Thermal Decomposition of Lichen Depsides

Siegfried Huneck*, Jürgen Schmidt

Institute of Plant Biochemistry of the Academy of Sciences of the GDR, Weinberg, GDR-4050 Halle/Saale, German Democratic Republic

Raffaele Tabacchi

Institute of Chemistry, University of Neuchâtel, Avenue de Bellevaux 51, CH-2000 Neuchâtel, Switzerland

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Lichen Depsides, Thermal Decomposition

The thermal decomposition of the following lichen depsides has been described: lecanoric acid, gyrophoric acid, evernic acid, perlatolic acid, planaic acid, confluentic acid, atranorin, 4-O-demethylbarbatic acid, and sekikaic acid. Main reaction products are decarboxylated compounds, phenolic units, rearranged depsides, and xanthones. Triethylammonium salts of depside carboxylic acids decompose at reasonably lower temperature than the corresponding free acids.

Introduction

Certain ethnic groups in Pakistan and other parts of the Himalaya use a glowing mixture of the lichen *Lethariella cladonioides* (Nyl.) Krog and *Juniperus* species as incense for sensual excitation. Because some lichens contain depsides and depsidones with an olivetol unit and *Juniperus* species synthesize *p*-menthane derivatives it might be that under pyrolytic conditions psychotropic active cannabinol derivatives could be built [1]. For this reason we were interested into the thermal decomposition of depsides from lichens.

The first who investigated the pyrolysis of lichen depsides were Schunck [2], Stenhouse [3] and Weigelt [4], who observed orcinol by heating lecanoric acid, evernic acid, and diploschistesic acid. Zopf [5] received a sublimate of two compounds, peltigronic acid and peltigeric acid on heating of peltigerin. Peltigronic acid was identified as methyl orsellinate by Huneck and Tümmler [6] later on. Koller [7] obtained a yellow compound which was considered to be 1,8-dimethyl-3,6-dihydroxyxanthone or 3,8-dimethyl-1,6-dihydroxyxanthone by pyrolysis of gyrophoric, lecanoric and evernic acids. Some years ago C. F. Culberson *et al.* [8] investigated the thermal stability of atranorin, anziaic acid, and perlatolic acid in the thallus of *Hypotrachyna partita* Hale and *H. prolongata* (Kurok.) Hale. They found methyl β-orcinolcarboxylate, anziol, olivetolcarboxylic acid, olivetol, and 4-O-methylolivetolcarboxylic acid as thermal decomposition products of the just mentioned acids.

These data indicate that depsides are split preferably at the ester bond, which is in agreement with the mass spectrometric fragmentation [9].

To get a deeper insight into the thermal decomposition of lichen depsides we pyrolysed numerous compounds and report on the results subsequently.

Results and Discussion

First preliminary TLC analyses showed that the pyrolysis leads to more and more complex mixtures with increasing temperature. On the other hand the depsides investigated decompose at reasonable rate only at temperatures above the melting point, *i.e.* between 170 and 230 °C. Thermal decomposition was carried out at constant temperature in a test tube immersed in a bath of Wood's metal. In the case of free acids decarboxylation occurred and the volume of carbon dioxide evolved was measured with an eudiometer. By this way the decarboxylation rate of the different compounds cold be compared quantitatively.

Lecanoric acid

Thermal decomposition of lecanoric acid (**1**) at 180 °C gave a brownish oil which was separated by preparative thin layer chromatography (PTLC) and yielded orcinol and lecanorol (**2**) as main compounds besides unidentified products. Lecanorol of m.p. 146–148 °C (from MeOH) shows the molecular ion

* Reprint requests to Dr. S. Huneck.

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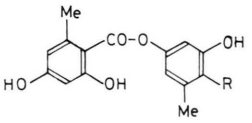

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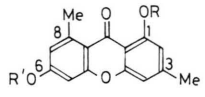

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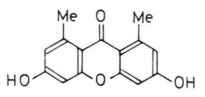

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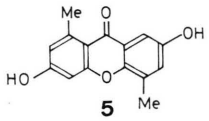

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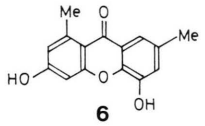

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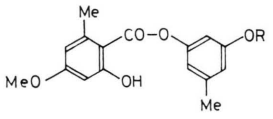

