Phytochemistry, Vol 22, No 1, pp 187–189, 1983
Printed in Great Britain

0031-9422/83/010187-03$03 00/0

TWO FURANOEUDESMANES FROM THE ESSENTIAL OIL OF MYRRH*

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(*Revised received* 17 *May* 1982)

Key Word Index—*Commiphora molmol*, Burseraceae lindestrene, furanoeudesma-1,3-diene, furanoeudesma-1,4-diene-6-one

Abstract—The identification of lindestrene, furanoeudesma-1,3-diene and furanoeudesma-1,4-diene-6-one, isolated from the essential oil of myrrh, was carried out by spectroscopic methods

INTRODUCTION

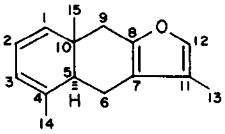
Knowledge about the constituents of the essential oil of myrrh, the resin of *Commiphora molmol* Engler, is scanty Only a few monoterpenes, phenols and aromatic aldehydes have been described in the literature and one author has reported the presence of the sesquiterpene hydrocarbon cadinene It was our intention to confirm these results by modern analytical methods, but none of these compounds was present in the investigated material Instead, we found that all the constituents of the oil were sesquiterpenes, especially furanosesquiterpenes of four different types In this paper, we report the characterization of two new furanoeudesmanes

RESULTS AND DISCUSSION

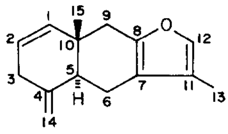
The essential oil from myrrh (quality DAB 8) was extracted with *n*-hexane The main component of the oil was the new furanoeudesmane, furanoeudesma-1,3-diene (**1**, 19 %), a colourless, unstable liquid with an intensive fragrance which was rapidly auto-oxidized in air at room temperature to give a resinous substance It was isolated from the non-polar fraction of the essential oil which also contained sesquiterpene hydrocarbons [2] and other unsubstituted furanosesquiterpenes, one of which was identified as the furanoeudesmene lindestrene (**2**) [3], a compound which had only been isolated from two plants of the Lauraceae

Compounds **1** and **2** showed very similar chromatographic behaviour (TLC, GLC and capillary GLC) suggesting that **1** was a non-polar derivative of furanoeudesmane **1** gave a positive Ehrlich colour reaction and had a molecular formula of $C_{15}H_{18}O$ ($[M]^+ m/z$ 214) These facts suggested the presence of a furan moiety and this was confirmed by the spectral data [4]

The mass spectrum of **1** showed the base peak at *m/z* 108, which is a characteristic of furanosesquiterpenes with an unsubstituted carbon atom in the α-position to the furan ring [4, 5] This fragment is formed by retro-Diels–Alder type ring cleavage The ^1H NMR spectrum also indicated the presence of the furano-grouping The α-proton of the furan ring appeared as a characteristic downfield signal at δ7 06 (*s*, *br*) A doublet at δ1 95 (*J* = 1 5 Hz) belonged to the β-methyl hydrogens In the IR spectrum the typical bands of a furan ring system were present at 1595, 1565 (C = C), 1145 and 1090 cm^{-1} (C–O–C) By comparing the chemical shifts in the ^{13}C NMR spectrum of **1** with those of menthofuran [6], lindenenol and lindenenyl acetate [7, 8], the assignment of the signals of the furan carbons (C–7, C–8, C–11, C–12) and of the β-methyl group (C–13) was possible (Table 1)



1



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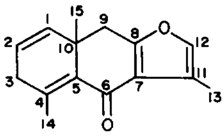

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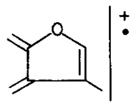

m/z 108
C_7H_8O

Table 1 ^{13}C NMR data of **1** and **3** ($CDCl_3$, TMS as internal standard)

