Phytochemistry, Vol. 24, No. 12, pp. 2959–2962, 1985.
Printed in Great Britain.

0031–9422/85 $3.00 + 0.00

BENZOXAZINONES FROM *COIX LACHRYMA-JOBI* VAR. *MA-YUEN*

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(*Revised received* 28 *May* 1985)

Key Word Index—*Coix lachryma-jobi* var. *ma-yuen*; Gramineae; roots; benzoxazinone; absolute configuration; X-ray analysis; ^{13}C NMR.

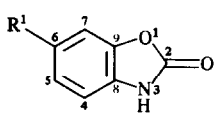
Abstract—The absolute configurations of 2-*O*-*β*-D-glucopyranosyl-7-methoxy-1,4(2H)-benzoxazin-3-one and three congeners isolated from *Coix lachryma-jobi* var. *ma-yuen* were determined by X-ray analysis and chemical correlation as the 2*R* type. ^{13}C NMR spectra of all congeners and coixol were fully assigned.

INTRODUCTION

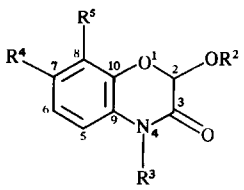
From the roots of the medicinal plant, *Coix lachryma-jobi*, coixol, (**1**) and two benzoxazinones (**2**, **3**) have been isolated [1–3]. From other genera of the Gramineae, several benzoxazinones (**4**–**12**) have also been isolated [4–11]. Among them, **7** has toxic properties to some aphids and the European corn borer, and **4** is known as a phytoalexin [12–14]. There is also the isolated occurrence of **1** in the Scrophulariaceae, in *Scoparia dulcis* [15].

In the course of a study on the constituents of the roots of *C. lachryma-jobi* L. var. *ma-yuen*, we have isolated five benzoxazinones (**2**–**6**) along with the benzoxazolinone, coixol (**1**). Although all of the compounds were previously isolated from gramineaous plants and their structures determined, the stereochemistry of the C-2 position has not yet been established.

In this paper, we report the results of X-ray analysis of compound **3** to ascertain the stereochemistry of the C-2 position and chemical derivation experiments that correlate the stereostructure of all compounds isolated from the above plant. ^{13}C NMR spectra of the compounds were also measured and all signals were assigned.



	R^1
1	OMe
12	H



	R^2	R^3	R^4	R^5
2	H	H	OMe	H
3	Glc	H	OMe	H
4	Glc	OH	OMe	H
5	Glc	OMe	OMe	H
6	Glc	H	OH	H
7	H	OH	OMe	H
8	Glc	H	OMe	OMe
9	Glc	OH	OMe	OMe
10	H	OH	H	H
11	Glc	OH	H	H

RESULTS AND DISCUSSION

Six compounds were isolated from the chloroform–methanol extract of the roots of cultivated *C. lachryma-jobi* var. *ma-yuen* and designated as compounds **1**–**6**. Compounds **1**–**3** and **6** were also isolated from the acetone extract. Compound **7** was not isolated, since it is fairly unstable and could be degraded to coixol (**1**) during processing of the harvested material [16].

Compound **1**, colourless needles (MeOH), mp 158–160°, $C_8H_7NO_3$ was identical with coixol [2, 3]. Since ^{13}C NMR data of **1** has not been reported, we measured ^{13}C NMR spectra and assigned all signals by the aid of proton selective decoupling. On irradiation of proton resonances at δ6.72 (*dd*, H-5), 6.97 (*d*, H-7) and 7.02 (*d*, H-4) carbon resonances of δ109.1, 97.1 and 109.9 appeared as singlets, assigning each signal to C-5, C-7 and C-4, respectively. Signals at δ155.1 and 155.4 were differentiated by the non-decoupled spectrum of **1**, in which the former signal appeared as a singlet, whereas the latter appeared as a multiplet due to long range C–H coupling with aromatic protons. Thus, the signal at δ155.4 was assigned to C-6 and δ155.1 to the C-2 carbonyl carbon. The remaining two singlet signals δ123.9 and 144.3 are unequivocally assigned to C-8 and C-9, respectively, by simple calculation from substituted benzene [17] (Table 1).

