Phytochemistry, Vol. 28, No. 11, pp. 3197–3200, 1989.
Printed in Great Britain.

0031–9422/89 $3.00 + 0.00

ALANGIFOLIOSIDE, A DIPHENYLMETHYLENE DERIVATIVE, AND OTHER PHENOLICS FROM THE LEAVES OF *ALANGIUM PLATANIFOLIUM* VAR. *TRILOBUM*

HIDEAKI OTSUKA, KAZUO YAMASAKI* and TATSUO YAMAUCHI†

Institute of Pharmaceutical Sciences, Hiroshima University School of Medicine, 1-2-3- Kasumi, Minami-ku, Hiroshima 734, Japan; †Department of Pharmacognosy, Faculty of Pharmaceutical Sciences, Fukuoka University, 8-19-1 Nanakuma, Jonan-ku, Fukuoka 814-01, Japan

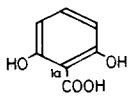
(*Received* 14 *March* 1989)

Key Word Index—*Alangium platanifolium* var. *trilobum*: Alangiaceae; flavonol glycoside; 2,6-dihydroxybenzoic acid henryoside; alangifolioside; 2D-NMR.

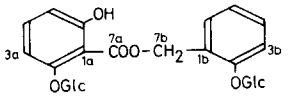
Abstract—From the methanolic extract of leaves of *Alangium platanifolium* var. *trilobum*, henryoside, 2,6-dihydroxybenzoic acid and alangifolioside, along with five known flavonol glycosides were isolated.

INTRODUCTION

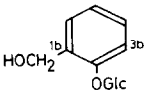
Alangium platanifolium Harms var. *trilobum* Ohwi is a deciduous shrub widely distributed in Japan. Another member of the genus, *A. lamarckii* Thwaites is an Indian medicinal plant, and is the only known source of ipecac alkaloids outside the Rubiaceae [1–3]. This plant also contains alangiside: a monoterpenoid lactam glucoside [4]. In a previous paper, we reported the isolation and the structure elucidation of 7-*O*-acetylloganic acid from the stem barks of *A. platanifolium* var. *trilobum* [5]. In the course of a continuing investigation, we have isolated several flavonol glycosides (**1**–**5**), 2,6-dihydroxybenzoic acid (**6**), henryoside (**7**): the ester of 2-*O*-glucopyranosyl-2,6-dihydroxybenzoic acid and salicin (**8**), and alangifolioside (**9**): a diphenylmethylene derivative from the leaves of this plant. This paper describes the isolation and structure elucidation of these compounds.



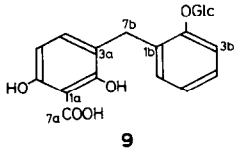
6



7



8 (Salicin)



9

*Author to whom correspondence should be addressed.

RESULTS AND DISCUSSION

The *n*-butanol soluble fraction of the methanol extract of the leaves of *A. platanifolium* var. *trilobum* was separated by Diaion CC and compounds were purified by the combination of silica gel CC, droplet counter-current chromatography (DCCC) and Sephadex LH-20 CC.

Compounds **1**–**5** were obtained as yellow needles and ^{1}H and ^{13}C NMR spectra of these compounds indicated that these are flavonol glycosides. Comparing physical date with the reported values, these were determined to be astragalin (**1**), nicotoflorin (**2**), clitorin (**3**), kaempferol 3-*O*-dirhamnopyranosylglucoside (**4**) and quercetin-3-*O*-dirhamnopyranosylglucoside (**5**).

Compound **6** was obtained as colourless needles. The ^{1}H NMR spectrum (CD_3OD) showed a doublet signal at δ6.27 (2H) and a triplet signal at δ7.12 (H), and ^{13}C NMR (CD_3OD) showed four signals for an aromatic ring (see Experimental and Table 1) and a carboxylic group. Although these data suggested **6** was 2,6-dihydroxybenzoic acid, melting points and other physical data were not identical with those of an authentic sample, presumably because of salt formation. After **6** was passed through Dowex 50W × 8 and crystallized from water, the resulting crystals were identical with an authentic sample of 2,6-dihydroxybenzoic acid in all aspects.