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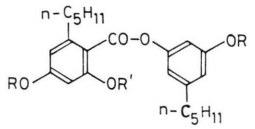

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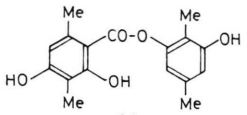
12: R = Me, R' = H
13: R = R' = Me



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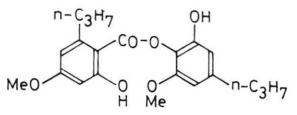

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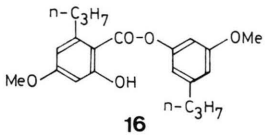

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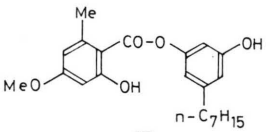

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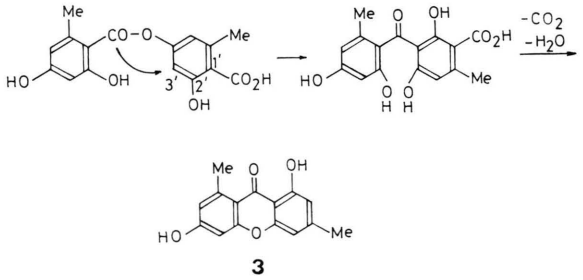
peak at *m/z* 274 ($C_{15}H_{14}O_5$) and two intensive peaks at *m/z* 151 ($C_8H_7O_3$, S-part) and *m/z* 124 ($C_7H_8O_2$, A-part) in the mass spectrum (MS). Structure 2 was confirmed by the ^{1}H NMR spectrum (200 MHz, acetone-d_6): 2.30 (3H, s, 6'-Me), 2.63 (3H, s, 6-Me), 6.35 (1H, d, J = 2.5 Hz, 3-H), 6.44 (1H, d, J = 2.5 Hz, 3'-H), 6.63 (2H, s, 5-H, 1'-H), 6.67 (1H, d, J = 2.5 Hz, 5'-H), 8.71, 9.47, 11.33 (3× 1H, 3× s, 3× −OH).

Gyrophoric acid

As mentioned in the introduction Koller [7] received a xanthone, $C_{15}H_{12}O_4$, of m.p. 260 °C by pyrolysis of gyrophoric, lecanoric, and evernic acids. Repeating the experiment with gyrophoric acid gave a yellow compound of m.p. 275–276 °C after chromatography, obviously identical with Koller's xanthone. This compound showed an intensive molecular ion peak in the MS at *m/z* 256 (100%, $C_{15}H_{12}O_4$) and a peak at *m/z* 227 (20, M−CO−H). The UV spectrum (in MeOH) with maxima at 205 (log ε 4.07), 234 (log ε 4.36), S 250 (log ε 4.16), 265 (log ε 3.88), 303 (log ε 4.08), and 346 nm (log ε 3.63) confirms the presence of a xanthone. Koller took formula 3 or 4 into consideration; other possible structures are 5 and 6. A decision between these structures was made upon addition of $AlCl_3$ by UV-spectroscopy: only structure 3 should give an $AlCl_3$ complex with a bathochromic shift of the long wave maxima. The spectrum observed had maxima at 208 (log ε 4.32), 218 (log ε 4.30), 234 (log ε 4.39), 255 (log ε 4.22), 276 (log ε 4.11), 336 (log ε 4.23), and 403 nm (log ε 3.74) with the following shifts: 303 → 336: 33 nm and 346 → 403: 57 nm. Hence the xanthone from gyrophoric acid must have structure 3, which was confirmed by the ^{1}H NMR spectrum (200 MHz, acetone-d_6): 2.40 (3H, s, 3-Me), 2.80 (3H, s, 8-Me), 6.60 (1H, s, 4-H), 6.25 (1H, s, 2-H), 6.78 (2H, s, 5-H, 7-H), 13.13 (1H, s, 1-OH). Xanthone 3 gave 1,6-diacetoxy-3,8-dimethylxanthone (**7**) by acetylation with acetic anhydride-sulphuric acid and 1-hydroxy-6-methoxy-3,8-dimethylxanthone [8] with diazomethane in 3 h: MS, *m/z* 270 (100%, $C_{16}H_{14}O_4$), 241 (13, M−CO−H), 227 (13); UV, λ_{max}^{MeOH} (log ε): 211 (4.51), 241 (4.67), 255 (4.55), 271 (4.37), 306 (4.45), 354 (4.00), UV, $\lambda_{max}^{MeOH+AlCl_3}$ (log ε): 206 (4.65), 221 (4.60), S 229 (4.65), 235 (4.67), 253 (4.52), 261 (4.55), 278 (4.58), 332 (4.58), 400 nm (4.09); bathochromic shifts: 306 → 332: 26 nm, 354 → 400: 46 nm. The 1-OH group is connected with the xanthone carbonyl group *via* a strong hydrogen bridge and cannot be methylated with diazomethane. The bathochromic shifts in the UV spectrum of **8** on addition of $AlCl_3$ prove again the structure of **3** and **8,** respectively.

