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STEROIDS, CHROMONE AND COUMARINS FROM *ANGELICA OFFICINALIS*

S. HARKAR, T. K. RAZDAN* and E. S. WAIGHT†

Department of Chemistry, Regional Engineering College, Hazratbal, Srinagar 190006, India; †Department of Chemistry, Imperial College of Sciene and Technology, London, U.K.

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Key Word Index—*Angelica officinalis*; Umbelliferae; root; pregnenolone; sitosterol; osthol; peucenin-7-methyl ether; furanocoumarins.

Abstract—From the ethyl acetate extract of the fresh roots of *Angelica officinalis* var. *himaliaca*, besides sitosterol, pregnenolone, peucenin-7-methyl ether, osthol and 18 furanocoumarins have been characterized by spectroscopic methods, including ^{13}C NMR, and some chemical transformations.

INTRODUCTION

The genus *Angelica* Hoffm. is well documented for the presence of coumarins [1]. Five species of the genus grow wild in northern temperate regions. *A. glauca* and *A. officinalis* var. *himaliaca* are found growing wild in the States of Jammu and Kashmir [2]. The former species has been reported [3] to contain isoimperatorin and prangolarin. Chatterjee and Sen Gupta [4] have identified furanocoumarins, namely archangelin, prangolarin, angelican and angelicin from a species procured from Kashmir. Although Chatterjee *et al.* subsequently reported the presence of ostruthol [5] and archangelenone [6] in *A. archangelica*, the exact identity of the plant species (from Kashmir) on which they worked is uncertain. This together with the known broad spectrum pharmacological properties of coumarins prompted us to study the detailed chemical composition of the fresh roots of the title plant.

RESULTS AND DISCUSSION

From the ethyl acetate fraction of the defatted ethanolic extract of fresh roots of *A. officinalis* var. *himaliaca*, 20 compounds (**2**–**21**), besides sitosterol‡, were recovered. The compounds were characterized, mainly by spectroscopic methods (UV, IR, ^1H NMR, high resolution mass spectrometry and ^{13}C NMR) and some chemical transformations, as well as comparison of the melting points with authentic samples or those in the literature.

Compound **2**, $[M]^+$ at m/z 316.2402, $C_{21}H_{32}O_2$, was shown to be an unsaturated steroid by positive Liebermann–Burchard and TNM tests. Its IR and UV spectra indicated the presence of a hydroxyl function, a double bond and an unconjugated carbonyl group. The ^1H NMR spectrum contained resonance signals at δ0.85 (3H, *s*) and 0.58 (3H, *s*) due to the methyl groups at C-18 and C-19, respectively, of a steroidal system [7], δ5.25 (1H, *br s*) due to the vinylic proton, and δ4.0 (1H, *s*, exch. D_2O), due to a hydroxyl function. A downfield methyl proton signal at δ2.0 suggested that this group was linked to the carbonyl carbon, because a shift of the ester carbonyl and the ketonic functions were observed at δ170.4 and 204.2, respectively, in the ^{13}C NMR spectrum of its acetate. The resonance signal at δ4.5 (1H, *d*, J = 6 Hz) was assigned to the carbinylic proton. The presence of a C-3 equatorial hydroxyl function in **2** was revealed by its facile acetylation to **22**, $[M]^+$ at m/z 358.2494, $C_{23}H_{34}O_3$ (calculated 358.2509); IR ν_{max} cm^{-1}: 1740 (C=O), 1245 (C–O–C); ^1H NMR: δ2.12 (3H, *s*, –O–CO–Me). The carbinylic proton in the ^1H NMR spectrum shifted downfield to δ4.60 (1H, *m*). Furthermore, after Jones oxidation, **2** gave a positive Zimmermann test, characteristic of C-3 keto steroids. The mass spectrum of **2** contained prominent peaks at m/z 301 $[M-Me]^+$, 298 $[M-H_2O]^+$, 283 $[M-H_2O-Me]^+$ and 255 $[M-COMe-H_2O]^+$. A detailed analysis of the mass spectrum showed that the compound was a Δ^5-steroid. Based on this evidence the compound was characterized as pregnenolone [8].

Compound **3**, $[M]^+$ at m/z 274.1200, gave a violet colour with alcoholic ferric chloride and showed UV absorption maxima (ethanol) characteristic of 5,7-dioxygenated chromones [9]. The presence of a chromone structure was also supported by its IR spectrum. It also revealed the presence of a chelated hydroxyl group; [IR ν_{max} cm^{-1}: 3450 (OH), 1660 (C=O); ^1H NMR: δ12.75 (1H, *br s* exch. D_2O)] and a geminal dimethyl group (1360, 1380 cm^{-1}). The ^1H NMR spectrum showed that the compound contained a 2-methylchromene nucleus by resonance signals at δ2.32 (3H, *s*) and 6.0 (1H, *s*) and also indicated the presence of a methoxy group at δ3.85 (3H, *s*) and an isopentenyl group at δ1.65 and 1.75 (3H, each, *s*, $=CMe_2$) 3.30 (2H, *d*, J = 8.7 Hz, Ar–CH_2–) and 5.20 (1H, *m*, –CH_2–C<u>H</u>=C–). The single proton singlet at δ6.32 was assigned to H-8. The mass spectral fragmentation exhibited features of a 5,7-dioxygenated-2-methyl chromone, indicating that the compound followed pathways I and II analogous to those of flavones [10]. The chromone was thus identified as peucenin-7-methyl ether.

On treatment with alkaline ammonium hydroxide

*To whom correspondence should be addressed.

‡Sitosterol (compound 1) is well known and is not illustrated.

followed by ferric chloride, compounds **4–21** produced a violet colour, indicating that all were coumarins [11]. Compounds **5–21** exhibited UV absorptions (Table 1) [12] and mass spectral fragmentations [13] characteristic of linear furanocoumarins. In the downfield region their ^{1}H NMR spectral patterns (Table 2) were identical. The resonance signals due to H-3 and H-4 appeared as doublets, J = 9–9.5 Hz; the signal due to H-3 was observed at δ6.20–6.33. The chemical shift of H-4 distinguished the C-8 and C-5 substituted furanocoumarins. In the spectra of **6–15** the resonance signal due to H-4 appeared at δ8.03–8.32, indicating that they were substituted at C-5 [14]; the singlet due to H-8 in these compounds appeared at δ7.03–7.29. On the other hand, the ^{1}H NMR spectra of **16–21** contained resonance signals due to H-4, relatively upfield at δ7.6–7.95, indicating that these compounds were substituted at C-8 [14, 15]; the chemical shift of H-5 was found at δ7.30–7.56. The furanoprotons appeared as doublets with J = 2.2 Hz. The resonance signals due to H-2′ and H-3′ were observed at δ7.49–7.89 and 6.66–7.21, respectively. The chemical shifts of the side-chain protons of **4–21**, excluding **5**, **6**, **15** and **20**, are tabulated in Table 3. The ^{13}C NMR shifts [16] of the compounds are given in Tables 4 and 5.

