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# TRITERPENES FROM THE SEED OF *ABIES FIRMA*

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**Key Word Index**—*Abies firma*; Pinaceae; seed; triterpenes; lanostane.

**Abstract**—Four new triterpenes having a lanostane-type skeleton, firmanoic acid [(24*E*)-3,23-dioxo-9β-lanosta-7,24-dien-26-oic acid], isofirmanoic acid [3,23-dioxo-9β-lanosta-7,25(27)-dien-26-oic acid], firmanolide [(17*S*,23*S*)-17,23-epoxy-3-oxo-9β-lanosta-7,24-dien-26,23-olide] and 23-*epi*-firmanolide [(17*S*,23*R*)-17,23-epoxy-3-oxo-9β-lanosta-7,24-dien-26,23-olide], were isolated from the seed of *Abies firma*. Their structures were established by spectral and chemical methods. In addition, the structures assigned for three previously reported diterpenes in this seed are revised here.

## INTRODUCTION

In a previous paper [1], we reported the identification of lower terpenoid constituents (mono-, sesqui- and diterpenes) in the seed extract of *Abies firma* Sieb. et Zucc. (Pinaceae). Further examination of this seed extract led to the isolation of several triterpenes. Among them, this paper deals with the structural elucidation of two triterpene acids, named firmanoic (**1a**) and isofirmanoic (**6a**) acids, and two triterpene lactones, firmanolide (**7a**) and 23-*epi*-firmanolide (**7b**).

## RESULTS AND DISCUSSION

On chromatographic separation, the triterpene acids and lactones were obtained from previously reported [1] acidic and neutral portions of the ether extract, respectively. The acids were purified by repeated chromatography after methylation with diazomethane while the lactones were separated by fractional recrystallization.

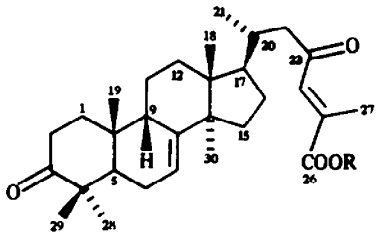
Methyl firmanoate (**1b**), mp 110–111°, $[\alpha]_D$ +23°, had a molecular formula of $C_{31}H_{46}O_4$ by HRMS, which showed also two salient fragment peaks at *m/z* 127 $[C_6H_7O_3]^+$ and *m/z* 325 $[M-C_6H_7O_3-2Me]^+$. Its IR and $^{13}C$ NMR (Table 2) spectra showed the presence of three carbonyl groups, ascribed to a saturated ketone (1695 $cm^{-1}$; 218.6 ppm), an unsaturated ketone (1680, 1610 $cm^{-1}$; 202.1 ppm) and an unsaturated ester (1720, 1260 $cm^{-1}$; 168.1 ppm). The $^1H$ NMR spectrum (Table 1) indicated signals for seven C-methyl groups involving one secondary and one vinylic methyls and two trisubstituted double bonds (δ 7.07 and 5.65), and thus this compound was a tetracyclic triterpene. The mass fragment at *m/z* 127, the proton signal at δ 7.07 spin-coupled only with the vinylic methyl signal at δ 2.22 by *J* = 1.5 Hz and a UV absorption maximum at 235 nm suggested the presence of a partial structure, –COCH=C(Me)COOMe, in the side chain. Further, another olefinic proton signal at δ5.65 was closely matched with that for C-7 double bond (δ5.50) of a lanostane triterpene, abieslactone (**2**) [2, 3], which has been found in the bark and leaves of some *Abies* species. By the above spectral features along with biogenetic considerations, the structure of methyl firmanoate was deduced as methyl (24*E*)-3,23-dioxo-9β-lanosta-7,24-dien-26-oate, **1b**.

Verification of this proposal was accomplished by the following chemical transformation. When exposed to light, **1b** was isomerized gradually into its 24*Z*-isomer, **3**, which was evidently differentiated from **1b** by proton chemical shifts of H-24 (δ6.11) and 27-Me (δ2.03) in the $^1H$ NMR. The 24*Z*-isomer was reduced with sodium borohydride to give two lactols, **4a** and **4b**, epimeric at C-23. The $^{13}C$ NMR spectrum of **4a** was in good agreement with that of **2** measured by us except for signals assigned to C(1)–C(5) and C(29) and also with that of the holostane triterpene **5** reported by Kalinovskii *et al.* [4] except for signals for the D-ring and side chain as shown in Table 2.