The mechanism of the formation of the xanthone **3** is an open question. Koller [7] discussed in the case of lecanoric acid the cleavage of the ester bond, the migration of the S-orsellinoyl moiety to C-3′ of the A-part of the molecule, followed by decarboxylation and dehydration to **3:** Scheme 1.



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Scheme 1. Formation of 1,6-dihydroxy-3,8-dimethylxanthone on pyrolysis of lecanoric acid.

Evernic acid

During a first experiment evernic acid was distilled in a "Kugelrohr" at 12 Torr; TLC showed the presence of unchanged evernic acid, orsellinic acid, and orcinolmonomethyl ether: MS, *m/z* 138 (100%, M^+), 123 (32, M−Me), 109 (91), 108 (79), 107 (91, M−OMe), 95 (60); ^{1}H NMR (200 MHz, $CDCl_3$): 2.27 (3H, s, −Me), 3.77 (3H, s, −OMe), 6.2−6.4 (3H, m, 3× arom. −H). Everninic acid and 2′-O-methylevernol (9), $C_{17}H_{18}O_5$, MS, *m/z* 302 (4%, M^+), 270 (20, M−MeOH), 197 (9), 165 (39), 164 (18), 138 (100), 123 (5), 109 (35), 108 (25), 107 (38), 95 (17) could also be detected. In a second experiment evernic acid was heated to 180 °C for 1 h and the residue of the pyrolysate chromatographed. The following compounds were isolated: orcinolmonomethyl ether, everninic acid, orcinol, lecanorol (**2**) and evernol (**10**), $C_{16}H_{16}O_5$. MS, *m/z* 288 (6%, M^+), 165 (92), 151 (20), 138 (32), 124 (100), 123 (46), 107 (13), 95 (22); ^{1}H NMR (200 MHz, $CDCl_3$): 2.45 (3H, s, −Me), 2.65 (3H, s, −Me), 3.85 (3H, s, −OMe), 6.35 (1H, s, arom. −H), 6.41 (1H, s, arom. −H), 6.9−7.1 (3H, m, 3× arom. −H). The formation of 2′-O-methylevernol and lecanorol can be explained by the reaction of two molecules of everninic and orsellinic acids, respectively; both compounds are present in the pyrolysate of evernic acid.

Perlatolic acid

Thermal decomposition of perlatolic acid at 160 °C in 1 h and chromatography of the pyrolysate gave olivetol, anziol (**11**), and 2′-O-methylperlatolol (**12**). Olivetol: MS, *m/z* 180 (71%, M^+); ^{1}H NMR (200 MHz, $CDCl_3$): 0.87 (3H, t, J = 7.5 Hz, −Me), 1.2−1.4 (4H, m, $-(CH_2)_2-$), 1.45−1.65 (2H, m, $-CH_2-$), 2.47 (2H, t, J = 7.5 Hz, benzyl. $-CH_2-$), 5.40 (2H, bs, 2× −OH), 6.15−6.35 (3H, m, 3× arom. −H). Anziol: MS, *m/z* 180 (65%), 138 (23), 137 (17), 124 (100), 123 (32); ^{1}H NMR (200 MHz, $CDCl_3$): 0.75−1.00 (6H, m, 2× −Me), 1.20−1.45 (8H, m, 2× $-(CH_2)_2-$), 1.45−1.75 (4H, m, 2× $-CH_2-$), 2.57 (2H, t, 6′-benzyl. $-CH_2-$), 2.95 (2H, t, 6-benzyl. $-CH_2-$), 6.35 (2H, d, 2× arom. −H), 6.50−6.70 (2H, m, 2× arom. −H), 6.95−7.10 (m, arom. −H), 11.53 (2H, bs, 2× phenol. −OH). Anziol was described by Culberson *et al.* [8] as thermal decomposition product of anziaic acid, but characterized only by its R_F-values in the three standard solvents A, B, and C. 2′-O-Methylperlatolol: MS, *m/z* 414 (4%, $C_{25}H_{34}O_5$), 252 (26), 221 (100), 196 (42), 194 (28), 177 (17), 164 (59), 149 (22), 138 (77), 123 (28), 108 (11); ^{1}H NMR (200 MHz, $CDCl_3$): 0.75−1.00 (6H, m, 2× −Me), 1.2−1.5 (8H, m, 2× $-(CH_2)_2-$), 1.5−1.8 (4H, m, 2× $-CH_2-$), 2.53 (2H, t, 6′-benzyl. $-CH_2-$), 3.00 (2H, t, 6-benzyl. $-CH_2-$), 3.82, 3.85 (2× 3H, 2× s, 2× −OMe), 6.4−7.0 (5H, m, 5 arom. −H), 11.52 (1H, s, −OH). Two A-parts of the molecule have been combined to 2′-O-methylperlatolol and two S-parts to anziol.