Table 1. UV absorption maxima of linear furanocoumarins

Compound	λ_{max} (EtOH)
5	240, 245, 289, 327
6	253, 262, 270, 310
7	209, 248, 259, 296
8	217, 247, 261, 309
9	217, 251, 266, 309
10	219, 248, 262, 305
11	220, 250, 265, 308
12	252, 261, 268
13	222, 255, 265, 310
14	225, 250, 270, 310
15	220, 250, 265, 310
16	243, 249, 262, 306
17	208, 247, 293, 262
18	243, 249, 263, 299
19	218, 248, 263, 300
20	244, 249, 264
21	224, 244, 267, 274, 317

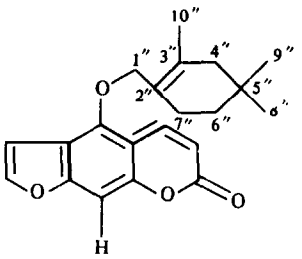
The IR spectrum of **6** ($[M]^+$ at m/z 338.1528, $C_{21}H_{22}O_4$) indicated the presence of a geminal dimethyl group and a tetra-substituted double bond. This was further confirmed by the ^{1}H NMR spectrum, which contained no signal in the olefinic region but showed the presence of two equivalent methyl groups at δ0.91 (6H, *s*) and a deshielded methyl group at 1.66. The latter signal indicated that this group was linked to a vinylic carbon. The two-proton singlets at δ1.87, 2.22 and 1.43 were assigned to H-4″, H-7″ and H-6″, respectively. The prominent peak at m/z 201 and the base peak at m/z 137 indicated a loss of $C_{10}H_{17}$ moiety from the molecular ion. By two-way typical retro-Diels–Alder fragmentation, the base peak ion gave rise to the fragments at m/z 95 and 81. This established the presence of a tetra-substituted cyclohexane moiety in **6**. The ^{1}H NMR signal at δ4.88 (2H, *s*) indicated that the side chain was attached to the aromatic ring through an oxymethylene function [15]. Based on the detailed spectral analysis, **6** was identified as archangelin [4, 17]. Support for this structure was also derived from ^{13}C NMR.

Compound **14**, $[M]^+$ at m/z 322.0606, $C_{16}H_{15}O_5Cl$, contained a hydroxyl function; IR ν_{max} cm^{-1}: 3350; ^{1}H NMR: δ2.90 (1H, *br s*, exch. D_2O). The ^{1}H NMR signal at δ4.1 (1H, *m*, CHOH) showed it to be secondary in nature. Further confirmation of this was derived from acetylation to **23**, whose ^{1}H NMR spectrum displayed the signal due to a carbinylic proton at δ5.30 (1H, *m*). The NMR spectra of **14** and **23** also accounted for two methyl groups and an oxymethylene function. The mass spectrum of **14** showed prominent peaks at m/z 322 $[M]^+$, 286 [M

Table 2. ^{1}H NMR chemical shifts of furobenzopyrone protons (δ values, $CDCl_3$)

Compound	H-3	H-4	H-5	H-8	H-2′	H-3′
5	6.33 (1H, *d*, 9 Hz)	7.76 (1H, *d*, 9 Hz)	7.46 (1H, 6)	7.29 (1H, *s*)	7.60 (1H, *d*, 2.2 Hz)	6.80 (1H, *d*, 2.2 Hz)
6	6.25 (1H, *d*, 9.5 Hz)	8.13 (1H, *d*, 9.5 Hz)	—	7.13 (1H, *s*)	7.57 (1H, *d*, 2.2 Hz)	6.95 (1H, *d*, 2.2 Hz)
7	6.26 (1H, *d*, 9 Hz)	8.24 (1H, *d*, 9 Hz)	—	7.13 (1H, *s*)	7.87 (1H, *d*, 2.2 Hz)	7.21 (1H, *d*, 2.2 Hz)
8	6.23 (1H, *d*, 9 Hz)	8.04 (1H, *d*, 9 Hz)	—	7.03 (1H, *s*)	7.57 (1H, *d*, 2.2 Hz)	6.96 (1H, *d*, 2.2 Hz)
9	6.23 (1H, *d*, 9.5 Hz)	8.1 (1H, *d*, 9.5 Hz)	—	7.26 (1H, *s*)	7.89 (1H, *d*, 2.2 Hz)	7.16 (1H, *d*, 2.2 Hz)
10	6.26 (1H, *d*, 9 Hz)	8.16 (1H, *d*, 9 Hz)	—	7.13 (1H, *s*)	7.63 (1H, *d*, 2.2 Hz)	6.96 (1H, *d*, 2.2 Hz)
11*	6.26 (1H, *d*, 9 Hz)	8.13 (1H, *d*, 9 Hz)	—	7.03 (1H, *s*)	7.53 (1H, *d*, 2.2 Hz)	6.93 (1H, *d*, 2.2 Hz)
12	6.32 (1H, *d*, 9.5 Hz)	8.32 (1H, *d*, 9.5 Hz)	—	7.17 (1H, *s*)	7.59 (1H, *d*, 2.2 Hz)	6.83 (1H, *d*, 2.2 Hz)
13	6.25 (1H, *d*, 9.5 Hz)	8.2 (1H, *d*, 9.5 Hz)	—	7.1 (1H, *s*)	7.6 (1H, *d*, 2.2 Hz)	7.0 (1H, *d*, 2.2 Hz)
14	6.2 (1H, *d*, 9 Hz)	8.20 (1H, *d*, 9 Hz)	—	7.1 (1H, *s*)	7.62 (1H, *d*, 2.2 Hz)	6.99 (1H, *d*, 2.2 Hz)
15	6.21 (1H, *d*, 9 Hz)	8.05 (1H, *d*, 9 Hz)	—	7.1 (1H, *s*)	7.59 (1H, *d*, 2.2 Hz)	6.98 (1H, *d*, 2.2 Hz)
16	6.28 (1H, *d*, 9.5 Hz)	7.72 (1H, *d*, 9.5 Hz)	7.23 (1H, *s*)	—	7.63 (1H, *d*, 2.2 Hz)	6.73 (1H, *d*, 2.2 Hz)
17	6.30 (1H, *d*, 9 Hz)	7.76 (1H, *d*, 9 Hz)	7.30 (1H, *s*)	—	7.70 (1H, *d*, 2.2 Hz)	6.80 (1H, *d*, 2.2 Hz)
18	6.30 (1H, *d*, 9 Hz)	7.79 (1H, *d*, 9 Hz)	7.56 (1H, *s*)	—	7.86 (1H, *d*, 2.2 Hz)	6.80 (1H, *d*, 2.2 Hz)
19	6.36 (1H, *d*, 9 Hz)	7.76 (1H, *d*, 9 Hz)	7.36 (1H, *s*)	—	7.72 (1H, *d*, 2.2 Hz)	6.82 (1H, *d*, 2.2 Hz)
20	6.13 (1H, *d*, 9 Hz)	7.60 (1H, *d*, 9 Hz)	7.16 (1H, *s*)	—	7.49 (1H, *d*, 2.2 Hz)	6.66 (1H, *d*, 2.2 Hz)
21*	6.32 (1H, *d*, 9 Hz)	8.03 (1H, *d*, 9 Hz)	—	—	7.72 (1H, *d*, 2.2 Hz)	6.86 (1H, *d*, 2.2 Hz)

