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Koelpinin-*A*, *B* and *C* — three triterpenoids from *Koelpinia linearis*

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Abstract

Three new triterpenoids, designated as koelpinin - *A*, *B* and *C* and characterised as 28-*nor*-lup-12,17-dien-3β,16α-diol,3β-acetoxy-28-*nor*-lup-12,17-dien-16α-ol and 28-*nor*-lup-12,17-dien-3β-ol-16-one, respectively, together with 30-*nor*-lup-3β-ol-20-one, taraxeryl acetate and germanicol, were isolated, from the aerial parts of *Koelpinia linearis*. ^{13}C-NMR shifts were assigned after performing APT and DEPT experiments.

Keywords: *Koelpinia linearis*; *Compositae*; *Nor*-triterpenoids; Koelpinin-*A*, *B* and *C*; 30-*nor*-lup-3β-ol-20-one; Taraxerylacetate; Germanicol

1. Introduction

Koelpinia linearis (Compositae) is reported to elaborate lupeol esters (Razdan, Qurishi & Khuroo, 1990; Razdan, Kachroo, Qurishi, Kalla & Waight, 1996) and a stigmastadienol derivative (Shah, Qurishi, Koul & Dhar, 1996). Herein, we report the isolation and characterisation of three new 28-*nor*-lup-12,17-dienes, designated as koelpinin-*A*, **1**; -*B*, **2** and -*C*, **3**, together with 30-*nor*-lup-3β-ol-20-one, **4** (Thompson & Bowers, 1965), taraxeryl acetate, **5** (Hui & Li, 1976) and germanicol, **6** (Yamada, Nakamura, Goto & Hirata, 1965). None of these compounds has been reported, so far, from the genus *Koelpinia*.

2. Results and discussion

The compounds **1**–**6** responded positively to LB, TCA (Bhargava & Sheshadari, 1973) and TNM tests for unsaturated triterpenoids. The ^{1}H-NMR (Table 1) of compounds **1**–**3**; M^+ at *m*/*z* 426.6240, $C_{29}H_{46}O_2$; 468.7105, $C_{31}H_{48}O_3$ and 424.5043, $C_{29}H_{44}O_2$, respectively; accounted for five tertiary and two secondary geminal methyls (ν_{max} 1370, 1380 cm^{-1}), δ 0.94 (6H, *d*, $J = 4.6$ Hz, H-29, H-30); characteristic of lupanes (Williams, Bhacca & Djerassi, 1963); a trisubstituted double bond (ν_{max} 3020, 1645, 820 cm^{-1}), δ 6.49–6.64 (1H, *t*, $J = 11.3$, 3.8 Hz, H-12), which was shown to be in heteroannular conjugation; λ_{max} (nm) 238, 244 (infl); 239, 250 (infl) and 308 (Williams & Fleming, 1988), respectively; and a carbinylic proton, δ 3.63, 4.49 and 3.63 (1H each, *dd*, $J = 7.6$, 4 Hz, H-3, Hui & Moon, 1977), respectively. The two extra vinylic carbon singlets at δ_C 152.6–158.7, in their ^{13}C-NMR confirmed the tetrasubstituted nature of the second double bond.

The HRMS of **1**–**3** exihibited the typical RDA-fragmentation of the ring C to give the respective ion radicals at *m*/*z* 208, 250 and 208 (A/B rings) and 218, 218 and 216 (D/E rings). The base peak ion at *m*/*z* 189 resulted from the loss of H_2O or HOAc from the prominent RDA-A/B ring ions at *m*/*z* 207 and 249. This fragmentation is characteristic of Δ^{12}-pentacyclic triterpenoids

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Table 1
^{1}H-NMR shifts ($CDCl_3$)

