

corrin compounds. Presumably it is the angular methyl group on C(1) that is responsible for the invariant conformation of ring A, but no force-field calculations have been carried out so far to test this suggestion.

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196. A Specific Synthesis of Ethyl (2Z)-2-Bromomethyl-2-butenolate and its Conversion into Mikanecic Ester¹⁾

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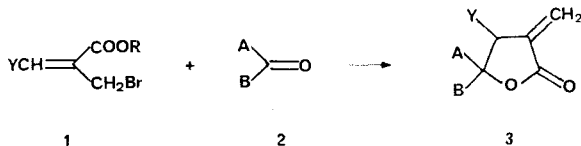
(28. IV. 76)

Eine spezifische Synthese von (2Z)-2-Bromomethyl-2-butensäure-äthylester und seine Umwandlung in Mikanezester¹⁾. – *Zusammenfassung.* Das Lithiumsalz **12**, hergestellt aus 2-Bromorthopropensäure-triäthylester (**11**) und *n*-Butyl-lithium, wurde mit Acetaldehyd umgesetzt, wobei 2-Methyliden-3-hydroxy-orthobutensäure-triäthylester (**13**) und daraus, durch saure Hydrolyse, 2-Methyliden-3-hydroxybutensäure-äthylester (**14**) entstand. Behandlung von **14** mit *N*-Bromsuccinimid und Dimethylsulfid lieferte den gewünschten (2Z)-2-Bromomethyl-2-butensäure-äthylester (**6**), der sich mit HBr zur entsprechenden Säure **4** hydrolysieren liess.

Die (2Z)-Konfiguration von **4** wurde aufgrund der *vicinalen* ¹H/¹³C Kopplungen zwischen H–C(3) und COOH bzw. CH₂Br im ¹³C-NMR-Spektrum bestätigt. Die ¹H-NMR-Signale der beiden Methylidenprotonen in **9**, **11**, **13** und **14** liessen sich mit Hilfe von additiven Entschirmungsbeiträgen der Substituenten um die Doppelbindung zuordnen.

1,4-Eliminierung von HBr aus (2Z)-2-Bromomethyl-2-butensäure-äthylester (**6**) mit Kalium-*t*-butylat ergab Mikanezsäure-diäthylester (**21**), der bei der Aufarbeitung teilweise zum Monoester **20** und zur Mikanezsäure¹⁾ (**19**) verseift wurde.

1. Introduction. – Some years ago it was discovered [1] that β-bromoesters of type **1** react readily with carbonyl compounds **2** under *Reformatsky* conditions to give α-methylidene-γ-butyrolactones (**3**). The reaction was found with methyl (2Z)-



¹⁾ The systematic name for mikanecic acid (**19**) is 4-vinyl-1-cyclohexene-1,4-dicarboxylic acid.

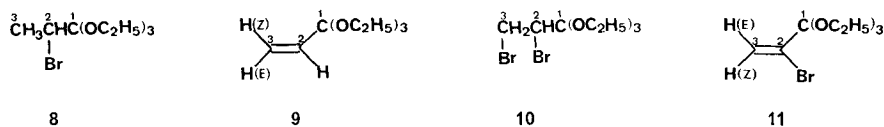
²⁾ Postdoctoral Fellow, 1974–1976.

2-bromomethyl-2-butenolate (**5**). This compound had been obtained as the minor product from the *N*-bromosuccinimide bromination of methyl (2*Z*)- or (2*E*)-2-methyl-2-butenolate along with the major product, methyl (2*E*)-2-methyl-4-bromo-2-butenolate (**7**) [2]. The separation of the two bromoesters **5** and **7** had been achieved only with difficulty. Recently a stereoselective synthesis of (2*E*)-2-methyl-4-halo-2-butenolates similar to **7** has been published [3]. We here report a specific synthesis of

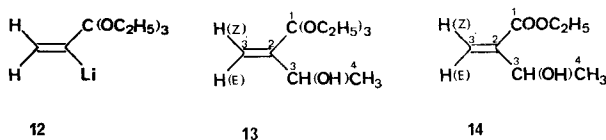


ethyl (2*Z*)-2-bromomethyl-2-butenolate (**6**) using a concept similar to that described for the preparation of (2*Z*)-2-chloromethyl-2-butenal [4].