Compound **7** was obtained as colourless needles, analysed for $C_{26}H_{32}O_{15}$ by HR-FABMS. The IR spectrum showed the presence of an aromatic ester bond (1710, 1650 and 1240 cm^{-1}) and aromatic rings (1610 and 1491 cm^{-1}). The H–H and C–H COSY spectra suggested the presence of two aromatic rings and of seven aromatic protons. One unit of the aromatic ring carbons and protons exhibited the similar NMR pattern to **6** and the NMR signals of the other unit resembled salicin (**8**) (Table 1). Accordingly, **7** is 2-*O*-glucopyranosyl-2,6-dihydroxybenzoic acid ester linked to the carbinol group of salicin, namely henryoside, which has been isolated from *Viburnum henryi* [6]. The reported physico-chemical data of henryoside were identical with **7**.

Table 1. ^{13}C NMR data of compounds 6–8 (DMSO-d_6, 100 MHz)

Carbon number	6	7	8
1a	101.8	111.9	
2a	160.3	155.3*	
3a	107.2	105.3	
4a	135.1	131.0	
5a	107.2	109.2	
6a	160.3	155.2*	
7a	172.3	165.8	
1b		125.3	131.3
2b		154.3*	154.6
3b		114.5	114.8
4b		128.4	127.3
5b		121.7	121.7
6b		127.5	127.6
7b		61.2	58.2
glucose			
		1,1′ 100.2, 100.9	1 101.4
		2,2′ 73.2	2 73.3
		3,3′ 76.4, 76.6	3 76.4
		4,4′ 69.5	4 69.6
		5,5′ 77.0	5 76.9
		6,6′ 60.6	6 60.7

*Signals may be interchanged.

Table 2. ^{13}C and ^{1}H NMR data of compound 9 (CD_3OD, 100 MHz and 400 MHz)

Carbon number and proton(s) at	^{13}C	^{1}H
1a	103.9 (*s*)	
2a	160.5 (*s*)	
3a	118.6 (*s*)	
4a	135.8 (*d*, 156)	6.99 (*d*, 8.5)
5a	106.6 (*d*, 161)	6.20 (*d*, 8.5)
6a	161.3 (*s*)	
7a	179.9 (*s*)	
1b	118.6 (*s*)	
2b	156.9 (*s*)	
3b	116.2 (*d*, 160)	7.13 (*dd*, 7.6, 1.6)
4b	128.0 (*d*, 159)	7.11 (*td*, 7.6, 1.6)
5b	123.3 (*d*, 161)	6.89 (*td*, 7.6, 1.6)
6b	131.3 (*d*, 159)	7.07 (*br*, *d*, 7.6)
7b	29.6 (*t*, 129)	3.89 (*d*, 15.5)
		3.95 (*d*, 15.5)
glucose		
1	102.8 (*d*, 160)	4.90 (*d*, 7.3)
2	75.0 (*d*, 146)	*
3	77.9 (*d*, 141)	*
4	71.4 (*d*, 145)	*
5	77.9 (*d*, 141)	*
6	62.6 (*t*, 143)	3.70 (*dd*, 5.1, 12.1)
		3.89 (*dd*, 1.8, 12.1)

Values in the parentheses are multiplicities and coupling constants in Hz.

*Signals overlapped each other.

Compound **9** was obtained as colourless needles, analysed for $C_{20}H_{22}O_{10}$ by HR-FABMS. The IR spectrum showed the presence of an aromatic carboxylic acid (1670 cm^{-1}) and aromatic rings (1625 and 1490 cm^{-1}). The ^{13}C NMR spectrum (CD_3OD) of **9** showed six signals for β-glucopyranosyl moiety, one methylene, one carboxylic acid and 12 aromatic carbons. Among the 12 aromatic carbon signals, six signals appeared as singlets, three of which were assigned to the oxygen substituted carbons by taking account of their chemical shifts. The chemical shifts of oxygen substituted carbons indicated that these were not in the vicinal positions each other. The ^{1}H NMR showed protons for glucosyl moiety and an isolated methylene, and six protons on the aromatic rings. The H–H COSY spectrum revealed the relationships of all six aromatic protons, such as two protons (δ6.20 and 6.99) are located *ortho* to each other and the other four protons are adjacent to each other. The C–H COSY spectrum confirmed the relation between proton and carbon atoms shown in Table 2.