*DMSO-d_6.



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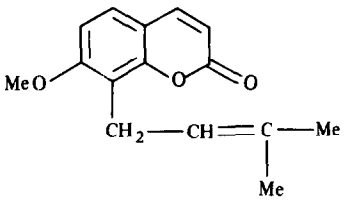

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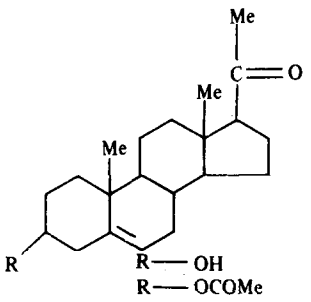

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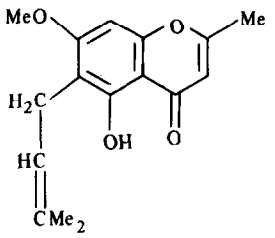


3

$-HCl]^+$, 245 and a base peak at *m/z* 202. Based on spectral evidence, **14** was identified as saxalin [18].

Compound **13**, $[M]^+$ at *m/z* 332.1254, $C_{18}H_{20}O_6$, was also shown to possess a secondary hydroxyl function; IR ν_{max} cm^{-1}: 3470; ^1H NMR: δ2.90 (1H, *br s*, exch. D_2O), 3.95 (1H, *m*, CHOH). On acetylation it formed **24** whose ^1H NMR spectrum contained the resonance signal at δ5.40 (1H, *m*), due to a carbinylic proton. The ^1H NMR spectrum of **13** contained signals at δ4.40 (1H, *dd*, J = 7.93 Hz) and 4.60 (1H, *dd*, J = 3.57 Hz) due to oxymethylene protons. This clearly indicated that the side chain of the compound was rigid. A two-proton quartet at δ3.49 (J = 9.92 Hz) and a triplet at 1.20 (3H, J = 3.96, 7.93 Hz) was characteristic of an ethoxy function, which must be attached to a tertiary carbon. The downfield chemical shift of H-4, δ8.2 ($CDCl_3$), indicated that **13** was substituted at C-5 [14]. The mass spectrum of **13** was in conformity with oxypeucedanin hydrate-3″-ethyl ether.

On the basis of the detailed study on the spectral data, other compounds were identified as psoralen (**5**), bergaptol (**7**), bergapten (**8**), isoimperatorin (**9**), oxypeucedanin (**10**), oxypuecedanin hydrate (**11**), isooxypeucedanin (**12**), ostruthol (**15**), xanthotoxol (**16**), xanthotoxin (**17**), imperatorin (**18**), heraclenol (**19**), 8-geranyloxypsoralen (**20**) and allo-isoimperatorin (**21**).

From the genus *Angelica*, pregnenolone, peucenin-7-methyl ether and oxypeucedanin hydrate-3″-ethyl ether have been characterized for the first time. Although compound **13** is believed to be present in *Ruta pinnata* and *R. oresgasme* [16], details of the characterization of this compound are reported for the first time. The C-8 isomer of this compound has been previously reported from *H. granatense* [19, 20]. The occurrence of mammalian hormones in plants is well established and there is sufficient evidence to support the occurrence of pregnenolone in plants [21] as well. The presence of ethyl ethers and chloro-compounds in plants is unusual. The former has been reported from the genus *Heracleum* [19] while the latter has been characterized from *A. saxatilis* [18]. Except for ostruthol and angelicin, we have not been able to obtain the compounds reported by Chatterjee *et al.* [4, 6].

EXPERIMENTAL

Mps. are uncorr. IR were recorded in KBr discs. ^1H NMR were run at 250 MHz and 60 MHz, MS at 70 eV and ^{13}C NMR at 62.896 MHz.

