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MORRONISIDE IN *SAMBUCUS* SPECIES

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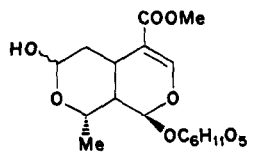
Key Word Index—*Sambucus nigra*; *S. racemosa*; *S. canadensis*; Caprifoliaceae; morroniside; iridoid glucoside.

Plants. Sambucus nigra L. (Caprifoliaceae). *Previous work.* None on iridoids.

Present work. Very young shoots (128 g), collected in April were processed by the method previously described.[1] Chromatography (silica gel; EtOAc–C_6H_6–EtOH, 4:1:1) of the glycoside fraction (530 mg) yielded cyanogenic glucosides[2] (60 mg) as the faster running band, and an iridoid glucoside in a slower moving fraction (285 mg). Further chromatography (SiO_2; $CHCl_3$–MeOH, 4:1) provided a homogeneous specimen of an amorphous glucoside (175 mg, 0·14%), tentatively identified by its PMR-spectrum as *morroniside*, an iridoid previously encountered in fruits of *Lonicera morrowii* A. Gray (Caprifoliaceae)[3] and of *Cornus officinalis* Sieb. et Zucc. (Cornaceae),[4] as well as in *Gentiana thunbergii* (G. Don) Grieseb. (Gentianaceae).[5] Acetylation (Ac_2O–Py) of the glucoside, followed by preparative TLC (SiO_2; Et_2O–C_6H_6, 1:3) provided the 7-anomeric pentaacetates. The faster running fraction (140 mg) was recrystallized from MeOH to give the *α-anomer*, m.p. 152–153° (corr.); $[\alpha]_D^{26}$ −73° (*c* 0·8, $CHCl_3$); λ_{max}^{EtOH} 237 nm (ε 12 400) [lit. m.p. 148–151°; $[\alpha]_D$ −73·5° (*c* 0·97, $CHCl_3$); λ_{max}^{EtOH} 236 nm (ε 12 200);[3] m.p. 150–153°; $[\alpha]_D^{23}$ −76° (*c* 1·0, $CHCl_3$);[4] m.p. 149°; $[\alpha]_D^{19}$ −77° (*c* 1·1, $CHCl_3$)[6]]. The slower running fraction (40 mg) was recrystallized 2× (EtOH) to give the *β-anomer*, m.p. 127–128°, spontaneously converted on standing at room temp. into an apparently more stable, crystalline modification, m.p. 144–145° (corr.); $[\alpha]_D^{26}$ −101° (*c* 0·4, $CHCl_3$); λ_{max}^{EtOH} 237 nm (ε 11 600) [lit. m.p. 127°; $[\alpha]_D^{19}$ −100° (*c* 1·0, in $CHCl_3$)[6]]. The PMR-spectra were in accord with those published.[6]



[1] ROSENDAL JENSEN, S., KJAER, A. and JUHL NIELSEN, B. (1973) *Acta Chem. Scand.* in press.
[2] ROSENDAL JENSEN, S. and JUHL NIELSEN, B. (1973) *Acta Chem. Scand.* in press.
[3] SOUZU, I. and MITSUHASHI, H. (1970) *Tetrahedron Letters* 191.
[4] ENDO, T. and TAGUCHI, H. (1973) *Yakugaku Zasshi* **93**, 30.
[5] INOUYE, H. and NAKAMURA, Y. (1971) *Yakugaku Zasshi* **91**, 755.
[6] INOUYE, H., TOBITA, S., AKIYAMA, Y., ITO, K. and SHINGU, T. (1973) *Chem. Pharm. Bull.* **21**, 846.

Young shoots of *S. racemosa* L. and *S. canadensis* L. (collected on 19 April and 1 May) were treated in the same way to give 0·1% and *ca* 0·05% morroniside, respectively. No cyanogenic glucosides were found in these species. Morroniside could not be detected either in fully developed foliage of the three species nor in green fruits of *S. nigra* (PMR and TLC of the glucoside fractions).

Sources. S. nigra (voucher numbers IOK 30/72; IOK 3/73; IOK 5/73; IOK 8/73–12/73): various localities on Sjælland, Denmark; *S. racemosa* (IOK 1/72; IOK 4/73): Geels Bakke near Copenhagen, Denmark. *S. canadensis* (IOK 158/72; IOK 7/73) Hørsholm Arboretum, Denmark. Vouchers have been deposited at the Botanical Museum of the University of Copenhagen, Denmark.

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3,4′-DIHYDROXYPROPIOPHENON-3-β-D-GLUCOPYRANOSID AUS *BETULA ALBA*

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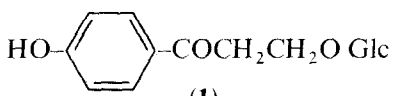
Aus den Blättern von *Betula alba* wurde das erstmals beobachtete 3,4′-Dihydroxypropiophenon-3-β-D-glucopyranosid (**1**) isoliert. Durch enzymatische Hydrolyse ging **1** in 3,4′-Dihydroxypropiophenon (**2**) über. **2** war erstmals bei der Synthese von Chromanon[1] als Nebenprodukt aufgetreten. Die früheren Autoren konnten jedoch nicht klären, ob es sich um 3,4′-Dihydroxypropiophenon oder 3,2′-Dihydroxypropiophenon handelte.



(**1**)

Die Strukturermittlung des Aglykons erfolgte durch IR-, NMR-, UV- und Massenspektroskopie von **2** und des **2**-diacetats. Die Verknüpfungsstelle der D-Glucose mit dem Aglykon wurde durch NMR-Spektroskopie des **1**-pentaacetats, durch UV-Spektroskopie von **1** und durch die Farbreaktion von **1** mit $FeCl_3$ ermittelt. Die D-Glucose wurde papierchromatographisch nachgewiesen und die Anzahl der Glucoseeinheiten durch

[1] MAYER, F. und VAN ZUTPHEN, L. (1924) *Chem. Ber.* **57**, 200.