Planaic acid

Planaic acid was pyrolyzed at 220 °C for 1 h and gave after chromatography decarboxyplanaic acid (2,4,2′-tri-O-methylanziol (**13**)) and di-O-methylolivetol. Decarboxyplanaic acid: $C_{26}H_{36}O_5$, MS, *m/z* 235 (100%), 194 (14), 152 (12), 138 (57); ^{1}H NMR (200 MHz, $CDCl_3$): 0.88 (3H, t, −Me), 0.89 (3H, t, −Me), 1.25−1.45 (8H, m, 2× $-(CH_2)_2-$), 1.5−1.8 (4H, m, 2× $-CH_2-$), 2.60, 2.70 (2× 2H, 2× t, 2× benzyl. $-CH_2-$), 3.82, 3.85, 3.88 (3× 3H, 3× s, 3× −OMe), 6.25−6.70 (5H, m, 5× arom. −H). Di-O-methylolivetol: MS, *m/z* 208 (91%, M^+), 179 (15), 166 (74), 152 (100), 137 (47), 123 (51), 122 (33), 121 (44), 109 (36); ^{1}H NMR (200 MHz, $CDCl_3$): 1.90 (3H, t, −Me), 1.2−1.4 (4H, m, $-CH_2-CH_2-$), 1.5−1.7 (2H, m, $-CH_2-$), 2.7 (2H, t, benzyl.

$-CH_2-$), 3.80 (6H, s, 2× $-OMe$), 6.30–6.45 (3H, m, 3× arom. $-H$).

Confluentic acid

From the pyrolysate of confluentic acid (180 °C, 15 min) only one compound could be identified: 4-O-methylolivetonide, MS, *m/z* 262 (100%, M^+), 248 (8), 233 (17), 191 (37), 177 (25), 164 (98), 150 (10), 135 (29).

Atranorin

Thermal decomposition of atranorin (230 °C, 15 min, then 250 °C, 30 min) gave orcinol, β-orcinol, 4-O-demethylbarbatol (**14**), methyl β-orcinolcarboxylate, methyl haematommate, and 3 unidentified compounds. 4-O-Demethylbarbatol, $C_{17}H_{18}O_5$, MS, *m/z* 302 (12%, M^+), 165 (100), 138 (38); ^1H NMR (200 MHz, acetone-d_6): 2.00, 2.25, 2.60 (3× 3H, 3× s, 3× $-Me$), 6.47, 6.55, 6.70 (3× 1H, 3× s, 3× arom. $-H$), 8.71, 11.83 (2× 1H, 2× s, 2× $-OH$). These results demonstrate that pyrolysis of atranorin leads to phenolic compounds which are capable to combine with *p*-menthane derivatives to potential psychotropically active cannabinol derivatives.

4-O-Demethylbarbatic acid

Pyrolysis of 4-O-demethylbarbatic acid at 190 °C for 10 min gave β-orcinol and 4-O-demethylbarbatol.