Extraction and isolation. Fresh roots of *A. officinalis* var. *himaliaca* Clarke (voucher No. 2180, ARN, Khillanmarg; 20.8.73, PGD Botany, University of Kashmir) were procured from Khillanmarg (Kashmir Valley). After hot extraction with EtOH and removal of the solvent, the residue was re-extracted successively with petrol (40–60°) and EtOAc. The EtOAc extract thus obtained was chromatographed on silica gel columns using gradient elution. The mixtures recovered during CC were

Table 3. ^{1}H NMR chemical shifts of side-chain protons (δ values, $CDCl_3$)

Compound	H-1″	H-2″	H-3″	H-4″	H-5″	OCH_2Me	OH
7	—	—	—	—	—	—	2.6 (1H, *br s*, exch. D_2O)
8	3.93 (3H, *s*, OMe)	—	—	—	—	—	—
9	4.86 (2H, *d*, J = 7 Hz)	5.40 (1H, *t*)	—	1.56 (3H, *s*)	1.66 (3H, *s*)	—	—
10	4.56 (2H, *m*)	3.36 (1H, *m*)	—	1.36 (3H, *s*)	1.39 (3H, *s*)	—	—
11*	4.53 (2H, *m*)	3.96 (1H, *m*)	—	1.33 (3H, *s*)	1.33 (3H, *s*)	—	2.53 and 3.03 (1H each, D_2O exch.)
12	5.10 (2H, *s*)	—	2.81 (1H, *m*)	1.17 (3H, *s*)	1.20 (3H, *s*)	—	—
13	4.6 (1H, *dd*, J = 3.57 Hz) 4.4 (1H, *dd*, J = 7.93 Hz)	3.95 (1H, *m*)	—	1.25 (3H, *s*)	1.3 (3H, *s*)	OCH_2 3.49 (2H*q*, J = 9.92 Hz) Me 1.2 (3H, *t*, J = 3.96, 7.93 Hz)	2.9 (1H, D_2O exch.)
14	4.7 (1H, *dd*, J = 3.12 Hz) 4.4 (1H, *dd*, J = 8.03, (4.9 Hz)	4.1 (1H, *m*)	—	1.70 (3H, *s*)	1.71 (3H, *s*)		2.9 (1H, D_2O exch.) 4.9 Hz)
16	—	—	—	—	—	—	3.50 (1H, *br s*, D_2O exch.)
17	4.23 (3H, *s*, OMe)	—	—	—	—	—	—
18	4.9 (2H, *d*, J = 7 Hz)	5.60 (1H, *t*, J = 8.5, 6 Hz)	—	1.73 (3H)	1.73 (3H)	—	—
19	4.56 (2H, *m*)	3.90 (1H, *m*)	—	1.30 (3H, *s*)	1.32 (3H, *s*)	—	2.73 and 3.53 (1H, each, D_2O exch.)
21*	3.73 (2H, *d*, J = 7 Hz)	3.20 (1H, *t*, J = 9, 6 Hz)	—	1.76 (3H, *s*)	1.89 (3H, *s*)	—	—

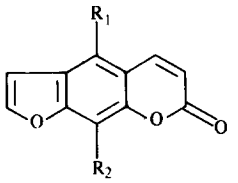
*DMSO-d_6.

Table 4. ^{13}C NMR shifts of furobenzopyrone nucleus (δ values, $CDCl_3$)

Compound	C-2	C-3	C-4	C-4a	C-5	C-6	C-7	C-8	C-8a	C-1′	C-2′
5	161.1	114.7	144.2	115.6	120.0	125.0	156.2	99.5	152.2	147.0	106.6
6	161.14	112.68	139.35	107.5	149.64	114.39	158.2	94.24	152.85	144.85	105.12
8	160.3	112.8	139.4	106.7	149.6	113.0	158.2	94.0	152.7	145.0	105.3
9	160.9	112.2	139.2	107.18	148.7	113.8	156.9	93.8	152.4	144.4	104.9
10	160.5	112.7	138.7	107.1	148.1	113.9	157.7	94.3	152.2	145.0	104.4
11	160.8	111.9	139.7	106.7	148.9	113.5	157.7	93.5	145.1	144.6	105.0
12	160.8	113.3	139.15	107.5	148.0	113.6	158.1	95.1	152.7	145.5	104.1
13	161.0	112.8	139.2	107.0	149.0	114.1	158.2	94.4	152.7	144.9	104.9
14	160.8	113.1	138.9	107.5	148.4	114.3	158.1	94.8	152.6	145.2	104.6
16	160.0	113.7	145.3	116.2	110.0	125.2	145.3	130.1	139.8	147.2	106.9
17	160.16	114.38	144.19	116.29	112.84	125.98	147.36	132.48	142.70	146.41	106.64
18	160.20	114.20	143.3	116.20	113.2	125.7	148.3	131.36	143.50	146.39	106.63
19	160.3	114.5	144.3	116.3	113.5	126.0	147.7	131.5	143.0	146.7	106.7

Table 5. ^{13}C NMR chemical shifts of side-chain carbons (δ values, $CDCl_3$)

Compound	C-1″	C-2″	C-3″	C-4″	C-5″	OCH_2Me
8	60.3	—	—	—	—	—
9	69.58	119.0	139.4	25.7	18.1	
10	72.2	61.0	58.1	24.5	19.1	
11	74.7	76.5	71.1	25.14	25.14	
12	75.0	208.6	37.4	17.9	17.9	
13	74.5	75.9	76.4	21.3	16.1	OCH_2Me 56.8, 21.5
14	74.3	76.5	71.3	28.6	29.2	
17	61.10	—	—	—	—	
18	69.91	119.75	139.2	25.70	18.02	
19	75.6	76.2	71.5	25.1	26.5	



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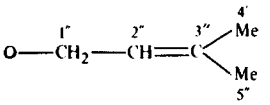
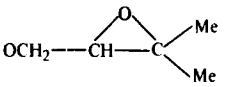
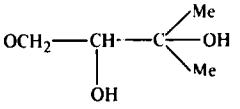
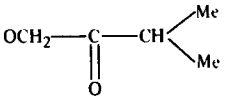
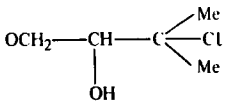
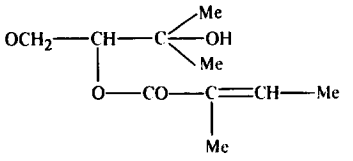
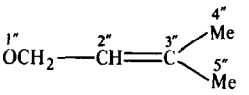
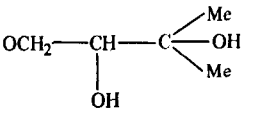
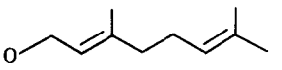
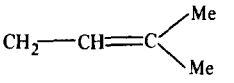
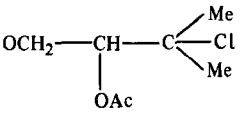
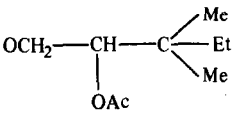
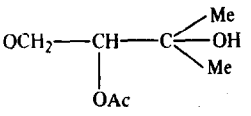
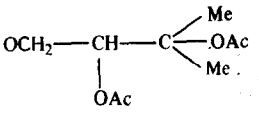
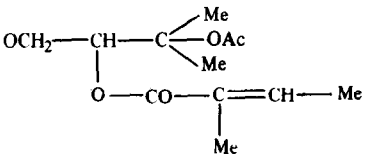
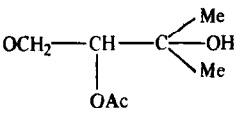
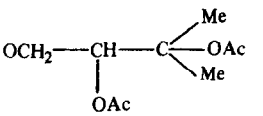
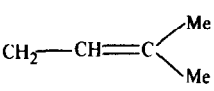
9		H
10		H
11		H
12		H
13		H
14		H
15		H

separated either by repeated CC or by prep. TLC on silica gel G.

