Phytochemistry, Vol 25, No 1, pp 207–211, 1986
Printed in Great Britain

0031 9422/86 $3.00 + 0.00

OXIRANYLPHENYL ESTERS FROM *PIMPINELLA DIVERSIFOLIA*

ALBERT T. BOTTINI, VASU DEV*, DAVID J. GARFAGNOLI, C. S. MATHELA†, A. B. MELKANI†, ANGELA A. MILLER* and NOEL S. STURM

Department of Chemistry, University of California, Davis, CA 95616, U.S.A.; *California State Polytechnic University, Pomona, CA 91768, U.S.A.; †Kumaun University, Nainital 263002, India

(*Received* 20 *April* 1985)

Key Word Index *Pimpinella diversifolia*; Apiaceae; 1,2,4-trisubstituted benzenes; ^{13}C NMR spectra.

Abstract—The major components of the essential oil from roots of *Pimpinella diversifolia*, gathered in the Kumaun Region of India, have been identified as the (+)-*Z*-2-methyl-2-butenoate (angelate) and (+)-isobutyrate esters of 4-methoxy-2-(*E*-3-methyloxiranyl)phenol. Aromatic ^{13}C NMR resonances of these compounds and their synthetic acetate analog, as well as those of 2-methoxy-4-(*E*-3-methyloxiranyl)phenyl acetate prepared from isoeugenol, were found to be in excellent agreement with calculated values. Comparison of the EIMS of the natural and synthetic products with those reported for compounds previously identified as 2-methoxy-4-(*E*-3-methyloxiranyl)phenyl esters indicates that they also have the 4-methoxy-2-(*E*-3-methyloxiranyl)phenyl structure.

INTRODUCTION

Several Apiaceae have yielded compounds identified as 2-methoxy-4-(*E*-3-methyloxiranyl)phenyl esters (**1**). Bohlmann and Zdero reported that they obtained the 2-methylbutyrate **1a** from *Pimpinella saxifraga* L. [1] and the (−)-*Z*-2-butenoate (angelate) **1b** from *Ligusticum mucronatum* Hort. [2]; Stahl and Herting reported that they obtained the *E*-2-methyl-2-butenoate (tiglate) **1c** as well as **1a** from *P. saxifraga* L. and *P. major* Huds. [3]. These structural assignments were based primarily on the EI mass spectra and ^{1}H NMR spectra of the compounds and, in all cases, there is no question concerning the identity of the three substituents on the benzene ring. However, the assigned orientation of the substituents appears to be based solely on an assumed relationship to isoeugenol, which is widely distributed among Apiaceae. Subsequent to these reports, two groups independently reported that (±)-4-methoxy-2-(*E*-1-propenyl)phenyl 2-methylbutyrate (**2a**) is an important component of the essential oil of *P. anisum* L. [4, 5]. Identification of **2a** was accomplished by both a detailed study of its ^{1}H and ^{13}C NMR spectra [4, 6] and its degradation to 2-hydroxy-5-methoxybenzaldehyde and (±)-2-methylbutyric acid [5].

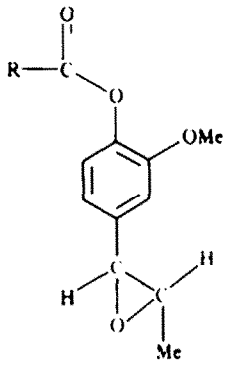
Pimpinella diversifolia DC. [7] is found at altitudes of 1500–3000 m in the Kumaun Region of the Himalayas. The ethanol extract of its seeds has been reported to be strongly fungitoxic [8], and the extract of the whole plant has been reported to possess spermicidal activity in rat semen [9]. Examination of the essential oil from seeds of *P. diversifolia* indicated the presence of carvone, geranyl acetate, limonene, myrcene, α-pinene, pulegone, santene, α-terpineol, terpineolic acid and unidentified coumarins [10], and two coumarins, iso-angenomalin and oxypeucedanin, have been isolated from the aerial part of the plant [11]. There has been no previous report on the chemical composition of the essential oils from roots of *P. diversifolia*.