H	1	2	3	4	7	8	9	10
H-2 (*m*)	–	–	–	–	–	–	–	–
H-3 (*dd*, *J* = 7.6, 4 Hz)	3.63	4.49	3.63	3.20	4.49	4.48	–	4.48 (*J* = 9, 6.5 Hz)
H-11 (*dd*, $W^{1/2}$ = 8.4, 6 Hz)	2.40	2.40	2.46	–	2.35	2.46	2.40 (submerged)	–
H-12 (*t*, *J* = 11.3, 3.8 Hz)	6.49	6.49	6.64	–	6.54	6.64	6.23 (*dd*, *J* = 11.3, 3.8 Hz)	–
H-15 (*d*, J = 9.2 Hz)	–	–	2.66	–	–	2.66	2.68	–
H-16 (*s*)	4.60	–	–	–	–	–	–	–
H-19 (*m*)	2.24	2.24	2.24	–	2.26	2.24	2.20	–
H-23 (*s*)	0.84	0.85	0.84	0.80	0.85	0.85	0.90	0.80
H-24 (*s*)	0.80	0.78	0.80	0.84	0.78	0.78	0.85	0.86
H-25 (*s*)	0.97	0.98	0.95	0.88	0.98	0.98	0.80	0.88
H-26 (*s*)	1.02	1.00	0.99	1.02	1.01	1.01	0.99	1.03
H-27 (*s*)	1.24	1.28	1.36	0.97	1.23	1.30	1.33	0.97
H-28 (*s*)	–	–	–	0.95	–	–	–	0.78
H-29 (*d*, *J* = 4.6 Hz)	0.95	0.94	0.94	2.15	0.94	0.94	0.93	2.15
H-30 (*d*, *J* = 4.6 Hz)	0.95	0.94	0.94	–	0.94	0.94	0.93	–
OAc-3β	–	2.01	–	–	2.01	2.01	–	–
OAc-16α	–	–	–	–	2.20	–	–	–

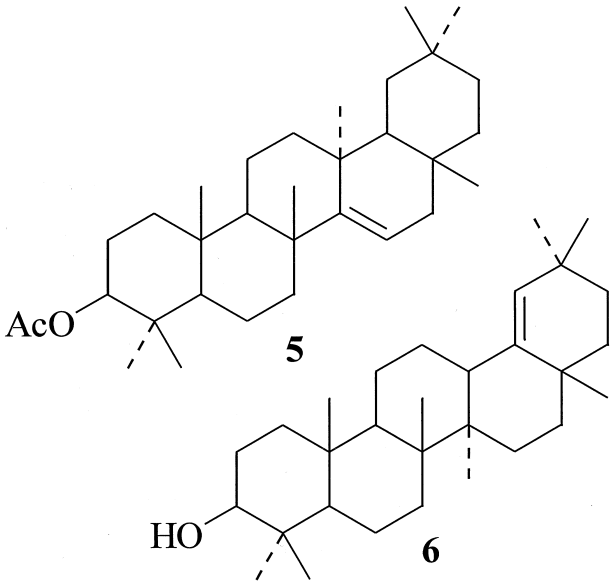
(Budzikiewicz, Wilson & Djerassi, 1963) and placed an oxygen function and the tetrasubstituted double bond in D/E rings and the second oxygen function (OH or OAc) in A/B rings, at the usual C-3 position. The lupane skeleton, in **1**–**3**, was fortified by the facile loss of $C_3H_7^{\cdot}$ from (M^+-H_2O), (M^+-HOAc) and RDA-D/E ring fragment ions (Thompson & Bowers, 1965). The presence of seven methyls only, their chemical shifts and heteroannular conjugation besides MS placed the tetrasubstituted double bond at C-17 (18). Thus **1**–**3** were derived from 28-*nor*-lup-12,17-diene and carried a hydroxyl or acetoxyl at C-3β equatorial position.