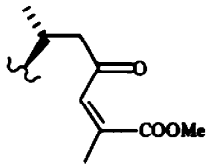
Methyl isofirmanoate (**6b**), mp 163–164°, $[\alpha]_D$ +24°, having the same molecular formula as that of **1b**, showed IR absorption bands at 1715 and 1700 $cm^{-1}$ (two ketones) and at 1725 $cm^{-1}$ (ester carbonyl). Its $^1H$ and $^{13}C$ NMR spectra (Tables 1 and 2) were very similar to those of **1b** except that the spectra exhibited the presence of a terminal methylene [$\delta_H$ 6.35 and 5.66; $\delta_C$ 134.3 (*s*) and 128.5 (*t*) ppm] and a methylene [$\delta_H$ 3.43 (*s*); $\delta_C$ 46.5 ppm

Table 1. $^1H$ NMR spectral data of **1b**, **6b**, **7a** and **7b**

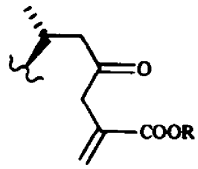
| H | 1b | 6b | 7a | 7b |
|---|---|---|---|---|
| 7 | 5.65 *dt* (7.6, 2.9) | 5.67 *dt* (7.6, 2.9) | 5.67 *dt* (7.6, 2.4) | 5.66 *dt* (7.6, 2.4) |
| 18 | 1.02 *s* | 1.04 *s* | 1.16 *s* | 1.17 *s* |
| 19 | 0.99 *s* | 1.00 *s* | 1.00 *s* | 1.00 *s* |
| 21 | 0.90 *d* (6.6) | 0.91 *d* (6.0) | 1.05 *d* (7.1) | 1.26 *d* (7.1) |
| 24 | 7.07 *q* (1.5) | 3.43 *s* | 6.71 *q* (1.7) | 6.65 *q* (1.7) |
| 27 | 2.22 *d* (1.5) | 5.66 and 6.35 each *d* (1.0) | 1.92 *d* (1.7) | 1.92 *d* (1.7) |
| 28 | 1.10 *s* | 1.10 *s* | 1.10 *s* | 1.10 *s* |
| 29 | 1.09 *s* | 1.10 *s* | 1.09 *s* | 1.09 *s* |
| 30 | 0.83 *s* | 0.83 *s* | 0.97 *s* | 0.98 *s* |
| OMe | 3.82 *s* | 3.77 *s* | | |



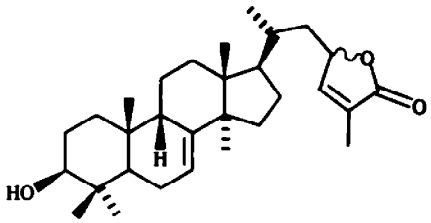
**1a** R = H
**1b** R = Me



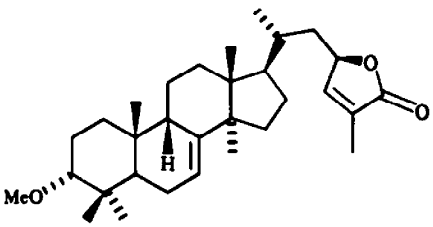
**3**



**6a** R = H
**6b** R = Me



**4a** 23*R*
**4b** 23*S*



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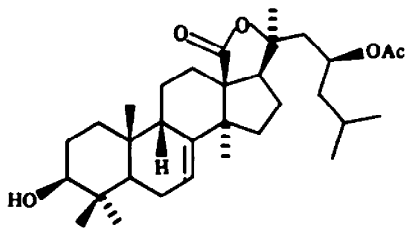
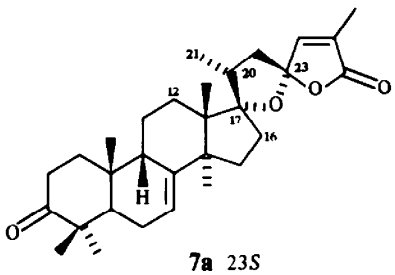
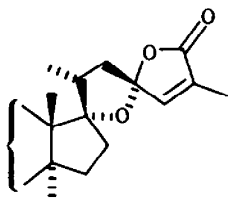