The precise structure of **9** was determined by inspection of C–H long-range couplings by a non-decoupled ^{13}C NMR experiment. In the non-decoupled ^{13}C NMR spectrum of **9** in methanol-d_4, the carbonyl carbon appeared as a singlet, suggesting that no proton is located within the range of two or three bond distances from the carbon and it must be placed at C-1a. The carbon signal at δ103.9 (C-1a) appeared as doublet (J = 5 Hz), indicating that the carbon is located in the positions where only one long range coupling (C-1a with C-5a-H) is allowed. Thus the two aromatic rings must be connected at C-3a and C-1b through a methylene bridge. The methylene carbon (C-7b) (*t*, J = 129 Hz) was further split as triplet by the long-range coupling (J = 5 Hz) with C-4a-H and C-6b-H. The C-3a (δ118.6) signal appeared as a quartet, actually a triplet of doublet, coupled with methylene protons (J = 7 Hz) and C-5a-H (J = 7 Hz), and the C-6b (δ131.3) signal was split as a quartet (actually *t*, *d*) of doublets, coupled with methylene protons (J = 7 Hz), C-4b-H (J = 7 Hz) and C-5b-H (J = 2 Hz). The non-decoupled spectrum was also used for the assignments of the carbon atoms bearing an oxygen function. The carbon signals, resonated at δ161.3 with a long-range coupling of *d*, *d* (J = 11, 2 Hz) was assigned to C-6a, and at δ160.5 with a long-range coupling of *t*, *d* (J = 10, 5 Hz) was to C-2a. Whereas the multiplet signal (δ 156.9) was reasonably attributed to C-2b, since complicated long-range couplings were at least expected between methylene protons, C-3b-H, C-4b-H and C-6b-H.

This structure was further confirmed by measurement of difference NOE spectrum. When irradiated at methylene protons, δ3.89 and 3.95, the intensities of two aromatic protons, a doublet at δ6.99 and a broad doublet at δ7.07, were significantly enhanced. The glucose position was also determined by this experiment. Since the irradiation of the anomeric proton at δ4.90 caused the increment of signal of an aromatic proton at δ7.13 (*d*, *d*), glucose is attached at the C-2b-hydroxyl group. This glucose must be in β-D series, because the anomeric proton signal appeared as a doublet (J = 7 Hz) and the sign of rotation power of this compound is minus. Thus the structure of this compound is **9** and is named alangifolioside. The structure was further confirmed by acetylation and methylation when it gave a hexaacetate methyl ester.

Methyl 2,6-dihydroxybenzoate has been found previously in *Acacia farnesiana* [7] and 2-methoxy-6-hydroxybenzoic acid ethyl ester in *Gloriosa superba* [8] and *Colchicum autumnale* [9]. Related compounds, the benzoyl ester and *p*-methoxy phenethyl amide of 2,6-dihydroxybenzoic acid were also obtained from *Aniba riparia* [10]. 2,6-Dihydroxybenzoic acid (**6**) is known as a synthetic material, detection of this compound by GC in *Viscum album* [11] and *Pinus* species [12], and by HPLC in avocado [13], have also been reported.

Compound **9** has a novel structure in that the two aromatic rings are connected by a methylene bridge. One plausible biosynthetic route is by the direct attack of the anion formed at the *para* position (3a or 5a) of the hydroxyl group of 2,6-dihydroxybenzoic acid (**6**) to the carbinol carbon of salicin (**8**), simultaneously losing an element of water.

