oberirdische Teile ergaben 5 mg **11** und nach Veresterung der polaren Anteile 40 mg **5** und 10 mg **7**.

3α-Tiglinoyloxy-stachen-20-säuremethylester (**7**). Farbloses Öl, IR: C≡C CO_2R 1720, 1640; CO_2R 1700, 1150 cm^{-1} MS: M^+ *m/e* 414.277 (0.3%) (ber. für $C_{26}H_{38}O_4$ 414.277); —$C_4H_7CO_2H$ 314 (8); $C_4H_7CO^+$ 83 (100).

$[\alpha]_D = -7.5°$ (*c* = 0.5).

3α-Tiglinoyloxy-9,11-dehydrostachensäuremethylester (**9**). *Farbloses* Öl, IR: C≡C CO_2R 1730, 1650; CO_2R 1700, 1160 cm^{-1} *MS*: M^+ *m/e* 412.261 (65%) (ber. für $C_{26}H_{36}O_4$ 412.261); —Me 397 (8); —$C_4H_7CO_2$ 312 (33); 312-.CH_3 297 (57); 312-.CO_2Me 253 (31); 297-HCO_2Me 237 (50); $C_4H_7CO^+$ 83 (100). $[\alpha]_D = -37.4°$ (C = 0.4).

20-Oxostachen (**10**). Farbloses Öl, IR: CHO 2720, 1710 cm^{-1} *MS*: M^+ *m/e* 286.230 (65%) (ber. für $C_{20}H_{30}O$ 286.230); —.CHO 259 (40) $C_4H_7^+$ 55 (100). 10 mg **10** in 3 ml MeOH reduzierte man mit 20 mg $NaBH_4$ und erhielt nach DC (E–P 1:3) 8 mg **11**, identisch mit authentischem Material (IR- und NMR-Spektrum und optische Rotation).

Viguiera cordifolia *Gray*. (Gesammelt in Mexico, Herbar Nr. 75/64) 400 g Wurzeln ergeben 100 mg α- und β-Pinen (*ca* 1:1), Spuren von Diinonen, 3 g **4**, **12** und **13** (*ca* 1:5:1). 500 g oberirdische Teile lieferten 700 mg **4**, **12** und **13** (*ca* 1:4:1).

Viguiera stenoloba *var.* chihuahuense. (Prof. Turker, Herbar Nr. 75/12): 237 g Wurzeln lieferten 1 mg **15**, 1 mg **16**, 3g **12** und **13** (*ca* 2:1) und 100 mg **17–20** (*ca* 5:1:1:1).

Viguiera grammatoglossa *DC*. (Gesammelt in Mexico Herbar.-Nr. 75/67) 150 g Wurzeln ergaben 80 mg α-Pinen, 1 g **4**, **12** und **13** (*ca* 1:1:1), 30 mg **10** und 20 mg **11** sowie in Spuren Diinone. 250 g oberirdische Teile lieferten 500 mg **4**, **12** und **13** (*ca* 1:1:1) 10 mg **10**, 10 mg **11** und 100 mg Germacren D.

Anerkennung—Der Deutschen Forschungsgemeinschaft danken wir für die Förderung dieser Arbeit, Herrn Prof. Dr. B. Turner, Austin, für Pflanzenmaterial.

LITERATUR

1. Bohlmann, F., Burkhardt, T., und Zdero, C. (1973) *Naturally Occurring Acetylenes*. Academic Press, London.
2. Bohlmann, F., und Ngo Le Van (1976) *Chem. Ber.* **109**, 1446.
3. McCrindle, R., Martin, A. und Murrary, R. D. H. (1968) *J. Chem. Soc.* (*C*.) 2349.
4. Bohlmann, F. und Ngo Le Van (1977) *Phytochemistry*, in press.

Phytochemistry, 1977, Vol. 16, pp. 1075–1078. Pergamon Press. Printed in England.

A NEW TRITERPENE, BETULAFOLIENPENTAOL, FROM *BETULA PLATYPHYLLA*

BYUNG HOON HAN and BYUNG JOON SONG
Natural Products Research Institute, Seoul National University, Chong No Ku, Seoul 110, Korea

(*Received* 24 *December* 1976)

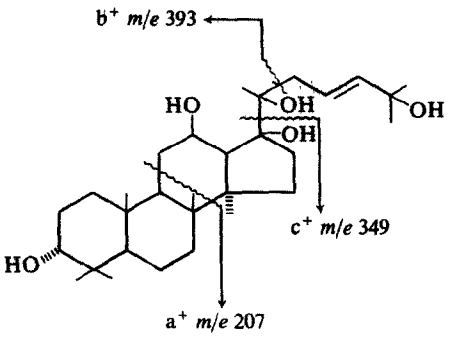
Key Word Index—*Betula platyphylla*; Betulaceae; triterpene; betulafolienpentaol.