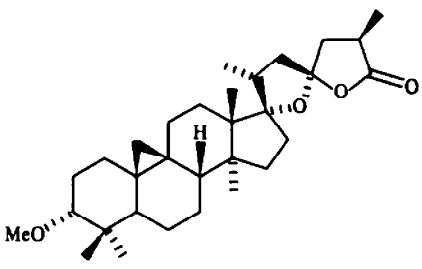
**5**



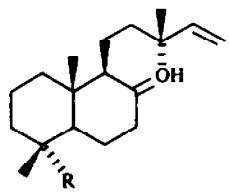
**7a** 23*S*



**7b** 23*R*



**8**



**9** R = Me
**10** R = $CH_2OAc$
**11** R = $CH_2OH$

Table 2. $^{13}$C NMR spectral data of **1b**, **3**, **6b**, **7a**, **7b**, **2**, **4a**, **4b** and **5**

| C | 1b | 3 | 6b | 7a | 7b | 2 | 4a | 4b | 5 |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 34.3* | 34.3* | 34.3* | 34.3* | 34.3* | 30.1 | 35.2 | 35.2 | 35.9 |
| 2 | 34.1* | 34.2* | 34.1* | 34.0* | 34.1* | 20.4 | 27.9 | 27.9 | 27.7 |
| 3 | 218.6 | 218.8 | 218.7 | 218.7 | 218.9 | 85.9 | 79.2 | 79.2 | 79.5 |
| 4 | 46.9 | 47.0 | 46.9 | 46.9 | 46.9 | 37.6 | 38.8 | 38.8 | 38.8 |
| 5 | 45.4 | 45.4 | 45.4 | 45.8 | 45.9 | 42.9 | 48.3 | 48.4 | 47.5 |
| 6 | 23.1 | 23.0 | 23.0 | 22.9 | 22.9 | 23.1 | 23.1 | 23.1 | 23.1 |
| 7 | 121.6 | 121.6 | 121.6 | 121.4 | 121.2 | 121.6 | 121.6 | 121.7 | 120.1 |
| 8 | 148.4 | 148.5 | 148.5 | 149.1 | 149.5 | 148.4 | 148.6 | 148.6 | 145.6 |
| 9 | 52.4 | 52.4 | 52.4 | 52.8 | 52.8 | 48.6 | 48.6 | 48.6 | 47.0 |
| 10 | 35.8 | 35.8 | 35.8 | 35.9 | 35.9 | 35.7 | 35.9 | 35.9 | 35.6 |
| 11 | 20.8 | 20.8 | 20.8 | 20.3 | 20.3 | 22.9 | 22.9 | 22.9 | 22.7 |
| 12 | 33.1 | 33.1 | 33.1 | 27.3 | 27.5 | 33.3 | 33.3 | 33.3 | 30.5 |
| 13 | 44.1 | 44.1 | 44.1 | 48.2 | 48.6 | 43.7 | 43.7 | 43.7 | 58.5 |
| 14 | 51.9 | 52.0 | 52.0 | 52.6 | 52.8 | 52.9 | 52.7 | 52.7 | 51.1 |
| 15 | 34.1 | 34.2 | 34.1 | 33.8 | 33.8 | 35.4 | 35.5 | 35.5 | 34.0 |
| 16 | 28.4 | 28.5 | 28.3 | 37.2 | 40.7 | 28.7 | 28.5 | 28.9 | 24.8 |
| 17 | 51.9 | 53.0 | 52.9 | 99.8 | 101.0 | 54.0 | 53.9 | 53.8 | 53.8 |
| 18 | 22.4 | 22.4 | 22.4 | 25.8 | 26.3 | 23.8 | 23.6 | 23.5 | 179.9 |
| 19 | 23.1 | 23.0 | 23.1 | 23.1 | 23.1 | 24.5 | 24.5 | 24.5 | 23.6 |
| 20 | 33.3 | 33.1 | 32.9 | 44.1 | 42.3 | 33.5 | 33.4 | 34.3 | 83.2 |
| 21 | 19.4 | 19.4 | 19.4 | 18.3 | 17.5 | 18.4 | 18.4 | 19.2 | 27.0 |
| 22 | 53.0 | 50.0 | 49.7 | 42.3 | 43.0 | 40.5 | 40.4 | 40.1 | 43.9 |
| 23 | 202.1 | 199.9 | 207.2 | 112.7 | 112.1 | 79.0 | 79.0 | 80.4 | 68.4 |
| 24 | 132.8 | 129.7 | 46.5 | 147.1 | 147.7 | 149.7 | 149.7 | 149.0 | 45.4 |
| 25 | 140.0 | 141.4 | 134.3 | 130.4 | 131.3 | 129.4 | 129.4 | 129.7 | 24.4 |
| 26 | 168.1 | 163.2 | 166.7 | 172.1 | 171.7 | 174.4 | 174.4 | 174.2 | 23.1 |
| 27 | 14.3 | 20.3 | 128.5 | 10.3 | 10.3 | 10.6 | 10.6 | 10.7 | 22.2 |
| 28 | 27.9 | 28.0 | 28.0 | 28.3 | 28.2 | 28.7 | 28.9 | 28.9 | 28.9 |
| 29 | 21.3 | 21.3 | 21.2 | 21.1 | 21.1 | 23.8 | 16.4 | 16.4 | 16.3 |
| 30 | 27.3 | 27.4 | 27.3 | 28.9 | 29.2 | 30.9 | 30.4 | 30.5 | 30.9 |
| OMe | 52.5 | 52.4 | 52.0 | | | 56.8 | | | |