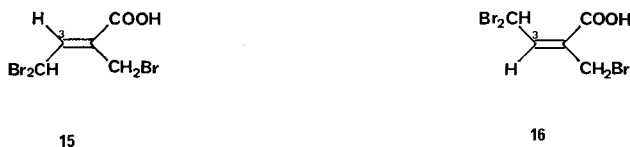
2. Preparation of (2*Z*)-2-bromomethyl-2-butenic acid (4**).** – Triethyl 2-bromo-orthopropenoate (**11**) was prepared according to the described procedure [5] *via* **8**, **9** and **10** with slight modifications. The lithium salt **12**, obtained by treatment



of **11** with butyl lithium, was condensed with acetaldehyde to give triethyl 2-methylidene-3-hydroxy-orthobutanoate (**13**; 82%), which was hydrolysed in a two-phase system to ethyl 2-methylidene-3-hydroxy-butanoate (**14**; 91%). Treatment with



N-bromosuccinimide and dimethyl sulfide [4] [6] converted **14** into the desired ethyl (2*Z*)-2-bromomethyl-2-butenolate (**6**; 87%). Hydrolysis of **6** with 48% aqueous HBr afforded the corresponding acid **4** in 85% yield, m.p. 111–112.5° [2].



3. Configuration of (2*Z*)-2-bromomethyl-2-butenic acid (4**).** – Previously the assignment of the (2*Z*)-configuration to **4** was based on comparison of the ¹H-NMR.

chemical shifts of H-C(3) and H₃-C(4) with those of equivalent protons in similar compounds [2]. A recent observation suggested caution with one of the arguments used, namely the one which said that a chemical shift of $\delta = 7.25$ for H-C(3) in **4** indicated a *cis* arrangement between this proton and the carboxyl group, assuming that a *trans* arrangement required a lower δ -value for H-C(3)³). This observation was that the stereoisomeric tribromoacids **15** and **16** showed very similar chemical shifts for H-C(3) ($\delta = 7.37$ and 7.40) [9]. However, the previous configurational assignment for **4** is now supported by ¹³C-NMR. measurements: The *vicinal* ¹H/¹³C coupling constants for H-C(3) are $J_{H-C(3)/C(1)} = 5.4$ and $J_{H-C(3)/C(3')} = 9$, visible in the signals at $\delta = 171.0$ (C(1)) and 23.2 (C(3')). This suggests a *cis* location for H-C(3) and -CO₂H as well as a *trans* arrangement for H-C(3) and -CH₂Br [10], both of which correspond with a (2*Z*)-configuration of **4**.

4. Assignment of ¹H-NMR. signals to protons at terminal double bonds. –

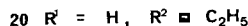
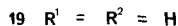
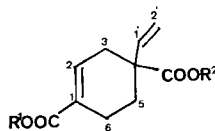
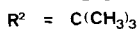
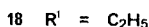
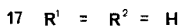
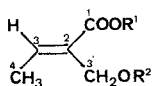
The following is an attempt to assign the ¹H-NMR. signals (CCl₄-solutions) in the $\delta = 5.3$ – 7.0 region of the propenoate (**14**) and orthopropenoate derivatives (**9**, **11** and **13**). The signals of orthoester **9** are assigned from the coupling pattern (similar to that known for ethyl propenoate [11]), analysed by spin simulation as an *ABX*-system, as follows: $\delta = 5.57$ ($J = 10$ and 17) to H-C(2), $\delta = 5.45$ ($J = 2.4$ and 17) to H(Z)-C(3) and $\delta = 5.29$ ($J = 2.4$ and 10) to H(E)-C(3) (for the signification of H(Z) and H(E) see the formula). According to the concept of *Pasqual et al.* [7] [8] (see also [12]), the following three approximate deshielding increments *Z* are calculated from these values for the -C(OC₂H₅)₃ (orthoester) group as a substituent on a double bond: $Z_{gem} = 0.32$, $Z_{cis} = 0.20$ and $Z_{trans} = 0.04$ ppm.