Compound **2** was identified as 2-hydroxy-7-methoxy-1,4(2H)-benzoxazin-3-one, previously isolated from the plants of the same genus by comparison of physical data and ^1H NMR spectra [3]. The proton signal at δ5.50 (J = 6 Hz, H-2), typical of this type of compound is to be noted. The ^{13}C NMR spectrum of the compound was assigned by selective and non-decoupled spectra in a similar manner to that used for compound **1**. (Table 1). The assignment was rationalized by comparisons of chemical shifts of each congener.

Compound **3** was identified as the 2-*O*-*β*-D-glucopyranoside of compound **2** by comparison of physical and spectral data with reported values [3]. The ^{13}C NMR spectrum of compound **3** showed the presence of the *β*-glucopyranosyl moiety and a reasonable glucosylation shift was observed at C-2 and C-3 (+4.2 and −2.8 ppm, respectively), which reconfirmed the structure [18]. As far

Table 1. ^{13}C NMR chemical shifts of compounds 1–6 in DMSO-d_6

C	1	C	2	3	4	5	6
		2	90.5	94.7	96.6	96.5	94.6
2	155.1	3	162.4	159.6	153.8	154.0	159.6
4	109.9	5	115.9	115.6	114.5	112.9	115.8
5	109.1	6	107.8	108.5	107.8	108.8	109.4
6	155.4	7	155.5	155.4	155.8	156.5	153.5
7	97.1	8	103.9	103.6	102.9	104.2	104.8
8	123.9	9	120.1	119.5	122.8	119.3	118.1
9	144.3	10	141.6	140.9	141.9	141.4	140.9
6-OMe	55.8	7-OMe	55.3	55.2	55.3	55.4	
		N–OMe				62.5	
	glucosyl carbons	1′		102.6	102.5	102.6	102.4
		2′		73.0	73.2	72.8	73.2
		3′		77.3*	77.3*	77.3*	77.2*
		4′		69.5	69.5	69.4	69.5
		5′		76.5*	76.6*	76.4*	76.5*
		6′		60.9	60.9	60.8	60.7

*Assignments may be interchanged in the vertical column.

as we know, the ^{13}C NMR assignment of this series of compounds was reported only for **7** [19]. The reported data (in DMSO-d_6) of C-9 and C-10 (of our numbering system) were contradictory to ours.

Compound **4** possessed an extra oxygen atom compared to **3**. The ^{13}C NMR spectrum of **4** is similar to that of **3**, including the multiplicity of the off-resonance decoupled spectrum. The most distinct difference in chemical shift of corresponding signals was observed at C-3 (−5.8 ppm). In the ^1H NMR spectrum of **4**, the NH signal was not observed. A red colour reaction with ferric chloride suggested the presence of a hydroxamic acid structure. From these facts, the only possible structure for **4** is 2-*O*-*β*-glucopyranosyl-4-hydroxy-7-methoxy-1,4(2H)-benzoxazin-3-one. This compound was previously isolated with no NMR data given [4], and later it was again reported with ^1H NMR data which is essentially identical to ours [5].

Compound **5** showed similar ^1H NMR and ^{13}C NMR spectra to those of compound **4**, with additional N–OMe signals (δ_H 3.89, δ_C 62.5). Comparison of physical constants and ^1H NMR spectral data of **5** with those of 2-*O*-*β*-glucopyranosyl-4,7-dimethoxy-1,4(2H)-benzoxazin-3-one proved that they are identical [8]. Compound **6** has no methoxyl signal in its NMR spectrum and is identical with 2-*O*-*β*-glucopyranosyl-7-hydroxy-1,4(2H)-benzoxazin-3-one by comparison of physical constants and ^1H NMR spectra [9].