EXPERIMENTAL

Mps: uncorr. ^{13}C and ^{1}H NMR for flavonol glycoside and Compound **6** were measured at 25 and 100 MHz, respectively, and those for other compounds were at 100 and 400 MHz. MS: 70 eV. 2,6-Dihydroxybenzoic acid was purchased from Tokyo Kasei Co. Ltd and Salicin was from Nakarai Tesque Co. Ltd.

Isolation. The plant materials (*Alangium platanifolium* var. *trilobum*) were collected in the vicinity of Hiroshima City (APHO-1-1985). The voucher specimen is deposited at Department of Pharmacognosy, Institute of Pharmaceutical Science, Hiroshima University School of Medicine.

The dried leaves (2.55 kg) were extracted with MeOH. The MeOH extract (270 g) was suspended in H_2O and partitioned with hexane, EtOAc and *n*-BuOH, successively. The *n*-BuOH extract (80 g) was separated by Diaion HP-20 CC with the solvent system of 20, 40, 60 and 80% MeOH in H_2O and then with MeOH.

The 60% MeOH fraction (11.68 g) was subjected to silica gel CC with $CHCl_3$–MeOH as eluent. The 15% MeOH fraction (3.58 g) was further separated by 5 runs of DCCC ($CHCl_3$–MeOH–H_2O–*n*-PrOH 9:12:8:1). Recrystallization of a **2**-rich fraction from H_2O gave 1.00 g of yellow needles. Final purification of 1 was achieved on Sephadex LH-20 CC (MeOH) to give 50 mg of yellow needles (MeOH). The 20% MeOH eluent (1.29 g) of silica gel CC was applied to 2 runs of DCCC ($CHCl_3$–MeOH–H_2O–*n*-PrOH 9:12:8:2) and **8**-rich fraction was further purified by Sephadex LH-20 CC to give 54 mg of amorphous powder. After half of this was passed through a Dowex 50W × 8 column, 23 mg of colourless needles were obtained from MeOH.

The 40% MeOH eluent (9.63 g) of the Diaion column was subjected to silica gel CC ($CHCl_3$–MeOH–H_2O). Compound **4** was concd in the 20% MeOH–0.2 ~ 0.4% H_2O fraction. This was recrystallized from $CHCl_3$–MeOH to give 1.15 g of yellow needles. In the 20% MeOH–0.1% H_2O fraction, **3** and **4** were abundant. Compound **4** was purified by DCCC ($CHCl_3$–MeOH–H_2O–*n*-PrOH, 9:12:8:2) and Sephadex LH-20 CC to give 14 mg of yellow needles ($CHCl_3$–MeOH). From the 20% MeOH eluent, 139 mg of colourless needles (**7**) (MeOH) was obtained, after purified by DCCC ($CHCl_3$–MeOH–H_2O–*n*-PrOH, 9:12:8:2). In 30% MeOH–1.6% H_2O fraction, **4** and **5** were concentrated. Compound **5** was purified by repeated DCCC ($CHCl_3$–MeOH–H_2O–*n*-PrOH, 9:12:8:2) to give 46 mg of yellow needles (H_2O).

The 20% eluent (9.51 g) of Diaion CC was subjected to Diaion CC again. The 15% MeOH fraction was purified by DCCC twice ($CHCl_3$–MeOH–H_2O, 5:6:4 and $CHCl_3$–MeOH–H_2O –*n*-PrOH, 9:12:8:2) to afford 130 mg of compound **6** as crystals (MeOH).