Using these values of Z_{cis} and Z_{trans} along with the corresponding increments given in [8] for -Br the signals of the bromo-orthoester **11** are assigned as follows: $\delta = 5.78$ to H(Z)-C(3) and $\delta = 6.22$ to H(E)-C(3) (calc. 5.74 and 6.00 , respectively). Since the two signals for the two H-C(3') in the hydroxy-orthoester **13** are quite similar in chemical shift ($\delta = 5.45$ and 5.33) they are not assigned individually. However, using the two possible assignments of these signals, *i.e.* $\delta = 5.45$ to H(E) and $\delta = 5.33$ to H(Z) of **13**, or *vice versa*, one can calculate two of the three deshielding increments *Z* for the -CH(OH)CH₃ group: accordingly Z_{cis} amounts to 0.04 or 0.16 ppm, and Z_{trans} to 0.00 or -0.12 ppm. These values together with the literature values for -COOR [8] can be used to assign signals in the hydroxy-ester **14** as follows: $\delta = 6.17$ to H(Z)-C(3') (calc. 6.43 or 6.31) and $\delta = 5.85$ to H(E)-C(3') (calc. 5.84 or 5.96). In a similar manner assignments for the previously reported [2] hydroxy acid corresponding to **14** can be made: in CDCl₃ $\delta = 6.37$ is attributed to H(Z)-C(3') (calc. 6.66 or 6.54) and $\delta = 5.93$ to H(E)-C(3') (calc. 6.00 or 6.12).

5. Conversion to mikanecic acid and its ethyl esters. – The observation that structural units such as serracinic acid (= (2*E*)-2-hydroxymethyl-2-butenic acid; **17**) may be precursors for the formation of mikanecic acid¹⁾ (**19**) has been

³) A more precise analysis can be made with the help of deshielding increments by the method of *Pasqual et al.* [7] [8]. The observed δ -values for H-C(3) in **4** and **6** (7.25 and 7.05) fit better for the (2*Z*)-configuration, as expressed in formulae **4** and **6** (calc. 7.07 and 6.84), than for the corresponding (2*E*)-isomers (calc. 6.52 and 6.36).

mentioned previously [13] [14]. Methyl mikanecate has also been isolated as a minor by-product of the saponification of the mixture of the bromoesters **5** and **7** (after reesterification with diazomethane) [2]. It was implied that **5** was the more probable precursor for isoprenic acid [2] which dimerized to mikanecic acid (**19**). The implication appeared reasonable, because 1,4-elimination of HBr from **5** involves depro-



tonation from an activated position (vinylogous to the ester group). We now confirm this point by isolating compounds having the mikanecic acid structure in about 50% yield from the treatment of ethyl (2*Z*)-2-bromomethyl-2-butenolate (**6**) with potassium *t*-butoxide⁴). The work-up procedure brought about partial saponification, so that a mixture of diethyl mikanecate (**21**, 33%), monoethyl mikanecate (**20**, 9%), and mikanecic acid (**19**, about 15%) was obtained. A minor by-product (4%) from this reaction was ethyl (2*E*)-2-*t*-butoxymethyl-2-butenolate (**18**).

This work was supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* and by *Sandoz AG*, Basel. We thank Mr. *W. Schwotzer* for spin simulation and Mr. *U. Vögeli* for ¹³C-NMR. measurements.

Experimental Part

General. See [9] [14].

Triethyl 2-bromo-orthopropenoate (8). For procedure see [5], yield 77%, b.p. 80–82°/10 Torr. – IR. (CCl₄): 2980 *s*, 2940 *m*, 2900 *m*, 2870 *m* sh, 1485 *w*, 1458 *m*, 1448 *m*, 1393 *m*, 1377 *m*, 1369 *m*, 1325 *m*, 1225 *s*, 1210 *s* sh, 1160 *m*, 1115 *s*, 1095 *s* sh, 1080 *s* sh, 1065 *s*, 1020 *m*, 980 *m*, 670 *w*, 650 *m*. – ¹H-NMR. (100 MHz, CCl₄): 1.17 (*X*₃ part of *ABX*₃, *J*_{*AX*} ≅ *J*_{*BX*} ≅ 7.2, 9H, 3 CH₃CH₂O); 1.67 (*d*, *J* = 7, 3H, 3H–C(3)); 3.59 (*B* part of *ABX*₃, *J*_{*BA*} = 9.5, *J*_{*BX*} ≅ 7.2, 3 CH₃–CH_AH_B–O) and 3.70 (*A* part of *ABX*₃, *J*_{*AB*} = 9.5, *J*_{*AX*} ≅ 7.2, 3 CH₃–CH_AH_B–O) (together 6H); 4.09 (*q*, *J* = 7, 1H, H–C(2)).