We describe here the isolation and characterization of the two major constituents (37% and 15%) of the essential oil from roots of pre-flowering *P. diversifolia*: (+)-4-methoxy-2-(*E*-3-methyloxiranyl)phenyl *Z*-2-methyl-2-butenoate (**3b**) and its (+)-isobutyrate analog **3d**.

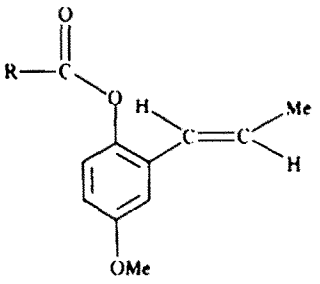
RESULTS AND DISCUSSION

Examination of the steam-volatile oil by GC/MS indicated the presence of at least 40 components. In contrast to the majority, the two present in largest amounts, **A** and **B**, both with relatively long GC retention times, had relatively simple fragmentation patterns that suggested they were not terpenes. They were obtained together by flash chromatography and separated by reverse phase HPLC.

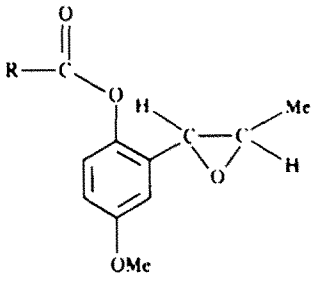
The HREIMS of the colourless oils indicated that $C_{15}H_{18}O_4$ is the molecular formula of the major component **A**, and that **B** has molecular formula $C_{14}H_{18}O_4$. Their 360 MHz ^{1}H NMR spectra (Table 1) have common bands for 11 protons and suggested that each compound was one of six possible benzenes substituted at C-1, C-2 and C-4 with methoxy, *E*-3-methyloxiranyl and either *Z*-2-methyl-2-butenoyloxy (**A**) or isobutyryloxy (**B**) groups. The 1,2,4-trisubstitution pattern on the benzene ring follows from the fine structure of the three signals at lowest field [12]. The ^{1}H NMR resonances at δ3.60, 2.92 and *ca* 1.4 showed the presence of a 3-methyloxiranyl group, and the ring-proton coupling of 2.0 Hz established the *E* stereochemistry [13, 14]. The presence of a 2-methyl-2-butenoyloxy group in **A** was shown by HREIMS peaks due to $C_5H_8O_2^+$, $C_5H_7O^+$ and $C_4H_7^+$ [15] and ^{1}H NMR resonances at δ6.28, 2.10 and 2.07. Comparison of these chemical shifts with those reported for angelates and tiglates [2, 3, 16] strongly suggested the *Z* stereochemistry, and this was confirmed by the ^{13}C NMR spectrum of **A** (Table 2).



1a R = CH(Me)Et
1b R = C(Me)=CHMe
1c R = C(Me)=CHMe
1d R = $CHMe_2$
1e R = Me



2



3

Table 1. ^{1}H NMR data of *P. diversifolia* products ($CDCl_3$, 360 MHz)

Protons	δ(ppm) 3b*	3d†	mult.	J (Hz)
H-6	7.00	6.94	*d*	8.7
H-5	6.83	6.80	*d,d*	3.1, 8.7
H-3	6.78	6.76	*d*	3.1
OMe	3.79	3.79	*s*	—
ArCHO	3.60	3.60	*d*	2.0
OCHMe	2.92	2.91	*q,d*	5.1, 2.0
OCHMe	1.40	1.42	*d*	5.1

*Other resonances at δ6.28 [*qq*, *J* = 7.2 and 1.2 Hz, HC(Me)=C], 2.10 [*dq*, *J* = 7.2 and 1.4 Hz, HC(Me)=C] and 2.07 [*p*, *J* ≈ 1.4 Hz, =C(Me)C=O].

†Other resonances at δ2.84 [*sept*, *J* = 7.2 Hz, Me_2CH], 1.335 and 1.326 [*doublets*, *J* = 7.2 Hz, Me_2CH].