C	1 (22 64 MHz)	C	3 (62 89 MHz)
1, 2, 3	135 6 *d* 122 1 *d* 120 1 *d*	1, 2, 4	133 8 *s*, *d* 120 5 *d*
4	136 9 *s*	3, 9	38 6 *t* 35 1 *t*
5	42 9 *d*	5, 7, 8	163 1 *s* 150 7 *s* 140 1 *s*
6, 9	36 7 *t* 19 8 *t*		
7	116 7 *s*	6	188 2 *s*
8	149 9 *s*	10	39 5 *s*
10	35 3 *s*	11	119 6 *s*
11	119 4 *s*	12	139 4 *d*
12	137 5 *d*	13	9 1 *q*
13	8 2 *q*	14, 15	28 0 *q* 20 9 *q*
14	20 4 *q*		
15	15 4 *q*		

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*This work has been taken from the Ph D thesis of P N [1]

The remaining four downfield signals at δ135 6 (*d* in off-resonance spectrum), 122 1 (*d*), 120 1 (*d*) and 136 9 (*s*) belonged to two more double bonds The multiplicity of the signals in the off-resonance spectrum indicated 1,1-di- and 1,1,2-trisubstitution, respectively, of these double bonds In the IR spectrum the expected band for a 1,2 *cis*-disubstituted olefin was observed at 725 cm^{-1}

The ^{1}H NMR spectrum of **1** showed that the two double bonds were conjugated, the olefinic protons having the coupling pattern of cyclohexadienes H-1 had only one neighbouring proton (H-2) and showed vicinal coupling It appeared at δ5 55 as a doublet ($J_{1,2}$ = 9 Hz) broadened by allylic coupling with H-3 H-2 gave a double doublet at δ5 81 ($J_{1\ 2}$ = 9 Hz, $J_{2,3}$ = 6 Hz), H-3 appeared as a multiplet at δ5 72, because it was coupled vicinally with H-2 and long-range coupled with H-1, H-5 and the protons of the methyl group at C-14 The eudesmanolide gazaniolide described by Bohlmann and Zdero [9] has the same structure in ring A The ^{1}H NMR data of the three olefinic protons of **1** were in excellent agreement with those of gazaniolide The diene structure was confirmed by the UV spectrum Besides the characteristic absorption of the isolated furano-grouping at 217 nm, there was another maximum at 263 nm This value was confirmed by incremental calculations [10] for a homoannular *S-cis*-diene

The ^{13}C NMR spectrum demonstrated that **1** consisted of a bicyclic terpene skeleton fused with a furan ring The signals at δ42 9 (*d* in off-resonance spectrum) and 35 3 (*s*) were assigned to bridge-head carbon atoms, one of which was substituted by a methyl group The homoannular conjugated diene arrangement indicated by the spectra was only possible in a six-membered skeleton of the eudesmane or eremophilane type A furanoeremophilane skeleton was excluded by FT-pseudo INDOR-decoupling experiments As the positions of the methyl groups in the furanoeudesmane skeleton are biogenetically fixed at C-4 and C-10, the positions of the double bonds could be defined From these results the structure of **1** was established as furanoeudesma-1,3-diene **1** was optically active

From the polar fractions of the essential oil of myrrh we separated another new furanosesquiterpene (**3**) of the eudesmane type by liquid chromatography on silica gel impregnated with silver nitrate The results of the spectral investigations led to the structure furanoeudesma-1,4-diene-6-one (**3**), a colourless, unstable oil The [M]$^+$ (*m/z* 228) agreed with the molecular formula $C_{15}H_{16}O_2$ and a positive Ehrlich colour test indicated a furano-grouping This was confirmed by the ^{1}H NMR spectrum The α-furan proton appeared at δ7 07, and the protons of the β-methyl group gave a doublet at δ2 25 (J = 1 5 Hz) In the ^{13}C NMR spectrum of **3**, the carbon atoms of the furan ring had similar chemical shifts to those described for **1** (Table 1)

