(4) *Conclusions*

In conclusion, insect fibrillar muscle oscillates by means of a myofibrillar automatism with ATP as the source of energy and with calcium and magnesium ions as necessary activators because any increase in length of myofibrils produces a delayed rise in tension and any decrease in length produces a delayed fall. Future work will have to show what relation (if any) exists between somewhat similar oscillatory phenomena of skeletal muscle described by ARMSTRONG et al.[61] and the oscillation of insect fibrillar muscle. Oscillations of tension have also been described in heart muscle[62] and smooth muscle[63] but these are almost certainly unrelated to myogenic oscillation since, unlike insect flight muscles, the vertebrate muscles do show fluctuations of the membrane potential in synchrony with the mechanical events. The mechanism of stretch activation and of the ATPase activation in relation to power output, as well as the nature of the highly efficient energy transfer from the ATP molecules to mechanical work, is still a mystery. But recently considerable progress has been achieved in studying the thermodynamics of contracting glycerinated skeletal muscle fibres (WEBER and PORTZEHL[42]) and of living striated muscle (e.g. MARÉCHAL[35], DAVIES[36], WILKIE[34]). Further research on the molecular level seems rather promising now that the efficient chemo-mechanical energy conversion and the mechano-chemical energy coupling can be studied directly on the working (oscillating) 'isolated' contractile machinery in vitro and under controlled chemical and mechanical conditions with ATP as the only source of energy, which is liberated by the ATPase of actin activated myosin[64].

Zusammenfassung. Während des Insektenfluges oszillieren die fibrillären Muskeln dank einem myofibrillären Automatismus. Oszillation der Myofibrillen ist in ATP-Salzlösungen selbst nach Isolierung der kontraktilen Strukturen möglich. Dies erlaubt In-vitro-Untersuchungen der mechano-chemischen Energiekoppelung der Muskelkontraktion.

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SPECIALIA

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The Synthesis of (±)-Maackiain

(−)-Maackiain (I) was isolated from *Maackia amurensis* Rupr. et Maxim. var. Buergeri (Maxim.) C. K. Schneid.[1], from *Andira inermis* (Wright) H. B. K.[2], and from *Swartzia Madagascariensis* Desv.[3]. By methylation I was converted into (−)-pterocarpin (II) which had been isolated from *Pterocarpus santalinus* L.[4]. Lately, (±)-maackiain I was obtained from *Sophora japonica* L.[5], and from *Dalbergia spruceana*[6].

In previous papers[7,8], the authors have reported the total synthesis of (±)-pterocarpin (II) via the methyl ether (III) of medicagol (IV), which was obtained by the procedure of WANZLICK's benzofurano-3′, 2′: 3, 4-coumarin synthesis[9]. In this paper we describe the synthesis of (±)-I from benzyl ether (V) of IV according to the modified procedure reported earlier[8].

In a manner similar to the experiment described earlier[7,10], the benzyl ether V (m.p. 251–253°, IR 1742 (α-pyrone), 1033, 940 cm^{-1} ($O-CH_2-O$) (Nujol), UV