Abstract—A new triterpene, betulafolienpentaol, 3α,12β,17,20,25-pentahydroxy dammar-23-*trans*-ene and two other known triterpenes were isolated from *Betula platyphylla*. The latter compounds were identified as betulafolientetraol and betulafolientetraol-A, respectively.

INTRODUCTION

Our previous reports described the isolation of five dammarane triterpenes from the unsaponifiable fraction of the fresh leaves of *Betula platyphylla* Sukatchev var. *mandshurica* [1–3]. Further work on the same fraction resulted in the isolation of another new triterpene, betulafolienpentaol (**3**), $C_{30}H_{52}O_5$, mp 203–204° in addition to two other known triterpenes, betulafolientetraol (**1**), $C_{30}H_{52}O_4$, mp 112–114° and betulafolientetraol-A (**2**), $C_{30}H_{52}O_4$, mp 125–127°.

Compounds (**1**), (**2**) and (**3**) showed positive Liebermann–Burchard reaction (red) and OsO_4 oxidation. Their IR spectra showed a strong absorption band at 3520 cm^{-1} (OH) but no bands assignable as carbonyl or carboxyl groups. Although direct comparison with an authentic specimen was not conducted, compound **1** was identified as betulafolientetraol [4] through its mp and its production of a five-membered ring ketone by HIO_4 oxidation. Compound **2** was identified as betulafolientetraol-A [5] by its mp and NMR spectrum. This paper describes the structural elucidation of the new triterpene (**3**).

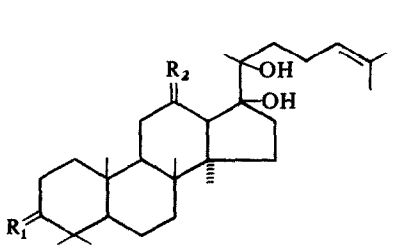


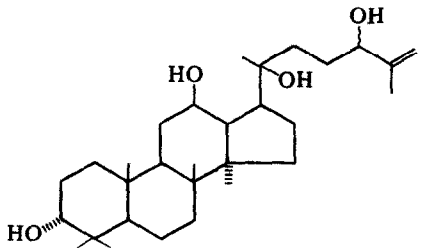
Scheme 1.

RESULTS

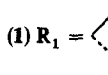
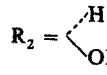
As shown in Scheme 2, compound **1** and its acetate (**7**) produced five-membered ring ketones (**4** and **6**) by HIO_4 oxidation. The carbonyl absorption in the IR spectrum of **4** at 1745 cm^{-1} could be clearly assigned to a five-membered ring ketone, because its Sarett oxidation product (**8**) gave distinctly separated carbonyl absorptions of five-membered and six-membered ring ketones at 1745 and 1705 cm^{-1}. Therefore **1** and **7** should have a glycol function on the C-17—C-20 bond.

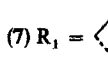
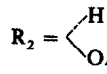
The pentaol (**3**) and the tetraol (**1**) produced the same ketonic compound (**4**) by HIO_4 oxidation. Thus the pentaol had the same tetracyclic skeleton as the tetraol. But based on the polarity difference between the pentaol and the tetraol on TLC, the pentaol possessed an addi-

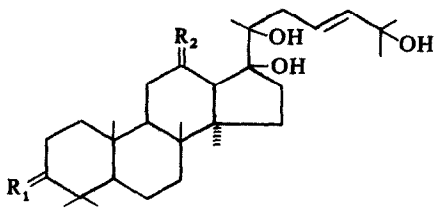


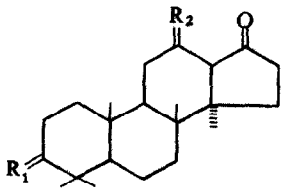


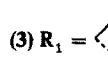
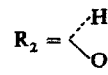
(2)

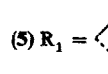
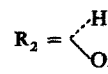
(1) R_1 =  R_2 = 

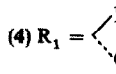
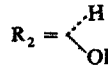
(7) R_1 =  R_2 = 

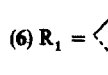
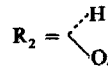




(3) R_1 =  R_2 = 

(5) R_1 =  R_2 = 

(4) R_1 =  R_2 = 

(6) R_1 =  R_2 = 

(8) $R_1 = O$ $R_2 = O$

Scheme 2.

tional hydroxyl group on its side chain. This evidence was confirmed by NMR and MS.