A singlet at δ188 2 was assigned to a carbonyl carbon atom The unusual high-field shift of the signal was caused by cross-conjugation with the furan ring and a further double bond For $\alpha\beta,\alpha'\beta'$-unsaturated ketones absorptions at δ190 are reported [11] The position of the C = O absorption value in the IR spectrum at 1655 cm^{-1} supported the olefinic cross-conjugation [10, 12, 13] Curcolone [14, 15] and lindenenone [16] have the same conjugated carbonyl systems, which are indicated in their IR spectra by very similar carbonyl absorptions at 1650 and 1653 cm^{-1} The position of the keto group in conjugation to the furan was confirmed by the mass spectrum The base peak *m/z* 122 was the fragment of the retro-Diels–Alder type ring cleavage and is characteristic of compounds with a keto group in the α-position to the furan [5, 17–19] The oxo function was put at either C-6 or C-9 The chemical shift value of the α-furan proton at δ7 07 in the ^{1}H NMR spectrum led to the C-6 position For the α-proton in 9-oxo derivatives, a deshielding effect caused by tautomerism is observed the shift is displaced downfield (δ7 2–7 4) [20] The cross-conjugated carbonyl system was verified by the UV spectrum ($\lambda_{\max}$ 259 and 286 nm) of curcolone ($\lambda_{\max}$ 261 and 292 nm) [14] The double bond conjugated to the 6-keto group was tetrasubstituted The hydrogens of the methyl group located on this double bond appeared at δ2 07 as a sharp singlet because there was no allylic coupling with an olefinic proton This double bond could only be in the $\Delta^{4\ 5}$-position The rest of the ^{1}H NMR and ^{13}C NMR data confirmed the furanoeudesmane skeleton

Compound **3** contained a second double bond which was not present in the furan ring system 1,2-*Cis*-disubstitution was deduced from the IR spectrum which had a typical band at 730 cm^{-1} (δ–CH = CH– out-of-plane 1,2-*cis*-disubstituted) and from the ^{13}C NMR spectrum The olefinic carbon atoms showed resonances at δ133 8 and 120 5 and gave doublets in the off-resonance spectrum In the ^{1}H NMR spectrum the two olefinic protons appeared together as a sharp singlet at δ5 62 Neighbouring methylene protons at C-3 gave a broad singlet at δ2 79 The isolated protons at C-9 gave an AB system with δ_A2 93 and δ_B2 70 (J_{AB} = 17 Hz) The magnetic non-equivalence of H-9a and H-9b was caused by the anisotropic effect of the keto group [10,21] Curculone with the same isolated methylene group at C-9 as **3** also showed an AB system with a coupling constant of 17 Hz Therefore **3** had the structure of furanoeudesma-1,4-diene-6-one

EXPERIMENTAL

Fractionation of the essential oil of myrrh The essential oil (22 g) was extracted with *n*-hexane, subjected to CC on Si gel 60 (500 g, 0 06–0 2 mm, column diameter 6 5 cm) and developed with petrol (bp 50–70°)–Et_2O mixtures of increasing polarity (2 1 17 3, 2 1 7 3, 2 1 1 1, 1 1 Et_2O) Fractions (346) each of 15 ml were collected and examined by TLC, GLC on two columns (SE 30, XE 60), and by the Ehrlich colour test The non-polar fractions contained furanoeudesma-1, 3-diene (**1**) besides α-copaene, bourbonene, furanodiene, β-elemene and lindestrene [22] The polar fractions contained furanoeudesma-1,4-diene-6-one (**3**) besides curzerenone and furanodiene-6-one [1]

Furanoeudesma-1,3-*diene* (**1**) **1** was separated from lindestrene (**2**) and the other accompanying sesquiterpenes by CC on $AgNO_3$ (10%), Si gel 60 (100 g, 0 06–0 2 mm), developed with *n*-hexane–Et_2O (9 1) and *n*-hexane–Et_2O (4 1) 108 mg **1**, colourless liquid, RR_t (XE 60) 1, RR_t (cap column) 1 0, R_f 0 29 (*n*-hexane) IR $\nu_{\max}^{\text{film}}$ cm^{-1} 3030 (= CH), 2970, 2930, 2900, 2870, 2850, 2810, 1645 (C = C), 1595 and 1565 (C = C, furan), 1453, 1440, 1385, 1365, 1145, 1090 (C–O–C, furan), 1045, 770, 725 (–CH = CH–, 1,2-*cis*-disubstituted), UV $\lambda_{\max}^{\text{EtOH}}$ (ε)nm 263 (4200) and 217 (7200), ^{1}H NMR (90 MHz, $CDCl_3$, TMS as int standard) δ7 06 (1H, *s* (*br*), α-furan-H), 5 46–5 88 (3H, *m*, olefin-H, H-1, H-2, H-3), 2 2–2 8 (5H, *m*, H-5, H_2-6, H_2-9), 1 95, (3H, *d*, J = 1 5 Hz, Me at furan), 1 87 (3H, *s*(*br*), vinyl Me at C-4), 0 84 (3H, *s*, Me at C-10), (250 MHz, $CDCl_3$) δ7 06 (1H, *s*(*br*), α-furan-H), 5 81 (1H, H-2, *dd*, J_1 = 9 Hz, J_2 = 6 Hz), 5 72 (1H, *m*, H-3), 5 55 (1H, *d*(*br*),