Known flavonol glycosides isolated. Astragalin (kaempferol-3-*O*-glucopyranoside) (**1**) [14]; mp 216–218°, $[\alpha]_D$ −51.2° (pyridine; *c* 0.26); ^{13}C NMR (DMSO-d_6): δ60.8, 69.8, 74.1, 76.3, 77.4, 93.5, 98.7, 100.8, 103.8, 115.0 × 2, 120.8, 130.8 × 2, 133.1, 156.1, 156.3, 159.9, 161.2, 164.0, 177.4. Nicotiflorin (kaempferol-3-*O*-rutinoside) (**2**) [14], mp 185–187°, $[\alpha]_D$ −40.1° (pyridine; *c* 0.32); ^{13}C NMR (DMSO-d_6): δ17.6, 66.9, 68.2, 69.9, 70.3, 70.6, 71.8, 74.1, 76.3, 75.7, 93.7, 98.7, 100.7, 101.3, 103.9, 115.0 × 2, 120.8, 130.8 × 2, 133.2, 156.4, 156.8, 159.8, 161.2, 164.1, 177.3. Kaempferol-3-*O*-neohesperidoside (**3**) [14], mp 203–206°, $[\alpha]_D$ −123.8° (pyridine; *c* 0.21); ^{13}C NMR (DMSO-d_6): δ17.2, 60.7, 68.2, 70.1, 70.5 × 2, 71.8, 77.2, 77.5 × 2, 93.6, 98.7 × 2, 100.5, 103.8, 115.0 × 2, 120.8, 130.6 × 2, 132.6, 155.9, 156.3, 159.8, 161.2, 164.5, 177.2. Clitorin [3-*O*-dirhamnopyranosyl (1→2, 1→6) glucopyranosylkaempferol] (**4**) [15], mp 204–206°, $[\alpha]_D$ −109.2° (pyridine; *c* 0.34); ^{13}C NMR (DMSO-d_6): δ17.2, 17.6, 66.8, 68.2 × 2, 70.3, 70.5 × 3, 71.8 × 2, 75.5, 77.0, 77.3, 93.7, 98.7 × 2, 100.5, 100.7, 103.9, 115.0 × 2, 120.9, 130.7 × 2, 132.5, 156.4, 156.8, 161.2, 164.1, 177.2. 3-*O*-Dirhamnopyranosyl (1→2, 1→6)glucopyranosyl quercetin (**5**) [16], mp >300°, $[\alpha]_D$ −99.2 (pyridine; *c* 0.24); ^{13}C NMR (DMSO-d_6): δ17.1, 17.6, 67.0, 68.1 × 2, 70.3, 70.5 × 3, 71.7, 75.6, 77.1 × 2, 93.5, 98.5, 98.6, 100.4, 100.6, 103.9, 115.0, 116.0, 121.1, 121.5, 132.6, 144.7, 148.2, 156.3, 156.5, 161.1, 177.1.

2,6-Dihydroxybenzoic acid (**6**). Colourless needles, mp 225–230° (decomp.) (MeOH); ^{1}H NMR (CD_3OD): δ6.27 (2H, *d*, *J* = 8 Hz), 7.12 (H, *t*, *J* = 8 Hz); ^{13}C NMR (CD_3OD): δ104.3 (*s*), 107.2 (*d*) × 2, 134.4 (*d*), 163.1 (*s*) × 2, 179.8. Authentic sample: mp 167–168°, ^{1}H NMR δ6.41 (2H, *d*, *J* = 8 Hz), 7.27 (H, *t*, *J* = 8 Hz); ^{13}C NMR: δ101.5 (*s*), 108.6 (*d*) × 2, 136.9 (*d*), 162.3 (*s*) × 2, 173.1 (*s*). Compound **6** (15 mg) + authentic sample (15 mg): ^{1}H NMR: δ6.36 (2H, *d*, *J* = 8 Hz), 7.21 (H, *t*, *J* = 8 Hz); ^{13}C NMR: δ102.8 (*s*), 108.1 (*d*) × 2, 135.8 (*s*), 162.7 (*s*) × 2, 175.9 (*s*). The methanol solution of compound **6** was passed through Dowex 50W × 8 (H) and then the eluent was evapd. The residue was crystallized from H_2O to give colourless needles, mp 165–167° (authentic sample, mp 167–168°), IR ν_{max}^{KBr} cm^{-1}: 3050, 1660, 1625, 1578, 1470, 1410, 1271, 1203, 1162, 1030, 813, 720, 695; UV λ_{max}^{MeOH} nm (log ε): 219 (4.25), 248 (4.00), 317 (3.64); EIMS *m/z* (rel. int.): 154 (53), 136 (85), 108 (100); HR-EIMS *m/z*: 154.0267 $[M]^+$ ($C_7H_6O_4$ requires: 154.0266), 136.0158 ($[M-H_2O]^+$, $C_7H_4O_3$ requires: 136.0158), 108.0205 ($[M-H_2O-CO]^+$, $C_6H_4O_2$ requires: 108.0211); ^{1}H NMR (DMSO-d_6): δ6.42 (2H, *d*, *J* = 8 Hz), 7.28 (H, *t*, *J* = 8 Hz), 10.77 (*s*, –OH); ^{13}C NMR: see Table 1. (Found: C, 54.77; H, 4.04. $C_7H_6O_4$ requires: C, 54.55, H, 3.92%).

