Present work. The aerial part was dried, powderized and extracted successively with light petroleum, $CHCl_3$ and ethanol. The light petroleum extract was saponified with 10% methanolic KOH. The unsaponifiable portion was taken into isopropyl ether and chromatographed on a silicic acid column, affording: *Octacosane*, $C_{28}H_{60}$; m.p. 60–62°, IR, NMR, m.m.p.; *Dotriacontane*, $C_{32}H_{66}$; m.p. 70–72, IR, NMR, m.m.p.; *Stigmasterol*, $C_{29}H_{48}O$; (M^+ 412), m.p. 150–154°; [α] −42·4°, IR, NMR, UV; Co-TLC and m.m.p. Stigmasteryl acetate $C_{31}H_{50}O_2$ (M^+ 454) m.p. 136–138° [α] −45°.

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Key Word Index—Clematis drummondii; Ranunculaceae; stigmasterol; alkanes.

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RHAMNACEAE

CHRYSOPHANOL AND β-AMYRIN IN THE FRUITS OF *KARWINSKIA HUMBOLDTIANA**

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Plant. Karwinskia humboldtiana, Zucc. *Occurence.* Northern part of Mexico. *Uses.* Medicinal,[1] has a progressive paralysing action. It is toxic to cattle and human beings.[2] *Previous work.* An unidentified quinone.[3]

Present work. The dried fruit was extracted twice with light petroleum, extracts were chromatographed on silicic acid: (β-amyrin, $C_{30}H_{50}O$ (M^+ 426), m.p. 197° (m.m.p. with authentic sample), [α], IR, NMR of triterpenol, and of its acetate. From the second extract was obtained chrysophanol—(1,8-dihydroxy-3-methylanthraquinone, $C_{15}H_{10}O_4$ (M^+ 254), m.p. 197° UV, IR, NMR (m.m.p. co-TLC and IR with authentic specimen).

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* Part XXI in the series "Mexican Medicinal Plants".

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Key Word Index—Karwinskia humboldtiana; Rhamnaceae; chrysophanol.

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SCHROPHULARIACEAE

FLORAL FLAVONOIDS OF THE *MIMULUS LUTEUS* COMPLEX

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THE *Mimulus luteus* complex of section *Simiolus* consists of three species: *M. luteus* L.,

M. cupreus Dombrain, and *M. tigrinus* Hort. and their varieties.[1,2] Previously, herbacitrin, i.e., herbacetin (8-hydroxykaempferol)7-glucoside, has been identified in the flowers of *M. luteus*.[3] The carotenoid pigments in the petals of *M. cupreus* and *M. tigrinus*[4] have been determined. The floral flavonoids of the *M. cardinalis* complex of section *Erythranthe* have also been determined.[5–7]

RESULTS AND DISCUSSION

The major floral flavonoids of 13 populations of the *Mimulus luteus* complex were investigated. Six of the populations belonged to *M. luteus*, four to *M. tigrinus* and three to *M. cupreus*.

Fresh flowers from all populations were pooled and a flavonoid extract prepared using standard procedures. This extract contained at least ten flavonoids, five of which were studied in detail. The five were found to be cyanidin 3-monoglucoside acylated with an unknown acid (not a cinnamic acid derivative), kaempferol 7-monoglucoside, quercetin 7-monoglucoside, a kaempferol 3-glycoside, and a quercetin 3-glycoside with undetermined numbers of glucose residues at the 3-positions. The remaining flavonoids were studied in less detail, but appeared to be kaempferol 7-diglycoside, quercetin 7-diglycoside, apigenin 7-glycoside, luteolin 7-glycoside, and herbacetin 7-glucoside. The finding of the latter confirms the previous report.

All the major floral flavonoids were found to be present in each of the three species, although individual populations of each species lacked one or more of them. Marked quantitative differences in the pigments occur between populations. In fact, each of the 13 populations could be distinguished on the basis of qualitative and quantitative differences in its floral flavonoid pigment complement.

Populations of a related complex, the *M. glabratus* complex also of section *Simiolus*, were surveyed. Comparisons showed that they too contained the 7-monoglucosides of kaempferol, quercetin and herbacetin. In contrast, the *M. cardinalis* complex of section *Erythranthe*[6] differs markedly from the *M. luteus* and *M. glabratus* complexes. The pelargonidins of the *M. cardinalis* complex are lacking in the other two complexes, while the kaempferol, quercetin and herbacetin of the *M. luteus* and *M. glabratus* complexes are lacking in the *M. cardinalis* complex.[7] Thus, the observed similarities and differences in floral flavonoids support the present taxonomic treatment of these species groups.

EXPERIMENTAL

Standard procedures were used for flavonoid extraction.[8] The flavonoids were purified by two-dimensional and one-dimensional paper chromatography. The flavonoids were hydrolysed. The aglycones were identified by paper chromatographic comparisons with authentic compounds (three solvents) and UV analysis.[9] The sugars were identified by paper chromatographic comparisons with known sugars.

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Cyanidin 3-monoglucoside, acylated. Acid hydrolysis gave cyanidin and glucose. Spectral analysis of the glycoside indicated that glucose was at the 3-position, and sequential acid hydrolysis indicated that it was a 3-monoglucoside. This pigment had a chromatographic mobility identical to authentic cyanidin 3-glucoside (four solvents) only after mild alkaline hydrolysis, indicating that it was acylated. The acylated and non-acylated glucoside had identical absorption spectra, indicating that the acyl group was not a cinnamic acid derivative. The nature of the acyl group was not determined.

Kaempferol and quercetin 7-monoglucosides. Acid hydrolysis gave the corresponding aglycones and glucose. The color reactions of these glycosides on paper chromatograms[10] and UV analysis indicated they were 7-glucosides, and R_f data indicated they were 7-monoglucosides.

Kaempferol and quercetin 3-glucosides. These were identified in a manner similar to the 7-monoglucosides, except that satisfactory R_fs were not obtained. Therefore, the number of glucose units at the 3-position cannot be stated.

Kaempferol and quercetin 7-diglycosides. Color reactions of these glycosides on paper chromatograms, and UV spectral data indicated these to be 7-diglycosides of kaempferol and quercetin. Their positions on two-dimensional paper chromatograms relative to the 7-monoglucoside derivatives mentioned above indicated that these are probably 7-diglycosides.

Apigenin and luteolin 7-glycosides. UV spectral data indicated these to be 7-glycosides of apigenin and luteolin.

Herbacetin 7-monoglucoside (herbacitrin). The color reactions on paper chromatograms, and UV spectral data confirmed the existence of this pigment in *M. luteus.*

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Key Word Index—Mimulus luteus; Scrophulariaceae; flower pigments; anthocyanins; flavonol glycosides; flavones.

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SOLANACEAE

CAFFEOYLPUTRESCINE IN *NICOTIANA TABACUM*

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Extensive studies have been made of the polyphenols of the leaves of tobacco resulting in the identification of many hydroxycinnamic acid derivatives.[1,2] However, there has been little work done on this class of compounds in the floral parts of the plant. Besides chloro-

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