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ABSCISIC ACID IN *AEGILOPS KOTSCHYI* CARYOPSES

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Key Word Index—*Aegilops kotschyi*; Gramineae; caryopsis; abscisic acid; germination inhibitor.

The glumes and hulls of *Aegilops kotschyi* (Gramineae) contain material which inhibits the germination of the seeds of this plant [1] and lettuce [1–2]. An extract also accelerates leaf abscission in cotton seedlings [2] and inhibits GA_3-promoted reducing sugar production [2–3]. An attempt was made to determine the amount of the inhibitor present in the caryopses and identify it as ABA.

It was found that an inhibitor exists in the acidic ethyl acetate fraction which was prepared from the two types of caryopses. This inhibitor repressed the production of GA_3-promoted reducing sugar. The R_f values of the acidic ethyl acetate fraction of each caryopsis type corresponding to the R_f of the synthetic marker ABA were eluted from the chromatograms. After methylation, the elutes were subjected to GLC. It was found that the extract of the caryopses had a peak at the R_t of 3·0 min which exactly corresponded to R_t of the marker (the *cis–trans* isomer). It thus appears that *cis–trans*—ABA is present in both types of caryopses, its concentration being 2·5 times higher in the smaller (6·2 ng/g dry wt) than in the larger one (2·5 ng/g dry wt), this probably being a contributing factor to the more marked dormancy of the former [3–4].

EXPERIMENTAL

Plant material. Aegilops kotschyi spikelets were collected in the Northern Negev of Israel in the summer of 1971. After dehulling, large and small caryopses were investigated separately.

Extraction. 5 g dehulled smaller and larger caryopses were homogenized in cold 80% MeOH. After shaking the extract for 24 hr in the cold, it was filtered and centrifuged for 20 min at 10000 *g*. The MeOH in the supernatant was removed under vac at 35° and the pH of the aq. layer adjusted to 8·5 with 5% $NaHCO_3$. This was extracted 4× light petrol (30°–40°) and then 4× EtOAc. The pH was then brought to 3·0 with 1 N HCl, and again extracted 4× EtOAc. The latter fractions were combined and evaporated to dryness.

Chromatography. Samples of the EtOAc fraction (equivalent to 1 g dry wt) were separated on Whatman no. 1 paper and with PrOH–NH_4OH–H_2O (10:1:1). The barley endosperm test for gibberellins and ABA [5] revealed the presence of an inhibitory zone at R_f corresponding to that of the synthetic marker (Sigma). The zones were eluted with MeOH and methylated with CH_2N_2 and separated by GLC column 1·8 m × 0·3 cm with 1·5% QF_1 on Gas Chrom Q, 60–80 mesh with N_2 (26 ml/min) at 200°.

REFERENCES

1. Waisel, Y. and Adler, Y. (1959) *Can. J. Botany* **37**, 741.
2. Wurzburger, J. and Leshem, Y. (1969) *New Phytol.* **68**, 337.
3. Wurzburger, J. and Leshem, Y. (1967) *Israel J. Botany* **16**, 181.
4. Wurzburger, J. and Koller, D. (1973) *New Phytol.* **72**, 1057.
5. Chrispeels, M. J. and Varner, J. E. (1967) *Plant Physiol.* **42**, 1008.

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A NEW NAPHTHAQUINONE FROM *TABEBUIA GUAYACAN*

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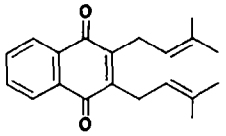
Key Word Index—*Tabebuia guayacan*; Bignoniaceae; 2,3-di(3,3-dimethylallyl)-1,4-naphthaquinone; α- and β-lapachones.

Plant: *Tabebuia guayacan* Hemsley. *Source*: Panama. *Previous work*: An early report [1] of lapachol in the wood of *T. guayacan* is the only reported investigation prior to the current work [2] in this laboratory. Other *Tabebuia* species have yielded several naphthaquinones, anthraquinones and prenylnaphthalene dimers [3–5]. *Present work.* Hammermilled heartwood was extracted successively with petrol bp 30–60°, Et_2O Me_2CO and MeOH. Recrystallization of cold petrol insolubles yielded lapachol (mp 136–137°) and preparative column chromatography of the filtrate (deactivated Si gel, C_6H_6) yielded a new compound as yellow needles (MeOH) mp 72–73°. Found: C, 81·2; H, 7·51 [Calc. for $C_{20}H_{22}O_2$: C, 81·6; H, 7·53]. UV λ_{max}^{EtOH} (log ε): 327 (3·25), 268 (4·20), 260 (4·19), 245 (4·25), ~243 (4·26) nm. IR: ν_{max}^{Nujol} 1660, 1615, 1590, 1460, 1290, 1280, 1160, 1100, 950, 345, 720 cm^{-1}. The 100 MHz NMR in $CDCl_3$ showed two vinyl gem dimethyl groups (*s* at δ1·70 and δ1·80), 2 equivalent

benzylic methylene groups (*d* at δ3·37, *J* 7 Hz), 2 vinyl protons (*t* at δ5·04, *J* 7 Hz) and four aromatic protons (2H, *m*, δ7·70–7·78; 2H, *m*, δ7·98–8·16). On the basis of these data the compound is considered to be 2,3-di(3,3-dimethylallyl)-1,4-naphthaquinone (1).