Henryoside (**7**). Colourless needles, mp 133–135° (MeOH), $[\alpha]_D$ −22.8° (pyridine; *c* 0.39), IR ν_{max}^{KBr} cm^{-1}: 3350, 2860, 1710, 1650, 1610, 1491, 1455, 1387, 1300, 1240, 1070, 900, 810, 755; UV λ_{max}^{MeOH} nm (log ε): 210 (4.49), 250 (3.77), 274 (3.47), 312 (3.33); HR-FABMS *m/z*: 607.1659 $[M+Na]^+$ (calcd. for $C_{26}H_{32}O_{15}Na$: 607.1638); ^{1}H NMR (DMSO-d_6): δ3.47 (2H, *m*, glc-6), 3.71 (2H, *m*, glc-6), 4.85 (H, *d*, *J* = 7 Hz, anomeric proton), 4.91 (H, *d*, *J* = 7 Hz, anomeric proton), 5.33, 5.46 (H each, *d*, *J* = 14 Hz, C-7b-H_2), 6.56 (H, *d*, *J* = 7 Hz, C-3a-H or C-5a-H), 6.66 (H, *d*, *J* = 7 Hz, C-5a-H or C-3a-H), 7.02 (H, *td*, *J* = 8, 1 Hz, C-5b-H), 7.14 (H, *br d*, *J* = 8 Hz, C-3b-H), 7.18 (H, *t*, *J* = 8 Hz, C-4a-H), 7.26 (H, *td*, *J* = 8, 2 Hz, C-4b-H), 7.52 (H, *dd*, *J* = 8, 2 Hz, C-6b-H); ^{13}C NMR: see Table 1. (Found: C, 52.49; H, 5.62. Calcd. for $C_{26}H_{32}O_{15}\cdot 1/2H_2O$: C, 52.61; H, 5.60%).

Alangifolioside (**9**). Colourless needles, mp 125–128° (MeOH), $[\alpha]_D$ −15.1° (pyridine; *c* 0.40); IR ν_{max}^{KBr} cm^{-1}: 3400, 1670, 1625, 1490, 1450, 1335, 1238, 1075, 1040, 812, 755; UV λ_{max}^{MeOH} nm (log ε): 218 (4.49), 252 (4.00), 275 (3.21), 322 (3.65); HR-FABMS *m/z*: 461.0970 $[M+K]^+$ ($C_{20}H_{22}O_{10}K$ requires: 461.0850);

^{1}H and ^{13}C NMR: see Table 2. (Found: C, 55.14; H, 5.45. $C_{20}H_{22}O_{10}\cdot 1/2H_2O$ requires: C, 55.68; H, 5.37%).