The NMR spectrum of the pentaol (3) showed three tertiary methyl signals markedly deshielded at δ 1.20 (3H, *s*), 1.30 (3H, *s*) and 1.33 (3H, *s*) together with five other methyl signals at δ 0·85 (3H, *s*), 0.90 (6H, *s*), 0·95 (3H, *s*) and 0.98 (3H, *s*). The three deshielded methyl signals could be assigned as the methyl groups oxygenated at their α-carbons and consequently as the C-21, C-26 and C-27 methyl groups.

The MS of the pentaol (3) supported an open side-chain structure, since it produced the ions derived from b^+ by successive dehydrations at *m/e* 393, 375, 357, 339, 321. (See Scheme 1).

One olefinic bond could be placed at C-23—C-24 from the evidence of the NMR spectrum since the two methyl signals for C-26 and C-27 appeared at lower magnetic field than that for the C-21 methyl groups.

Confirmation of the side chain structure of the pentaol (3) was obtained by oxidation of 3 with OsO_4 to give the 3α,12β,17,20,23,24,25-heptaol follwed by treatment with HIO_4 to yield acetone derived from C-25, C-26 and C-27. The production of acetone from the pentaol was shown by the formation of a 2,4-dinitrophenylhydrazone. The olefinic bond was shown to be *trans* from the chemical shift at δ 5.08 (2H, *br s*) of the olefinic protons of the pentaol (3), which agreed well with the calculated value. Based on the above discussions, the final structure of the pentaol can be formulated as 3α,12β,17,20,25-pentahydroxydammar-23-*trans*-ene (3), a new tritepene, to which we assign the name betulafolienpentaol.

EXPERIMENTAL

Mps were taken on a heat block apparatus and are uncorr. Optical rotations were measured in MeOH, UV spectra were recorded in MeOH and IR spectra in KBr-disk. NMR spectra were obtained in $CDCl_3$ using TMS as internal standard at 100 MHz.

Extraction and isolation. Fresh leaves (20 kg) of *Betula platyphylla* Sukatchev var. *mandshurica* (synonym: *Betula latifolia* Komarov) were extracted with hot MeOH. The MeOH extract was concnd to dryness, dissolved in a small amount of H_2O and partitioned with Et_2O. The Et_2O extract was concnd to dryness and saponified by boiling with 5% NaOH in 50% MeOH. After removal of MeOH the unsaponifiable substance was extracted several times with Et_2O and evaporated to dryness. The unsaponifiable fraction was chromatographed on a Si gel column with C_6H_6–EtOAc (1:1). After exhaustive elution with the eluent, the column was extracted with hot MeOH. The MeOH extract contained compounds (1), (2) and (3). The mixture of the compound, eluted with $CHCl_3$–MeOH (15:1) and gave compounds 1, 2 and 3 in crystalline state after working up in the usual way.

Compound 1. $C_{30}H_{52}O_4$, recrystallized from EtOAc, mp 112–114°, $[\alpha]_D^{24}$ +12.0, Liebermann–Burchard reaction +ve (red), TLC R_f 0.7 ($CHCl_3$–MeOH 15:1), +ve HIO_4 oxidation, UV λ_{max}: 204 nm; IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1650, 970 (—CH=C<).

Compound 2. $C_{30}H_{52}O_4$, recrystallized from MeOH, mp 125–127°, $[\alpha]_D^{24}$ +15.0, Liebermann–Burchard reaction +ve (red), TLC R_f 0.45 ($CHCl_3$–MeOH 15:1), −ve HIO_4 oxidation, UV λ_{max}: 204 nm; IR ν_{max}^{KBr} cm^{-1}: 3520, 3240 (OH), 1650 (>C=CH$_2$), NMR: δ 0.83 ppm (3H, *s*), 0.88 (6H, *s*), 0.93 (3H, *s*), 0.96 (3H, *s*), 1.16 (3H, *s*), 1.72 (3H, *s*) all tertiary methyl proton signals and δ 4.85 ppm (1H, *br s*) and 4.95 (1H, *br s*) for exo-methylene group.