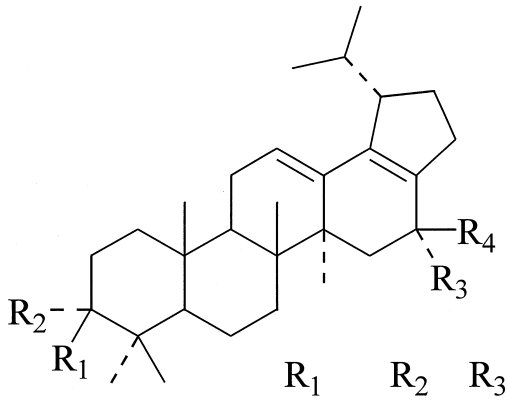
The compounds **1** and **2** displayed a downfield carbinylic proton resonance signal at δ 4.60 (1H, *s*). **2** resisted acetylation with Ac_2O–C_5H_5N, at room temperature, but **1** formed monoacetate which was identical (mp, cotlc, ^{1}H-NMR) to **2**. However, on heating with Ac_2O–C_5H_5N both formed a diacetate **7**, M^+ at *m*/*z* 510.6398, $C_{33}H_{50}O_4$, ν_{max} 1730, 1740 cm^{-1}, δ 2.01, 2.20 (3H each). On Sarett oxidation **2** readily gave the acetoxy ketone **8**; M^+ at *m*/*z* 466.6160, $C_{31}H_{46}O_3$, δ_C 218.9 (C═O), 170.2, 21.3 (OAc) whose ^{1}H-NMR displayed a doublet at δ 2.66 (2H, $J = 9.5$ Hz, H-15). The chemical shift and multiplicity of the downfield carbinylic proton, the resistance to acetylation and the ease of oxidation of **2** (Schreiber & Eschemnoser, 1955; Grinner, 1960; Fried & Edwards, 1972; Razdan, Kachroo, Harkar & Koul, 1982) placed the hydroxyl at C-16 α axial position in **1** and **2**.

On treatment with Ac_2O–C_5H_5N, at room temperature, **3** formed a monoacetate which was identical to **8**. On Sarett oxidation, it gave a diketone **9**; M^+ at *m*/*z* 422.5924, $C_{29}H_{42}O_2$, δ 2.40 (2H, *m*, H-2), 2.68 (2H, *d*,

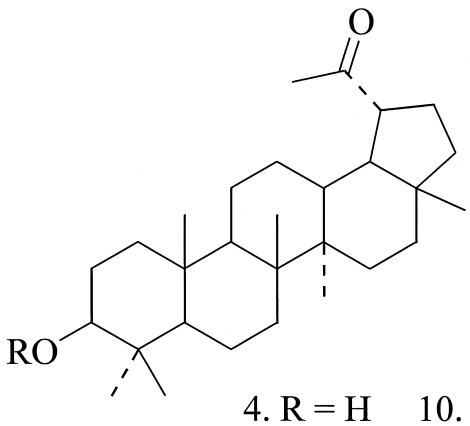
Table 2
^{13}C-NMR chemical shifts ($CDCl_3$)