Triethyl orthopropenoate (9). For procedure see [5] (commercial potassium *t*-butoxide was used), yield 73%, b.p. 74–74.5°/29 Torr. – IR. (CCl₄): 3100 *w*, 3035 *w*, 2985 *s*, 2935 *s*, 2900 *s*, 2880 *m* sh, 1485 *w*, 1460 *w*, 1450 *m*, 1410 *s*, 1390 *m*, 1370 *w*, 1290 *w*, 1220 *s*, 1175 *s* sh, 1160 *s* sh, 1070 *vs* br., 1050 *s* sh, 990 *s*, 945 *s*. – ¹H-NMR. (100 MHz, CCl₄): 1.13 (*t*, *J* = 7, 9H, 3 CH₃CH₂O), 3.40 (*q*, *J* = 7, 6H, 3 CH₃CH₂O), 5.19–5.72 (*ABX* pattern, 3H); simulation gives 5.29 for *X* part, *J*_{*XB*} = 2.4, *J*_{*XA*} = 10.0 (H(*E*)-C(3)), 5.45 for *B* part, *J*_{*BA*} = 17.0, *J*_{*BX*} = 2.4 (H(*Z*)-C(3)), 5.57 for *A* part, *J*_{*AB*} = 17.0, *J*_{*AX*} = 10.0 (H–C(2)).

Triethyl 2,3-dibromo-orthopropenoate (10). The bromination of 6.96 g (40 mmol) of **9** according to [5] was performed at –30° in the presence of CaO to prevent acid hydrolysis of the ortho ester. The crude residue, which still contained CaO, was used directly for the next step described in the following experiment. A sample was treated with carbon tetrachloride and filtered for

⁴) This result has been preliminarily mentioned in footnote ⁷) of [14].

NMR. measurement. – $^1\text{H-NMR}$. (60 MHz, CCl_4): 1.33 (X_3 part of ABX_3 , $J_{AX} \cong J_{BX} \cong 7$, $\sim 9\text{H}$, $3\text{CH}_3\text{CH}_2\text{O}$), 3.1–4.6 (m including signal at 3.72, AB part of ABX_3 , $J_{AX} \cong J_{BX} \cong 7$, $\sim 9\text{H}$, $3\text{CH}_3\text{CH}_2\text{O}$, $\text{H-C}(2)$ and $2\text{H-C}(3)$); signals corresponding to about 10% of **11** were also present.

Triethyl 2-bromo-orthopropenoate (11). The crude residue obtained in the preceding experiment (which contained up to 36 mmol of triethyl 2,3-dibromo-orthopropenoate (**10**) and up to 4 mmol of triethyl 2-bromo-orthopropenoate (**11**)) was treated with a solution of 2.80 g (50 mmol) of KOH in 25 ml of absolute ethanol. After stirring during 20 h, 100 ml of ether were added and the mixture was filtered through Celite. The filtrate was washed with saturated NaCl solution, dried over K_2CO_3 , evaporated and distilled to give 7.89 g (78% from **9**) of **11** as a colourless oil, b.p. $57\text{--}60^\circ/\text{l Torr}$. – IR. (CCl_4): 2985s, 2935m, 2905m, 2875w sh, 1630w, 1485w, 1460w, 1448w, 1395w, 1375w, 1340w, 1225s, 1160m sh, 1118s, 1100s sh, 1065s, 1050s sh, 1025m sh, 920m, 875w, 685w. – $^1\text{H-NMR}$. (60 MHz, CCl_4): 1.20 (t , $J = 7$, 9H, $3\text{CH}_3\text{CH}_2\text{O}$); 3.43 (q , $J = 7$, 6H, $3\text{CH}_3\text{CH}_2\text{O}$); 5.78 (d , $J = 1.5$, 1H, $\text{H}(Z)\text{-C}(3)$); 6.22 (d , $J = 1.5$, 1H, $\text{H}(E)\text{-C}(3)$).