Although the structure of all compounds **1**–**6** had already been determined, no studies have been made as to the absolute configuration of C-2. Thus, we established the stereochemical correlation between all of the compounds by means of X-ray analysis and chemical conversion.

A computer-generated perspective drawing of the final X-ray model of compound **3** with the hydrogens is shown Fig. 1. The X-ray study defined only the relative configuration and the enantiomer shown assumes that the glucose

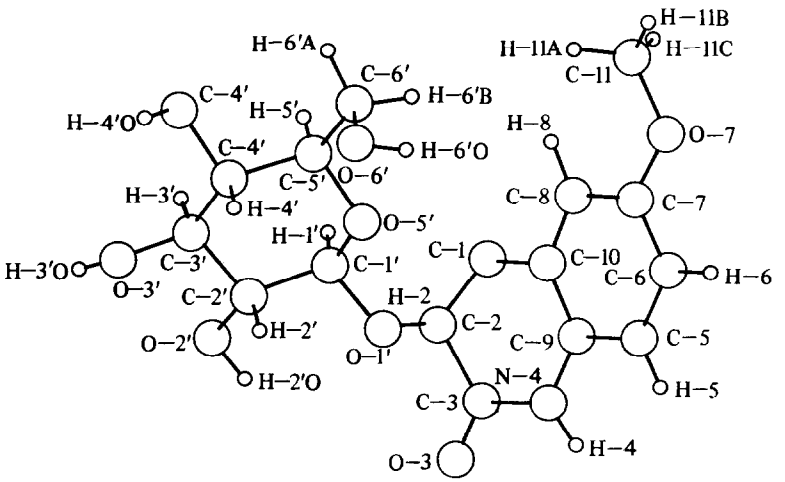


Fig. 1.

is in D-series. This assumption was justified by the measurement of optical rotation of glucose obtained by acid hydrolysis of compound **3**, $[\alpha]_D^{15} = +48.2°$ (standard D-glucose, $[\alpha]_D^{15} = +47.8°$). Since the glucose was confirmed to be D-type, the absolute structure of **3** was definitely determined to be 2*R* (Fig. 1).

Treatment of compound **4** with Zn–HCl gave a corresponding reduced product which was identical with naturally obtained compound **3**, with respect to mp and spectroscopic data. Since the optical rotation of these two compounds did not show any significant discrepancy, compound **4** must have the same *R* configuration at the C-2 position. The absolute configuration of compounds **5** and **6** was determined by methylation of compounds **4** (2*R*) and **6** with diazomethane to give compounds **5** and **3** (2*R*), respectively. Therefore, these two compounds (**5** and **6**) also have 2*R* configurations. The CD curves of compounds **3**–**6** exhibited a positive Cotton effect at similar wavelength (231–234 nm), which is in agreement with the above results. Thus, the glucosides have the same 2*R* configuration, while the C-2 hydroxy compound (**2**) is optically inactive since this position is a hemiacetal and readily interconvertible like an anomeric centre of a sugar.

In the biosynthesis of 1,4-benzoxazin-3-one from *Zea mays* the aromatic moiety originated from anthranilic acid and the C-3 of the oxazinone moiety was proved to come from C-1 of ribose by tracer and degradation experiments [20, 21]. As to the origin of the C-2 of the oxazinone skeleton, C-2 of ribose was strongly suggested, although direct proof has not been obtained. Even if the C-2 of ribose is introduced into the C-2 of the benzoxazinone skeleton, prediction of the predominant configuration is impossible, since the biosynthesis would include the fission of a C–C bond between the C-2 and C-3 carbons of the ribosyl moiety and the epimerization of the C-2 of the free form of the oxazinones occurs readily. The orientation of the *O*-glucosyl moiety is possibly controlled by a glucosyltransferase but this assumption needs to be clarified.

EXPERIMENTAL

All mps are uncorr. ^{1}H NMR spectra were measured at 100 MHz and ^{13}C NMR at 25 MHz.