*Assignments may be interchanged.

(*t*)] taking the place of the olefin at C-24 and vinylic methyl group in **1b**. These spectral data, and the absence of a UV absorption maximum above 205 nm, suggested methyl isofirmanoate to be an isomer of **1b**, in which the double bond at C-24 migrated to C-25(27), thus the structure was determined as methyl 3,23-dioxo-9$\beta$-lanosta-7,25(27)-dien-26-oate, **6b**.

Firmanolide (**7a**), mp 193–195°, $[\alpha]_D$ −8°, and 23-*epi*-firmanolide (**7b**), mp 193–195°, $[\alpha]_D$ +24°, having the same molecular formula, $C_{30}H_{42}O_4$, were supposed to be stereoisomers because of the close similarity of their IR and NMR spectra to each other. The IR and $^{13}$C NMR spectra of both **7a** and **7b** showed the presence of a saturated carbonyl group (1700 cm$^{-1}$; *ca* 219 ppm), an $\alpha,\beta$-unsaturated butyrolactone (1760 cm$^{-1}$; *ca* 172 ppm) and two trisubstituted double bonds [*ca* 121 and 147 ppm (each *d*); *ca* 130 and 149 ppm (each *s*)], the last of which was also confirmed by their two olefinic proton signals at *ca* $\delta$5.7 and 6.7 in the $^1$H NMR spectra (Table 1). In addition, the absence of a hydroxyl band in their IR spectra and the appearance of two $^{13}$C signals at *ca* 100 (*s*) and 112 (*s*) ppm assigned to carbons bearing one and two oxygen atoms each indicated that firmanolides involved a cyclic ether linkage, most likely lactol ether, in their molecules. Upon basic hydrolysis followed by acidification, both the compounds were isomerized to afford a mixture of the compounds **7a** and **7b** in a ratio of *ca* 3:2, suggesting that the structures of firmanolides differed only in the configuration of the acetal carbon. From the above facts coupled with other $^1$H and $^{13}$C NMR spectral features: the presence of one vinylic, one secondary and five tertiary methyl groups and the identity of the chemical shifts of carbon atoms constructing A- and B-rings with those of **1b**, firmanolides were proposed to be C-23 epimers of 17,23-epoxy-3-oxo-9$\beta$-lanosta-7,24-dien-26,23-olide, tentatively represented by the structures **7a** and **7b**.

The configuration at C-17 of both the compounds was supposed to be *S*, because the C-12 carbon signal of **7a** and **7b** resonated at higher field ($\Delta$ 6 ppm) as compared with that of **1b** owing to the upfield shift caused by the C(17)-$\alpha$-oxygen atom [5] in each case and also abietospirane (**8**) [6], isolated from *Abies alba*, had been established to have a similar lactol ether moiety with 17*S* configuration by X-ray analysis. A similar effect [7] of the lactone oxygen on the carbon chemical shift of C-16 was recognized in the case of firmanolides. Namely, the carbon signal of C-16 for **7a** was more shielded as compared with that of **7b** ($\Delta$ 3.5 ppm), indicating that the former had 23*S* and the latter 23*R* configurations as represented by the stereostructures **7a** and **7b**. This was further supported by another finding, that the proton signal of 21-Me of **7b**

($\delta$1.26) was more deshielded than that of **7a** ($\delta$1.05) by the anisotropic effect of the lactone oxygen atom.