Triethyl 2-methylidene-3-hydroxy-orthobutanoate (13). To a stirred solution of 1.265 g (5 mmol) of triethyl 2-bromo-orthopropenoate **11** in 25 ml of dry tetrahydrofuran were added, during 30 min at -75° , 2.3 ml of a 2.2N *n*-butyl lithium solution in hexane ($\sim 5\text{mmol}$). After 0.5 h a solution of 0.78 g (17.7 mmol) of acetaldehyde in 5 ml of tetrahydrofuran was added during 30 min at -75° . The solution was stirred for 0.5 h, allowed to warm to RT., and treated with saturated NaCl solution and ether. The organic layer was washed with saturated NaCl solution until neutral, dried over K_2CO_3 , and evaporated. Distillation of the residue afforded 900 mg (82%) of **13** as a colourless oil, b.p. $80^\circ/9\text{ Torr}$ (bulb to bulb distillation). – IR. (CCl_4): 3620w, 3550w, 2985s, 2935m, 2905m, 2880w sh, 1485w, 1460w sh, 1450m, 1395m br., 1370w, 1300w, 1265m, 1180m sh, 1150s sh, 1130s sh, 1115s sh, 1070s br., 940m, 920w, 900w. – $^1\text{H-NMR}$. (60 MHz, CCl_4): 1.17 (t , $J = 7.5$, $3\text{CH}_3\text{CH}_2\text{O}$) and 1.23 (d , $J = 6.5$, $3\text{H-C}(4)$) (together 12H); 2.88 (d , $J = 3.5$, 1H, OH); 3.45 (q , $J = 7.5$, 6H, $3\text{CH}_3\text{CH}_2\text{O}$); 4.30 ($q \times d$ with broadened lines, $J = 6.5$ and 3.5 , 1H, $\text{H-C}(3)$); 5.33 (d , $J = 2$, 1H, $\text{H-C}(3')$); 5.45 ($d \times d$, $J = 2$ and 1.5 , 1H, $1\text{H-C}(3')$). After addition of D_2O : 2.88 absent, 4.30 (q with broadened lines, $J = 6.5$). – MS. (70 eV): 173 (9, $M\text{-C}_2\text{H}_5\text{O}$), 147 (8, $M\text{-C}_4\text{H}_7\text{O}$), 129 (11, $M\text{-C}_2\text{H}_5\text{O-C}_2\text{H}_4\text{O}$), 127 (22, $M\text{-C}_2\text{H}_5\text{O-C}_2\text{H}_4\text{-H}_2\text{O}$), 119 (10, $M\text{-C}_4\text{H}_7\text{O-C}_2\text{H}_4$), 101 (19, $M\text{-C}_2\text{H}_5\text{O-C}_2\text{H}_4\text{O-C}_2\text{H}_4$), 100 (9), 99 (37, $M\text{-C}_2\text{H}_5\text{O-C}_2\text{H}_4\text{-H}_2\text{O-C}_2\text{H}_4$), 98 (26), 97 (15), 91 (15, $M\text{-C}_4\text{H}_7\text{O-C}_2\text{H}_4\text{-C}_2\text{H}_4$), 83 (37, $M\text{-C}_2\text{H}_5\text{O-C}_2\text{H}_4\text{O-C}_2\text{H}_4\text{-H}_2\text{O}$), 82 (12), 81 (34, $M\text{-C}_2\text{H}_5\text{O-C}_2\text{H}_4\text{-H}_2\text{O-C}_2\text{H}_4\text{-H}_2\text{O}$), 73 (12, $M\text{-C}_4\text{H}_7\text{O-C}_2\text{H}_4\text{-C}_2\text{H}_4\text{-H}_2\text{O}$), 72 (5), 71 (9), 70 (8), 69 (12), 63 (20, $M\text{-C}_4\text{H}_7\text{O-C}_2\text{H}_4\text{-C}_2\text{H}_4\text{-C}_2\text{H}_4$), 56 (9), 55 (61), 54 (25), 53 (35), 52 (12), 51 (12), 50 (10), 46 (27), 45 (100), 44 (83), 43 (71), 42 (20), 41 (14).

