results of electrophoresis, paper chromatography and UV data are outlined in Table 1.

The three bisulphate groups are most probably present on the flavonoid moiety. Thus, on treatment with β-glucuronidase (free of sulphatase), the original material gave rise to a single product (brown on chromatograms under UV). Acidification (0·05 N HCl) of the product gave three intermediates along with rhamnetin. The intermediates disappeared after 10 min heating. The acidity of $AlCl_3$ was apparently high enough to dissociate the sulphate groups, and shifts due to $AlCl_3$ are therefore of no diagnostic value in this particular case.

It is concluded that (*F*) is rhamnetin-3′-glucuronide esterified with potassium bisulphate in positions 3,5 and 4′. Although the presence of a bisulphate group on the glucuronic acid is doubted, yet the possibility should not be excluded. This is the second report of such a highly esterified flavonoid [3], while esterification with one mole of potassium bisulphate has been reported in other moisture-loving plants [4–6]. The presence of such a flavonoid in *Tamarix* is thus not all that surprising, in view of the fact that *Tamarix* species are found in marshy habitats. Furthermore, it has been argued that the formation of flavonoid esters is associated with the adaptability of plants to these environments [7, 8].

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N-N′-DI-O-TOLYLETHYLENDIAMINE FROM *CACHRYS SICULA*

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Key Word Index—*Cachrys sicula*; Umbelliferae; *N-N′*-di-o-tolyl-ethylendiamine.

Plant. Cachrys sicula L. or *Hippomarathrum pterochlaenum* Boiss [1]. Endemic species from the Mediterranean region, very common in the S. of Spain. *Previous work.* None. *Present work.* From an acidic fraction of the methanol extract of the whole dried plant, a compound was isolated in 0,01% yield. This compound was shown to be, by UV, IR and NMR, *N-N′*-di-o-tolylethylendiamine. The structure of this diamine, hitherto not isolated from a natural source, was supported by direct comparison (m.p., m.m.p., IR and NMR) with a synthetic sample [2].

EXPERIMENTAL

Plants were collected in Lucena (Córdoba, Spain) June 1973. Legit et determinavit Dr. J. Borja. Voucher specimens (no. 15742) were deposited in the Herbarium Faculty of Pharmacy (Ciudad Universitaria, Madrid).

The whole dried plant (410 g) was extracted 3 × MeOH: after removal of the solvent *in vacuo*, the residue was extracted 3× 200 ml 1% HCl. The acidic fraction was basified with ammonia and extracted with $CHCl_3$ giving 380 mg solid. Preparative TLC of this residue [SiO_2/$CHCl_3$ with $Ce^{IV}(SO_4)_2$ as spray reagent] gave 50 mg of *N-N'*-di-o-tolylethylendiamine.

N-N'-Di-o-tolylethylendiamine. Recrystalization from *n*-pentane gave m.p. 70–71°, λ_{max} 247 nm (log ε 4·46), 291 (3·77); in EtOH. ν_{max} 3460, 3420, 1612, 1592 cm^{-1} in $CHCl_3$. NMR ($CDCl_3$, TMS) δ, 2·10 (s, 6 H, 2 Me-aryl), 3·46 (s, 4 H, N-CH_2-CH_2-N), 3·30 (broad band removed with D_2O, 2 NH), 6·64 (*m*, 4 H aromatic protons ortho or ortho and para to NH), 7·05 (*m*, 4 H aromatic protons meta to NH). The lack of equivalence of the 4 meta protons showed the probable structure. MS: *m/e* 240 (M^+, 30) (found 240·1632 ± 0·0027; calc. for $C_{16}H_{20}N_2$: 240·1626) 121 (89), 120 (100), 118 (19), 106 (17), 91 (49), 79 (4), 78 (3), 77 (10), 65 (23).

N-N'-Di-p-tolylethylendiamine was also prepared [2] giving the following NMR data: 2·22, 3·30 (*s*, 4 H, N-CH_2-CH_2-N), 3·55 (s, removed with D_2O, 2 NH), 6·53 and 6·96 (*m*, 4 H, aromatic protons meta, equivalents, from NH).

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TRITERPENOID SAPOGENINS OF *SCHIMA MERTENSIANA*

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Key Word Index—*Schima mertensiana*; Theaceae; oleanene-type sapogenols; primulagenin A; dihydropriverogenin A; A_1-barrigenol; barringtogenol C; R_1-barrigenol.

Plant. *Schima mertensiana* Koidz. (Theaceae); syn. *S. boninensis* Nakai. *Source*. The Bonin Islands, Japan. *Previous work*. On related species. *S. kankawaensis* Hay (A_1-barrigenol)[1] and *S. liukiuensis* Nakai (A_1-barrigenol, R_1-barrigenol)[2].

Present work. The MeOH extractive of the bark of *S. mertensiana* was partitioned between *n*-BuOH–H_2O. The saponin mixture obtained from the *n*-BuOH soluble portion after ordinary working-up procedures was subjected to acid hydrolysis followed by treatment with alkali and silica-gel chromatography. Primulagenin A (3β,16α,28-trihydroxy-olean-12-ene)[3], dihydropriverogenin A (3β,16α,22α,28-tetrahydroxy-olean-12-ene)[4], A_1-barrigenol (3β,15α,16α,22α,28-pentahydroxy-olean-12-ene)[5], barringtogenol C (3β,16α,21β,22α,28-pentahydroxy-olean-12-ene)[6], and R_1-barrigenol (3β,15α,16α,21β,22α,28-hexahydroxy-olean-12-ene)[5] were obtained in the respective yields of 2·2, 6·0, 35·8, 7·2 and 13·3% (from the total sapogenol mixture), and identified with the authentic specimens by direct comparison (m.m.p., IR, TLC). This is the first time that primulagenin A, dihydropriverogenin A and barringtogenol C have been isolated from *Schima* species.

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