In addition to the above triterpenes, some triterpenes having rearranged lanostane skeletons have been isolated from the same source. These will be reported in the near future.

In the previous paper [1], we erroneously reported the presence of manool, 19-acetoxymanool and torulosol, but they should be revised to 13-*epi*-manool (**9**), 18-acetoxy-13-*epi*-manool (**10**) and 13-*epi*-torreferol (**11**) [8], respectively (see Experimental).

## EXPERIMENTAL

*General.* Mps: uncorr; $^1$H and $^{13}$C NMR: $CDCl_3$ containing TMS as an internal standard.

*Isolation of methyl firmanoate* (**1b**) *and methyl isofirmanoate* (**6b**). A part (7.4 g) of the previously reported acidic portion [1] from the ether extract of the seed was chromatographed on a silica gel (310 g) column eluting with EtOAc–$C_6H_6$ (1:2 → 2:3) to fractionate a mixture of diterpene acids (2.5 g), of firmanoic and isofirmanoic acids (840 mg) and of other unknown triterpene acids (3.9 g). After treatment with diazomethane at −15°, the second fraction was purified on LiChroprep RP-8 ($H_2O$–MeOH, 1:10) and silica gel ($Et_2O$–$CHCl_3$, 1:50, and EtOAc–hexane, 1:5) to give **1b** (560 mg) and **6b** (80 mg).

**1b**, mp 110–111° (needles from $CHCl_3$–hexane), $[\alpha]_D$ +23° (*c* 0.76, $CHCl_3$); UV $\lambda_{max}^{EtOH}$ nm (log $\varepsilon$): 235 (4.10); IR $\nu_{max}^{KBr}$ cm$^{-1}$: 2960, 2860, 1720, 1695, 1680, 1610, 1460, 1440, 1380, 1355, 1260, 1150, 1115, 1060, 950, 735; HRMS *m/z* (rel. int.): 482.3398 $[M]^+$ (calc. for $C_{31}H_{46}O_4$: 482.3398) (11), 467 $[M-Me]^+$ (34), 326 (27), 325 $[M-C_6H_7O_3-2Me]^+$ (100), 127 $[C_6H_7O_3]^+$ (60), 121 $[C_9H_{13}]^+$ (24), 105 (19), 69 (21), 55 (19); $^1$H NMR (400 MHz): Table 1; $^{13}$C NMR (25.15 MHz): Table 2.

**6b**, mp 163–164° (plates from hexane), $[\alpha]_D$ +24° (*c* 0.48, $CHCl_3$); IR $\nu_{max}^{KBr}$ cm$^{-1}$: 2960, 2880, 1725, 1715, 1700, 1620, 1465, 1440, 1380, 1360, 1340, 1315, 1195, 1145, 1060, 950, 815; MS *m/z* (rel. int.): 482 $[M]^+$ (14), 467 (37), 326 (24), 325 (100), 127 (17), 121 (22), 95 (17), 81 (17), 55 (17), 41 (23); $^1$H NMR (400 MHz): Table 1; $^{13}$C NMR (25.15 MHz): Table 2.

Their corresponding acids, **1a** (mp 202–205°) and **6a** (mp 140–141°) were obtained from the esters by hydrolysis in 1 M aq. methanolic NaOH followed by acidification with 5% HCl.

*Preparation of compounds* **4a** *and* **4b**. A $CHCl_3$ soln of **1b** (150 mg) was allowed to stand for 2 weeks in the light. After evaporation of the solvent, the residue was chromatographed by prep. TLC on silica gel ($Et_2O$–$CHCl_3$, 1:50) to give **3** ($R_f$ 0.58, 30 mg) and recovered **1b** ($R_f$ 0.77, 110 mg).

