spectra.

ACORA-6,8-DIENE (**1**).—Colorless oil, ir spectrum (CCl_4) 2960, 2920, 2860, 1470, 1380 cm^{-1}; (Found: M^+ 204,188, $C_{15}H_{24}$ requires 204.188); ms *m/z* (rel. int.) 204 (M^+, 17), 161 ($M-C_3H_7$, 24), 105 ($C_8H_9^+$, 100);

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+76 \quad +78 \quad +87 \quad +183} \quad (c=0.13, CHCl_3)$$

ACORA-6,8(15)-DIENE (**2**).—Colorless oil, ir spectrum (CCl_4) 2960, 2880, 1480, 1390, 890 cm^{-1}; (Found: M^+ 204.188, $C_{15}H_{24}$ requires 204.188); ms *m/z* (rel. int.) 204 (M^+, 27), 189 ($M-CH_3$, 3), 161 ($M-C_3H_7$, 100), 133 (22), 120 (44), 119 (61), 105 (68), 91 (78).

ACORA-4(14),8-DIENE (**3**).—Colorless oil, ir spectrum (CCl_4) 3060, 2960, 2920, 1650, 1460, 1430, 1390, 1370, 900 cm^{-1}; (Found: M^+ 204.188, $C_{15}H_{24}$ requires 204.188); ms *m/z* (rel. int.) 204 (M^+, 24), 189 ($M-CH_3$, 7), 161 ($M-C_3H_7$, 100), 133 (41), 119 (67), 105 (98), 94 (97), 93 (88), 91 (98), 79 (90);

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+47 \quad +49 \quad +55 \quad +94} \quad (c=0.8, CHCl_3)$$

Derivatives: 5 mg **3** in 1 ml $CHCl_3$ stirred with 10 mg *m*-chloroperbenzoic acid and tlc (Et_2O-petrol, 1:10) gave 3 mg **4**. Colorless oil, ir spectrum (CCl_4) 3075, 2960, 2930, 2865, 1645, 1465, 1435, 1380, 895, 850 cm^{-1}; (Found: M^+ 220.182, $C_{15}H_{24}O$ requires 220.182); ms *m/z* (rel. int.) 220 (M^+, 3), 205 (4), 202 (4), 177 (63), 159 (50), 133 (95), 107 (86), 93 (85), 91 (100), 79 (88).

8-DESMETHYL ACOR-6-EN-8-ONE (**5**).—Colorless oil, ir spectrum (CCl_4) 2960, 2940, 2870, 1685, 1610, 1470, 1380, 1233, 1150 cm^{-1}; (Found: M$^+$ 206.167, $C_{14}H_{22}O$ requires 206.167); ms *m/z* (rel. int.) 206 (M$^+$, 28), 191 (M-CH_3, 6), 163 (M-C_3H_7, 18), 135 (24), 122 ($C_8H_{10}O^+$, 100), 107 (44), 94 (44), 93 (45), 91 (44), 97 (58);

$$[\alpha]^{\lambda}_{24°} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+3 \quad +3 \quad +5 \quad +11} \quad (c=1.0, CHCl_3)$$

Cmr ($CDCl_3$) (C-1-C-14) δ 60.3 d, 28.1 t, 30.3 t, 46.4 d, 48.0 s, 160.8 d, 128.5 d, 200.1 s, 35.0 t, 20.1 t, 30.5 d, 15.3 q, 22.6 q, 22.7 q.

PREPARATION OF **1** AND **2**.—To 20 mg **5** in 1 ml Et_2O excess of methyl lithium was added at room temperature. After addition of dilute H_2SO_4, the carbinol obtained was heated with a trace of *p*-toluene sulfonic acid. Tlc (SiO_2, $AgNO_3$ coated) afforded ~ 5 mg of **1** and 5 mg of **2**, their pmr spectra being identical with those of the natural compounds.