Plant material. C. lachryma-jobi L. var. *ma-yuen* Stapf was cultivated at Yasufuruichi (Hiroshima City) and harvested in November, 1982.

Extraction and separation of compounds. Dried and powdered roots (3.5 kg) of the plant were extracted with hexane, Me_2CO and a mixture of MeOH–$CHCl_3$ (2:1), successively. The MeOH–$CHCl_3$ extract was suspended in H_2O and extracted with *n*-BuOH to give an extract (40 g) which was chromatographed on highly porous polymer (DIAION, HP 20, Mitsubishi Chemical Ind. Co.) with a stepwise increase of MeOH content in H_2O (10, 20, ... 100%). The 70% MeOH fraction was further chromatographed on silica gel. Elution with $CHCl_3$–MeOH afforded **1** (340 mg). From the above Me_2CO extract compound **1** (1.2 g) was also obtained by silica gel chromatography (Me_2CO–C_6H_6). The 50 to 60% MeOH fraction was chromatographed on silica gel ($CHCl_3$–MeOH) to afford **2** (1.1 g), which was also obtained from the Me_2CO extract (170 mg). Another fraction of the silica gel chromatography was further purified by silica gel ($CHCl_3$–MeOH), Sephadex LH-20 (MeOH) and HPLC (30% MeOH), to afford **5** (40 mg). On concn of the 40–50% MeOH fraction, **3** (1.3 g) was obtained as crystals. From the mother liquid, additional **3** (1.1 g) and **4** (720 mg) were obtained by silica gel CC eluting with 20–30% MeOH in $CHCl_3$ and 30–60% MeOH in $CHCl_3$, respectively. Compound **3** was further obtained from the Me_2CO (540 mg). The 20–30% MeOH fraction was chromatographed on silica gel ($CHCl_3$–MeOH–H_2O, 75:15:2) to afford **6** (4 mg). From the Me_2CO extract, **6** (36 mg) was also obtained by repeated chromatography on silica gel and Sephadex LH-20.

6-Methoxybenzoxazolin-2-one (*coixol*, **1**). Mp 158–160° (MeOH) (lit. [3] 155–156°); EIMS *m/z*: 165.0430 $[M]^+$ (calc. for $C_8H_7NO_3$: 165.0425); UV λ_{max}^{EtOH} nm (log ε): 233 (4.01), 291 (3.78); IR ν_{max}^{KBr} cm^{-1}: 3020, 1770, 1630, 1495, 1320, 1205, 1140, 1095, 970; ^{1}H NMR (DMSO-d_6): δ3.79 (3H, *s*, OMe), 6.72 (1H, *dd*, *J* = 2, 9 Hz, H-5), 6.97 (1H, *d*, *J* = 2 Hz, H-7), 7.02 (1H, *d*, *J* = 9 Hz, H-4), 11.44 (1H, *br*, NH).

*2-Hydroxy-7-methoxy-*1,4(2H)*-benzoxazin-3-one* (**2**). Mp 196–198° (MeOH) (lit. [3] 196–199°); EIMS *m/z*: 195.0534 $[M]^+$ (calc. for $C_9H_9NO_4$: 195.0531); UV λ_{max}^{EtOH} nm (log ε): 258 (4.06), 286 sh (3.78); IR ν_{max}^{KBr} cm^{-1}: 3150, 1680, 1510, 1160, 1030; ^{1}H NMR (DMSO-d_6): δ3.71 (3H, *s*, OMe), 5.50 (1H, *d*, *J* = 6 Hz, H-2), 6.59 (1H, *dd*, *J* = 3, 9 Hz, H-6), 6.63 (1H, *d*, *J* = 3 Hz, H-8), 6.88 (1H, *d*, *J* = 9 Hz, H-5), 7.95 (1H, *d*, *J* = 6 Hz, OH), 10.65 (1H, *s*, NH).