Characterization of the compounds. Sitosterol (**1**), mp 135°, gave a positive Liebermann–Burchard (LB) test for sterols. Its identity was confirmed by co-TLC and mmp with an authentic sample.

Pregnenolone (**2**), $[M]^+$ *m/z* 316.2404, $C_{21}H_{32}O_2$, mp 180°, (lit. mp 193°), $[\alpha]_D^{20}$ +28° (*c* 0.1 in EtOH). Positive LB and TNM tests. IR ν_{max} cm^{-1}: 3420 (OH), 1720 (C=O), 1680, 840 (–C=CH). MS *m/z*: 316 $[M]^+$, 301 $[M-Me]^+$, 283 $[M-H_2O-Me]^+$, 255 $[M-COMe-H_2O]^+$, 213, 231, 205, 175, 161, 159, 167, 147, 133, 121, 119. **2** (0.04 g) in pyridine (1 ml) was treated with Ac_2O (2 ml) and left overnight. After usual work-up, **22** (0.035 g), mp 120°, was recovered. IR ν_{max} cm^{-1}: 1740, 1725, 1245, 1610, 840. ^1H NMR ($CDCl_3$, 250 MHz): δ0.64 (3H, *s*, H-19), 1.0 (3H, *s*, H-18), 2.0 (3H, *s*, H-21), 2.12 (3H, *s*, OCOMe), 4.60 (1H, *m*), 5.38 (1H, *d*, J = 8.9 Hz, H-6). MS *m/z*: 358 $[M]^+$, 343 $[M-Me]^+$, 298 $[M-HOAc]^+$, 283 $[M-HOAc-Me]^+$, 255, 231, 224, 205, 134, 133, 121, 120. ^{13}C NMR ($CDCl_3$): δ37.1 (C-1), 27.8 (C-2), 73.9 (C-3), 38.14 (C-4), 139.8 (C-5), 122.3 (C-6), 31.9 (C-7), 38.9 (C-8), 50.0 (C-9), 36.7 (C-10), 21.1 (C-11), 31.4 (C-12), 44.0 (C-13), 56.9 (C-14), 22.9 (C-15), 24.5 (C-16), 63.7 (C-17), 13.2 (C-18), 19.3 (C-19), 209.2 (C=O), 21.3 (CO-$\underline{C}H_3$), 170.4 (O-$\underline{C}$OMe), 21.3 (OCO$\underline{C}H_3$).

	R_1	R_2
16	H	OH
17	H	OMe
18	H	
19	H	
20	H	
21	H	
23		H
24		H
25	OAc	H

	R_1	R_2
26		H
27		H
28		H
29	H	OAc
30	H	
31	H	
32	OAc	

Peucenin-7-methyl ether (**3**). Mp 100°, (lit. 102°); $[M]^+$ *m/z* 274.1200 (calc. for $C_{16}H_{18}O_4$, 274.1205), violet colour with alcoholic $FeCl_3$. UV λ_{max} nm: 258, 240, 238, 210. IR ν_{max} cm^{-1}: 3450 (OH), 1660, 1580, 1500, 1460 (aromatic), 1380, 1360 (geminal dimethyl), 1220, 1200, 1650, 1110, 960, 840, 820. MS *m/z*: 274 $[M]^+$, 259 $[M-Me]^+$, 231, 219, 206, 205, 189 and 177. ^{13}C NMR: δ105.07 (C-2), 112.69 (C-3), 182.33 (C-4), 166.18 (C-5), 108.7 (C-6), 162.69 (C-7), 89.3 (C-8), 158.3 (C-8a), 156.4 (C-4a), 21.30 (C-2Me), 55.7 (C-7 OMe), 25.65 (C-1'), 122.02 (C-2'), 131.63 (C-3'), 20.23 (C-4'), 17.65 (C-5').

Osthol (**4**). Mp 83°, $[M]^+$ *m/z* 244.1123 (calc. for $C_{15}H_{16}O_3$, 244.1099). UV λ_{max}^{EtOH} nm: 318, 247, 245. IR ν_{max} cm^{-1}: 1600, 1495 (aromatic); 1715 (α:β-unsaturated δ-lactone), 1385, 1365 (geminal dimethyl). ^1H NMR ($CDCl_3$, 60 MHz): δ1.86 (3H, *s*, H-4'), 1.83 (3H, *s*, H-5'), 3.5 (2H, *d*, *J* = 7 Hz, H-1'), 3.96 (3H, *s*, OMe), 5.23 (1H, *m*, H-2'), 6.20 (1H, *d*, *J* = 9 Hz, C-3H), 6.96 (1H, *d*, *J* = 8.5 Hz, C-6H), 7.46 (1H, *d*, *J* = 8.5 Hz, C-5H) and 7.80 (1H, *d*, *J* = 9 Hz, C-4H). MS *m/z*: 244 $[M]^+$, 229 $[M-Me]^+$, 214, 213, 175.

Psoralen (**5**). Mp 156° (lit. mp 156°), $[M]^+$ *m/z* 186.0310 (calc. for $C_{11}H_6O_3$, 186.0316). IR ν_{max} cm^{-1}: 1710, 1600, 1560, 870.