Sekikaic acid

Thermal decomposition of sekikaic acid at 170 °C for 1 h yielded divaricatinic acid, 3-O-methyl-4-hydroxydivarinol, 3-O-methyldivarinol, decarboxysekikaic acid (**15**), and 2′-O-methyldivaricatol (**16**). 3-O-Methyl-4-hydroxydivarinol, $C_{10}H_{14}O_3$, MS, *m/z* 182 (M^+); ^1H NMR (200 MHz, $CDCl_3$): 0.95 (3H, t, J = 7.5 Hz, $-Me$), 1.5–1.8 (2H, m, $-CH_2-$), 2.50 (2H, t, benzyl. $-CH_2-$), 3.90 (3H, s, $-OMe$), 5.20 (1H, bs, $-OH$), 6.35, 6.45 (2× 1H, 2× d, J = 4 Hz, 2-H, 5-H), 11.15 (1H, bs, $-OH$). 3-O-Methyldivarinol, $C_{10}H_{14}O_2$, MS, *m/z* 166 (86%, M^+), 138 (100); ^1H NMR (200 MHz, $CDCl_3$): 0.95 (3H, t, J = 7.5 Hz, $-Me$), 1.5–1.8 (2H, m, $-CH_2-$), 2.50 (2H, t, J = 8 Hz, benzyl. $-CH_2-$), 3.80 (3H, s, $-OMe$), 4.75 (1H, bs, $-OH$), 6.2–6.4 (3H, m, 2-H, 4-H, 6-H). Decarboxysekikaic acid, $C_{21}H_{26}O_6$, MS, *m/z* 193 (8%), 182 (18), 166 (91), 153 (26), 151 (23), 138 (100), 137 (45), 123 (8), 107 (23); ^1H NMR (200 MHz, $CDCl_3$): 1.95 (6H, t, 2× $-Me$), 1.4–1.9 (4H, m, 2× $-CH_2-$), 2.60 (2H, t, benzyl. $-CH_2-$), 2.95 (2H, t, benzyl. $-CH_2-$), 3.83, 3.98 (2× 3H, 2× s, 2× $-OMe$), 5.45 (1H, bs, $-OH$), 6.40–6.75 (4H, m, 4× arom. $-H$), 11.34 (1H, s, $-OH$). 2′-O-Methyldivaricatol, $C_{21}H_{26}O_5$, MS, *m/z* 358 (5%, M^+), 193 (97), 166 (94), 151 (28), 149 (24), 138 (100), 137 (54), 123 (11), 109 (17), 107 (26); ^1H NMR (200 MHz, $CDCl_3$): 0.95 (6H, t, 2× $-Me$), 1.55–1.90 (4H, m, 2× $-CH_2-$), 2.60, 3.02 (2× 2H, 2× t, 2× benzyl. $-CH_2-$), 3.83, 3.85 (2× 3H, 2× s, 2× $-OMe$), 6.30–6.75 (5H, m, 5× arom. $-H$), 11.52 (1H, bs, $-OH$).

Triethylammonium salts of depside carboxylic acids and pyrolysis of triethylammonium sphaerophorate.

During the preparation of triethylammonium salts of depside and depsidone carboxylic acids it was observed that these salts decompose under evolution of gas at reasonably lower temperatures than the original carboxylic acids: Table I.

Table I. Decomposition temperature of depside and depsidone carboxylic acids and the corresponding triethylammonium salts.

Compound	Decomposition (°C) of the carboxylic acid	triethylammonium salt
Lecanoric acid	184 (m.p.)	143 (m.p.)
Evernic acid	180	135
4-O-Demethylbarbatic acid	176–177 (m.p.)	155–157 (m.p.)
Barbatic acid	187 (m.p.)	135–137 (m.p.)
Divaricatic acid	180	130
Confluentic acid	180	93–95 (m.p.)
Diffractaic acid	200	155
Psoromic acid	265 (m.p.)	173–175 (m.p.)