*2-O-β-Glucopyranosyl-7-methoxy-*1,4(2*H*)*-benzoxazin-3-one*. Mp 250–251° (MeOH), (lit. [3], 245°); FAB-MS *m/z*: 358.1127 $[M+H]^+$ (Calc. for $C_{15}H_{19}NO_9 + H = 358.1139$); UV λ_{max}^{EtOH} nm (log ε): 261 (4.05), 285 inf (3.89); IR ν_{max}^{KBr} cm^{-1}: 3300, 1690, 1605, 1510, 1160, 1080, 1020: $[\alpha]_{max}^{24} = +31.4°$ (pyridine *c* 0.86); CD $[\theta]_{233} + 153$ (EtOH; *c* 0.021); ^{1}H NMR (DMSO-d_6): δ3.70 (3H, *s*, OMe), 4.59 (1H, *d*, *J* = 7 Hz, anomeric H), 5.66 (1H, *s*, H-2), 6.60 (1H, *dd*, *J* = 3, 8 Hz, H-6), 6.73 (1H, *d*, *J* = 3 Hz, H-8), 6.88 (1H, *d*, *J* = 8 Hz, H-5), 10.75 (1H, *s*, NH).

*2-O-β-Glucopyranosyl-4-hydroxy-7-methoxy-*1,4(2H)*-benzoxazin-3-one* (**4**). Mp 166–168° (MeOH–H_2O); FAB-MS *m/z*: 374.1100 $[M+H]^+$ (Calc. for $C_{15}H_{19}NO_{10} + H = 374.1087$); UV λ_{max}^{EtOH} nm (log ε): 280 sh (3.98), 290 (4.00); IR ν_{max}^{KBr} cm^{-1}: 3300, 1604, 1500, 1070, 1020. $[\alpha]_D^{24} = -59.2°$ (pyridine; *c* 0.76); CD $[\theta]_{231} + 86$ (EtOH; *c* 0.022). ^{1}H NMR (DMSO-d_6): δ3.66 (3H, *s*, OMe), 4.53 (1H, *d*, *J* = 7 Hz, anomeric H), 5.77 (1H, *s*, H-2), 6.52 (1H, *dd*, *J* = 3, 9 Hz, H-6), 6.60 (1H, *d*, *J* = 3 Hz, H-8), 7.26 (1H, *d*, *J* = 9 Hz, H-5).

*2-O-β-Glucopyranosyl-4,7-dimethoxy-*1,4-(2H)*-benzoxazin-3-one* (**5**). Mp 91–93° (powder). FAB-MS *m/z*: 388.1268 $[M+H]^+$ (Calc. for $C_{16}H_{21}NO_{10} + H = 388.1243$); UV λ_{max}^{EtOH} nm (log ε): 262 (3.97), 285 sh (3.84). IR ν_{max}^{KBr} cm^{-1}: 3300, 1690, 1500, 1510, 1080–1000 (br) $[\alpha]_D^{24} = 0°$, $[\alpha]_{436}^{24} = -25.0°$ (pyridine; *c* 0.88); CD $[\theta]_{233} + 191$ (EtOH; *c* 0.023). ^{1}H NMR (DMSO-d_6): δ3.75 (3H, *s*, 7-OMe), 3.89 (3H, *s*, N–OMe), 4.61 (1H, *d*, *J* = 7 Hz, anomeric H), 5.90 (1H, *s*, H-2), 6.74 (1H, *dd*, *J* = 3, 9 Hz, H-6), 6.80 (1H, *d*, *J* = 3 Hz, H-8), 7.18 (1H, *d*, *J* = 9 Hz, H-5).