Table 2. ^{13}C NMR data of *P. diversifolia* products ($CDCl_3$, 50.3 MHz)

Carbon	δ(ppm) 3b*	d†	Carbon	δ (ppm) 3b*	3d†
C=O	166.1‡	176.5‡	HC_{ar}	114.2	114.2
C_{ar}	157.6‡	157.6‡	HC_{ar}	109.9	109.8
C_{ar}	142.4‡	142.4‡	OC	58.4	58.4
C_{ar}	131.2‡	131.1‡	OC	55.6	55.6
HC_{ar}	122.8	122.6	OC	55.4	55.2
			Me	17.7	17.8

*Other resonances at δ 141.0 (Me CH=C), 126.8‡ [C=C(Me)CO_2], 20.7 (Me) and 16.0 (Me).

†Other resonances at δ34.1 (Me_2CH) and 19.1 (Me_2C).

‡Lower intensity signal.

which has no signal below δ16 ppm characteristic of tiglate [16, 17]. The presence of an isobutyryloxy group in **B** was suggested by the *m/z* 43 base peak (i-$C_3H_7^+$) and the prominent peak at *m/z* 71 (i-$C_3H_7CO^+$) in its LREIMS and confirmed by the ^{1}H NMR resonances at δ2.86 and *ca* 1.34. Significantly, the *gem*-dimethyl of **B** exhibited not one but two doublets separated by 0.009 ppm. This indicated that they were influenced by one or both chiral centres of the oxiranyl group, which would only be likely if the oxiranyl and acyl groups were *ortho* [18]. The remaining ^{1}H NMR resonance at δ3.79 in the spectra of **A** and **B** is characteristic of a methoxy group, which must be on the benzene ring.

When the aromatic ^{1}H NMR chemical shifts for **1**, **3** and their four possible isomers were calculated using the parameters listed by Silverstein *et al.* [12] for acyloxy, methoxy and, for the oxiranyl group, alkoxymethyl, the same values, and those in best agreement with the spectra of **A** and **B**, were obtained for **1** and **3**: H-3, δ6.75; H-5, 6.75; H-6, 7.05. This together with the likely *ortho* relationship of the isobutyryloxy and oxiranyl groups in **B** indicated that the *P. diversifolia* products are **3b** and **3d**.

Comparison of the aromatic parts of the ^{13}C NMR spectra of **A** and **B** (Table 2) with the calculated aromatic parts of the ^{13}C NMR spectra of **1**, **3** and their four isomers (Table 3) gave even stronger evidence that the compounds are **3b** and **3d**. Two methods were used to calculate the spectra. For **1** and **3**, ^{13}C parameters [19] of

Table 3. Calculated ^{13}C NMR frequencies for 1,2,4-trisubstituted benzenes*

Substituents				Chemical shifts (ppm)†						
C-1	C-2	C-4	Method	C-1	C-2	C-3	C-4	C-5	C-6	ΣΔ‡ (ppm)
OAc	OMe	C_3H_5O	A	139.4	151.5	108.9	136.5	118.1	122.6	19.3
OAc	OMe	C_3H_5O	B	139.3	151.2	110.1	135.7	118.2	122.7	18.1
OAc	C_3H_5O	OMe	A	141.6	130.6	111.1	157.1	114.2	123.1	3.4
OAc	C_3H_5O	OMe	B	140.8	131.3	112.5	156.9	114.2	122.3	5.5
OMe	OAc	C_3H_5O	B	150.6	139.9	120.4	129.5	124.4	112.4	21.6
OMe	C_3H_5O	OAc	B	154.6	123.8	120.0	143.1	121.5	114.8	22.8
C_3H_5O	OAc	OMe	B	122.5	149.6	106.9	160.0	111.1	127.9	18.9
C_3H_5O	OMe	OAc	B	120.1	158.3	106.9	151.3	113.5	127.9	18.9

*See text for methods used.

†The reverse of original assignments to C-5 (122.9) and C-6 (120.7) of 2-methoxyphenyl benzoate [20] and to C-1 (137.3) and C-4 (138.5) of isoeugenol 3-methylbutyrate [4] were used in the calculations.