Alangifolioside hexaacetate methyl ester. About 6 mg of compound **9** was treated with Ac_2O–pyridine at 20° overnight, followed by ethereal CH_2N_2. The reaction mixture was evapd to dryness and purified by prep. TLC (6 mg) (silica gel, developed with C_6H_6–Me_2CO, 4:1 and eluted with $CHCl_3$–MeOH, 19:1). EIMS *m/z* (rel. int.): 688 (<1) $[M]^+$, 657 (<1), 615 (<1), 331 (25), 169 (100), 109 (56), 43 (71); HR-EIMS *m/z*: 688.1973 $[M]^+$ ($C_{33}H_{36}O_{16}$ requires: 688.2002), 657.1798 ($[M-MeO]^+$, $C_{32}H_{33}O_{15}$ requires: 657.1818), 615.1729 [$[M-MeO-Ac$ (ketene)]$^+$, $C_{30}H_{31}O_{14}$ requires: 615.1714], 331.1047 [Glc $(Ac)_4^+$ oxonium ion, 331.1028 calcd. for $C_{14}H_{19}O_9$]; ^{1}H NMR ($CDCl_3$): δ1.90, 2.02, 2.05, 2.07 (3H each, alcoholic Ac × 4), 2.23, 2.26 (3H each, *s*, phenolic Ac × 2), 3.80 (H, *d*, J = 10 Hz), 3.84 (3H, *s*), 3.85 (H, *d*, J = 10 Hz), 4.16 (H, *dd*, J = 12, 2 Hz), 4.27 (H, *dd*, J = 12, 5 Hz), 5.10 ~ 5.30 (5H, sugar protons), 6.90 ~ 7.05, 7.17 ~ 7.21 (6H, aromatic protons); ^{13}C NMR ($CDCl_3$): δ20.4, 20.6 (Ac × 6), 29.2, 52.3, 61.9, 68.4, 71.1, 72.1, 72.8, 99.2, 115.4, 120.8, 123.6, 127.8, 128.7, 130.9, 131.7, 133.2, 148.0, 154.5 × 2, 168.4, 169.1 × 2, 169.3 × 2, 170.2, 170.5.

Acknowledgements—We thank Ms N. Kubo, Ms K. Katayama and the late Prof. H. Yoshida (Hiroshima University) for elemental analyses.

REFERENCES

1. Battersby, A. R., Kapil, R. S., Bhakuni, D. S., Popli, S. P., Merchant, J. R. and Salgar, S. S. (1966) *Tetrahedron Letters* 4965.
2. Pakrashi, S. C. and Achari, B. (1970) *Experientia* **26**, 933.
3. Achari, B., Ali, E., Dastidar, P. P. G., Sinha, R. R. and Pakrashi, S. C. (1980) *Planta Med.* Suppl. 5.
4. Shoeb, A., Raj, K., Kapil, R. S. and Popli, S. P. (1975) *J. Chem. Soc. Perkin I* 1245.
5. Nakamoto, K., Otsuka, H. and Yamasaki, K. (1988) *Phytochemistry* **27**, 1856.
6. Jensen, S. R., Nielsen, B. J. and Norn, V. (1979) *Phytochemistry* **18**, 904.
7. Demole, E., Enggist, P. and Stoll, M. (1969) *Helv. Chim. Acta* **52**, 24.
8. Clewer, H. W. B., Green, S. J. and Tutin, F. (1915) *J. Chem. Soc.* **107**, 835.
9. Santavy, F. and Reichstein, T. (1952) *Pharm. Acta Helv.* **27**, 71.
10. Barbosa-Filho, J. M., Yoshida, M., Gottlieb, O. R., Barbosa, R. de C. S. B. C., Giesbrecht, A. M. and Young, M. C. M. (1987) *Phytochemistry* **26**, 2615.
11. Krzaczek, T. (1977) *Ann. Univ. Mariae-Curie-Sklodowska, Sect. D* **32**, 281; *Chem. Abstr.* **89**, 56433y.
12. Krzaczek, T. and Urbaniak, L. (1985) *Acta Soc. Bot. Pol.* **54**, 429.
13. Torres, A. M., Mau-Lastovicka, T. and Rezeaiyan, R. (1987) *J. Agric. Food Chem.* **35**, 921.
14. Markham, K. R., Ternai, B., Stanley, R., Geiger, H. and Mabry, T. J. (1978) *Tetrahedron* **34**, 1989.
15. Morita, N., Arisawa, M., Nagase, M., Hsu, H.-Y. and Chen, Y.-P. (1977) *Yakugaku Zasshi* **97**, 649.
16. Buttery, B. R. and Buzzell, R. I. (1975) *Can. J. Botany* **53**, 219.