DAUCA-3,11-DIEN-2-ONE (**6**).—Colorless oil, ir spectrum (CCl_4) 2960, 2920, 2850, 1710, 1650, 1430, 1380, 900 cm^{-1}; (Found: 218.167, $C_{15}H_{22}O$ requires 218.167); ms *m/z* (rel. int.) 218 (M$^+$, 14), 203 M-CH_3, 12), 175 (M-C_3H_7, 68), 161 (28), 147 (30), 136 (46), 134 (43), 121 (48), 107 (63), 105 (58), 93 (81), 91 (79), 82 (80), 79 (66), 69 (61), 68 (77), 67 (78), 55 (100), 53 (81); pmr (C_6D_6) δ 2.81 d and 2.26 d br (1-H), 5.94 ddq (4-H), 2.05 m and 1.88 m (5-H), 1.88 m (6-H), 2.64 ddd br (7-H), 1.60 m (8-H), 1.31 ddd and 1.10 ddd br (9-H), 4.93 dq and 4.75 d br (12-H), 1.58 s br (13-H), 0.78 s br (14-H), 2.03 s br (15-H) [*J* (Hz): 1,1′=15.5; 1′,14=1; 4,5=6.5; 4,5′=4,15=1; 6,7=7,8=7,8′~10; 8,9=6; 8,9′=12; 8′,9=1.5; 8′,9′=7; 9,9′=13; 12,12′=12,13=1.5];

$$[\alpha]^{\lambda}_{24°} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-23 \quad -26 \quad -32 \quad -68} \quad (c=0.41, CHCl_3)$$

2-ISOPROPENYL-5,6,7-TRIMETHOXY BENZOFURANE (**9**).—Colorless oil, ir spectrum (CCl_4) 2960, 2940, 2860, 2840, 1623, 1490, 1470, 1450, 1435, 1425, 1320, 1220, 1200, 1180, 1140, 1050, 1010 cm^{-1}; (Found: 248.105, $C_{14}H_{16}O_4$ requires 248.105); ms *m/z* (rel. int.) 248 (M$^+$, 100), 233 (M-CH_3, 72), 218 (10), 205 (6), 190 (30), 175 (24); pmr ($CDCl_3$): δ 6.77 s (3-H), 6.68 s (4-H), 5.66 s br and 5.04 s br (9-H), 2.10 s br (10-H), 4.09 s, 3.89 s, and 3.81 s (OCH_3).

5-ACETO-6,7-DIMETHOXYBENZOFURANE (**10**).—Colorless oil, ir spectrum (CCl_4) 3000, 2960, 2940, 2860, 1680, 1620, 1605, 1550, 1503, 1470, 1380, 1330, 1300, 1275, 1260, 1223, 1205, 1170, 1150, 1130 cm^{-1}; (Found: 220.074, $C_{12}H_{12}O_4$ requires 220.074); ms *m/z* (rel. int.) 220 (M$^+$, 100), 205 (M-CH_3, 84), 177 (11), 149 (38), 135 (12); pmr ($CDCl_3$) δ 6.32 d (2-H), 6.64 dd (3-H), 7.52 s br (4-H), 2.54 s (9-H), 3.91 s and 3.86 s (OCH_3) [(Hz) 2,3=2; 3,4=0.5].

11-ACETOXYCALEPRUNA-1,4E,9-TRIEN-6-OL (**11**).—Colorless oil, ir spectrum (CCl_4) 3600, 2945, 2920, 2820, 1734, 1460, 1375, 1220 cm^{-1}; ms *m/z* (rel. int.) (cims, isobutane) 263 (M+1−H_2O, 18), 221 (M+1−AcOH, 26), 203 (221−H_2O, 100);

$$[\alpha]^{\lambda}_{24°} = \frac{589 \quad 578 \quad 548 \quad 436\,\text{nm}}{+6 \quad +9 \quad +10 \quad +21} \quad (c=0.2, CHCl_3)$$

6-HYDROXY-NORCALEPRUNA-1,4E,8E-TRIEN-10-ONE (**12**).—Colorless oil, ir spectrum (CCl_4) 3580, 2960, 2925, 2860, 1710, 1465, 1380 cm^{-1}; ms *m/z* (rel. int.) gc/cims (isobutane) 223 (M+1, 2), 205 (M+1−H_2O, 21), 139 (M-CH_2CH=$CHCOCH_3$, 100).