δ_C	1	2	3	4	7	8	9
1	38.7	38.5	38.1	39.2	38.9	38.4	39.6
2	25.6	23.8	25.4	25.2	23.6	23.8	34.2
3	77.5	80.4	77.4	76.3	80.8	80.5	217.1
4	38.2	40.7	38.6	38.4	40.5	40.2	47.5
5	55.1	48.6	55.0	55.2	55.4	55.3	55.9
6	18.4	18.2	18.3	18.1	18.5	18.5	19.6
7	34.2	32.3	34.2	34.2	32.3	32.6	34.0
8	41.2	39.9	41.5	41.1	39.4	41.3	41.3
9	50.7	48.5	50.7	50.1	48.2	38.3	48.9
10	36.3	38.5	36.0	36.3	38.7	38.2	39.8
11	31.9	32.2	31.5	22.6	32.2	31.9	32.7
12	128.6	128.5	130.9	28.7	129.1	131.4	131.6
13	149.2	149.3	151.8	37.5	149.6	151.9	151.7
14	45.4	45.5	51.4	43.6	49.3	51.2	51.8
15	28.3	28.6	33.5	27.4	26.9	33.2	33.3
16	78.2	78.2	219.5	35.5	82.3	218.9	219.1
17	154.3	154.5	158.7	42.9	152.9	157.9	157.8
18	152.6	152.6	155.5	48.2	154.8	155.8	155.7
19	47.5	47.5	48.2	47.9	47.7	48.3	48.6
20	28.0	28.0	28.2	207.3	29.2	28.4	28.3
21	30.6	30.6	31.2	31.0	31.6	31.2	31.4
22	48.9	48.8	48.3	40.1	46.2	48.3	48.3
23	28.2	27.3	28.2	28.5	27.4	28.3	28.1
24	15.6	15.2	15.6	15.4	15.8	15.5	15.5
25	16.7	17.1	16.7	16.2	17.3	16.5	16.5
26	18.9	18.9	19.2	15.9	18.6	19.1	19.2
27	20.3	20.5	23.8	14.5	20.9	23.8	23.6
28	–	–	–	18.4	–	–	–
29	16.9	16.8	16.8	23.5	16.4	16.5	16.5
30	17.8	17.8	17.6	–	17.8	17.4	17.5
OAc (3β)	–	170.0 (C═O)	–	–	170.4	170.2	–
	–	21.2 (CH_3)	–	–	21.3	21.3	–
OAc (16α)	–	–	–	–	172.2	–	–
	–	–	–	–	22.5	–	–





	R_1	R_2	R_3	R_4
1.	OH	H	OH	H
2.	OAc	H	OH	H
3.	OH	H	=O	
7.	OAc	H	OAc	H
8.	OAc	H	=O	
9.	=O		=O	



4. R = H 10. R = OAc

$J = 9.2$, H-15); identical (mmp., cotlc) to the diketone prepared similarly from **1**.

The compounds **1**–**3** were thus characterised as 28-*nor*-lup-12,17-dien-3β,16α-diol; 3β-acetoxy-28-*nor*-lup-12,17-dien-16α-ol and 28-*nor*-lup-12,17-dien-3β -ol-16-one, respectively. The ^{13}C-NMR shifts (Table 2) have been assigned by known techniques (Levy & Nelson, 1972; Cheung & Williams, 1969; Dantanarayan, Kumar, Muthukuda & Wazeer, 1982; Stothers, 1972; Wenkert, Baddeley, Burfitt & Moreno, 1978), including APT and DEPT (90°) methods.

3. Experimental

Mps are uncorr., $[\alpha]_D$ was measured in $CHCl_3$; IR on KBr discs, UV in MeOH, ^{1}H-NMR at 250 and 90 MHz, MS at 70 eV and ^{13}C-NMR, APT and DEPT (90°) on Brucker instrument.

3.1. Isolation of *1*–*6*

The hot MeOH extract of aerial parts of *Koelpinia linearis* was defatted with Pet. ether (bp 40–60°C) and the residue was dissolved in EtOAc, filtered and filterate subjected to CC over silica get after concentration. The column was developed with C_6H_6–EtOAc (19:1), to give fraction A, and (9:1) to give fraction B. The fraction A, contained three components (TLC, silica gel G, C_6H_6–EtOAc–MeOH: 15:4:1 from which **2**, **3** and **4** were recovered by rechromatrography followed by disc chromatography on silica gel G, using C_6H_6–EtOAc–$CHCl_3$ (14:4:3). The fraction B on disc-chromatography (C_6H_6–EtOAc–MeOH, 12:4:3) gave **1**, **5**, **6**. The compounds were purified by recrystalisation.

3.1.1. Koelpinin-A, *1*

Mp 235–237°C (MeOH–C_6H_6), $[\alpha]_D^{25}$ + 21.2 *C* (0.2), M^+ at *m/z* 426.6240 (calculated for $C_{29}H_{46}O_2$, 426.5207), UV: λ_{max} (nm) 238, 244 (infl). IR: ν_{max} cm^{-1} 3480 (*br*, OH), 3020, 1645, 840 (–CH=C), 1370, 1380 (*d*, –CMe_2), 1240, 1160. ^{1}H-NMR ($CDCL_3$): Table 1. MS: *m/z* at 426 (M^+, 408 (M^+-H_2O), 375 (M^+-H_2O-C_3H_7), 335, 218 (RDA-D/E rings), 208 (RDA-A/B rings), 207, 189 (100%), 175, 135, 121, 109, 95, 83, 44.