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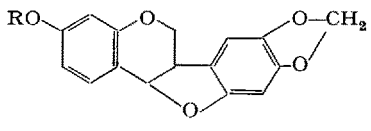
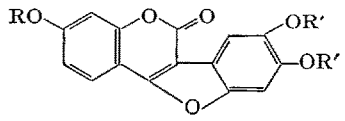
λ_{EtOH}^{max} nm ($\log\varepsilon$): 246 (4.30), 280 (3.88), 295 (3.80), 347 (4.37). Found: C, 71.20; H, 3.79. $C_{23}H_{14}O_6$ requires: C, 71.50; H, 3.65%) was obtained from 7-benzyloxy-5′,6′-dihydroxybenzofurano-3′,2′:3,4-coumarin (VI)[10,11] with methylene iodide. For reductive cleavage of the coumarin bridge, V was treated in tetrahydrofuran with lithium aluminum hydride to give 2-(2-hydroxy-4-benzyloxyphenyl)-3-hydroxymethyl-5,6-methylenedioxy-benzofuran (VII) (m.p. 135–136°, IR 3450, 3100 (OH), 1035, 930 cm^{-1} (O–CH_2–O) (Nujol), UV λ_{max}^{EtOH} nm ($\log\varepsilon$): 269 (4.11), 321 (4.35). Found: C, 70.80; H, 4.76. $C_{23}H_{18}O_6$ requires: C, 70.76; H, 4.65%), which was readily transformed to a diacetate (m.p. 127–128°, IR 1760, 1740 (C=O), 1030, 945 cm^{-1} (O–CH_2–O) (Nujol). Found: C, 68.08; H, 4.74. $C_{27}H_{22}O_8$ requires: C, 68.35; H, 4.67%). VII was dehydrated in boiling diethylene glycol to afford the ether (VIII) (m.p. 167–168°, IR 1624, 1603, 1510 (C=C, phenyl), 1022, 938 cm^{-1} (O–CH_2–O), UV λ_{max}^{EtOH} nm ($\log\varepsilon$): 253 (4.01), 270 (4.03), 324 (4.33), 357 (4.10). Found: C, 73.97; H, 4.36. $C_{23}H_{16}O_5$ requires: C, 74.18; H, 4.33%). The ether VIII was hydrogenated in acetic acid with 10% Pd-C as catalyst. It absorbed exactly 2 moles of hydrogen: 1 mole within 2 h and the other within 10 h. The obtained crystals, m.p. 199–200°, were identical with natural (±)-maackiain I in the mixed melting point and the spectral characteristics (synthetic sample, m.p. 199–200°, IR 3570, 3380, 3230 (broad) (OH), 1615, 1600, 1505 (phenyl), 1030, 930 cm^{-1} (O–CH_2–O) (Nujol), UV λ_{max}^{EtOH} nm ($\log\varepsilon$): 280 (3.57), 286 (3.63), 310 (3.85). Found: C, 65.50; H, 4.38. $C_{16}H_{12}O_5 \cdot {}^1/_2H_2O$ requires: C, 65.53; H, 4.46%) (natural sample[12], m.p. 200–201°) (lit.[5], m.p. 195–196°, IR 3460 to 3540 (OH), 1617, 1600, 1509 (phenyl), 1033, 928 cm^{-1} (O–CH_2–O) (Nujol), UV λ_{max}^{EtOH} nm ($\log\varepsilon$): 281 (3.58), 287 (3.65), 310 (3.86)). Its acetate (IX) (m.p. 152–153°, IR 1747 (C=O), 1031, 935 cm^{-1} (O–CH_2–O) (Nujol), UV λ_{max}^{EtOH} nm ($\log\varepsilon$): 278 (3.46), 284 (3.53), 311 (3.82). Found: C, 66.51; H, 4.21. $C_{18}H_{14}O_6$ requires: C, 66.25; H, 4.32%) (natural samples[12], m.p. 152–152.5°) (lit.[5], m.p. 159–160°) was obtained by a usual method. A methyl ether prepared by methylation of synthetic (±)-I was identified with synthetic (±)-II[8] by the mixed melting point and the spectral characteristics.

On the other hand, catalytic debenzylation of V with hydrogen gave medicagol IV in good yield (m.p. 323–325°, IR 3210 (OH), 1700 (α-pyrone), 1032, 939 cm^{-1} (O–CH_2–O) (Nujol), UV λ_{max}^{EtOH} nm ($\log\varepsilon$): 245 (4.29), 270 (3.91), 297 (3.85), 310 (4.03), 348 (4.46), $\lambda_{max}^{EtOH-NaOAc}$ nm ($\log\varepsilon$): 246 (4.28), 2.67 (3.93), 297 (3.90), 310 (4.01), 349 (4.43), 362 (4.42). Found: C, 65.08; H, 2.79. $C_{16}H_8O_6$ requires: C, 64.87; H, 2.72%) (lit., m.p. 324–325°[13], m.p. 326 to 327°[14]), whose properties were identical with those described by the American authors[13,14]. Acetylation of IV gave an acetate (X) (m.p. 266–267°, IR 1746sh, 1715 (C=O), 1028, 941 cm^{-1} (O–CH_2–O) (Nujol), UV λ_{max}^{EtOH} nm ($\log\varepsilon$): 245 (4.15), 276 (3.81), 284 (3.83), 298 (3.71), 310 (3.50), 348 (4.37). Found: C, 63.80; H, 3.09. $C_{18}H_{10}O_7$ requires: C, 63.91; H, 2.98%) (lit., m.p. 262–263°[13], m.p. 271°[14]).

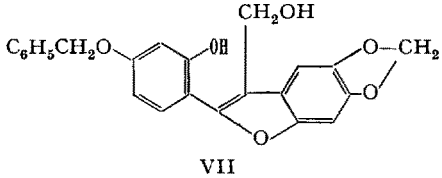
As a result, the oxygen pattern of the aromatic rings of I and IV must be the same. The close structural relationship between the 2 compounds suggests a similar biosynthetic pathway.



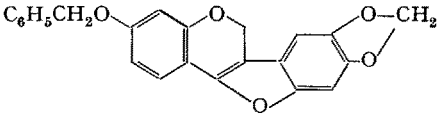
I R = H
II R = Me
IX R = Ac



III R = Me R′–R′ = CH_2
IV R = H R′–R′ = CH_2
V R = $CH_2C_6H_5$ R′–R′ = CH_2
VI R = $CH_2C_6H_5$ R′ = H
X R = Ac R′–R′ = CH_2



VII



VIII

Zusammenfassung. Die Synthese von (±)-Maackiain aus Medicagol-benzyläther wird beschrieben. Sie sind mit den entsprechenden Naturstoffen aus *Sophora japonica* L. identisch.

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