Compound 3 (*Betulafolienpentaol*). $C_{30}H_{52}O_5 \cdot H_2O$, recrystallized from MeOH, mp 203–204°, −ve nitrogen test, +ve Liebermann–Burchard reaction (red), +ve HIO_4 and OsO_4 oxidation. TLC R_f 0.2 ($CHCl_3$–MeOH 15:1). UV λ_{max}: 204 nm; IR ν_{max}^{KBr} cm^{-1}: 3250, 3240 (OH), 1650, 970 (>C=CH), NMR: δ 0.85 ppm (3H, *s*), 0.90 (6H, *s*), 0.95 (3H, *s*), 0.98 (3H, *s*), 1.20 (3H, *s*), 1.30 (3H, *s*) and 1.33 (3H, *s*) for eight tertiary methyl proton signals and δ 5.7 ppm (2H, *br s*) olefinic protons. MS *m/e*: 474 (M^+-H_2O), 456 (M^+-2H_2O), 438 (M^+-3H_2O), 420 (M^+-4H_2O), 402 (M^+-5H_2O), 393 (b^+; M^+-$C_6H_{11}O$, side chain), 375 (b^+-H_2O), 357 (b^+-2H_2O), 339 (b^+-3H_2O), 321 (b^+-4H_2O), 349 (c^+; M^+-$C_8H_{15}O_2$), 331 (c^+-H_2O), 313 (c^+-2H_2O), 295 (c^+-3H_2O), 207 (a^+) and 189 (a^+-H_2O) (see Scheme 1). (Found: C, 70.49; H, 11.13 $C_{30}H_{52}O_5 \cdot H_2O$ requires; C, 70.59; H, 10.59%).

HIO_4 Oxidation of the tetraol (1) *and pentaol* (3). The tetraol (1) 160 mg) was dissolved in 10 ml MeOH and 0.1 mol HIO_4 (5 ml) in MeOH was added. After standing 18 hr with occasional stirring, periodate and iodate were removed by addition of a $Ba(OH)_2$ soln and subsequent filtration of the ppt. The filtrate was concnd to a small vol. and extracted with Et_2O. After removal of Et_2O, the residue was chromatographed on a Si gel column with $CHCl_3$–Et_2O (1:6) yielding the oxidation product 4 as prisms, mp 236–237° (decomp.). IR ν_{max}^{KBr} cm^{-1}: 3460 (OH), 1745 (5-membered ring ketone). The same ketonic compound (4) was obtained from the pentaol (3) by the same oxidation process.

Sarett oxidation of the ketonic compound (4). Compound 4 was dissolved in C_5H_5N (1 ml) and CrO_3–C_5H_5N complex (1 ml) was added dropwise in the ice-bath over 1 hr. After standing 18 hr at room temp., the reaction mixture was diluted with CH_2Cl_2–Et_2O (1:2), and filtered through a glass filter. The filtrate was washed with H_2O several times and the ethereal layer was dried with Na_2SO_4. The triketonic compound (8) was obtained as an amorphous material after evaporation of solvent. IR ν_{max}^{KBr} cm^{-1}: 1745 (5-membered ring ketone) and 1705 (6-membered ring ketone).

Acetylation of the tetraol (1) *and the pentaol* (3). The tetraol (1) (200 mg) was dissolved in C_5H_5N (5 ml) and Ac_2O (1 ml) was added, and stood 18 hr at room temp. After working up in the usual way, the acetate (7) was obtained. The pentaolacetate (5) was also obtained by the same process from the pentaol (3). The acetates were used for further reaction without purification.

HIO_4 Oxidation of tetraolacetate (7) *and pentaolacetate* (5). Tetraolacetate (7) was oxidized to the corresponding keto-acetate (6) by periodate. The oxidation was carried out by the method previously mentioned. The same ketoacetate (6) was also obtained by the same oxidation process of pentaolacetate (5). A portion of ketoacetate (6) was saponified by boiling with 5% alcoholic NaOH soln in a sealed tube. The saponified products were identical with the ketonic compound (4) on TLC.