Archangelin (**6**). Mp 130° (lit. mp 132°), $[M]^+$ *m/z* 338.1528 (calc. for $C_{21}H_{22}O_4$, 338.1502). IR ν_{max} cm^{-1}: 1725, 1620, 1525, 1480, 1380, 1360, 720. MS *m/z*: 338 $[M]^+$, 201, 173, 145, 137 (100), 95, 81. ^1H NMR ($CDCl_3$, 250 MHz) of side-chain protons: δ0.91 (6H, *s*, H-8'' and H-9''), 1.66 (3H, *s*, H-10''), 1.43 (2H, *s*, H-6''), 1.87 (2H, *s*, H-4''), 2.22 (2H, *s*, H-7''), 4.88 (2H, *s*, H-1''). ^{13}C NMR of side-chain carbons: δ73.66 (C-1''), 133.2 (C-2''), 124.48 (C-3''), 35.68 (C-4''), 46.2 (C-5''), 26.1 (C-6''), 29.1 (C-7''), 28.1 (C-8''), 19.4 (C-9'') and 28.1 (C-10'').

Bergaptol (**7**). Mp 276° (lit. mp 277–278°), $[M]^+$ *m/z* 202.0202 (calc. for $C_{11}H_6O_4$, 202.0249). IR ν_{max} cm^{-1}: 3310, 1714, 1598, 1492. **7** (0.038 g) on acetylation with Ac_2O (1 ml) and pyridine (0.5 ml) gave **25**, mp 151–153°, $[M]^+$ *m/z* 244, $C_{13}H_8O_5$. IR ν_{max} cm^{-1}: 1745, 1246, 1714, 1590, 1490. ^1H NMR ($CDCl_3$, 60 MHz): δ2.13 (3H, *s*, –OCOMe), 6.26 (1H, *d*, *J* = 9 Hz, H-3), 7.13 (1H, *s*, H-8), 7.21 (1H, *d*, *J* = 2.2 Hz, H-3'), 7.87 (1H, *d*, *J* = 2.2 Hz, H-2'), 8.20 (1H, *d*, *J* = 9 Hz, H-4).

Bergapten (**8**). Mp 180° (lit. mp 188°), $[M]^+$ *m/z* 216.0416 (calc. for $C_{12}H_8O_4$, 216.0406). IR ν_{max} cm^{-1}: 1725, 1607, 1500, 880. MS *m/z* (rel. int.): 216 $[M]^+$, 201 (100), 185, 173, 145, 132, 76.

Isoimperatorin (**9**). Mp 108° (lit. mp 109°), $[M]^+$ *m/z* 270.0882 (calc. for $C_{16}H_{14}O_4$, 270.0875). IR ν_{max} cm^{-1}: 1725, 1680, 1590, 1500, 1480, 1360, 1380, 1170, 820. Identity was confirmed by mmp and co-TLC with an authentic sample.

Oxypeucedanin (**10**). Mp 142–143°, $[M]^+$ *m/z* 286.0845 (calc. for $C_{16}H_{14}O_5$, 286.0841). IR ν_{max} cm^{-1}: 1720, 1603, 1386, 1362. **10** (0.05 g) was dissolved in MeOH (20 ml) and treated with oxalic acid (20 mg). The reaction mixture was refluxed at 100° for 2.5 hr, cooled and filtered. The filtrate after usual work-up gave a product, mp 134–136°, identical with **11**.

Oxypeucedanin hydrate (**11**). Mp 134° (lit. mp 134–135°), $[M]^+$ *m/z* 304.0942 (calc. for $C_{16}H_{16}O_6$, 304.0946). IR ν_{max} cm^{-1}: 3400, 1716, 1604, 1500, 1389, 1370. Identity of **11** was confirmed by co-TLC and mmp with an authentic sample. **11** (0.09 g) in pyridine (1.5 ml) was treated with Ac_2O (3 ml) and the mixture left overnight. Half of the reaction mixture was removed and after usual work-up gave **26** (0.04 g), mp 115°, $[M]^+$ *m/z* 346, $C_{18}H_{18}O_7$; ^1H NMR ($CDCl_3$, 60 MHz): δ1.33 (6H, *s*, H-4'' and H-5''), 2.06 (3H, *s*, H-2''), 3.76 (1H, *s*, H-3'', exch. D_2O), 4.60 (2H, *m*, H-1''), 5.36 (1H, *m*, H-2''), 6.13 (1H, *d*, *J* = 9 Hz, H-3), 6.90 (1H, *d*, *J* = 2.2 Hz, H-3'), 7.03 (1H, *s*, H-8), 7.56 (1H, *d*, *J* = 2.2 Hz, H-2'), 8.13 (1H, *d*, *J* = 9 Hz, H-4). The other half of the reaction mixture was heated at 100° for 3 hr and worked up for the recovery of **27** (0.042 g), $[M]^+$ *m/z* 388, $C_{20}H_{20}O_8$; ^1H NMR ($CDCl_3$, 60 MHz): δ1.66 (6H, *s*, H-4'' and H-5''), 2.16 (6H, *s*, H-2'' and H-3'' –OAc), 4.46 (2H, *m*, H-1''), 5.33 (1H, *m*, H-2'', –C<u>H</u>–OAc), 6.16 (1H, *d*, *J* = 9 Hz, H-3), 6.93 (1H, *d*, *J* = 2.2 Hz, H-3'), 7.06 (1H, *s*, H-8), 7.60 (1H, *d*, *J* = 2.2 Hz, H-2'), 8.16 (1H, *d*, *J* = 9 Hz, H-4).

Isooxypeucedanin (**12**). Mp 140° (lit. mp 146°), $[M]^+$ *m/z* 286.0837 (calc. for $C_{16}H_{14}O_5$, 286.0841); IR ν_{max} cm^{-1}: 1720, 1620, 1590, 1490, 1385, 1361. MS *m/z* (rel. int.): 286, 215, 202, 189, 201 (100), 173, 145, 132, 71, 69, 43.

Oxypeucedanin hydrate-3''-ethyl ether (**13**). Mp 92°, $[M]^+$ *m/z* 332.1254 (calc. for $C_{18}H_{20}O_6$, 332.1260). IR ν_{max} cm^{-1}: 3470, 1715, 1620, 1525, 1435, 1350, 810, 860. MS *m/z* (rel. int.): 332, 286, 215, 202 (100), 201, 174, 145, 113, 89, 87, 85. On acetylation with Ac_2O–pyridine, it afforded **24**, mp 80°, $[M]^+$ *m/z* 374, $C_{20}H_{20}O_7$. IR ν_{max} cm^{-1}: 1730, 1715, 1245, 1620, 1320, 1435, 810. ^1H NMR ($CDCl_3$, 60 MHz): δ1.27 (6H, *s*, H-4'' and H-5''), 1.29 (3H, *t*, *J* = 7.93, 3.90 Hz, $OCH_2C\underline{H}_3$), 2.1 (3H, *s*, OCOMe), 3.45 (2H, *q*, *J* = 9 Hz, $OC\underline{H}_2Me$), 4.5 (2H, *d*, *J* = 7.9 Hz, H-1''), 5.25 (1H, *m*, H-2''), 6.25 (1H, *d*, *J* = 9 Hz, H-3), 7.0 (1H, *d*, *J* = 2.2 Hz, H-3'), 7.1 (1H, *s*, H-8), 7.5 (1H, *d*, *J* = 2.2 Hz, H-2'), 8.23 (1H, *d*, *J* = 9 Hz, H-4).