3.1.2. Koelpinin-B, *2*

Mp 222–223°C (C H–MeOH), $[\alpha]_D^{25}$ + 13.8° *C* (0.04), M^+ at *m/z* 468.7105 (calculated for $C_{31}H_{48}O_3$, 468.4790). UV: λ_{max} (nm) 239, 250 (infl). IR: ν_{max} cm^{-1} 3460 (OH, *br*), 3010, 1730 (OAc), 1645, 1370, 1380 (*d*), 1250, 1160, 1020, 880. ^{1}H-NMR ($CDCl_3$): Table 1. MS: *m/z* at 468 (M^+), 408 (M^+-HOAc), 355 (M^+-HOAc-C_3H_7), 315, 250 (RDA-A/B rings), 249, 218 (RDA-D/E rings), 189 (100%) 175, 135, 121, 109, 95, 59, 44.

*3.1.3. Koelpinin-C, **3***

Mp 208–209°C (C_6H_6–MeOH), $[\alpha]_D^{25}$ + 6.5 *C* (0.01), M^+ at *m/z* 424.5043 (calculated for $C_{29}H_{44}O_2$ 424.3341). UV: λ_{max} 308 nm. IR: ν_{max} cm^{-1} 3440 (OH), 3010, 1705 (C═O), 1650, 1370, 1380, 1250, 1020, 870. ^{1}H-NMR ($CDCl_3$): Table 1. MS: *m/z* at 422 (M^+), 404 (M^+-H_2O), 361, 216 (RDA-D/E rings), 208 (RDA-A/B rings), 207 (RDA-A/B^+), 189 (100%) 173, 133, 123, 119, 95, 44.

*3.2. Acetylation of **1**, **2**, **3***

1, **2** and **3** in C_5H_5N (2 ml) were treated with Ac_2O (3 ml) and left overnight, at room temperature After usual work up **1** formed monoacetate identical with **2**; **2** did not undergo any change. The compound **3** gave monoacetate **8**, mp 189–190°C, M^+ at *m/z* 466.6160 (calculated for $C_{31}H_{46}O_3$, 466.2401). UV: λ_{max} 307 nm. IR: ν_{max} cm^{-1} 3050, 1730, 1650, 1370, 1360, 1250, 1020, 870. ^{1}H-NMR: Table 1. MS: *m/z* at 466, 406 (M^+-HOAc), 363, 323, 295, 250, 249, 216, 189 (100%), 173, 133, 105, 81, 44.

The compound **2** and monoacetate of **1** were heated with C_5H_5N and Ac_2O, on a water bath for 6 h. After usual work up colourless crystals of **7**, mp 216–217°C, M^+ at *m/z* 510.6398 (calculated for $C_{33}H_{50}O_4$; 510.7406) were recovered UV: λ_{max} 247, 250 (infl.) nm. IR: ν_{max} cm^{-1} 3010, 1730, 1740 (2 × AOC), 1645, 1380, 1370, 1245, 870. ^{1}H-NMR ($CDCl_3$): Table 1. MS: *m/z* at 510 (M^+), 450, (M^+-HOAc), 407 (M^+-HOAc-$C_3H_7^{\cdot}$), 367, 260 (RDA, D/E rings), 250, 249, (RDA-A^+/B rings), 217, 189 (100%), 177, 135, 109, 59, 44.