‡ΣΔ is the sum of the absolute values of the differences between the calculated values and observed values for the *P. diversifolia* products assuming the best possible agreement.

the *E*-1-propenyl group [20] were subtracted from the spectra of isoeugenol 3-methylbutyrate [4] and of 4-methoxy-2-(*E*-1-propenyl)phenyl 2-methylbutrate (**2a**) [4] and the parameters for *E*-3-methyloxiranyl were then added (method A). The latter parameters were taken to be the average for the oxiranyl group [20] (C-1, 9.3; *o*, −3.0; *m*, −0.1; *p*, −0.5 ppm) and the 3,3-dimethyloxiranyl group [21] (C-1, 8.3; *o*, −2.0; *m*, −0.4; *p*, −1.0 ppm). For all six isomers, parameters for the *E*-3-methyloxiranyl group were added to the spectra calculated for *m*- and *p*-methoxyphenyl acylate by group additivity [19] and the spectrum reported for *o*-methoxyphenyl benzoate [20] (method B). Note that addition of *E*-1-propenyl group parameters to the reported spectrum of *o*-methoxyphenyl benzoate and the calculated spectrum of *p*-methoxyphenyl acylate gives values for the aromatic resonance of isoeugenol 3-methylbutyrate and **2a** in very good agreement with the reported values: ada, 0.9 ppm; greatest deviation, 2.3 ppm. When original assignments are corrected, as noted in a footnote to Table 3, the ada and greatest deviation become 0.5 and 1.4 ppm. Note also that the aromatic resonances of phenyl esters show very little change with change in acyl or aroyl group [17, 20]. The average substituent effects for 13 such groups are: C-1, 22.6; *o*, −7.0; *m*, 0.9; *p*, −2.8 ppm; greatest deviations are: C-1, 0.4; *o*, 0.8; *m*, 0.2; *p*, 0.3 ppm. Thus we could expect that the aromatic parts of the ^{13}C NMR spectra of **1b**, **1d** and their acetate analog **1e**—or **3b**, **3d** and their acetate analog **3e**—would be essentially the same.

Epoxidation of isoeugenol acetate and 4-methoxy-2-(1-propenyl)phenyl acetate (**2e**) with *m*-chloroperbenzoic acid [22] gave **1e** and **3e**. Comparison of their ^{13}C NMR spectra (Table 4) with those calculated for **1** and **3** and those observed for the *P. diversifolia* products confirmed that they are **3b** and **3d**.

The EIMS of the acetate **3e**, like that of the *P. diversifolia* products and the compounds previously identified as **1a** [1, 3], **1b** [2] and **1c** [3], showed a strong peak at *m/z* 162 (21.5% of BP 137). In contrast, the *m/z* 162 peak in the EIMS of **1e** was very weak (< 0.5% of BP 137). This difference, which is probably due to the relative ease of water loss from the *o*-substituted phenol radical cation [23] that forms when **3** loses the acyl group on electron impact indicates that the 2-methylbutyrate

Table 4. ^{13}C NMR data of **1e** and **3e** ($CDCl_3$, 50.3 MHz)

Compound	Chemical shifts (ppm)					
	C-1	C-2	C-3	C-4	C-5	C-6
1e*	139.3	151.1	108.8	136.7	117.9	122.5
3e†	142.4	131.0	110.0	157.7	114.2	122.7

*Other resonances at δ17.7 (MeCH), 20.5 (MeCO), 55.7 (MeO), 55.7 and 59.1 (CH–CH) and 168.9 (C=O). *Cf.* Table 3, lines 1 and 2.

†Other resonances at δ17.7 (MeC), 20.6 (MeCO), 55.5 (OMe), 55.2 and 59.3 (CH–CH) and 169.5 (C=O). *Cf.* Table 2 and lines 3 and 4 of Table 3.

obtained from *P. saxifraga* [1, 3] and *P. major* [3] is **3a** rather than **1a** and suggests that the angelate and tiglate identified as **1b** [2, 3] and **1c** [3] are probably **3b** and **3c**. In this regard, the optical rotations at three wavelengths of **3b** from *P. diversifolia* are consistent with the possibility that it is the enantiomer of the *L. mucronatum* product [2].

The unusual 'isoisoeugenol' structures **2** and **3** have now been shown to be produced by four members of the genus *Pimpinella*. Conceivably, the biosynthetic pathway to **2** and **3** may involve *o*-coumarate and the rarely if ever encountered 5-methoxy-*o*-coumarate [24] and may compete with the biosynthesis of coumarins [25] from those intermediates.