$J = 9$ Hz, H-1), 2 2–2 8 (5H, *m*, H-5, H_2-6, H_2-9), 1 95 (3H, *d*, $J = 1\ 5$ Hz, Me at furan), 1 87 (3H, *s*(*br*), vinyl. Me at 4-C), 0 84 (3H, *s*, tert Me at C-10), ^{13}C NMR—see Table 1, MS (70 eV) *m/z* (rel int) 214 $[M]^+$ ($C_{15}H_{18}O$) (50), 199 (25), 118 (26), 108 (100), 91 (18), 79 (21), 77 (17), 43 (14), $[\alpha]_D^{20}$ 59° ($c = 0\ 82$, $CHCl_3$), $C_{15}H_{18}O$ calc 214 1358, found 214 1376 (MS)

Furanoeudesma-1,4-*diene*-6-*one* (**3**) **3** was separated from the accompanying sesquiterpenes by CC on $AgNO_3$ (10%)–Si gel 60 (80 g, 0 06–0 2 mm), developed with *n*-hexane–Et_2O (7 3) and *n*-hexane–Et_2O (3 2) 45 mg **3**, colourless liquid, RR_t (cap column), 1 65, R_f 0 63 (*n*-hexane–Et_2O, 7 3) IR ν_{max}^{film} cm^{-1} 3030 (=CH), 2960, 2930, 2870, 2805, 1673, 1655 (C=O), 1618, 1560 (C=C, furan), 1453, 1433, 1420, 1380, 1265, 1245, 1098, 1075, 1045 (C–O–C, furan), 910, 880, 730 (–CH=CH–, 1,2-*cis*-disubstituted), UV λ_{max}^{EtOH} (ε)nm 286 (2300), 259 (2400) and 214 (7100), ^1H NMR (90 MHz, $CDCl_3$/TMS) δ7 07, (1H *s* (*br*), α-furan -H), 5 62 (2H, s, H-1, H-2), 2 79 (2H, *s* (*br*), H-3), 2 82 (2H, AB system, δ_A2 93, δ_B2 70 $J_{AB} = 17$ Hz, H-9a, H-9b), 2 25 (3H, *d*, $J = 1\ 5$ Hz, Me at furan), 2 07 (3H, *s*, vinyl Me at C-4), 1 21 (3H, *s*, tert Me at C-10), (90 MHz, C_6D_6 TMS as int standard) δ6 79 (1H, *s* (*br*), α-furan-H), 5 31 (2H, *s*, H-1, H-2), 2 41 (2H, *s* (*br*), H_2-3), 2 54 (2H, AB-system, δ_A2 68, δ_B2 40, $J_{AB} = 16\ 5$ Hz, H-9a, H-9b), 2 28 (3H, *d*, $J = 1\ 2$ Hz, Me at furan), 2 07 (3H, *s*, vinyl Me at C-4), 1 06 (3H, *s*, tert Me at C-10), ^{13}C NMR Table 1, MS (70 eV) *m/z* (rel int) 228 $[M]^+$ ($C_{15}H_{16}O_2$), (25), 213 (29), 198 (16), 123 (13), 122 (100), 94 (33), 91 (11), 66 (12), 65 (12), 39 (10) $C_{15}H_{16}O_2$ calc 228 1150, found 228 1159 [MS]

Acknowledgement—We thank Dr V Formaček, Fa Bruker, Forchheim, West Germany, for NMR measurements and discussions of the results

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