

ence of A_m for C over the range given is in accordance with that found for $[\text{Rh}(\text{dip})_2\text{Cl}_2]\text{ClO}_4$.⁸ In contrast with this, we found that a salt of composition $\text{Tl}(\text{dip})(\text{NO}_3)_2\text{ClO}_4$ had not only a lower conductance than C and D, but also a strong concentration dependence, as would be expected if extensive ion association had occurred. Because of this difference we conclude that B, C, and D probably all retain two molecules of dipyrindyl in nitrobenzene. A and B on solution give species containing one perchlorate ion, while solutions of C and D contain the six coordinate ion $[\text{Tl}(\text{dip})_2\text{NO}_3]^{+}$. D is thus analogous to the mixed perchlorate-nitrate complexes of diphenylmethylarsineoxide with cobalt(II), in that, as might have been expected, it is the nitrate which is preferentially coordinated.⁶

None of the compounds reported here are isomorphous.

Conductivity measurements were made with a Radiometer conductivity meter, Type C DM 2d; infrared absorption spectra with a Beckman I.R.8 infrared spectrophotometer.

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The Non-volatile Acids of Succulent Plants Exhibiting a Marked Diurnal Oscillation in their Acid Content

II. Demonstration of Piscidic Acid as one of the Predominating Acids in *Opuntia ficus-indica* L.*

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The present paper represents a new attempt to elucidate the nature of the organic acids found in plants with a typical "crassulacean acid metabolism". In fact, this special form of metabolism was first demonstrated in an *Opuntia* species (in 1804) by the famous Swiss plant physiologist, de Saussure.¹

The organic acids of a few *Opuntia* species have been investigated by several scientists, but until recently only oxalic, malic, and citric acid had been reported.² During screening tests for phorbic acid, carried out in this laboratory in February 1965, it was noticed that an ethyl ester mixture, prepared from the non-volatile acids of *Opuntia ficus-indica* L., produced a dominating peak on the gas chromatogram with a longer retention time than either citric or phorbic acid ethyl ester. In order to carry out a closer investigation of this substance, 15 kg of *Opuntia ficus-indica* L. was supplied from the Canary Islands.

For the investigation we applied mainly the same methods as we had used on earlier occasions for corresponding purposes:^{3,4} isolation of the non-volatile acids over their lead salts, esterification of the acid mixtures, fractionation of the ester mixtures in high vacuum, and examination of the individual fractions by various methods, like gas chromatography, investigation of the solid esters by means of classical organic chemical methods,

* A more extensive survey will be published later in *Meddelelser fra Norsk Farmaceutisk Selskap*.

conversion of the liquid esters into hydrazides etc.

The investigation revealed that *Opuntia ficus-indica* L. contains at least 7 non-volatile acids, among which are the earlier detected malic and citric acids.

From the ester mixture we also isolated two solid ethyl esters. The first of these esters separated from the crude ester mixture before fractionation. The yield after drying was 6.5 g. After recrystallization, first from ethyl acetate and then twice from water, the substance was found to consist of microscopic white needles or rods, which melted at 207°C. (Found: C 54.91; H 5.72; OC₂H₅ 15.36. Calc. for C₁₃H₁₆O₇: C 55.0; H 5.64; OC₂H₅ 15.85). The substance corresponds to *piscidic acid monoethyl ester*.

From the two highest boiling fractions of the ethyl ester mixtures, we isolated a second solid ester, that after recrystallization from 30% ethanol consisted of colourless, rather thick, often pointed rods, that melted at 135°C. The yield of pure ester was nearly 5.0 g. (Found: C 57.80; H 6.49; OC₂H₅ 28.35. Calc. for C₁₅H₂₀O₇: C 57.75; H 6.42; OC₂H₅ 28.80). The substance corresponds to *piscidic acid diethyl ester*.

Piscidic acid monoethyl ester was isolated for the first time by Freer and Clover⁵ from the bark of *Piscidia erythrina* L., but according to these authors piscidic acid does not form a diethyl ester. In order to investigate this question more thoroughly, we obtained 5 kg of the bark of *Piscidia erythrina* L., and from this we prepared two solid esters which were found to be identical with the two solid esters isolated from *Opuntia ficus-indica* L. The solid esters isolated from the two species were subjected to the following tests and analyses: melting point and mixed melting point determinations, elementary analyses, IR-spectrometry, gas chromatography, determination of saponification equivalent, potentiometric titration, and determination of optical rotation.

Opuntia ficus-indica L. is the second plant with a typical "crassulacean acid metabolism" in which piscidic acid was found in the tissue of the fresh plant. The first plant of this type in which the same acid was demonstrated, was *Agave americana* L.³

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Studien über die NMR-Spektren der CH₂-Protonen in einigen Mercaptal- und Mercaptol-essigsäuren

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Die magnetische Äquivalenz und Nicht-Äquivalenz der Protonen einer aliphatischen -CH₂-Gruppe und ihre Bedeutung für die NMR-Spektren ist zum Gegenstand vieler experimentellen und theoretischen Untersuchungen gemacht worden, ohne dass man eine endgültige Erklärung ihrer Ursachen erreicht hat.¹⁻⁵ Eine Erweiterung des experimentellen Materials besonders mit neuen Verbindungstypen muss daher wertvoll sein. Im folgenden werden die Resultate einiger preliminären Untersuchungen über das Verhalten der Methylenprotonen in der -SCH₂COOH-Gruppe einiger Mercaptal- und Mercaptolessigsäuren mitgeteilt.