Saxalin (**14**). Mp 158° (lit. Mp 159–160°), $[M]^+$ *m/z* 322.0606 (calc. for $C_{16}H_{15}O_5Cl$, 322.0608). IR ν_{max} cm^{-1}: 3350, 1720, 1610, 1580, 825, 750. MS *m/z* (rel. int.): 322, 286, $[M-HCl]^+$, 245, 216, 202 (100), 201. On acetylation with Ac_2O–pyridine **14** gave **23**, mp 140°, $[M]^+$ *m/z* 364, $C_{18}H_{17}O_6Cl$. IR ν_{max} cm^{-1}: 1740, 1715, 1245, 1610, 1580, 1380, 1370, 820. ^1H NMR ($CDCl_3$, 60 MHz): δ1.69 (6H, *s*, H-4'' and H-5''), 2.1 (3H, *s*, OCOMe), 4.5 (2H, *d*, *J* = 7.5 Hz, H-1''), 5.3 (1H, *m*, H-2''), 6.2 (1H, *d*, *J* = 9 Hz, H-3), 6.95 (1H, *d*, *J* = 2.2 Hz, H-3'), 7.1 (1H, *s*, H-8), 7.55 (1H, *d*, *J* = 2.2 Hz, H-2'), 8.19 (1H, *d*, *J* = 9 Hz, H-4).

Ostruthol (**15**). Mp 137° (lit. mp 136–137°), $[M]^+$ *m/z* 386.1317 (calc. for $C_{21}H_{22}O_7$, 386.1365). IR ν_{max} cm^{-1}: 3450, 1720, 1620, 1580, 1460, 1380, 1360, 820, 760. MS *m/z* (rel. int.): 386 $[M]^+$, 371 $[M-Me]^+$, 368 $[M-H_2O]^+$, 286, 271, 244, 229, 202 (100), 201, 185, 174, 173, 167, 157, 145. ^1H NMR ($CDCl_3$, 250 MHz): δ1.37 (3H, *s*, H-4''), 1.34 (3H, *s*, H-5''), 2.01 and 1.97 (3H, *dq*, *J* = 7.49, 2.49, 3.34 and 1.66 Hz, respectively, H-4''), 1.88 (3H, *t*, *J* = 2.49, 7.49 Hz, H-5''), 4.84 and 4.46 (2H, *dd*, *J* = 4.46, 4.01 and 8.9, 8.6 Hz respectively, H-1''), 5.45 (1H, *dd*, *J* = 4.6 Hz, H-2''), 6.12 (1H, *ddd*, *J* = 2.3 Hz, H-3''). On heating with Ac_2O–pyridine for 5 hr, **15**, after usual work-up, yielded **28**, mp 110°, $[M]^+$ *m/z* 428, $C_{23}H_{24}O_8$; IR ν_{max} cm^{-1}: 1750, 1720, 1245, 1620; ^1H NMR ($CDCl_3$, 60 MHz): δ2.0 (3H, *s*, OCOMe).

Xanthotoxol (**16**). Mp 247° (lit. mp 251–252°), $[M]^+$ *m/z* 202.0240 (calc. for $C_{11}H_6O_4$, 202.0249). IR ν_{max} cm^{-1}: 3280 (OH), 1710, 1600, 1495. MS *m/z* (rel. int.): 202, 201 (100), 173, 145. On acetylation with Ac_2O–pyridine at room temp., **16** afforded **29**, mp 186°; IR ν_{max} cm^{-1}: 1740, 1600, 1590, 1245. ^1H NMR ($CDCl_3$, 60 MHz): δ2.35 (3H, *s*, OCOMe), 6.28 (1H, *d*, *J* = 9.5 Hz, H-3), 6.73 (1H, *d*, *J* = 2.2 Hz, H-3'), 7.73 (1H, *s*, H-5), 7.63 (1H, *d*, *J* = 2.2 Hz, H-2'), 7.72 (1H, *d*, *J* = 9.5 Hz, H-4).

Xanthotoxin (**17**). Mp 147° (lit. mp 147°), $[M]^+$ *m/z* 216 (calc. for $C_{12}H_8O_4$, 216.0432). IR ν_{max} cm^{-1}: 1710, 1610, 1585, 1400, 1290, 1090, 870, 750. MS *m/z* (rel. int.): 216 $[M]^+$, 201 $[M-15]^+$, (100), 185, 173.

Imperatorin (**18**). Mp 102° (lit. mp 102–103°), $[M]^+$ 270.0882 (calc. for $C_{16}H_{14}O_4$, 270.0875). IR ν_{max} cm^{-1}: 1718, 1595, 1497, 1380 and 1360. MS *m/z*: 270 $[M]^+$, 255 $[M-Me]^+$, 202, 201, 173, 145. The identity of the compound was confirmed by co-TLC and mmp.

