Table 2. Cyanogenesis in Gymnosperms

Order and family*	No. examined/ No. positive	Species tested (* means positive)
Coniferales Pinaceae	46:0	*Araucaria araucana* (Mol.) K.Koch, *Cedrus atlantica* Manetti, *C. deodara* (Royle ex Lamb.) Loud., *Chamaecyparis lawsonia* (A.Murr.) Parl. var. "lutea compacta", *C. obtusa* (Sieb. & Zucc.) Sieb. & Zucc. var. "nana", *C. pisifera* (Sieb. & Zucc.) Sieb. & Zucc. var. "filifera nana", *C. thyoides* (L.) Britton, Sterns & Pogg. var. "glauca", *Cryptomeria japonica* (L.f) D. Don var. "spirilis" var. "vitellina", *Cunninghamia lanceolata* (Lamb.) Hook, *Juniperus communis* L. var. "nana", *J. conferta* Parl., *J. horizontalis* Moench., *J. procumbens* Sieb., *J. sabina* L. var. "tamariscifolia", *J. scopulorum* Sarg., *J. squamata* D. Don, *Larix decidua* Mill., *L. gmelini* (Rupr.) Litvinov., *L. leptolepis* (Sieb. & Zucc.) Murr., *Libocedrus decurrens* Torr., *Picea abies* (L.) Karst, *P. bicolor* (Maxim) Mayr., *P. glauca* (Moench) Voss., *Pinus aristata* Engelm., *P. ayacahuite* Ehrenb., *P. banksiana* Lamb., *P. bungeana* Zucc., *P. cembra* L., *P. cembroides* Zucc., *P. coulteri* D. Don, *P. jeffreyi* A.Murr., *P. mugo* Turra, *P. nigra* Arnold, *P. parviflora* Sieb. & Zucc., *P. peuce* Griseb., *P. pinea* L., *P. ponderosa* Dougl., *P. radiata* D.Don, *P. strobus* L. var. "prostata", *P.* sylvestris L., *Pseudolarix amabilis* (Nelson) Rehder, *Sciadopitys verticillata* (Thunb.) Sieb. & Zucc., *Sequoia sempervirens* (Lamb.) Endl. var. "adpressa", *Taxodium ascendens* Brongn. var. "nutans", *T. distichum* (L.) Rich., *Tsuga canadensis* (L.) Carr. var. "albo-spica" var. "pendula"
Taxaceae	2:0	*Taxus baccata* L. var. "expansa", *Podocarpus andinus* Poepp. ex. Endl.

* Arranged according to Kew "Handlist of Conifers".

material (*ca* 1.0 g of terminal pinnae or needles) with 2–3 drops of toluene in a sealed tube with a filter paper strip, which had been pre-treated with either sodium picrate [8,14] or copper ethylacetoacetate in $CHCl_3$ [9], suspended from the stopper and incubating the tube at 35° for 3 hr. Any change in the colour of the paper was observed.

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BENZYL ISOTHIOCYANATE IN *CYCLICOMORPHA SOLMSII* (CARICACEAE)

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Key Word Index—*Cyclicomorpha*; Caricaceae; chemotaxonomy; benzyl isothiocyanate.

Plant. Seeds of *Cyclicomorpha solmsii* were collected in January, 1976, by Mr. Jurgen Griesbach of the German Agricultural Mission at about the 1500 m level on Mt. Kenya, Kenya from trees about 27 m tall. Several plants were grown from the seeds by the Horticulture department at the Hawaii Agricultural Experiment Station. The leaves of these young plants fit the description of that of *C. solmsii* [1]. However, flowering plants have not

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been observed by the authors. *Previous work.* Benzyl isothiocyanate (BITC) was first identified in the seeds of *Carica papaya* L. [2], and later from other parts of the plant [3]. Gmelin and Kjaer [4] reported that BITC was the only isothiocyanate found in *Carica* and *Jarilla*, suggesting that this compound could be characteristic of the Caricaceae. The concentrations of BITC were examined in macerated seeds of six species of *Carica*, one in *Jarilla* and three in *Jacaratia* [5]. Both *Carica* and *Jarilla* contain high levels of BITC ranging from 1.37 to 1.96% in the macerated embryo and endosperm. However, only 2–4 ppm was found in all three *Jacaratia* species. The striking quantitative differences suggest the possible use of BITC content as a chemotaxonomic criterion.

Present work. Quantitative determination of BITC in seeds of *C. solmsii* was performed according to our previous publication [5], except that BITC in the sample was further confirmed by GC–MS. A Finnigan 3000 Peak Identifier interphased with Varian 1400 Gas Chromatograph was used and the mass spectrum obtained from the sample was identical to that of authentic BITC. Content of BITC was 1.29% of the fr. wt of the embryo and endosperm.

The Caricaceae contains only four genera; we have now surveyed all the genera in this family. *Carica*, *Jarilla* and *Cyclicomorpha* have high levels of BITC in the macerated seeds, but *Jacaratia* has only trace amounts. BITC also appears to be the only isothiocyanate in Caricaceae [4].

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STRUCTURAL DETERMINATION OF SECONDARY ALCOHOLS FROM PLANT EPICUTICULAR WAXES*

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Key Word Index—Angiosperms; gymnosperms; epicuticular waxes; secondary alcohols; TMSi ethers; GC–MS; structural determination; ultrastructure.

In the course of our investigations on the possible relationship between the ultrastructure and chemical composition of plant waxes [1, 2], we needed a rapid method for identifying secondary alcohol constituents. Although the presence of these components in waxes can readily be established by preliminary TLC (Si gel G, C_6H_6, R_f 0.32) and GLC on packed columns used to determine their homologue content, these methods give no information on the position of the OH group. In the past this information has been obtained from purely physical methods [3–6,7 and refs. cited therein] or from chemical degradation after conversion to the corresponding ketone [8–11] but more recently MS of either the free alcohol [12–16] or derived ketone [13, 17–20] has been used. A quantitative assessment of positional isomers is possible from the MS of the ketone [19, 20]. Since our main requirement was for a direct GC–MS method, most of these techniques were not applicable. The free alcohols can be analysed directly by GLC but their MS are complicated by the presence of several fragment ions derived from cleavage of the OH group [21] making reliable quantitative assessment of positional isomers difficult.

In this paper we report the use of TMSi ether derivatives for the facile and unambiguous GC–MS determination of long chain secondary alcohols which occur in plant waxes. Such derivatives have already been employed for locating mid-chain OH groups in other classes of lipid [22–26] and a detailed MS study has recently been published using a series of synthetic secondary alcohol TMSi ethers [21].

The MS of wax secondary alcohol TMSi ethers show the expected ions viz m/e 73 > 75 > 103 > 129 > 89 and at the upper end a weak M^+ (*ca* 1–2% rel. intensity) and a more intense M^+-15 (*ca* 5% rel. intensity) are observed. In the middle of the spectrum only prominent ions corresponding with cleavage α to the TMSi group occur and these fragments thus enable the position of the OH group and isomer content of the original alcohol to be determined (see footnote Table 1). In asymmetrical alcohols the TMSi-containing fragment derived from the shorter chain end is stronger than that from the longer chain end and is the base peak of the spectrum. The spectra are markedly different from those given by primary alcohol TMSi ethers which have the same MW but show an intense M^+-15 (>50% rel. intensity) and ions m/e 75 > 73. In addition silylation produces a marked improvement in peak shape and resolution by GLC compared with the corresponding free alcohols.

The secondary alcohol contents and compositions of

* For the previous paper in this series see Ref. [2].

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