*2-O-β-Glucopyranosyl-7-hydroxy-*1,4(2H)*-benzoxazin-3-one* (**6**). Mp 267–269° (MeOH); FAB-MS *m/z*: 344.0961 $[M+H]^+$ (Calc. for $C_{14}H_{17}NO_9 + H = 344.0985$); UV λ_{max}^{EtOH} nm (log ε): 263 (4.00), 286 inf (3.84); IR ν_{max}^{KBr} cm^{-1}: 3300, 1690, 1520, 1080, 1010; $[\alpha]_D^{24} = +22.3°$ (pyridine; *c* 0.63). CD $[\theta]_{234} + 180$ (EtOH; *c* 0.020). ^{1}H NMR (DMSO-d_6): δ4.55 (1H, *d*, *J* = 7 Hz, anomeric H), 5.61 (1H, *s*, H-2), 6.43 (1H, *dd*, *J* = 2, 8 Hz, H-6), 6.53 (1H, *d*, *J* = 2 Hz, H-8), 6.77 (1H, *d*, *J* = 8 Hz, H-5), 9.42 (1H, *s*, OH), 10.76 (1H, *s*, NH).

Single-crystal X-ray diffraction study of **3**. Suitable crystals of compound **3** in the form of rods could be grown by slow evapn of aq. MeOH solns. A crystal of dimensions (0.20 mm × 0.25 mm × 0.12 mm) was used for all X-ray measurement on a Rigakudenki AFC-5 diffractometer with graphite-monochromated CuK α radiation. Integrated intensities were measured in the range $2\theta \leqslant 130°$ with $\theta - 2\theta$ scan, giving 1311 independent reflections. The data were corrected for Lorenz-

polarization factors, but not for absorption. Crystal data; $C_{15}H_{19}NO_9$, triclinic, space group P1, $a = 8.048$ (1) Å, $b = 9.684$ (1) Å, $c = 5.612$ (1) Å, $\alpha = 99.18$ (1)°, $\beta = 111.85$ (1)° and $\gamma = 71.33$ (1)°, $V = 384.37$ (8) Å^3 (by least-squares refinement with 24 reflections, $\lambda = 1.54178$ Å), $Z = 1$, $D_x = 1.544$ g/cm^3, $D_m = 1.55$ g/cm^3. The structure was solved by the direct method using the MULTAN programme [22]. Difference-synthesis revealed the positions of all H atoms. The structure was refined by block-diagonal least-squares, with anisotropic temp. factors for non-H atoms and isotropic temp. factors for H atoms. The weighing scheme employed was $W = 1/\sigma^2$ (Fo) for $|Fc| \geq 2\sigma|Fo|$ and $W = 0$ for $|Fo| \geq 2\sigma|Fo|$or$|\Delta F| \geq 3\sigma|Fo|$. σ (Fo) was estimated by the relation σ (Fo) = $[\sigma_1{}^2$ (Fo) + c$|Fo|^2]^{1/2}$, where σ_1 (Fo) is the E.S.D. depending on the counting errors [23], c being 0.00085. The refinement converged at $R = 0.023$ ($W \neq 0$), $R_w = 0.032$. Final atom coordinates, a list of temp. factors, H atom positions and final structure factors have been deposited at the Cambridge Crystallographic Data Centre.

Identification of D-*glucose from* **3**. Compound **3** (50 mg) was refluxed in 2 N H_2SO_4–EtOH for 2 hr. The neutralized reaction mixture was chromatographed over highly porous polymer (DIAION HP-20) and silica gel to afford D-glucose (15.2 mg), $[\alpha]_D^{20} = +48.2°$ (H_2O; *c* 1.01); authentic D-glucose $[\alpha]_D^{20} = +47.8°$ (H_2O; *c* 1.0).

Chemical correlation of **3**–**6**. Compound **4** (100 mg) was treated with Zn (200 mg) in 5% HCl for 12 hr. The reaction mixture was neutralized with satd $NaHCO_3$ soln and filtered. The filtrate was chromatographed over DIAION HP-20, eluting with H_2O and 50% MeOH successively. The MeOH eluate was chromatographed over silica gel using $CHCl_3$–MeOH to afford **3** (50 mg); $[\alpha]_D^{20} = +31.9°$ (pyridine; *c* 0.83), identical with naturally obtained compound **3**. Compound **4** (30 mg) was methylated with CH_2N_2–Et_2O followed by chromatography over silica gel and Sephadex LH-20, to afford **5** (18 mg), $[\alpha]_D^{20} = 0°$, $[\alpha]_{436}^{20} = -24.6°$ (pyridine; *c* 0.82), identical with naturally obtained compound **5**. Compound **6** (30 mg) was methylated with CH_2N_2–Et_2O followed by chromatography over silica gel and Sephadex LH-20 to afford **3** (7 mg), $[\alpha]_D^{20} = +30.0°$ (pyridine; *c* 0.43), identical with naturally obtained compound **3**.