*3.3. Sarett oxidation of **1**, **2** and **3***

1, **2** and **3** in $CHCl_3$ were stirred with freshly prepared CrO_3–C_5H_5N complex at room temperature for 2 h. After usual work up the products were recovered and crystalised from petrol–MeOH. **1** and **3** gave identical diketone **9**, mp 185–186°C, M^+ at *m/z* 422.5924 (calculated for $C_{29}H_{42}O_2$, 422.4730). UV: λ_{max} 310, 260 (infl.) nm. IR: ν_{max} cm^{-1} 3015, 1705, 1695, 1640, 1370, 1360, 1045, 890. ^{1}H-NMR ($CDCl_3$): Table 1. MS: 422 (M^+), 407 (M^+-CH_3), 394 (M^+-CH_3-$CO^{\cdot}$), 379, 216 (RDA-D/E), 206 (RDA-A/B) 205 (100%), 190, 173, 162, 133, 113, 105, 95, 94, 44. The compound **2** formed a monoketone, mp 189–190°C, which had UV, IR, ^{1}H-NMR and MS similar to **8**. Its identity was confirmed by Co-TLC and mmp.

*3.3.1. 30-nor-lupan-3β-ol-20-one, **4***

Mp 238–239°C, lit. (Thompson & Bowers, 1965) 237–239°C $[\alpha]_D^{25}$ − 10.2 (C.O. 30), M^+ at *m/z* 428.4996 (calculated for $C_{29}H_{48}O_2$ 428. 3581). IR: ν_{max} cm^{-1} 3457, 3200, 1687 (C═0), 1037, 870. ^{1}H-NMR ($CDCl_3$): Table 1. MS: *m/z* at 428 (M^+), 413 (M^+-CH_3), 410 (M^+-H_2O), 395 (M^+-H_2O-CH_3CO), 207, 189 (100%). On acetylation with C_5H_5N–Ac_2O at room temperature (overnight) it gave colourless needles of **10**, mp 276–277°C (MeOH–$CHCl_3$) M^+ at *m/z* 470.3627 (calculated for $C_{31}H_{50}O_3$, 470.3647) IR: ν_{max} cm^{-1} 3200, 1722 (OAc), 1705 (C═O), 1245, 870. ^{1}H-NMR ($CDCl_3$): Table 1. MS: *m/z* at 470 (M^+), 410 (M^+-HOAc), 395, 231, 207, 189, (100%), 157, 133, 105, 95, 94, 44.

*3.3.2. Taraxeryl acetate, **5***

Mp 301–302°C (C_6H_6–EtOAc), lit. (Hui & Li, 1976) 304–205°, M^+ *m/z* 468.3310 (calculated for $C_{32}H_{52}O_2$ 468.3381). IR: ν_{max} cm^{-1} 1720, 1638, 1243, 815. ^{1}H-NMR ($CDCl_3$): δ 0.82 (3H, *s*, H-28), 0.86 (3H, *s*, H-25), 0.88 (3H, *s*, H-23), 0.90 (3H, *s*, H-24), 0.91 (3H, *s*, H-26), 0.95 (6H, *s*, H.30), 1.07 (3H, *s*, H-27), 2.04 (3H, *s*, $OCOCH_3$), 4.46 (1H, *dd*, $J = 11.6$, 6.5 Hz, H-3) 5.53 (1H, *dd*, $J = 8.3$, 3.7 Hz, H-15). MS: *m/z* at 468 (M^+), 453, 408 (M^+-HOAc), 344, 329, 284, 269, 204 (100%). On acetylation with C_5H_5N–Ac_2O, at room temperature (overnight), colourless compound, **11**, mp 278–279°C (MeOH–$CHCl_3$) was recovered. IR: ν_{max} cm^{-1} 3030, 1375, 1640, 1258, 868. ^{1}H-NMR ($CDCl_3$): δ 0.73 (3H, *s*, H-23), 0.84 (3H, *s*, H-28), 0.85 (3H, *s*, H-25), 0.91 (3H, *s*, H-24), 0.93 (3H, *s*, H-26), 0.96 (3H, *s*, H-29), 1.02 (3H, *s*, H-30), 1.08 (3H, *s*, H-27), 2.05 (3H, *s*, $OCOCH_3$) 4.49 (1H, *dd*, $J = 11.5$, 6.2 Hz, H-3), 4.86 (1H, *s*, H-19). MS: *m/z* at 468, 453 (M^+-CH_3), 408 (M^+-HOAc), 231, 218, 207, 204, 189 (100%).