$\text{C}_{11}\text{H}_{22}\text{O}_4$ (218.297) Calc. C 60.52 H 10.16% Found C 60.20 H 10.21%

Ethyl 2-methylidene-3-hydroxybutanoate (14). A solution of 981 mg (4.5 mmol) of triethyl 2-methylidene-3-hydroxy-orthobutanoate (**13**) in 10 ml of ether was stirred during 0.5 h with 10 ml of 0.25N aqueous H_2SO_4 . The aqueous layer was extracted with ether and the combined organic solutions were washed with 5% NaHCO_3 solution and with saturated NaCl solution, dried over K_2CO_3 , and evaporated. Distillation of the residue afforded 590 mg (91%) of **14** as a colourless oil, b.p. $70^\circ/9\text{ Torr}$ (bulb to bulb distillation). – IR. (CCl_4): 3615w, 3540m, 2985s, 2940m, 2910m, 2875w, 1710s br., 1632m, 1480m, 1468m, 1450m, 1400m br., 1373s, 1328s, 1295s br., 1270s, 1175s, 1155s, 1090s, 1040m sh, 1030s, 955s, 930m, 900m, 865w. – $^1\text{H-NMR}$. (60 MHz, CCl_4): 1.25 (d , $J = 6.5$, $3\text{H-C}(4)$) and 1.28 (t , $J = 7.5$, $\text{CH}_3\text{CH}_2\text{O}$) (together 6H); 3.33 (d , $J = 4.5$, 1H, OH); 4.20 (q , $J = 7.5$, $\text{CH}_3\text{CH}_2\text{O}$) and 4.57 (m , $\text{H-C}(3)$) (together 3H); 5.85 (t , $J = 1.5$, 1H, $\text{H}(E)\text{-C}(3')$); 6.17 (finely split s, 1H, $\text{H}(Z)\text{-C}(3')$). On addition of D_2O : 3.33 absent; 4.57 (q , $J = 6.5$). – MS. (70 eV): 129 (48, $M\text{-CH}_3$), 115 (7, $M\text{-C}_2\text{H}_5$), 101 (71, $M\text{-CH}_3\text{-C}_2\text{H}_4$), 99 (41, $M\text{-C}_2\text{H}_5\text{O}$), 98 (35), 97 (21), 87 (6), 84 (6), 83 (100, $M\text{-CH}_3\text{-C}_2\text{H}_4\text{-H}_2\text{O}$), 82 (5), 81 (31), 73 (33, $M\text{-C}_4\text{H}_7\text{O}$), 72 (7), 71 (23), 70 (18), 69 (8), 56 (9), 55 (48, $M\text{-C}_2\text{H}_5\text{O-C}_2\text{H}_4\text{O}$), 54 (13), 53 (19), 45 (26, $M\text{-C}_4\text{H}_7\text{O-C}_2\text{H}_4$), 44 (14), 43 (40), 42 (5), 41 (10).

$\text{C}_7\text{H}_{12}\text{O}_3$ (144.173) Calc. C 58.32 H 8.39% Found C 57.98 H 8.63%

Ethyl (2Z)-2-bromomethyl-2-butenate (6) and (2Z)-2-bromomethyl-2-butenic acid (4). To a solution of 2.160 g (12 mmol) of *N*-bromosuccinimide in 40 ml of dry methylene chloride was added at 0° under N_2 a solution of 933 mg (15 mmol) of dimethylsulfide in 4 ml of methylene chloride

while a yellow solid separated. A solution of 576 mg (4 mmol) of ethyl 2-methylidene-3-hydroxybutanoate (**14**) was added, and the mixture was stirred at RT. during 6 h. It was then diluted with cold pentane, and poured into cold saturated NaCl solution. The aqueous phase was extracted with pentane, and the combined organic extracts were washed with saturated NaCl solution, dried over MgSO_4 , and evaporated. Distillation of the residue at $40^\circ/0.1$ Torr afforded 721 mg (87%) of $^1\text{H-NMR}$. pure **6**. – IR. (CCl_4): 2990 *m*, 2970 *w* sh, 2940 *w*, 2910 *w*, 2875 *w*, 2850 *w*, 1723 *s*, 1653 *m*, 1480 *w*, 1448 *m*, 1385 *m*, 1370 *m*, 1352 *w*, 1280 *s* sh, 1272 *s*, 1220 *m*, 1175 *s*, 1162 *s*, 1128 *m*, 1098 *w*, 1055 *m*, 1025 *w*, 870 *w*, 670 *w*. – $^1\text{H-NMR}$. (60 MHz, CCl_4): 1.32 (*t*, $J = 7.5$, 3H, $\text{CH}_3\text{CH}_2\text{O}$); 1.93 (*d*, $J = 7.5$, 3H, 3H–C(4)); 3.87 (*s*, 2H–C(3')) and 3.90 (*q*, $J = 7.5$, $\text{CH}_3\text{CH}_2\text{O}$) (together 4H); 7.05 (*q*, $J = 7.5$, 1H, H–C(3)).