EXPERIMENTAL

Plant material. Pimpinella diversifolia DC. was collected from Dwali, Almora District, elevation 2727 m, in June. The identity of the plant was confirmed by Dr. B. M. Wadhwa, R.B.G. Kew, London (herbarium no. H6/2035/82).

Isolation of **3b** *and* **3d**. Roots (1.3 kg) of the freshly collected plants were finely chopped and steam distilled. The essential oil was extracted from the NaCl-satd distillate with petrol, bp 40–60°, and the organic soln was dried (Na_2SO_4) and concd by distillation. Removal of the last traces of solvent at red. pres. left 0.37 g (0.28%) of essential oil.

The oil was analysed using a 30 m × 0.25 mm (J. & W.) fused

silica capillary column, liquid phase DB-5, with He as the carrier gas in a Hewlett–Packard 5840A GC interfaced with a Hewlett–Packard 5985 mass spectrometer at California State University, Sacramento. The column temp. was maintained at 60° for 1 min, and then programmed at 2.5°/min for the next 29 min and 3°/min up to 74 min. The eluant was sampled repeatedly by the mass spectrometer, EI conditions, 70 eV. The two major components, subsequently identified as **3b** and **3d**, had retention times of 52.3 and 47.4 min and were estimated on the basis of their GC response to make up 37% and 15% of the oil.

The major components were isolated together by flash chromatography (SiO_2, hexane–$CHCl_3$) and separated on a C-18 prep. HPLC column using MeOH–H_2O (7:3) as the mobile phase. The yield from 0.36 g of oil was 71 mg (20%) of **3b** and 30 mg (8%) of **3d** as colourless oils.

(+)-4-*Methoxy*-2-(*E*-3-*methyloxiranyl*)-*phenyl Z*-2-*methyl*-2-*butenoate* (**3b**). HREIMS (probe) 50 eV, *m/z* (rel. int.): 262.1241 $[C_{15}H_{18}O_4]^+$ (3.4), 162.0673 $[C_{10}H_{10}O_2]^+$ (100), 147.0463 $[C_9H_7O_2]^+$ (52.0), 131.0498 $[C_9H_7O]^+$ (6.0), 119.0487 $[C_8H_7O]^+$ (31.0), 100.0520 $[C_5H_8O_2]^+$ (9.0), 83.0508 $[C_5H_7O]^+$ (19.6) [$C_{15}H_{18}O_4$ requires: 262.1205]. LREIMS (GC/MS) *m/z* (rel. int.): 262.1 [M]$^+$ (1.4), 162 [M − $C_5H_8O_2$]$^+$ (13), 83 $[C_5H_7O]^+$ (100), 55 $[C_4H_7]^+$ (51). ^1H and ^{13}C NMR: Tables 1 and 2.

$$[\alpha]_{23^\circ}^{\lambda} = \frac{578 \quad 546 \quad 436}{+44^\circ \quad +49^\circ \quad +77^\circ} \text{ (CDCl}_3\text{, } c \text{ 1.7)}$$

(+)-4-*Methoxy*-2-(*E*-3-*methyloxiranyl*)*phenyl isobutyrate* (**3d**). LREIMS (GC/MS) *m/z* (rel. int.): 250 [M]$^+$ (19), 180 [M − C_4H_6O]$^+$ (49), 163 [M − $C_4H_7O_2$]$^+$ (38), 162 [M − $C_4H_8O_2$]$^+$ (48), 151 [M − C_4H_6O − CHO]$^+$ [26] (44), 137 $[C_8H_9O_2]^+$ (100), 71 $[C_4H_7O]^+$ (26), 43 $[C_3H_7]^+$ (21). ^1H and ^{13}C NMR: Tables 1 and 2. $[\alpha]_{23^\circ}^{436} + 56^\circ$ ($CDCl_3$, *c* 0.8).