**3**, mp 164–165° (needles from hexane), UV $\nu_{max}^{EtOH}$ nm (log $\varepsilon$): 234 (3.84, shoulder); IR $\nu_{max}^{KBr}$ cm$^{-1}$: 2970, 2880, 1725, 1695, 1685, 1615, 1435, 1370, 1355, 1245, 1190, 1130, 950, 760; HRMS *m/z* (rel. int.): 482.3383 $[M]^+$ (calc. for $C_{31}H_{46}O_4$: 482.3398) (8), 467 (11), 325 (100), 137 (33), 127 (75), 105 (29), 69 (30), 55 (34), 43 (31), 41 (32); $^1$H NMR (100 MHz): $\delta$6.11 (1H, *q*, *J* = 2 Hz), 5.60 (1H, *dt*, *J* = 7.5 and 3 Hz), 2.03 (3H, *d*, *J* = 2 Hz), 0.90 (3H, *d*, *J* = 6 Hz), 3.80, 1.09, 1.09, 1.02, 0.99, 0.81 (each 3H, *s*); $^{13}$C NMR (25.15 MHz): Table 2.

$NaBH_4$ reduction of **3** in EtOH followed by chromatography of the product by prep. TLC on silica gel ($Et_2O$–$CHCl_3$, 1:10) yielded lactols **4a** ($R_f$ 0.43) and **4b** ($R_f$ 0.40) in a ratio of *ca* 1:1.

**4a**, mp 210–225° (amorphous from MeOH), MS *m/z* (rel. int.): 454 $[M]^+$ (18), 421 (69), 327 (65), 107 (76), 105 (72), 81 (69), 55 (100), 41 (73); IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3400, 2940, 2880, 1745, 1450, 1370, 1090, 1055, 1025; $^1$H NMR (100 MHz): $\delta$7.04 (1H, *t*, *J* = 1.5 Hz), 6.57 (1H, *m*, $W_{1/2}$ = 13 Hz), 4.99 (1H, *br d*, *J* = 9 Hz), 3.21 (1H, *dd*, *J* = 7 and 8 Hz), 1.92 (3H, *t*, *J* = 1.5 Hz), 1.02, 0.99, 0.93, 0.87 (signals of six Me groups).

**4b**, mp 228–229° (fine needles from MeOH), MS *m/z* (rel. int.): 454 $[M]^+$ (30), 439 (54), 421 (100), 107 (52), 95 (65), 55 (68), 41 (56); IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3470, 2940, 2880, 1760, 1740, 1440, 1370, 1090, 1060, 1020; $^1$H NMR (100 MHz): $\delta$ 7.12 (1H, *t*, *J* = 1.5 Hz), 6.57 (1H, *m*, $W_{1/2}$ = 13 Hz), 4.95 (1H, *m*, $W_{1/2}$ = 12 Hz), 3.23 (1H, *dd*, *J* = 7 and 8 Hz), 1.92 (3H, *t*, *J* = 1.5 Hz), 1.04, 1.01, 0.99, 0.92, 0.87 (signals of six Me groups)

*Isolation of firmanolide* (**7a**) *and* 23-epi-*firmanolide* (**7b**). The EtOAc eluate of the reported neutral portion [1] on a silica gel column was further purified on silica gel using $Et_2O$–$CHCl_3$ (1:40) to give a mixture of firmanolides (220 mg) as a solid. Fractional recrystallization of the mixture from $CHCl_3$ gave pure **7a** and **7b**, which showed $R_f$ values 0.65 and 0.56 on silica gel TLC ($Et_2O$–$CHCl_3$, 1:20), respectively.

**7a**, mp 193–195° (needles), $[\alpha]_D$ −8° (*c* 0.48, $CHCl_3$); IR $\nu_{max}^{KBr}$ cm$^{-1}$: 2950, 2880, 1760, 1700, 1460, 1380, 1320, 1105, 955, 870, 755; HRMS *m/z* (rel. int.): 466.3092 $[M]^+$ (calc. for $C_{30}H_{42}O_4$: 466.3085) (25), 451 $[C_{29}^{\cdot}H_{39}O_4]^+$ (25), 297 $[C_{21}H_{29}O]^+$ (29), 273 $[C_{19}H_{29}O]^+$ (26), 271 $[C_{19}H_{27}O]^+$ (26), 137 $[C_8H_9O_2]^+$ (42), 119 $[C_9H_{11}]^+$ (33), 111 $[C_7H_{11}O]^+$ (100), 105 $[C_8H_9]^+$ (30), 69 (43), 55 (45), 43 (36), 41 (51); $^1$H NMR (400 MHz): Table 1; $^{13}$C NMR (25.15 MHz): Table 2.