Acknowledgements—We thank Professor Y. Ogihara and Dr. M. Ogawa of Nagoya City University for measurement of CD spectra, Dr. A. Ogiso and T. Takagaki of Sankyo Co. Ltd. for MS measurement and Professor O. Tanaka of this Institute for optical rotations. Financial support from Hiroshima Prefecture for the cultivation of medicinal plants is also acknowledged.

REFERENCES

1. *Dictionary of Chinese Materia Medica* (Zhong Yao Da Ci Dian) (1977) p. 2647. Jiangsu New Medical College, Shanghai Scientific and Technological Publisher, Shanghai.
2. Koyama, T. (1955) *Yakugaku Zasshi* **75**, 702.
3. Shigematsu, S., Kouno, I. and Kawano, N. (1981) *Yakugaku Zasshi* **101**, 1156.
4. Wahlroos, O. and Virtanen, A. I. (1959) *Acta Chem. Scand.* **13**, 1906.
5. Gahgan, H. E. and Mumma, R. O. (1966) *Chem. Ind.* 1967.
6. Hofman, J. and Hofmanova, O. (1969) *Eur. J. Biochem.* **8**, 109.
7. Tipton, C. L., Klun, J. A., Husted, R. R. and Pierson, M. D. (1969) *Biochemistry* **6**, 2866.
8. Hofman, J. and Hofmanova, O. (1970) *Tetrahedron Letters* 3213.
9. Hofman, J. and Hofmanova, O. (1969) *Tetrahedron Letters* 5001.
10. Hofman, J. and Masojidkova, M. (1973) *Phytochemistry* **12**, 207.
11. Virtanen, A. I. and Hietala, P. K. (1960) *Acta Chem. Scand.* **14**, 499.
12. Argandona, V. H., Luza, J. H., Niemeyer, H. M. and Corcuera, L. J. (1980) *Phytochemistry* **19**, 1665.
13. Klun, J. A. and Brindley, T. A. (1966) *J. Econ. Entomol.* **59**, 711.
14. Klun, J. A., Tipton, C. L. and Brindley, T. A. (1967) *J. Econ. Entomol.* **60**, 1529.
15. Chen, C.-M. and Chen, M.-T. (1976) *Phytochemistry* **15**, 1997.
16. Bredenberg, J. B., Honkanen, E. and Virtanen, A. I. (1962) *Acta Chem. Scand.* **16**, 135.
17. Stothers, J. B. (1972) *Carbon-13 NMR Spectroscopy*, p. 197. Academic Press, New York.
18. Kasai, R., Suzuo, M., Asakawa, J. and Tanaka, O. (1977) *Tetrahedron Letters* 175.
19. Ioannon, Y. M., Dauterman, W. C. and Tucker, W. P. (1980) *Phytochemistry* **19**, 1607.
20. Reimann, J. E. and Byerrum, R. U. (1964) *Biochemistry* **3**, 847.
21. Tipton, C. L., Wang, M.-C., Tsao, F. H.-C., Tu, C.-C. L. and Husted, R. R. (1973) *Phytochemistry* **12**, 347.
22. Main, P., Hull, S. E., Lessinger, L., Germain, G., Decleroq, J. P. and Woolfson, M. M. (1978) *MULTAN* 78. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Universities of York, England and Louvaine, Belgium.
23. Grant, D. S., Killean, R. C. G. and Lawrence, J. L. (1969) *Acta Crystallogr.* **B25**, 374.