The oily triethylammonium salt of sphaerophorin gave sphaerophorol, decarboxysphaerophorin (**17**), and orcinol monomethyl ether after thermal decomposition at 180 °C for 10 min. A further component seems to be 2′-O-methylevernol (**9**) according to the ^{1}H NMR spectrum (200 MHz, acetone-d_6): 2.35, 2.65 (2× 3H, 2× s, 2× −Me), 3.83, 3.87 (2× 3H, 2× s, 2× −OMe), 6.44, 6.48 (2× 1H, 2× d, 2× arom. −H), 6.7–6.8 (3H, m, 3× arom. −H). Sphaerophorol, $C_{22}H_{28}O_5$, MS, *m/z* 372 (4%, M^+), 208 (28), 165 (100), 151 (5), 138 (88), 124 (92), 109 (35), 108 (23), 107 (35); ^{1}H NMR (200 MHz, $CDCl_3$): 0.88 (3H, t, −Me), 1.3 (8H, bs, $-(CH_2)_4-$), 1.6 (2H, m, $-CH_2-$), 2.58 (2H, t, benzyl. $-CH_2-$), 2.65 (3H, s, 5-Me), 3.85 (3H, s, −OMe), 5.55 (1H, bs, 2′-OH), 6.40 (2H, s, 2× arom. −H), 6.40–6.65 (3H, m, 3× arom. −H), 11.51 (1H, s, −OH).

Comparison of the rate of decarboxylation of depside carboxylic acids

Fig. 1 shows that the rate of decarboxylation of the depsides investigated decreases in the following order: lecanoric acid, evernic acid, planaic acid, sekikaic acid, perlatolic acid. Obviously methylation in 4-position and substitution of the 6-methyl group by a longer aliphatic chain renders decarboxylation more difficult.

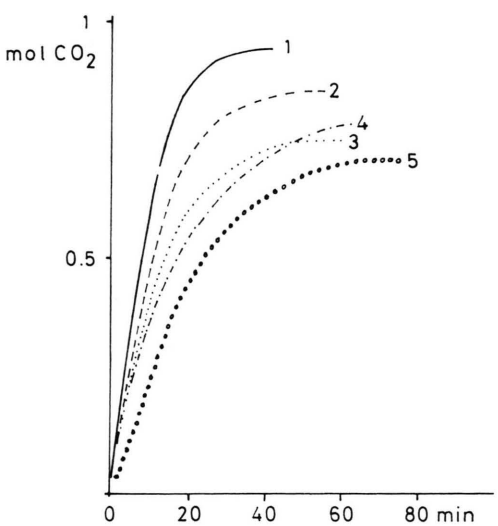

Fig. 1. Rate of decarboxylation of lecanoric acid (1, 180°), evernic acid (2, 180°), planaic acid (3, 220°), sekikaic acid (4, 170°), and perlatolic acid (5, 180°).

Experimental

Lecanoric acid

Lecanoric acid (1.013 g) gave a brownish oil (0.792 g) after thermal decomposition. PTLC (silica gel PF 254+366, 1 mm, *n*-hexane:Et_2O:HCO_2H = 4:6:1) yielded orcinol (0.065 g) and lecanorol, 2 (0.033 g).

Gyrophoric acid

The pyrolysate (0.8 g) of gyrophoric acid (1 g) was chromatographed over silica gel (35 g, with 5% H_2O): *n*-hexane:ethyl acetate = 17:3 (400 ml) eluted 1,6-dihydroxy-3,8-dimethylxanthone (**3**), IR ν_{max}^{KBr}: 674, 840, 850, 916, 1010, 1060, 1090, 1130, 1160, 1212, 1270, 1294, 1394, 1402, 1460, 1508, 1602, 1642, 2950, 3350 cm^{-1}.

1,6-Diacetoxy-3,8-dimethylxanthone (**7**): needles of m.p. 148–150 °C (MeOH–H_2O).

1-Hydroxy-6-methoxy-3,8-dimethylxanthone (**8**): yellowish needles of m.p. 197–198 °C ($CHCl_3$–MeOH), IR, ν_{max}^{KBr}: 674, 802, 834, 870, 902, 960, 1048, 1156, 1210, 1280, 1340, 1390, 1420, 1454, 1504, 1562, 1610, 1650, 2950, 3450 cm^{-1}.

Evernic acid

Evernic acid (1 g) yielded a brown resin (0.7 g) on thermal decomposition which was chromatographed over silica gel (30 g, with 5% H_2O). Benzene (250 ml) eluted 2′-O-methylevernol (**9**) in needles of m.p. 165–167 °C (from Et_2O). Further elution with benzene (500 ml) gave evernol (**10**).