2-*Methoxy*-4-(3-*methyl*-2-*oxiranyl*)*phenyl acetate* (**1e**). The epoxidation method of ref. [22] was used to convert 2.90 g of isoeugenol acetate, mp 80–81° (lit. [27] mp 80.7–81.3°), to 2.65 g of **1b**, $n^{30}D$ 1.5185. (Found: C, 64.53; H, 6.39. $C_{12}H_{14}O_4$ requires: C, 64.85; H, 6.35%.) LREIMS (GC/MS) *m/z* (rel. int.): 222 [M]$^+$ (4.3), 180 [M − C_2H_2O]$^+$ (27), 163 (2.4), 162 (< 0.5), 151 [M − C_2H_2O − CHO]$^+$ [26] (39), 137 $[C_8H_9O_2]^+$ (100). ^1H NMR (360 MHz, $CDCl_3$): δ6.99 (*d*, 1H, *J* = 8.1 Hz), 6.87 (*dd*, 1H, *J* = 1.5, 8.1 Hz), 6.83 (*d*, 1H, *J* = 1.5 Hz), 3.81 (*s*, 3H), 3.56 (*d*, 1H, *J* = 1.8 Hz), 2.99 (*qd*, 1H, *J* = 4.9, 1.8 Hz), 2.30 (*s*, 3H), 1.43 (*d*, 3H, *J* = 4.9 Hz). ^{13}C NMR: Table 4.

4-*Methoxy*-2-(*E*-3-*methyloxiranyl*)*phenyl acetate* (**3e**). The procedure used in ref. [28] to convert allybenzene to propenylbenzene (160°, KOH–$HOCH_2CH_2OH$) was used to convert 35.1 g of 2-allyl-4-methoxyphenol [29, 30] to a 70:30 mixture of the *E*- and *Z*-isomers of 4-methoxy-2-propenylbenzene, bp 78–93°/0.1 mm (lit. [30] bp 110–114°/3 mm), from which 5.8 g of the higher boiling *E* isomer was obtained by fractional distillation. Treatment with excess Ac_2O and a trace of NEt_3 gave the acetate **2e** as a viscous, colourless liquid after evaporation of solvent at 42°/0.4 mm, $n^{23}D$ 1.5443. (Found: C, 70.01; H, 6.85. $C_{12}H_{14}O_3$ requires: C, 69.88; H, 6.84%.)

Epoxidation [22] of 3.50 g of **2e** gave 2.7 g of **3e**, bp 94–95/0.4 mm, $n^{18}D$ 1.5185. (Found: C, 64.57; H, 6.27. $C_{12}H_{14}O_4$ requires: C, 64.85; H, 6.35%.) LREIMS (GC/MS) *m/z* (rel. int.): 222 [M]$^+$ (13) 180 [M − C_2H_2O]$^+$ (45), 163 [M − $C_2H_3O_2$]$^+$ (12), 162 [M − $C_2H_4O_2$]$^+$ (30), 151 [M − C_2H_2O − CHO]$^+$ [26] (53), 137 $[C_8H_9O_2]^+$ (100). ^1H NMR (360 MHz, $CDCl_3$): δ6.95 (*d*, 1H, *J* = 8.8 Hz), 6.79 (*dd*, 1H, *J* = 3.0, 8.8 Hz), 6.75 (*d*, 1H, *J* = 3.0 Hz), 3.76 (*s*, 3H), 3.58 (*d*, 1H, *J* = 1.8 Hz), 2.93 (*qd*, 1H, *J* = 5.2, 1.8 Hz), 2.30 (*s*, 3H), 1.42 (*d*, 3H, *J* = 5.2 Hz). ^{13}C NMR: Table 4.

Acknowledgements— This work was supported in part by grants from the Faculty Research Committee, University of California, Davis, the Herman Frasch Foundation, administered by the American Chemical Society (to ATB), the National Science Foundation and the University Grants Commission, India, to VD as U.S.-India Exchange Scientist, and the University Grants Commission, India (to CSM). High resolution mass spectra were obtained at the Bio-organic, Biomedical Mass Spectrometry Resource (A. L. Burlingame, Director) supported by NIH Division of Research Resources Grant RR01614. NMR spectra were obtained at the University of California, Davis, NMR Facility; the NT-200 spectrometer used for determination of the ^{13}C NMR spectra was purchased in part by NSF grant CHE 79-04832 to the Department of Chemistry. We are grateful to Professor David Forkey for assistance in obtaining the GC/MS data and the Council of Scientific and Industrial Research, India, for a fellowship to ABM.