A mixture of this ester and 8 ml of 48% aqueous HBr was heated under reflux during $1\frac{1}{2}$ h, cooled and extracted with ether. The ethereal solution was dried over MgSO_4 , and evaporated, and the residue was recrystallized from ether/pentane to give 530 mg (85%) of (2*Z*)-2-bromomethyl-2-butenic acid (**4**), m.p. 111–112.5°, with spectral data identical to those previously reported [2]. $^{13}\text{C-NMR}$. (25.2 MHz, CDCl_3): 171.0 (C(1)); 145.9 (C(3)); 129.7 (C(2)); 23.2 (C(3')); 14.8 (C(4)). – Proton coupled ^{13}C -spectrum: the signal at 23.2 appears as $d \times t$ ($J = 9$ and 155) and the signal at 171.0 as $d \times t$ ($J = \sim 5.4$ and 5). – Selective decoupling: Irradiation at 4.25 ($\text{H}_2\text{C}(3')$) converted the signal at 171.0 into *d* ($J = 5.4$)⁵. Thus $J_{\text{C(1)}/\text{H-C(3)}} = 5.4$ and $J_{\text{C(3')}/\text{H-C(3)}} = 9$.

4-Vinyl-1-cyclohexene-1,4-dicarboxylic acid (mikanecic acid) (**19**), its monoethyl (**20**), and diethyl esters (**21**). To a solution of 497 mg (2.4 mmol) of ethyl (2*Z*)-2-bromomethyl-2-butenate (**6**) in 10 ml of *t*-butyl alcohol were added 336 mg (3 mmol) of potassium *t*-butoxide. The mixture was stirred during 5 h and then treated with ether and saturated NaCl solution. The basic aqueous layer was extracted with more ether, the combined organic extracts were washed with saturated NaCl solution, dried over MgSO_4 , and evaporated to give 244 mg of an oil. The work-up of the combined aqueous layers will be described below. Purification by thick layer chromatography of the residue from the organic layer using pentane/ether 2:1 gave 138 mg which consisted mainly of **21** (according to $^1\text{H-NMR}$). Rechromatography with hexane/acetone 5:1 gave two fractions, the less polar of which contained 30 mg of a colourless oil with an $^1\text{H-NMR}$. spectrum corresponding to ethyl (2*E*)-2-*t*-butoxymethyl-2-butenate (**18**) (yield $\sim 4\%$). – IR. (CCl_4): 2985 *s*, 2930 *m*, 2905 *m*, 2870 *m*, 1715 *s*, 1658 *m*, 1480 *m*, 1460 *m* sh, 1445 *m*, 1400 *w* sh, 1385 *m*, 1375 *m*, 1362 *s*, 1335 *w*, 1280 *s*, 1230 *s*, 1192 *s*, 1170 *m*, 1155 *m* sh, 1137 *s*, 1090 *m*, 1060 *s*, 1022 *m*, 950 *w*, 895 *m*. – $^1\text{H-NMR}$. (60 MHz, CCl_4): 1.18 (*s*, $(\text{CH}_3)_3\text{C-O}$) and 1.25 (*t*, $J = 7$, $\text{CH}_3\text{CH}_2\text{O}$) (together $\sim 12\text{H}$); 1.87 (*d*, $J = 7.5$, 3H, 3H–C(4)); 4.03 (*s*, 2H–C(3')) and 4.12 (*q*, $J = 7$, $\text{CH}_3\text{CH}_2\text{O}$) (together 4H); 6.92 (*q*, $J = 7.5$, 1H, H–C(3)); some additional signals due to a slight impurity were present in the 1 ppm region.