Perlatolic acid

The pyrolysate (1.7 g) of perlatolic acid (2 g) was chromatographed over silica gel (35 g, with 5% H_2O) and the column eluted with a *n*-hexane–Et_2O gradient; further separation by PTLC gave anziol (**11**) and 2′-O-methylperlatolol (**12**): oil, IR, ν_{max}^{KBr}: 724, 810, 860, 900, 968, 1004, 1060, 1160, 1212, 1262, 1330, 1384, 1468, 1500, 1614, 1662, 2980, 3200 cm^{-1}.

Planaic acid

Planaic acid (0.717 g) gave an oil (0.65 g) after pyrolysis which yielded decarboxyplanaic acid (**13**), m.p. 52–53 °C after PTLC.

Confluentic acid

Confluentic acid (0.5 g) yielded a sticky oil (0.4 g) after thermal decomposition from which crystals separated after some days at room temperature. These crystals were removed and recrystallized from

n-pentane: 4-O-methylolivetonide in flat needles of m.p. 54–55 °C.

Atranorin

The pyrolysate (1.7 g) of atranorin (2 g) gave the following compounds after separation by PTLC (silica gel PF 254+366, 1 mm, $CHCl_3$:MeOH = 47.5:2.5): R_F 0.17: orcinol (0.04 g), R_F 0.27: β-orcinol (0.04 g), R_F 0.35: unidentified prisms of m.p. 153–154 °C, no reaction with KOH or *p*-phenylenediamine, MS, *m/z* 332 (22%, M^+ ?), R_F 0.42: 4-O-demethylbarbatol, R_F 0.53: atranol (0.04 g) in needles of m.p. 105–107 °C (from Et_2O–*n*-hexane), KOH yellow, *p*-phenylenediamine yellow-orange, MS, *m/z* 152 (M^+); ^1H NMR (200 MHz, acetone-d_6): 2.24 (3H, s, –Me), 6.30 (2H, s, 2× arom. –H), 10.26 (1H, s, –CHO), R_F 0.67: methyl β-orcinolcarboxylate (0.382 g) in needles or plates of m.p. 137–139 °C (from benzene), MS, *m/z* 196 (100%, M^+), 164 (98, M–MeOH), 136 (98, M–MeOH–CO); ^1H NMR (200 MHz, $CDCl_3$): 2.10 (3H, s, 6-Me), 2.46 (3H, s, 3-Me), 3.95 (3H, s, $-CO_2Me$), 5.2 (1H, bs, 4-OH), 6.24 (1H, s, 5-H), 12.05 (1H, s, 2-OH), R_F 0.98: methyl haematommate (0.086 g) in needles of m.p. 150–152 °C (from $CHCl_3$–MeOH), KOH and *p*-phenylenediamine yellow, MS, *m/z* 210 (76%, M^+); 182 (33, M–CO), 178 (41, M–MeOH), 150 (100, M–MeOH–CO), 122 (51, M–MeOH–2CO), ^1H NMR (200 MHz, acetone-d_6): 2.55 (3H, s, –Me), 4.00 (3H, s, $-CO_2Me$), 6.49 (1H, s, arom. –H), 10.31 (1H, s, –CHO).

4-O-Demethylbarbatic acid

4-O-Demethylbarbatic acid (1 g) was pyrolysed under N_2. The sublimate gave β-orcinol (0.02 g) in prisms of m.p. 155–157 °C, MS, *m/z* 138 (M^+) after repeated crystallization from Et_2O–*n*-hexane. The brown oily residue yielded 4-O-demethylbarbatol of m.p. 152–155 °C after chromatography.

Sekikaic acid

The pyrolysate (0.8 g) of sekikaic acid (1 g) was separated by PTLC (silica gel PF 254+366, 1 mm, $CHCl_3$:MeOH = 48:2): R_F 0.19: divaricatinic acid (0.01 g) in needles of m.p. 154 °C, MS, *m/z* 210 (76%, M^+), 192 (100, M–H_2O), 164 (56, M–H_2O–CO); ^1H NMR (200 MHz, $CDCl_3$): 0.96 (3H, t, –Me), 1.62 (2H, m, $-C\underline{H}_2-$Me), 2.90 (2H, t, benzyl. $-CH_2-$), 3.84 (3H, s, –OMe), 6.35, 6.37 (2H, 2× d, 3-H, 5-H), 11.62 (1H, bs, –OH), R_F 0.39: 3-O-methyl-4-hydroxydivarinol, oil (0.04 g), R_f 0.55: 3-O-methyldivarinol, MS, *m/z* 166 (87%, M^+), 138 (100, M–C_2H_4); ^1H NMR (200 MHz, $CDCl_3$): 0.95 (3H, t, –Me), 1.5–1.8 (2H, m, $-C\underline{H}_2-$Me), 2.50 (2H, t, benzyl. $-CH_2-$), 3.80 (3H, s, –OMe), 4.75 (1H, bs, –OH), 6.25–6.40 (3H, m, 3× arom. –H), R_F 0.80: decarboxysekikaic acid, R_F 0.96: 2′-O-methyldivaricatol.