APOCALEPRUNA-1,4E-DIEN-6,9-OLIDE (**13**).—Colorless oil, ir spectrum (CCl_4) 2960, 2920, 2850, 1780, 1635, 1465, 1380, 1220 cm^{-1}; ms *m/z* (rel. int.) gc/cims (isobutane) 195 (M+1, 100), 137 (195-CH_2COO, 4), 123 (195-CH_2CH_2COO, 5), 99 ($C_5H_7O_2$, 5); EI: 179 (M-Me, 6), ($C_5H_7O_2$, 100); $[\alpha]_D$ +3 (c=0.06, $CHCl_3$).

6β,10-OXIDOCALEPRUNA-1,4E-DIEN-9β-OL (**14**).—Colorless oil, ir spectrum (CCl_4) 3600, 2960, 2920, 2860, 1460, 1375, 985, 920 cm^{-1}; ms *m/z* (rel. int.) gc/cims (isobutane) 221 (M+1−H_2O, 100), 203 (221−H_2O, 12).

6,9-OXIDO CALEPRUNA-1,4E-DIEN-10-OL (**15**).—Colorless oil, ir spectrum (CCl_4) 3540, 3080, 2960, 2920, 2865, 1640, 1470, 1380, 980, 925 cm^{-1}; (Found: M-H_2O, 218.162, $C_{15}H_{22}O$ requires 218.162); ms *m/z* (rel. int.) 221 (M−, 2), 218 (M−CH_3 H_2O, 6), 203 (221−H_2O, 4), 161 (8), 121 (26), 81 (40), 71 (46), 69 (68), 57 (100); cims (isobutane) 221 (M+1−H_2O, 100);

$$[\alpha]^{\lambda}_{24°} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-3.5 \quad -4.9 \quad -5.3 \quad -7.0} \quad (c=0.43, CHCl_3)$$

cmr ($CDCl_3$) δ 110.7 t (C-1), 147.2 d (C-2), 136.1 d (C-4), 133.0 d (C-5), 82.6 s (C-6), 85.6 d (C-9), 71.2 s (C-10), 24.4 q, 26.8 q, 27.1 q, 27.1 q, 27.5 q (CH_3).

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LITERATURE CITED

1. F.C. Seaman, *Bot. Rev.*, **48**, 121 (1982).
2. F. Bohlmann and C. Zdero, *Phytochemistry*, **21**, 2263 (1982).
3. F. Bohlmann and J. Jakupovic, *Phytochemistry*, **18**, 119 (1979).
4. F. Bohlmann and K.H. Knoll, *Phytochemistry*, **18**, 877 (1979).
5. P. Naegeli, *Tetrahedron Lett.*, 2127 (1978).
6. M. Pesaro and J.P. Bachmann, *J. Chem. Soc. Chem. Commun.*, 203, (1978).
7. F. Bohlmann, K.H. Knoll, C. Zdero, P.K. Mahanta, M. Grenz, A. Suwita, D. Ehlers, N. LeVan, W.R. Abraham, and A.A. Natu, *Phytochemistry*, **16**, 965 (1977).
8. F. Bohlmann and W.R. Abraham, *Phytochemistry*, **18**, 1851 (1979).
9. F. Bohlmann and K.H. Knoll, *Phytochemistry*, **17**, 319 (1978).
10. W. Herz and R.P. Sharma, *J. Org. Chem.*, **40**, 192 (1975).

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