(1)

This structural assignment was confirmed by synthesis. Naphthalene-1,4-diol (30 g) was reacted with 2-methylbut-3-en-2-ol (30 g) in air, in refluxing 2% citric acid (1 L, 20 hr.). The reaction mixture was cooled, extracted with ether, washed with water, dried and concentrated. The concentrate was preparatively chromatographed (deactivated Si gel, benzene) and the first yellow band was collected, concentrated, and recrystallized as yellow needles (MeOH), mp 73–74° (9 g). This compound was identical in all respects with 1 (UV, IR, NMR, mmp).

Continued preparative chromatography (SiO_2, C_6H_6) of the *T. guayacan* pet. Et_2O solubles yielded small amounts of dehydro-α-lapachone, orange needles (MeOH) mp 148°; α-lapachone, yellow needles (MeOH) mp 116°; and β-lapachone, orange needles (MeOH) mp 155–156°. The identity of these compounds was determined by direct comparison to authentic samples and recorded values [3,4].

REFERENCES

1. Wise, L. E., Rittenhouse, R. C., and Garcia, C. (1951) *Tappi* **34**, 185.
2. Manners, G., Jurd, L., and Stevens, K. (1974) *J. Chem. Soc. Chem. Comm.*, 388.
3. Burnett, A. R. and Thomson, R. H. (1967) *J. Chem. Soc.* (C) 2100.
4. Burnett, A. R. and Thomson, R. H. (1968) *J. Chem. Soc.* (C) 850.
5. Dietrichs, H. H. (1965) *Naturwissenschaften* **51**, 408.

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TRITERPENOIDS AND FLAVONOIDS OF *DALBERGIA SERICEA* BARK

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Key Word Index—*Dalbergia sericea*; Leguminosae; triterpenoids; 3β, 16β-dihydroxy-olean-12en-29 or 30-oic acid; flavonoids; ψ-baptigenin; 7-hydroxy-6-methoxy-3′,4′-methylenedioxyisoflavone; liquiritigenin; isoliquiritigenin.

Plant. Dalbergia sericea; *Geographical source*: Darjeeling (Himalayas). *Previous work.* Tirucallol acetate, glutinol, taraxerol and sitosterol from light petrol extract of the bark [1].

Present work. The air dried and ground bark (3·35 kg) was successively extracted with boiling light petrol (60–80°), C_6H_6, Me_2CO and alcohol. The light petrol and C_6H_6 extracts found to be similar (TLC), were mixed, concentrated and chromatographed over silica gel to yield 7 compounds, in the following order: (a) tirucallol acetate (1·3 g) from light petrol–C_6H_6, 9:1 eluates; (b) glutinol (350 mg) from light petrol–C_6H_6, 3:1 fraction; (c) taraxerol (650 mg) from light petrol–C_6H_6, 7:3 eluates; (d) sitosterol (500 mg) from benzene eluates; details of their identification have already been reported [1]. In addition C_6H_6–EtOAc, 10:1 fractions yielded a mixture, separated by rechromatography over silica gel to afford (e) erythrodiol (35 mg), mp 236–237°, $[\alpha]_D$ + 70·2° (*c*, 0·78, $CHCl_3$), positive LB, TNM tests, diacetate, mp 188–189° and (f) betulin (110 mg) as thin rectangular rods (MeOH), mp 254–255°, $[\alpha]_D$ +17·8° (*c*, 0·68, $CHCl_3$), positive LB, TNM tests, diacetate, mp 214–216°, $[\alpha]_D$ + 19·8 (*c*, 1·3 $CHCl_3$). Finally (g) a white waxy solid (85 mg) was eluted by C_6H_6–EtOAc, 5:2. ν_{max} (film) 1725 cm^{-1}, positive LB, TNM tests, gave sitosterol on saponification and was obviously an ester.

Acetone extract. On concentration and keeping in the refrigerator it deposited a solid (150 mg). This was purified on SiO_2 gel column to yield (h) ψ-baptigenin (120 mg) in C_6H_6–EtOAc, 3:2 eluates, mp 295–296°, gave negative tests for flavones and positive test for isoflavone; acetate, mp 163–164°, methyl ether, 177–178°; (i) another compound contaminated with (h) (15 mg) appeared in the later fractions of the same eluates. MS showed peaks in addition to those corresponding to (h), at 312 (M+), 298, 297, 229, 166, 156·5. These suggested (i) to contain an additional methoxyl as compared to (h) and the strong (M-15) peak suggested the location of the methoxyl at 6 [2,3] and hence (i) is considered to be 7-hydroxy-6-methoxy-3′,4′-methylenedioxyisoflavone and this was confirmed by TLC with an authentic sample earlier reported from *D. riperia* [4] and *Pterodon appariciol* [5].

The mother liquor from acetone extract on chromatography over silica gel afforded 5 more compounds: (j) from C_6H_6–EtOAc, 8:2 fractions, colourless needles (45 mg), mp 268–269° (MeOH), positive LB, TNM tests, ν_{max} (nujol) 3545, 1686, 1282, 1224, 1163, 1116, 1086, 1045, 1036, 1000, 890, 825, 808 & 726 cm^{-1}; MS (% abundance) M^+ 472(12), 454(10), 264(98), 246(99), 219(99), 218(78), 217(97), 207(100), 201(69), 175(81), 171(98), 149(69), 145(74), 131(97) and 121(96); (Found: C, 75·9;