Heraclenol (**19**). Mp 117–118° (lit. mp 117–118°), $[M]^+$ *m/z* 304.1005 (calc. for $C_{16}H_{16}O_6$, 304.0946). IR ν_{max} cm^{-1}: 3540, 1720, 1605, 1595, 1491, 1386, 1370, 870. MS *m/z* (rel. int.): 304 $[M]^+$, 289, 245, 202, 201 (100), 173, 145. On acetylation with Ac_2O–pyridine at room temp., **19** afforded **30**, $[M]^+$ *m/z* 346, $C_{18}H_{18}O_7$, mp 101–102°; IR ν_{max} cm^{-1}: 1750, 1600, 1590 and

1245. ^{1}H NMR ($CDCl_3$, 60 MHz): δ1.36 (3H, *s*, H-4″), 1.41 (3H, *s*, H-5″), 2.30 (3H, *s*, CH–OAc–C–OH), 2.46 (1H, *br s*, D_2O exch. –C–OH), 4.63 (2H, *m*, H-1″, Ar–OC$\underline{H}_2$), 5.20 (1H, *m*, H-2″, OCH_2–C$\underline{H}$–), 6.33 (1H, *d*, J = 9 Hz, H-3), 6.80 (1H, *d*, J = 2.2 Hz, H-3′), 7.36 (1H, *s*, H-5), 7.70 (1H, *d*, J = 2.2 Hz, H-2′), 7.78 (1H, *d*, J = 9 Hz, H-4). On heating with Ac_2O–pyridine for 5 hr, **19** afforded **31**, mp 65°, $[M]^+$ m/z 388, $C_{20}H_{20}O_8$; ^{1}H NMR ($CDCl_3$, 60 MHz): δ1.42 (3H, *s*, H-4″), 1.50 (3H, *s*, H-5″), 2.30 (3H, *s*, OAc), 2.36 (3H, *s*, OAc), 4.63 (2H, *m*, Ar–OC$\underline{H}_2$), 5.26 (1H, *m*, H-2″, –OCH_2–C$\underline{H}$OAc), 6.26 (1H, *d*, J = 9.5 Hz, H-3), 6.80 (1H, *d*, J = 2.2 Hz, H-3′), 7.30 (1H, *s*, H-5), 7.60 (1H, *d*, J = 2.2 Hz, H-2′), 7.70 (1H, *d*, J = 9.5 Hz, H-4).

8-*Geranyloxypsoralen* (**20**). Mp 53°, $[M]^+$ m/z 338.1512 (calc. for $C_{21}H_{22}O_4$, 338.1502). IR ν_{max} cm^{-1}: 1710, 1600, 1560, 1490, 1380, 1360. ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.53, 1.63, 1.69 (3H, each *s*, side-chain methyls), 4.69 (2H, *d*, J = 8.5 Hz, Ar–OC$\underline{H}_2$), 5.43 (2H, *t*, methine), 2.0 (4H, *d*, –CH_2–CH_2–CH), 6.13 (1H, *d*, J = 10 Hz, H-3), 6.66 (1H, *d*, J = 2.2 Hz, H-3′), 7.16 (1H, *s*, H-5), 7.49 (1H, *d*, J = 2.2 Hz, H-4), 7.60 (1H, *d*, J = 10 Hz, H-4). The identity of the compound was confirmed by co-TLC and mmp with an authentic sample.

Allo-isoimperatorin (**21**). Mp 213° (lit. mp 228–230°). $[M]^+$ m/z 270.0882 (calc. for $C_{16}H_{14}O_4$, 270.0875). IR ν_{max} cm^{-1}: 3310, 1720, 1600, 1470, 1430, 1380, 1365, 1120, 650. MS m/z (rel. int.): 270, 255, 202, 201, (100), 145. On acetylation with Ac_2O–pyridine, **21** afforded **32**, mp 129°, $[M]^+$ m/z 312, $C_{18}H_{16}O_5$; IR ν_{max} cm^{-1}: 1750, 1600, 1590, 1380, 1360, 1245, 820. ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.63 (3H, *s*, H-4″), 1.79 (3H, *s*, H-5″), 2.43 (3H, *s*, OAc), 3.60 (2H, *d*, J = 7 Hz, H-1″), 5.12 (1H, *t*, J = 9.6 Hz, H-2″), 6.26 (1H, *d*, J = 9.5 Hz, H-3), 6.79 (1H, *d*, J = 2.2 Hz, H-3′), 7.60 (1H, *d*, J = 2.2 Hz, H-2′), 7.9 (1H, *d*, J = 9.5 Hz, H-4).

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REFERENCES

1. Murray, R. D. H. (1978) *Progress in the Chemistry of Organic Natural Products*, Vol. 35. Springer, New York.
2. Hooker, J. D. (1900) *Flora of British India*, Vol. 2, p. 707. Reeve, New York.
3. Kapoor, S. K., Sharma, Y. N. and Zaman, A. (1972) *Phytochemistry* **11**, 475.
4. Chatterjee, A. and Sen Gupta, S. (1964) *Tetrahedron Letters* 1961.
5. Chatterjee, A. and Dutta, S. (1968) *Science Cult.* **34**, 460.
6. Chatterjee, A. and Basa, S. C. (1973) *Indian J. Chem.* **11**, 407.
7. Roy, S., Dutta, A. K. and Chakraborty, D. P. (1982) *Phytochemistry* **21**, 2417.
8. Windholz, M. (ed.) (1976) *The Merck Index*, No. 7533, p. 1001. Merck, New York.
9. Robeson, D. J., Ingham, J. L. and Harborne, J. B. (1980) *Phytochemistry* **19**, 2171.
10. Mabry, T. J. and Markham, K. R. (1975) in *The Flavonoids* (Harborne, J. B., Mabry, T. J. and Mabry, H., eds.), p. 79. Chapman & Hall, London.
11. Feigl, F. (1960) *Spot Tests in Organic Analysis*, p. 250. Elsevier, New York.
12. Lee, H. K. and Soine, T. O. (1969) *J. Pharm. Sci.* **6**, 681.
13. Sheshadri, T. R. and Vishwapaul (1973) *J. Sci. Ind. Res.* **32**, 227.
14. Steck, W. and Mazurek, M. (1972) *Lloydia* **35**, 418.
15. Razdan, T. K., Kachroo, V., Harkar, S. and Koul, G. L. (1982) *Phytochemistry* **21**, 923.
16. Elgamal, M. H. A., Elewa, N. H., Elkhrisky. E. A. M. and Duddeck, H. (1979) *Phytochemistry* **18**, 139.
17. Chatterjee, A. and Dutta, S. (1968) *Indian J. Chem.* **6**, 415.
18. Avramenko, L. G. and Nikonov, G. K. (1971) *Khim. Prir. Soedin.* **7**, 830.
19. Gonzalez, A. G. and Barroso, B. (1975) *Chem. Abstr.* **83**, 4914.
20. Tondon, S. and Rastogi, R. P. (1979) *J. Sci. Ind. Res. (India)* **38**, 434.
21. Bennett, R. D., Heftmann, E. and Winter, B. J. (1969) *Naturwissenschaften* **56**, 463.