OsO_4 Oxidation of pentaol (3). The pentaol (3) (200 mg) was dissolved in C_6H_6 (4 ml) and 140 mg OsO_4 in C_6H_6 was added. After standing at room temp. for 48 hr, H_2S gas was introduced into the soln for the removal of OsO_4. After addition of a small amount of MeOH–$CHCl_3$ (1:1), the reaction mixture was filtered through a glass filter. The filtrate was concnd to a small vol. and purified on a Sil gel column, eluting with $CHCl_3$–MeOH (4:1). Finally about 80 mg glycol was obtained after concn the eluent mixture. This glycol was suspended in dioxane (0.5 ml) and 0.1 mol HIO_4 soln (0·5 ml) was added and the mixture stood 18 hr at room temp. To this reaction mixture, 50 mg 2,4-dinitrophenyl hydrazine in H_2O (1 ml) was added. The reaction product was identical to acetone-2,4-dinitrophenylhydrazone by coTLC. R_f 0.24, solvent system: CCl_4–Hexane–EtOAc (10:2:1).

Acknowledgement—The authors are grateful to Dr. Tchang Bok Lee, College of Agriculture, Seoul National University for the identification of the plant used in this work.

REFERENCES

1. Han, B. H., Chi, H. J. and Han, Y. N. (1973) *Kor. J. Pharmacog.* **4**, 167.
2. Chi, H. J. and Han, B. H. (1975) *J. Pharm. Soc. Korea* **19**, 159.
3. Chi, H. J. (1974) *J. Pharm. Soc. Korea* **18**, 11.
4. Fischer, F. G. and Seiler, N. (1960) *Ann. Chem.* **644**, 146.
5. Ikekawa, N., Ohta, A., Seki, N. and Takahashi, A. (1972) *Phytochemistry* **11**, 3037.

Phytochemistry, 1972, Vol. 16, pp. 1078–1080. Pergamon Press. Printed in England.

TRITERPENE GLYCOSIDES AND QUERETAROIC ACID IN ORGAN PIPE CACTUS*

HENRY W. KIRCHER
Department of Nutrition and Food Science, University of Arizona, Tucson, AZ 85721, U.S.A.

(*Received* 7 *October* 1976)

Key Word Index—*Lemairocereus thurberi*; Cactaceae; organ pipe cactus; triterpene glycosides; queretaroic acid; *Drosophila* breeding; chemical ecology.

Abstract—The concentration of triterpene glycosides in mature stems of organ pipe cactus was shown to decrease from the surface to the inner portions of the plant. In addition to the previously described oleanolic acid and thurberogenin, queretaroic acid was also shown to be present as an aglycone, and glucose and rhamnose were two of the constituent sugars. Addition of the glycosides to the medium inhibited the maturation of *Drosophila nigrospiracula*, a fly which cannot breed in organic pipe cactus.

INTRODUCTION

Organ pipe cactus (*Lemairocereus thurberi*) grows in Sonora and Baja California, Mexico and in Organ Pipe National Monument, Arizona. The decaying tissues of the plant serve as a breeding site for *Drosophila mojavensis* but cannot be used by *D. nigrospiracula* [1]. The cactus has been reported to lack alkaloids and contain oleanolic acid (1) and thurberogenin (2) as glycosides [2, 3]; betulin and calenduladiol were later isolated from a neutral fraction [4, 5]. Our interest in organ pipe cactus was initiated by the *Drosophila* ecology [6] and the lack of information about other lipids in the cactus.

RESULTS AND DISCUSSION

The cross section of a mature stem of organ pipe cactus is shown in Fig 1. The skin refers to the tough, wax-coated outer layer of translucent material covering the plant, the photosynthetic layer is a gelatinous, bright green tissue under the skin, the transition zone is where green gradually changes to the yellow of the cortex, a dry-appearing, soft, partly fibrous tissue extending inward to the woody, cylindrical rib, whose center is filled with a soft pith. The composition of each

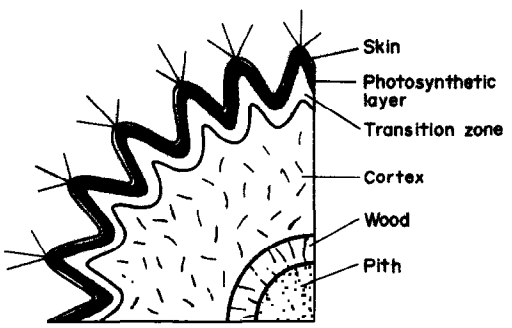


Fig. 1. Cross section of organ pipe cactus; 1/4 of mature stem.

* Arizona Agricultural Experiment Station Journal Article No. 2672.