*3.3.3. Germanicol, **6***

Mp 175–176°C (MeOH–$CHCl_3$), lit. (Yamada et al., 1965) 176–177°, M^+ at *m/z* 426.3926 (calculated for $C_{30}H_{50}O$, 426.3936), $[\alpha]_D^{25}$ + 6.0 (C.O. 40). IR: ν_{max} cm^{-1} 3600, 3030, 2940, 2850, 1630, 1450, 1360, 1040, 855 ^{1}H-NMR ($CDCl_3$): δ 0.75 (3H, *s*, H-23), 0.77 (3H, *s*, H-25), 0.88 (3H, *s*, H-24), 0.95 (6H, *s*, H-28), 0.98 (3H, *s*, H-28), 1.03 (3H, *s*, H-29), 1.08 (3H, *s*, H-30), 3.96 (1H, *dd*, $J = 11.5$, 6.2 Hz, H-3), 4.86 (1H, *s*, H-19), MS: *m/z* at 426 (M^+), 411 (M^+-Me), 408, (M^+-H_2O), 231, 218, 189, 77.

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References

Bhargava, K. K., & Sheshadari, T. R. (1973). *Curr. Science*, *42*, 59.

Budzikiewicz, H., Wilson, J. M., & Djerassi, C. (1963). *J. Am. Chem. Soc*, *85*, 3688.

Cheung, H. T., & Williams, D. G. (1969). *Tetrahedron*, *25*, 119.

Dantanarayan, A. P., Kumar, N. S., Muthukuda, M., & Wazeer, M. I. M. (1982). *Phytochemistry*, *21*, 2065–2068.

Fried, J., & Edwards, J. A. (1972). *Organic reactions in steroid chem*, *vol. 1*. New York: Van Nostrand Reinhold.

Grinner, G. (1960). *Ann. Chem*., *13*, 636.

Hui, W. H., & Li, M. M. (1976). *Phytochemistry*, *15*, 563.

Hui, W. H., & Moon, L. M. (1977). *Phytochemistry*, *16*, 111.

Levy, G. C., & Nelson, G. L. (1972). *C-13NMR for organic chemists*. New York: Wiley.

Razdan, T. K., Kachroo, V., Harkar, S., & Koul, G. L. (1982). *Tetrahedron*, *38*, 991.

Razdan, T. K., Kachroo, P. K., Qurishi, M. A., Kalla, A. K., & Waight, E. S. (1996). *Phytochemistry*, *41*, 1437–1438.

Razdan, T. K., Qurishi, M. A., & Khuroo, M. A. (1990). In *Proc. XVIIth IUPAC Symp. on Natural Products, ND* (p. 254).

Schreiber, J., & Eschemnoser, A. (1955). *Helv. Chem. Acta*, *38*, 1529.

Shah, W. A., Qurishi, M. A., Koul, S. K., & Dhar, K. L. (1996). *Phytochemistry*, *41*, 595–597.

Stothers, J. B. (1972). ^{13}C-*NMR spectroscopy*. New York: Academic Press.

Thompson, M. J., & Bowers, W. S. (1965). *Phytochemistry*, *7*, 845.

Wenkert, E., Baddeley, G. V., Burfitt, I. R., & Moreno, L. N. (1978). *Org. Magn. Reson*, *11*, 337.

Williams, D. H., Bhacca, N. S., & Djerassi, C. (1963). *J. Am. Chem. Soc*, *85*, 2810.

Williams, D. H., & Fleming, I. (1988). In *Spectroscopic methods in organic chemistry* (pp. 9–17). UK: Tata McGraw-Hill.

Yamada, T., Nakamura, S., Goto, T., & Hirata, Y. (1965). *Chem. Soc. Jpn*, *86*, 1315.