REFERENCES

1. Bohlmann, F. and Zdero, C. (1969) *Tetrahedron Letters* 1003
2. Bohlmann, F. and Zdero, C. (1971) *Chem. Ber.* **104**, 2033.
3. Stahl, E. and Herting, D. (1976) *Phytochemistry* **15**, 999.
4. Kubeczka, K.-H., Massow, F. v. and Smith, M. A. R. (1976) *Z. Naturforsch.* **31b**, 283.
5. Carter, G. T., Schnoes, H. K. and Liechtenstein, E. P. (1977) *Phytochemistry* **16**, 615.
6. Massow, F. v. and Smith, M. A. R. (1976) *J. Chem. Soc. Perkin Trans.* 2, 977.
7. Chopra, R. N., Nayar, S. L. and Chopra, I. C. (1956) *Glossary of Indian Medicinal Plants*, p. 193. CSIR, New Delhi.
8. Pandey, D. K., Tripathi, N. N., Tripathi, R. D. and Dixit, S. N. (1983) *Int. J. Crude Drug Res.* **21**, 177.
9. Setty, D. S., Kamboj, V. P. and Khanna, N. M. (1977) *Indian J. Exp. Biol.* **15**, 231.
10. Asraf, M., Rafi, A. and Bhatty, M. K. (1979) *Pak. J. Sci. Ind. Res.* **22**, 265.
11. Bhatia, C. B., Banerjee, S. K. and Handa, K. L. (1978) *J. Indian Chem. Soc.* **55**, 198.
12. Silverstein, R. M., Bassler, G. C. and Morrill, T. C. (1981) *Spectrophotometric Identification of Organic Compounds*, 4th edn, Chap. 4. Wiley, New York.
13. Benassi, R., Lazzeretti, P., Mosetti, I., Taddei, F. and Torre, G. (1973) *Org. Magn. Reson.* **5**, 391.
14. Villa, L., Schenetti, L. and Taddei, F. (1973) *Org. Magn. Reson.* **5**, 593.
15. Thomas, A. F. and Willhalm, B. (1976) *Org. Mass. Spectrom.* **11**, 831.
16. Brouwer, C. H. and Stothers, J. B. (1972) *Can. J. Chem.* **50**, 601.
17. Sequin, U. (1981) *Helv. Chim. Acta* **64**, 2654.
18. Whitesides, G. M., Holtz, D. and Roberts, J. D. (1964) *J. Am. Chem. Soc.* **86**, 2628.
19. Wehrli, F. W. and Wirthlin, T. (1978) *Interpretation of Carbon-13 NMR Spectra*, pp. 45–47. Heydon, Philadelphia.
20. *Sadtler Standard ^{13}C NMR Spectra* (1976) Sadtler Research Laboratories, Philadelphia.
21. Hevesi, L., Nagy, J. B., Krief, A. and Derouane, E. G. (1977) *Org. Magn. Reson.* **10**, 14.
22. Imuta, M. and Ziffer, H. (1979) *J. Org. Chem.* **44**, 1351.
23. McLafferty, F. W. (1980) *Interpretation of Mass Spectra*, 3rd edn, pp. 193–194. University Science Books, Mill Valley, CA.
24. Vorovskii, V. V., Dubinin, N. S. and Dranik, L. I. (1975) *Nek. Probl. Farm. Nauki Prakt., Mater. S'ezda Farm. Kaz.*, (Dubinin, N. S., ed.) pp. 231–232. Nauchn. O-vo. Farm. Kaz.:

Alma-Ata, USSR [*Chem. Abstr.* **86**, 185916v (1976)].
25. Torssell, K. B. G. (1983) *Natural Product Chemistry*, pp. 88–91. Wiley, New York.
26. Fetizon, M., Henry, Y., Aranda, G., Audier, H. E. and De Luzes, H. (1974) *Org. Mass Spectrom.* **8**, 201.
27. Levi, L. (1958) *Perfum. Essent. Oil Rec.* **49**, 512.
28. Koch, H. P. (1948) *J. Chem. Soc.* 1123.
29. White, W. N. and Slater, C. D. (1961) *J. Org. Chem.* **36**, 3631.
30. Bell, A., Knowles, M. B. and Tholstrup, C. E. (1951) U.S. Patent 2682474 [*Chem. Abstr.* **48**, 11090d (1954)].