The more polar fraction was purified by bulb to bulb distillation at $55^\circ/0.005$ Torr to give 102 mg (33%) of diethyl 4-vinyl-1-cyclohexene-1,4-dicarboxylate (**21**, diethyl mikanecate) as a colourless oil, with $^1\text{H-NMR}$. and IR. spectra in agreement, as far as reported, with those described previously [14]. – $^1\text{H-NMR}$. (60 MHz, CCl_4): 5.07 ($d \times d$, $J = 1.2$ and 18.5, H(Z)–C(2')) and 5.10 ($d \times d$, $J = 1.2$ and 10, H(E)–C(2')) (together 2H); 5.92 ($d \times d$, $J = 10$ and 18.5, 1H, H–C(1')); 6.88 (*m*, with visible splitting of 2, 1H, H–C(2)); for the rest of the signals see [14].

The combined aqueous layers were acidified with concentrated HCl to pH ~ 1 and extracted with ether. The extract was washed with saturated NaCl solution until neutral, dried over MgSO_4 , and evaporated to give 101 mg of a solid residue. Thick layer chromatography using ether/pentane 3:1 as eluant afforded 25 mg (9%) of crude 4-ethoxycarbonyl-4-vinyl-1-cyclohexene-1-carboxylic acid (**20**, ethyl mikanecate) as a colourless solid, after recrystallization from ether/pentane, m.p. 110–112°. – IR. (CCl_4): 3600–2300 *m*, 1722 *s*, 1690 *s*, 1650 *m*, 1425 *m* br., 1365 *w*, 1277 *m*, 1258 *m* sh, 1215 *m* br. sh, 1175 *m* sh, 1090 *m* br., 1020 *w*, 922 *w*. – $^1\text{H-NMR}$. (100 MHz, CDCl_3): 1.23 (*t*, $J = 7$, 3H, $\text{CH}_3\text{CH}_2\text{O}$), 1.5–3.1 (*m*, 6H, 2H–C(3), 2H–C(5), 2H–C(6)); 4.14 (*q*, $J = 7$, 2H, $\text{CH}_3\text{CH}_2\text{O}$); 5.11 (*d*, $J = 17.5$, H(Z)–C(2')) and 5.17 (*d*, $J = 11$, H(E)–C(2')) (together

⁵) The power of irradiation was 450 Hz with offset of 300. The coupling constant was corrected using Pachler's equation [15].

2H); 5.91 ($d \times d$, $J = 11$ and 17.5, 1H, H-C(1')); 7.1 (m , 1H, H-C(2)). – MS. (70 eV): 224 (24, M), 206 (25, $M - H_2O$), 178 (7), 152 (13), 151 (100, $M - CO_2C_2H_5$), 150 (27), 149 (7), 134 (6), 133 (43, $M - CO_2C_2H_5 - H_2O$), 132 (7), 123 (9), 107 (6), 106 (7), 105 (42), 104 (6), 103 (6), 98 (9), 91 (17), 79 (21), 78 (7), 77 (15).

Elution of the more polar fraction gave 26 mg of a colourless solid which according to its 1H -NMR. spectrum [14] consisted mainly of 4-vinyl-1-cyclohexene-1,4-dicarboxylic acid (**19**, *mikanecic acid*), the impurities giving rise to signals in the 1–1.5 ppm region, yield up to 15%. Recrystallization from ether/pentane gave a colourless solid, m. p. $\sim 225^\circ$, lit. [14] m. p. 239–240°.

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Errata

Helv. **58**, 969 (1975), Abhandlung Nr. 163 von L. Balásperi, B. Penke, Gy. Papp, G. Dombi und K. Kovács: auf S. 972, 6. Zeile von oben: anstatt $C_{26}H_{41}N_2O_4$ (445,59) lies $C_{26}H_{40}N_2O_4$ (444,60).

Helv. **59**, 1018 (1976), Abhandlung Nr. 107 von W. Stegmann, P. Gilgen, H. Heimgartner und H. Schmid, Schema 4 und Fussnote 9, S. 1022: Die Formel **10d** entspricht nicht der im Text angegebenen (*E*)-Konfiguration. H und H_5C_2O an C(1') sind demnach in Formel **10d** zu vertauschen.