Triethylammonium salts of depside carboxylic acids

The triethylammonium salts were prepared by reaction of the carboxylic acids with triethylamine in acetone.

Triethylammonium lecanorate, $C_{22}H_{29}NO_7$, m.p. 143–145 °C (dec.) (rhombic crystals from acetone), IR, ν_{max}^{KBr}: 704, 830, 900, 972, 1000, 1070, 1140, 1168, 1192, 1250, 1280, 1310, 1350, 1450, 1580, 1644, 1690, 2650, 2950 cm^{-1}.

Triethylammonium evernate, $C_{23}H_{31}NO_7$, m.p. 82–84 °C (dec.) (prisms from Et_2O), IR, ν_{max}^{KBr}: 704, 750, 800, 892, 954, 998, 1036, 1060, 1076, 1156, 1202, 1250, 1270, 1312, 1360, 1440, 1580, 1650, 2480, 2650, 2950 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): 1.35 (9H, t, $-N(CH_2-\underline{Me})_3$), 2.65, 2.67 (2× 3H, 2× s, 2× –Me), 3.15 (6H, q, $-N(C\underline{H}_2-Me)_3$), 3.85 (3H, s, –OMe), 6.40 (2H, s, 3′-H, 5′-H), 6.47, 6.62 (2H, 2× d, 3-H, 5-H), 11.56 (1H, bs, –OH).

Triethylammonium confluentate, $C_{34}H_{51}NO_8$, m.p. 93–95 °C (dec.) (amorphous).

Triethylammonium 4-O-demethylbarbatate, $C_{24}H_{33}NO_7$, m.p. 155–157 °C (dec.) (prisms from acetone), IR, ν_{max}^{KBr}: 808, 830, 1082, 1110, 1150, 1260, 1300, 1364, 1410, 1450, 1590, 1640, 2650, 2950 cm^{-1}.

Triethylammonium barbatate, $C_{25}H_{35}NO_7$, m.p. 135–137 °C (dec.) (rhombic crystals from Et_2O), IR, ν_{max}^{KBr}: 736, 806, 830, 880, 1000, 1042, 1080, 1150, 1230, 1270, 1290, 1362, 1440, 1502, 1570, 1600, 1642, 2440, 2600, 2960 cm^{-1}.

Triethylammonium divaricatate, $C_{27}H_{39}NO_7$, m.p. 54–56 °C (plates from Et_2O), IR, ν_{max}^{KBr}: 718, 750, 846, 890, 1032, 1150, 1200, 1218, 1250, 1268, 1334, 1364, 1430, 1460, 1580, 1640, 1720, 2640, 2940 cm^{-1}.

Triethylammonium diffractate, $C_{26}H_{37}NO_7$, m.p. 110–112 °C (prisms from acetone–Et_2O), IR, ν_{max}^{KBr}: 756, 790, 810, 844, 1000, 1080, 1140, 1220, 1268, 1320, 1362, 1450, 1570, 1590, 1716, 2950 cm^{-1}.

Triethylammonium salt of sphaerophorin, $C_{29}H_{43}NO_7$ (oil).

Thermal decomposition of the triethylammonium salt of sphaerophorin gave sphaerophorol, decarboxysphaerophorin, and orcinol monomethyl ether after chromatography over silica gel. Sphaerophorol: needles of m.p. 52–54 °C (from H_2O), MS, *m/z* 208 (42%, M^+), 137 (26), 124 (100, M–C_6H_{12}); ^1H NMR (200 MHz, $CDCl_3$): 0.88 (3H, t, –Me), 1.30 (8H, bs, $-(CH_2)_4-$), 1.67 (2H, m, $-CH_2-$), 2.50 (2H, t, benzyl. $-CH_2-$), 6.15–6.30 (3H, m, 3× arom. –H).

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