**7b**, mp 193 – 195° (fine needles), $[\alpha]_D$ +24° (*c* 0.67, $CHCl_3$); IR $\nu_{max}^{KBr}$ cm$^{-1}$: 2950, 2880, 1755, 1700, 1465, 1375, 1330, 1105, 1080, 1030, 970, 930, 875, 770, 760; MS *m/z* (rel. int.): 466 $[M]^+$ (32), 111 (100); $^1$H NMR (400 MHz): Table 1; $^{13}$C NMR (25.15 MHz): Table 2.

*Identification of* 13-epi-*manool* (**9**), 18-*acetoxy*-13-epi-*manool* (**10**) *and* 13-epi-*torreferol* (**11**). Compound **9**, a gum, $[\alpha]_D$ +37.5° (*c* 3.07, $CHCl_3$); the 3,5-dinitrobenzoate, mp 120–121°, $[\alpha]_D$ +31.5° (*c* 1.72, $CHCl_3$), and compound **11**, mp 152–154°, $[\alpha]_D$ +46° (*c* 0.25, $CHCl_3$), were identical in all respects (mp, $[\alpha]_D$, MS, IR and $^1$H NMR) with 13-*epi*-manool and 13-*epi*-torreferol reported in ref. [8], respectively. Compound **10**, a gum, $[\alpha]_D$ +36° ($CHCl_3$), showed the following spectral data: MS *m/z* (rel. int.): 330 ($[M-H_2O]^+$, 20), 257 (34), 135 (58), 107 (38), 95 (49), 93 (36), 81 (38), 43 (100), 41 (36); IR $\nu_{max}^{neat}$ cm$^{-1}$: 3455, 3090, 1730, 1640, 1450, 1380, 1245, 1040, 995, 920, 895; $^1$H NMR (60 MHz): $\delta$5.83 (1H, *dd*, *J* = 10, 18 Hz), 5.13 (1H, *dd*, *J* = 2, 18 Hz), 4.95 (1H, *dd*, *J* = 2, 10 Hz), 4.77, 4.47 (each 1H, *br s*), 3.70 (2H, *ABq*, *J* = 10 Hz, $\Delta_\nu$ = 12.5 Hz), 2.00, 1.23, 0.80, 0.70 (each 3H, *s*). The presence of an acetoxyl group indicated by the above spectra as well as the close similarity of the $^1$H NMR spectrum of **10** with that of **11** except for the chemical shift of a signal as *ABq* [$\delta$3.25 (*J* = 10, $\Delta_\nu$ = 18.5 Hz) for **11**] due to a methylene group bearing an oxygen atom suggested that **10** was 18-*O*-acetyl derivative of **11**. Hydrolysis of **10** with 2 M ethanolic KOH gave **11**, confirming the structure, and thus **10** was determined as 18-acetoxy-13-*epi*-manool.

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## REFERENCES

1. Kaneko, N., Hasegawa, S. and Hirose, Y. (1985) *Phytochemistry* **24**, 185.
2. Kutney, J. P. and Westcott, N. D. (1971) *Tetrahedron Letters* 3463.

3. Allen, F. H., Isaacs, N. W., Kennard, O. and Motherwell, W. D. S. (1973) *J. Chem. Soc. Perkin II* 498.
4. Kalinovskii, A. I., Sharypov, V. F., Afiyatullov, Sh. Sh., Kuznetsova, T. A., Stonik, V. A. and Elyakov, G. B. (1983) *Bioorg. Khim.* **9**, 1558.
5. Parrilli, M., Adinolfi, M. and Mangoni, L. (1979) *Gazz. Chim. Ital.* **109**, 611.
6. Steglich, W., Klaar, M., Zechlin, L. and Hecht, H. J. (1979) *Angew. Chem.* **91**, 751.
7. Gonzáles, A. G., Francisco, C. G., Freire, R., Hernández, R., Salazar, J. A. and Suárez, E. (1976) *Tetrahedron Letters* 1897.
8. Sayama, Y., Kyogoku, K. and Murayama, H. (1971) *Agric. Biol. Chem.* **35**, 1068.